Difference of phosphorus availability and its chemical mechanism under long-term different fertilization in black soil of China

Qiong Wang

Promoteurs : Prof. Gilles Colinet
Prof. Shu-Xiang Zhang (CAAS, China)

2022

COMMUNAUTÉ FRANÇAISE DE BELGIQUE
UNIVERSITÉ DE LIÈGE – GEMBLOUX AGRO-BIO TECH

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Dissertation originale présentée (ou essai présenté) en vue de l'obtention du grade de docteur en sciences agronomiques et ingénierie biologique

Promoteurs: Prof. Gilles Colinet & Prof. Shu-Xiang Zhang
Année civile: 2022

Résumé

Qiong Wang. (2022). “Difference of phosphorus availability and its chemical mechanism under long-term different fertilization in black soil of Chia” (PhD Dissertation in English). Gembloux, Belgique, Gembloux Agro-Bio Tech, University of Liège, 164 pages, 13 tables, 29 figures

Résumé en Français

L'application d'engrais contenant du phosphore (P) est une pratique agricole importante pour augmenter la capacité d'approvisionnement du sol en P et le rendement des cultures. Sur le long terme, la fertilisation a considérablement augmenté le niveau de P du sol et cette accumulation constitue tant un gaspillage des ressources qu’une source de pollution diffuse des eaux en Chine. La valorisation du P déjà présent dans le sol par les plantes cultivées est devenue une question cruciale pour définir une stratégie durable de fertilisation des sols. La transformation du P dans le sol est un processus complexe qui fait intervenir des réactions physiques, chimiques et biologiques. Cependant, il y a un manque de recherche systématique sur cette question et l'analyse des facteurs qui conditionnent l'effet de la fertilisation sur la disponibilité du P du sol est nécessaire.

Dans la première partie de nos recherches, nous avons valorisé une expérience de fertilisation menée depuis 29 ans sur un sol noir, dans la province de Jilin en Chine. Cette étude a évalué de manière exhaustive les formes de P dans le sol, quantifié la contribution de celles-ci à la disponibilité du P, et identifié les relations entre fertilisation et formes de P. Ensuite, nous avons analysé les changements de formes de P en fonction de la profondeur par la méthode séquentielle modifiée de Hedley. Cette deuxième étude a permis d'identifier la distribution verticale des différentes formes de P, le risque environnemental de perte de P, et les principaux facteurs pédologiques affectant les formes de P à chaque profondeur de sol. Enfin, nous avons réalisé des expériences pour étudier les caractéristiques de l'adsorption-désorption du P et identifier les mécanismes et les propriétés du sol qui affectent la disponibilité du P, avec et sans engrais P. Tous ces résultats visent à expliquer l'effet des différents traitements de fertilisation sur la disponibilité du phosphore.

Les principales conclusions sont les suivantes :

L’étude de l’évolution des formes de P au cours du temps a montré que la fertilisation a favorisé l'accumulation des fractions de P labile et mi-labile dans le sol et inversément a diminué la proportion de P stable dans le sol, en particulier dans les traitements engrais chimiques (NPK) et engrais plus fumier (NPKM). En outre, l'analyse XANES a montré que le P inorganique (Pi) était dominé par les phosphates d'aluminium (Al-P) et le phosphate de calcium monobasique monohydraté (MCP) pour le traitement NPK, tandis que les formes dominantes pour le traitement NPKM étaient Al-P, MCP et le phosphate tricalcique (TCP). Les fractions $NaHCO_3$-Pi et NaOH-Pi semblent être les sources potentielles de P extrait par résine, qui conditionne la disponibilité du P. L'analyse de redondance (RDA) a montré que la matière organique du sol (SOM) et les oxydes de fer et d'alumine liés à la matière organique (Fep+Alp) étaient les principaux facteurs influençant l'évolution des fractions de P. Ils ont contribué à augmenter l'activité du P du sol et à réduire la fixation du P.

L'étude des formes de P à l'échelle verticale a montré que le traitement NPKM à long terme a augmenté de manière significative la teneur en P total, ainsi que la concentration en P-Olsen qui a largement dépassé le seuil environnemental (50,6 mg kg^{-1}) sur l'épaisseur du profil (60 cm). Le Pi était la forme principale de P dans le profil de sol. Dans des conditions de limitation des apports, le P labile et le P stable étaient les principales fractions à montrer une réduction dans le sol. L'application d'engrais P a principalement favorisé l'accumulation des fractions labile et mi-labile. De plus, le P extrait par résine, le $NaHCO_3$-Pi, le NaOH-Pi et le P extrait par HCl dilué (dil.HCl-Pi) augmentent en profondeur lorsqu'un excès de P est observé dans la couche supérieure. La distribution et la disponibilité des fractions de P du sol ont été affectées par les propriétés du sol dans le profil. Pour la couche arable (0-20 cm), l'augmentation de la matière organique du sol (MOS), du fer extractible par la méthode mehlich-3 (M3-Fe), et de l'Alp, causée par la fertilisation, ont été les principaux facteurs des différenciation des fractions de P. Pour le sous-sol (20-60cm), ce sont les composants minéraux du sol, c'est-à-dire les oxydes libres de Fe/Al et le $CaCO_3$, qui ont été les principaux facteurs influençant les fractions de P.

En comparaison avec le sol sans apport de P, les valeurs de la capacité d'adsorption maximale (Q_m) et du pouvoir tampon maximal du P du sol (MBC) ont diminué, tandis que le ratio de désorption (D_r) et la capacité de désorption maximale (D_m) ont augmenté pour les modalités avec apports d'engrais. La fertilisation pourrait ainsi réduire l'adsorption du P par le sol sol. L'apport de P sur le long terme a augmenté de manière significative la teneur en P total et en SOM et a diminué les teneur en Fe_d+Al_d. D'une part, SOM, Fe_d+Al_d et P total dans le sol sans apports, et par ailleurs Fe_d+Al_d, Fe_p+Al_p, pH et SOM dans les sols avec apports, étaient les principaux facteurs influençant les différences dans les paramètres caractéristiques d'adsorption et de désorption du P.

En conclusion, les formes de P étaient les facteurs les plus importants affectant le coefficient d'activation du P (PAC). $NaHCO_3$-Pi et NaOH-Pi, étaient les sources potentielles de P-résine qui détermine la disponibilité du P du sol. La fertilisation, en particulier en présence d'un amendement organique, pourrait améliorer la disponibilité du P principalement en augmentant les fractions de P hautement actives et en diminuant la capacité d'adsorption du P par le sol. Les résultats de l'expérimentation sur le terrain ont confirmé que la modification de la SOM et des oxydes Fe/Al causée par la fertilisation étaient les principaux facteurs affectant la disponibilité du P. De plus, un apport excessif de P n'augmenterait plus le rendement des cultures, mais générerait potentiellement des problèmes environnementaux en augmentant le risque de perte de P vers l'environnement.

Mots-clés: Expérience à long terme; disponibilité du P; formes de P; adsorption-désorption du P; mobilité du P; seuil environnemental

Abstract

Qiong Wang. (2022). "Difference of phosphorus availability and its chemical mechanism under long-term different fertilization in black soil of China" (PhD Dissertation in English). Gembloux, Belgique, Gembloux Agro-Bio Tech, University of Liège, 164 pages, 13 tables, 29 figures

Abstract: Application of phosphorus (P) fertilizer is an important agricultural measure to increase soil P supply capacity and crop yields. Long-term P fertilization has greatly increased the soil P level, which also lead to waste of phosphate rock resources and diffuse source of water pollution in China. The activation of existing soil P by crop plants has become a major issue in the sustainable management of soil fertilization. The transformation of P in soil is a complex process depending on physical, chemical, and biological reactions. However, there is a lack of systematic research in the process and factor analysis of the effect of P fertilizer on the soil P availability is needed.

In this study, a 29-year fertilization experiment on a black soil in Gongzhuling City, Jilin Province in China was sampled. Firstly, we analyzed the changes of P forms with multiple methods and soil properties in topsoil on time scale. This part comprehensively evaluated the P forms, quantified contribution rate of P forms to P availability, and identify the effects of fertilization on P forms. Secondly, we analyzed the changes of P forms with modified Hedley sequential method and soil properties on vertical scale. This part identified the vertical distribution of different P forms, the environmental risk of P loss, and the main soil factors affecting the P forms at each soil depth. Finally, we performed batch experiments to investigate the characteristics of P adsorption-desorption and identify the mechanism of soil properties affecting the availability of P without and with P fertilizers. All these results will expound the effect of different fertilizer treatments on P availability. The main conclusions are as follows:

The experiment of P forms on the time scale showed that fertilization promoted the accumulation of labile P and mid-labile P fraction in the soil, decreased the proportion of stable P in the soil, especially in the chemical fertilizers (NPK) plus manure (NPKM) treatment. Further, XANES analysis showed that accumulated inorganic P (Pi) were dominated by aluminum phosphate (Al-P) and monobasic calcium phosphate monohydrate (MCP) for NPK treatment, and by Al-P, MCP and tricalcium phosphate (TCP) for NPKM treatment. $NaHCO_3$-Pi and NaOH-Pi were the potential sources of resin-Pi, which decided the P availability. Redundancy analysis (RDA) test showed that soil organic matter (SOM) and organic-bound iron and alumina oxide (Fe_p+Al_p), increased by fertilization, were the main factors influencing the transformation of P fractions. These soil factors increased activity of soil P fractions and reduced the P fixation in soil.

The experiment of P forms on the vertical scale showed that long-term NPKM treatment significantly increased total P content. and Olsen-P concentration far exceeded environmental threshold for soil Olsen-P (50.6 mg kg^{-1}) in the 0–60 cm soil profile. Pi was the main form in soil profile. Under the conditions of P deficiency, labile and stable P were the main reduced P fractions in the soil. The application of P fertilizer mainly promoted the accumulation of labile and mid-labile P. Moreover, resin-extracted P (resin-P), $NaHCO_3$-Pi, NaOH-Pi and dilute HCl-extracted P (dil.HCl-Pi) would move to deeper soil layer when excess P was accumulated in the topsoil. The distribution and availability of soil P fractions were affected by soil properties in the profile. For topsoil (0-20 cm), the increase of SOM, mehlich-3 extractable iron (M3-Fe), and Alp caused by fertilization, were the main factors influencing the differences in the P fractions. For subsoil (20-60 cm), soil mineral components, i.e., free Fe/Al oxide and $CaCO_3$, were the main factors influencing the P fractions.

In comparison with soil without P fertilizers, the values of maximum adsorption capacity (Q_m) and maximum buffering capacity of soil P (MBC) were decreased, while desorption ratio (Dr) and maximum desorption capacity (D_m) increased in the soil with P fertilizers. It indicated that fertilization could reduce the adsorption of soil to P. Long-term P input significantly increased the content of total P and SOM and decreased the Fe_d+Al_d when compared to that in the soil without P fertilizers. SOM, Fe_d+Al_d and total P in the soil without P fertilizers, as well as Fe_d+Al_d, Fe_p+Al_p, pH and SOM in the soil with P fertilizers, respectively, were the main factors influencing the differences in P adsorption and desorption characteristic parameters.

In conclusion, P forms were the most important factors affecting P activation coefficient (PAC). $NaHCO_3$-Pi and NaOH-Pi were the potential sources of resin-Pi and drove the P availability. Fertilization, especially in the presence of organic amendment, could improve P availability mainly by enhancing the high active P fractions and decreasing the P adsorption capacity of soil. Field experiment results confirmed that the change of SOM and Fe/Al oxides caused by fertilization were the main factors affecting P availability. Moreover, excessive P input would not significantly increase crop yield, but increase the soil available P to levels which exceed the environmental threshold and increase the risk of P loss to environment.

Keywords: long-term experiment; P availability; P forms; P adsorption-desorption; P mobility; environmental threshold

Acknowledgments

It is the time I have to say goodbye! In the past five years, I had a precious time in the Chinese Academy of Agricultural Sciences and Liege University. I finished my thesis and studies, and gained lots of valuable lesson. Looking back on the hard and happy journey, I have received great help from many teachers, classmates, and family members. I would like to express my heartfelt thanks here!

Firstly, I would like to express my deepest gratitude to my supervisors, Prof. Shu-Xiang Zhang and Prof. Gilles Colinet. They devoted a lot of time and energy on the research design, data analysis, paper writing and provided many opportunities for academic exchange at home and abroad, built a broad learning platform, improved my ability of independent learning and thinking, thank you very much!

I would also like to express my gratitude to my thesis committee and jury members. Thanks for taking their valuable time to read, evaluate and give pertinent suggestions to my research and thesis. Thanks for all your valuable time and genuine help.

I would also like to thank Prof. Ming-Gang Xu, Prof. Wen-Ju Zhang, Prof. Chang-Ai Lu, Prof. Ying-Hua Duan, Prof. Hui-Min Zhang, Prof. Nan Sun, Prof. Gu Feng, Prof. Qi-Mei Lin, Prof. Jin Liu, Ming-Jun Zhang and Hua-Ping Shen, and other teachers, from the Chinese Academy of Agricultural Science and China Agricultural University. Thanks for their patient help and guidance during the whole period of Ph.D. study time.

Thanks to team members, Xiao-Ying Zhan, Qi-Hua Wu, Wei-Wei Zhang, Yan-Hua Chen, Nai-Yu Zhang, Le-Wang, Zhen-Han Qin, Yu-Wen Jin and other students give enthusiastic help in experiment analysis and article revision. Thanks to my classmates and friends, Xing-Juan Zhu, Hui-Min Guo, Xue-Mei Zhao, Yu-Ling Ma, Yu-Zhi Li, Qing-Shan Shen, Sheng-Ping Li, Hu Xu, Xiao-Jun Song, Yan Wang, Shuo Liang, Shu-Hui Wang, Ran Li, Xiao-Fang Ji, Yan-Fang Tian, and other people who gave the help and accompany in my life.

I want to express my heartfelt thanks to my family members, who fully always support me to do anything I like. Specially, I want to thank my boyfriend, Zhe Zhang, we knew each other at my lowest point, he gave me most encouragement and help, made me outgoing and strong, and his inclusivity and support have been driving me forward.

Finally, I would sincerely like to thank all the people who helped me to carry it out successfully. Thanks for the support of National Natural Science Foundation of China (41977103 and 41471249), National Key Research and Development Program of China (2021YFD1500205) and the Reform and Development Fund of the Beijing Academy of Agriculture and Forestry Sciences, China (YZS201905).

Qiong Wang
June, 2022 in Beijing, China

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List of Abbreviations

AP	Soil available phosphorous
CK	No fertilizer
NK	Chemical nitrogen and potassium fertilizer
NP	Chemical nitrogen and phosphorous fertilizer
NPK	Chemical nitrogen, phosphorous and potassium fertilizer
NPKM	Chemical NPK combined with manure
NPKS	Chemical NPK combined with straw
K	Potassium
N	Nitrogen
P	Phosphorus
PAC	Phosphorus activation coefficient
Pi	Inorganic phosphorus
Po	Organic phosphorus
Resin-P	Phosphorus extracted by resin
$NaHCO_3$-P	Phosphorus extracted by $NaHCO_3$
NaOH-P	Phosphorus extracted by NaOH
Dil.HCl-P	Phosphorus extracted by 1 M HCl
Conc.HCl-P	Phosphorus extracted by 12 M HCl
Residual P	Residual phosphorus
Ca-P	Calcium phosphate
Ca_2-P	Dicalcium phosphate
Ca_8-P	Octacalcium phosphate
Ca_{10}-P	Decacalcium phosphate
Fe-P	Iron phosphate [$FePO_4 \cdot 2H_2O$]
Al-P	Aluminum phosphate ($AlPO_4$)
DCP	Dibasic calcium phosphate ($CaHPO_4 \cdot 2H_2O$)
MCP	Monobasic calcium phosphate monohydrate [$Ca(H_2PO_4)_2 \cdot H_2O$]
TCP	Tricalcium phosphate [$Ca_3(PO_4)_2 \cdot xH_2O$]
HAP	Hydroxyapatite
IHP	Inositol hexaphosphate
XANES	X-ray absorption near-edge structure
NMR	Nuclear magnetic resonance
Q_m	Maximum adsorption capacity
K_Q	Adsorption constant
D_m	Maximum Desorption capacity
D_r	The desorption ratio

MBC	Maximum buffering capacity of soil P
DPS	Degree of soil P sorption
$DPS_{M\text{-}P}$	Calculated by Mehlich-3 extractable P, Fe and Al
$DPS_{O\text{-}P}$	Calculated by Olsen-P and Q_m
SOM	Soil organic matter
M3-Ca	Ca extracted by Mehlich-3 extraction
M3-Mg	Mg extracted by Mehlich-3 extraction
M3-Fe	Fe extracted by Mehlich-3 extraction
M3-Al	Al extracted by Mehlich-3 extraction
Fe_d	Crystalline iron oxide
Al_d	Crystalline aluminum oxide
Fe_o	Amorphous iron oxide
Fe_o	Amorphous aluminum oxide
Fe_p	Organic-bound iron oxide
Al_p	Organic-bound aluminum oxide
RDA	Redundancy analysis
BRT	Least significant difference
LSD	Least significant difference
Topsoil	Top 20 cm soil
Subsoil	Soil below 20 cm
OM	organic manure
CF	chemical fertilizer

Chapter I

General Introduction

Abstract

In agricultural production system, the scientific management of rational soil phosphorus (P) level is the focus of soil science and environmental at home and aboard. Soil P availability is affected by many factors. Application of phosphate fertilizer is the most important measure to increase P availability. Moreover, P availability is directly decided by the change of P forms and adsorption-desorption, which are related to soil properties. Until now, knowledge about chemical mechanism of P availability and the quantitative relationship between them are not clear. This chapter provided an overview of the thesis frame structure with a brief description of P availability index, P form and P adsorption-desorption and their influence factors. Based on the above review, we point out the knowledge gap in the related researches, and then presented the study objectives and strategies of this thesis.

Keywords: phosphorus availability; P forms; P adsorption-desorption; soil properties

1. Background

Phosphorus (P) is one of the necessary macro-nutrients and consists of most important organic compounds (e.g., nucleic acids, phospholipids, nucleoproteins, ATPases, etc.) (Sun, 2004). P is essential to plant growth and development by participating in the physiological activities in many ways (such as photosynthesis, respiration, and decomposition) (Childers et al., 2011; Hawkesford et al., 2012). However, the most soil P are absorbed and fixed by iron (Fe) and aluminum (Al) oxides, calcium carbonate ($CaCO_3$) and exist in the form of insoluble phosphate, it's hardly to be directly used by plants under natural conditions (Shen, 2014a, b). In most farmland, the natural P supply capacity of soil often cannot meet the needs of plant growth and development (Wang et al., 2021; Wu et al., 2020; Daly et al., 2015; Kong et al., 2014). Application of P fertilizer is an important agricultural measure to increase and stabilize crop yield, improve soil P supply capacity, and ease the shortage of P resources (Malhi et al., 2015; Zhang et al., 2015; Ma et al., 2009). In recent decades, the production of phosphate fertilizer has been improved continuously with the development of industry in China, and the consumption of P fertilizer increased in agricultural production (Sattari et al., 2014; Lu, 2004). Statistics show that the production of P fertilizer has increased from 0.12 million ton in 1962 to 15.0 million ton in 2017 in China (National Bureau of Statistics, 2018). The high output of P fertilizer, especially the gradual substitution of high concentration P fertilizer for low concentration P fertilizer, has greatly promoted the application of P fertilizer, increasing the accumulation of soil P in most parts of China (Fig.1-1) (Ma, 2018; Ma et al., 2016; Sattari et al., 2014). The average soil P balance in farmland increased from 10.6 kg P_2O_5 ha^{-1} in 1980 to 96.4 kg P_2O_5 ha^{-1} in 2012, the soil P surplus was mainly distributed in North China and the Lower-Middle Reaches of the Yangtze River (Ma et al., 2016). It is concluded that long-term, and high-intensity application of P fertilizers has greatly improved the soil P level, resulting in the accumulation of soil P in China.

Phosphate rock, a non-renewable mineral resource, can only meet the needs of human beings in 100 years in the world (Obersteiner et al., 2013). Moreover, the most phosphate rock resources were low-quality, and distributed unevenly in China (Lu, 2003). Therefore, scientific P application experiment is important to improve the effectiveness of P fertilizers and reduce the waste of phosphate rock resources. This experiment will provide theoretical basis for realizing high efficient utilization of nutrient resources and maintaining ecological environment security

The mobility of soil P determines its ability to migrate to water. The key point to reduce soil P environmental pollution is to control P fertilizer input and accumulation of soil P, reduce the P mobility and improve the utilization efficiency of P resources. Therefore, it's important to study the P accumulation, P forms and mobility under different fertilization. This will correctly evaluate environmental risk of soil P, solve the resource and environment problems restricting the sustainable development of farmland and realize the development of circular agriculture.

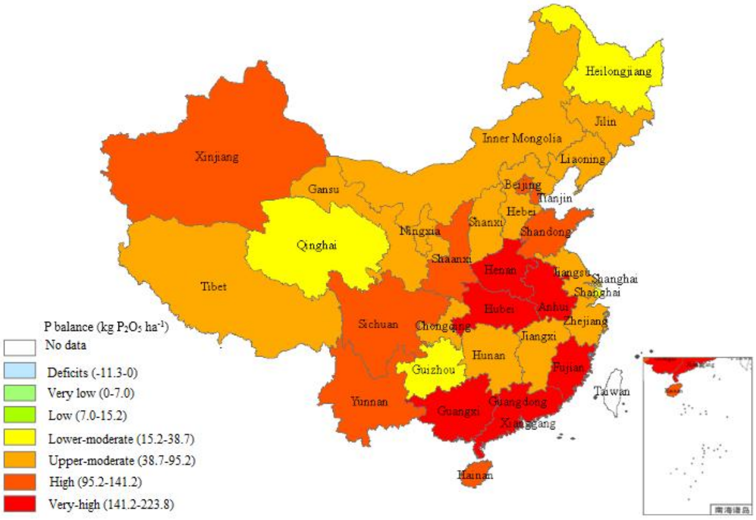


Figure 1-1 Soil P balance in 2012 in China (Ma, 2018)

2. Literature review

2.1 Availability of soil phosphorus and its evaluation index

Soil P exists in a variety of chemical fractions and all these P fractions are in multiple equilibrium system. The transformation from stable P pools to to plant-available P pools is the process of soil P availability.The transformation of soil P fractions can be classified into processes of P fixation and release (Fig. 1-2). The fixation process includes P precipitation, sorption and immobilization, and the release process includes desorption, dissolution, and mineralization (Shen et al., 2011; Frossard et al., 2010).

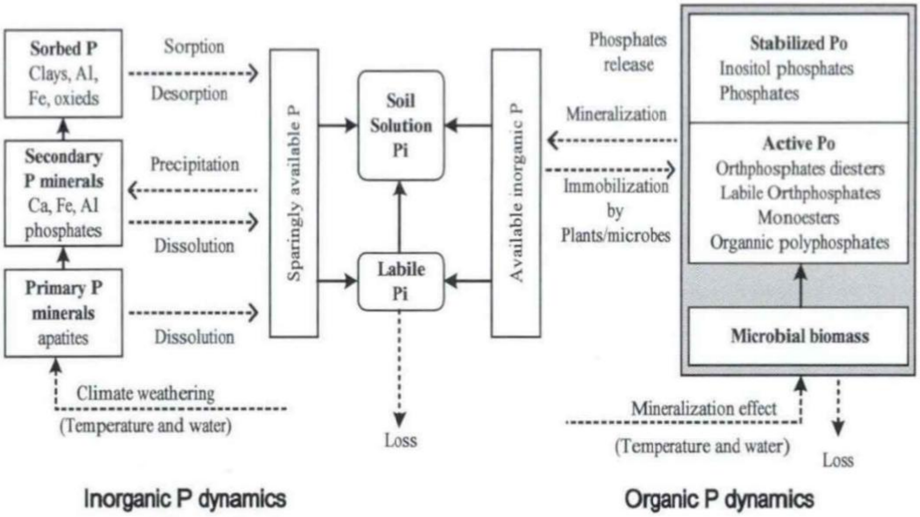


Figure 1-2 P dynamic in soil (Shen et al., 2011)

The soil available P (AP) is defined as the most effective part of soil P pool, which can be absorbed and utilized directly by plant and indicate the growth status of crops (Wang et al., 2013; Lu, 1980). AP, determined by specific method, is a quantitative index instead of a specific form (Shen, 1998). At present, AP is important to evaluate the abundance and loss risk of soil P, guide the rate of P application (Bai et al., 2018; Renneson et al., 2015; Zhang et al., 2015; Li et al., 2013; Li et al., 2010; Lu, 1999).

Many methods were used to determine the AP. Bray1-P (HCl+NH_4F method) is usually to evaluate the P availability in acid soil (Bray, 1945). Olsen-P, measured by Olsen ($NaHCO_3$, pH=8.5) method, is widely used because of its advantage of versatility, especially in slightly acidic, neutral, and calcareous soils (Olsen, 1954). Resin-P (extracted with resin) shows a strong correlation with plant growth and is also widely used (Page, 1982). Mehlich3-P, obtained by action of acetic acid and fluoride compounds, strongly correlate with plant P uptake, or yield (Beauchemin et al., 2003a; Mallarino, 2003; Ziadi et al., 2001; Sharpley et al., 1996). $CaCl_2$-P, extracted with 0.01 mol L^{-1} $CaCl_2$, shows a strong correlation with dissolved reactive P concentrations in runoff, and can be used to characterize the risk of soil loss (McDowell et al., 2002; Sharpley, 1995).

Olsen-P can characterize soil P supply status and guide the application of P fertilizer, and provide a scientific basis for the P fertilizer management (Takahashi and Anwar, 2007; Vu et al., 2008). Olsen-P is mainly affected by long-term different fertilization in farmland soil. Due to the continuous P uptake by crop growth, the soil Olsen-P content decreased gradually under long term without P fertilizer. Many studies had confirmed this conclusion (Xu et al., 2015; Wang et al., 2018). Wu (2018) found that the annual decline rate of Olsen-P is 0.37,0.33 and 0.43 mg kg^{-1}, respectively, in CK, N and NK treatments under 23-year long-term experiments in red soil. Zhang et al (2021) found that without P input, the Olsen-P content kept decreasing with experimental years in rate of 0.14 mg $kg^{-1}year^{-1}$ in alkaline soil in China. Similar results were also reported in black soil, after 30 years without P input, the Olsen-P content decreased 35.8%-70% than that in initial year (Wang et al., 2022; Hao et al., 2015). However, some researches showed opposite results, especially when the soil Olsen-P content was lower than 3 mg kg^{-1}, which was affected by P uptake by crops, soil properties and climate change (Selles et al., 1995; Lu, 2003; Ma et al., 2009). The application of mineral or organic P fertilizer increase the content of Olsen-P, and the improvement of soil P fertility was more obvious especially under the combination of NPK fertilizers with manures (NPKM) (Nikitishen et al., 2008; Huang, 2017; Yang et al., 2009; Li et al., 2010; Wang et al., 2010a). Li et al (2019) found that the order of Olsen-P increasing rate were mineral P fertilizer (NP, PK, NPK) < NPK plus straw returning (NPKS) < NPKM and manures (M) in red soil after a 25-year long-term experiment. A similar result was also report in cinnamon soil, higher increasing rate of Olsen-P was found in NPKM than that in NP treatment (Yang et al., 2015). Moreover, under the same P input, the Olsen-P content in NPKM was 2.1 times higher than that in NPK treatment in surface soil in a calcareous soil (Yan et al., 2018).

In addition to P input, the change of Olsen-P was affected by soil properties (SOM, pH, mineral composition, etc.) and environmental factors (temperature, moisture) (Wang et al., 2019; Sun et al., 2015; Ma et al., 2016; Campos et al., 2018; Chen et al., 2016). Shen (2014b) reported that the change in Olsen-P showed significant positive correlation with SOM under different cropping systems in China. The possible reason was that high SOM showed strong adsorption capacity with metal oxides, which reduce the fixation of soil to P and increase the content and proportion of soil Olsen-P (Siddique et al., 2003; Wang et al., 2008; Yusran, 2010). Soil pH and base cation affect soil P activity (Simonsson et al., 2018). Soil silicates, carbonates, especially iron oxides, were significantly correlated with Olsen-P content (Hinsinger, 2001; Zhou et al., 2001; Sanchez et al., 2014). Changes in soil pH affect the chemical fixation and precipitation-dissolution processes of P, changing the content of Olsen-P (Jing et al.,2014; Hoffland, 1989; Devau et al., 2011; Andersson et al., 2015). Liu (2013) reported that high temperature could increase Olsen-P content, especially when the temperature was 25 and 35°C, the Olsen-P content was significantly higher than that under 5 and 15°C. The possible reasons were that the increase of temperature would increase the adsorption strength and adsorption capacity of soil to P. Moreover, the temperature would affect the activity of soil microorganisms, which in turn affects soil Olsen-P (Du et al.,1993; Rui et al., 2012).

Phosphorus activation coefficient (PAC), is the conversion ratio of total P to Olsen-P, which characterizes the availability of P (Tang et al., 2012). The high PAC value indicates the high availability of soil P, meanwhile, the low PAC value means strong fixation capacity of soil to P (Jia and Li, 2011). The PAC<2% indicates the lower conversion rate of soil total P and capacity and supply intensity of available P (Huang et al., 2016; Wang et al., 2014). PAC value is affected by P input and fertilization regime. It was found that with the increase of P application, the PAC value also increased, and there was a significant positive correlation between them (Zhang et al., 2008; Chen et al., 2010). Many studies reported a higher PAC value was found with P fertilizers than without P fertilizers, especially in NPKM, and the PAC value showed strong correlation with crop yield and the amount of P uptake (Wang et al., 2018; Lu et al., 2015, 2016; Chen et al., 2010). Moreover, soil factors were considered as another important drivers in the change of PAC. A research found that the variance of PAC was mainly affected by soil factors (29.53%), P fertilizer increased the PAC value by changing soil properties in three croplands in China (Wu et al., 2017). Moreover, based on 14 experiment sites in China, Jia and Li (2011) explored that soil pH, CEC, clay and sand content showed directly positive contribution, while SOM showed directly negative contribution on PAC. Meanwhile, Huang et al (2009) analyzed vegetable garden soil with three parent material types and found that the PAC value ranged in different kinds of soil and the difference was up to 3.8 times.

Above, the influence factors for the difference in P availability are multiple and complex under different fertilization. It’s important to explore the difference mechanism of P availability.

2.2 Soil P accumulation and loss

In agricultural production, long-term excessive input of P fertilizers lead to P input exceeding crop uptake and promote the accumulation of P in the soil (Tiecher et al., 2020; Ye et al., 2018). Average soil P balance increased from 10.6 kg P_2O_5 ha^{-1} in1980 to 96.4 kg P_2O_5 ha^{-1} in 2012 (Ma, 2018). High amount of accumulated P significantly increase available P content in topsoil. Available P increased by 0.47–10.76 $mg{\cdot}kg^{-1}$ with an average surplus of 100 kg $P{\cdot}hm^{-2}$ in China (Zhan et al., 2015).A great quantity accumulated soil P promote the migration of soil P to water through erosion, runoff and leaching in vertical profile (Liu et al., 2019; Borovec et al., 2018; Huang et al., 2016; Andersson et al., 2015). Meanwhile, it results in soil and water bodies of P non-point source pollution.

Soil P level is the most important factor affecting P loss in farmland. The runoff amount of P showed positive correlation with P fertilizers (Haden et al., 2007). Zhang et al (2011) found the runoff amounts of TP and PP were affected by P fertilizers and accumulation of soil P. Liu et al (2019) reported that application of high organic fertilizers increased soil TDP leaching and promoted P migration down to soil profile. The possible reasons are the input of organic fertilizers directly provided P, but also promoted the release of active P by activating the fixed P (Zhu et al., 2018). Soil properties showed significant effects on P loss. The leaching risk of paddy soil in dry land is lower than that in dry land (Summers et al. 2001). Soil with high SOM, Olsen-P showed great P loss potential (Sommers et al. 1979).

Although there are many studies on the effects of P fertilizer on soil P accumulation and leaching, most of them focused on the change of P content in leaching solution by indoor model test. The change of P fraction in soil profile and its influencing factors have not been systematically studied until now.

Soil P adsorption saturation (DPS), soil test P and model prediction and evaluation are usually used to assess soil P loss risk. DPS considers both soil P concentration and P sorption capacity and is another index to indicate the risk of releasing P into solution (Kleinman, 2017; Nair et al., 2014, 2004; McDowell et al., 2002; Sharpley, 1995). The soil DPS can be calculated with many equations, and the most commonly equations were calculated with Mehlich-3 P (M3-P), Al (M3-Al), and Fe (M3-Fe; mmol kg^{-1}) or decided by the content of Olsen-P and maximum adsorption capacity (Q_{max}) (Jalali and Jalali, 2016; Sharpley et al., 2020). The higher DPS value, the stronger potential P release capacity of soil to surface runoff and water (Nair et al., 2014; Sharpley, 2020, 1996; Sims et al., 2005; Vadas et al., 2005).

The change point between Olsen-P and $CaCl_2$-P is considered as environmental threshold. When Olsen-P content exceeds this critical value, it will increase the risk of P leaching and overland flow (Heckrath et al. 1995). The environmental threshold varies greatly under different soil types and framing patterns. Bai et al. (2013) reported the environmental threshold in red soil and loessial soil were 90.2 and 39.6 mg kg^{-1}, respectively. Under sugarcane rotation systems, the environmental threshold was 85 mg kg^{-1} (Mardamootoo et al., 2012).

The evaluation of P loss risk varied in different soil types and planting systems. Comprehensive evaluation of environmental threshold with multiple methods is important to rational control of soil P and the accurate control of soil P loss risk.

2.3 Soil P fraction and its availability

In the P biogeochemical cycle, soil P exists in a variety of fractions including inorganic P (Pi) and organic P (Po), and all these P fractions are in multiple equilibrium system. Existing P fractions directly determine P dynamics and bioavailability (Condron and Newman, 2011; Lei et al., 2007; Huang et al., 2005).

Pi is the main soil P form, accounting for about 60%-80% in most cultivated land. Pi is dominated by primary mineral apatite and secondary mineral inorganic phosphate, and can also be divided into mineral Pi, adsorbed Pi, and water-soluble Pi (Huang, 2000). The primary mineral Pi fractions in soil exist in the form of crystal lattice, including apatites, strengite, and variscite and are very stable (Shen et al., 2011). The soil secondary mineral Pi mainly exists in the soil in precipitated Pi, adsorbed Pi, and water-soluble Pi (Pierzynski et al, 2005). Precipitated Pi is combined with iron (Fe), aluminum (Al) or calcium (Ca) in the soil, mainly including calcium phosphate (Ca-P), Fe-P, Al-P (Oelkers and Valsami-Jones, 2008). Absorbed Pi is adsorbed on the surface of clay minerals and organic compounds through van der Waals force and chemical bond energy (Mclaughlin et al., 2011). The adsorption matrix of soil P is affected by soil types, with hydrated oxides and amorphous Fe and Al oxides in acidic soil, physical clay, $CaCO_3$, free Fe oxides (Fe_d) in calcareous soils (Zhao et al., 2006; Cao and Li, 1988). The water-soluble Pi is dominated by orthophosphate, which can be directly absorbed by crops, but its content in the soil is very low (Bucher, 2007). In most soils, orthophosphate is dominated by $H_2PO_4^-$ in soil solution with pH=3-7, and HPO_4^{2-} in soil pH=7-12; there is litter PO_4^{3-} when the soil pH is below 11 (Sanyal et al., 1991; Gao et al., 2001; Yu et al., 2003).

Soil Po generally accounts for 7-60% of total P, and is related to the content of organic carbon in soil (Oehl et al., 2004). Po can be divided into non-biological and biological Po (Yan et al., 2016; Liu et al., 2013; Condron et al., 2005). Non-biological Po refers to some P compounds with high activity and stability, while biological Po refers to P components fixed by microorganisms. According to P structure, Po includes orthophosphate phosphomonoester, orthophosphate phosphodiester and phosphonate (Cade-Menun et al., 2000). The structure of orthophosphate phosphomonoester is $ROPO_3^{2-}$. R is carbon group, and one carbon group together with one orthophosphoric acid. The structure of orthophosphate phosphodiester is $R_1(RO)PO_2^-$, two carbon groups together with one orthophosphoric acid. The structure of phosphonates is $RP(O)(OH)_2$, including 2-aminoethylphosphoric acid (AEP), herbicides agent. Soil Po dominate by orthophosphate phosphomonoester, where inositol phosphate (IHP) accounts for the highest proportion (Dalal, 1977). It mainly includes myo inositol phosphate (myo-IHP), chiro-IHP, scyllo-IHP and neo-IHP. Myo-IHP, also named phytic acid, is the most common Po compound in the organophosphorus component.

P dynamics were frequently explored via sequential extraction technique, which character different inorganic P (Pi) and organic P (Po) fractions based on their solubility (Condron and Newman, 2011; Tiessen and Moir 2007) (Fig.1-3).

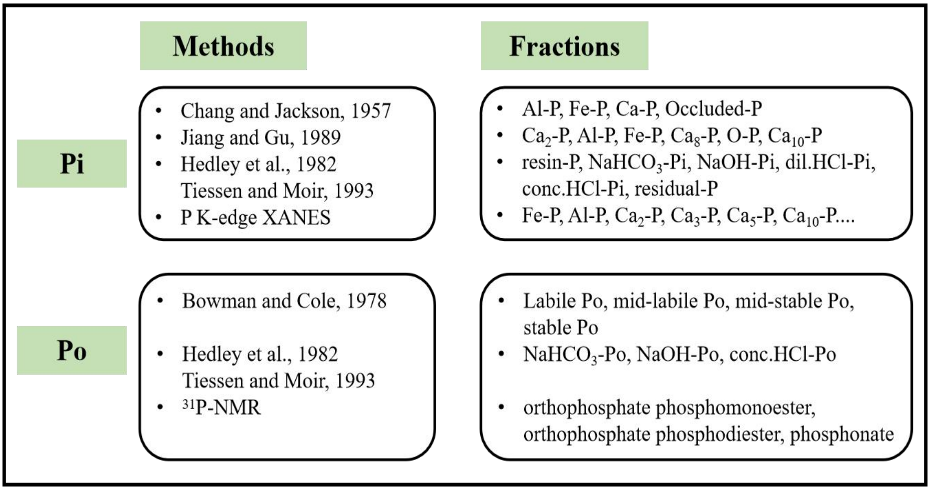


Figure 1-3 Measurement method of P forms

Chang and Jackson (1957) classified the Pi into: Al-P, Fe-P, Ca-P and the reductant-soluble phosphate. This method is suitable for neutral and acidic soils.

Jiang and Gu (1989) established a sequential extraction method of Pi forms suitable for calcareous soil, according to the high proportion of Ca-P and its different availability in alkaline soil. It further divided Pi forms into dicalcium phosphate (Ca$_2$-P), octacalcium phosphate (Ca$_8$-P) and decacalcium phosphate (Ca$_{10}$-P), Al-P, Fe-P and occluded-P (O-P). Ca$_2$-P and Al-P are considered as the most effective P sources, Fe-P and Ca$_8$-P are slow P sources, and O-P, Ca$_{10}$-P can’t directly be used by plant (Jiang and Gu, 1989). Specific composition and availability of soil Pi were affected by soil types and fertilization regimes. Wang (2019) found that the Pi forms used by plants mainly came from Ca$_8$-P, Al-P, Fe-P in the depletion state of P in calcareous fluvo-aquic soil. Yang et al. (2019) reported that the Al-P with high solubility is the potential source of available P, then is Ca-P in black soil. A study showed that the order of contribution rate of P fractions to Olsen-P is: Ca$_2$-P, Ca$_8$-P and Fe-P in yellow soil (Zhang et al., 2016). Wang et al. (2014) reported that Al-P/Fe-P showed significant linear positive correlation with Olsen-P, and its change decided the P availability in red soil.

Hedley sequential extraction method and its modification by **Tiessen and Moir** is widely used to characterize soil P fractions (Fig. 1-4) (Hedley et al., 1982; Tiessen and Moir, 1993). According to the method, 9 different kind of P fractions are extracted, including: (1) Resin-P, extracted through the anion exchange resin membrane, is immediately used by plant; (2) NaHCO$_3$-P (Pi and Po), extracted with 0.5 mol L^{-1} NaHCO$_3$ (pH=8.5), NaHCO$_3$-Pi is released by ligand exchange with bicarbonate ion, and available to plants in a short period, $NaHCO_3$-Po that can be uptake by plants after being mineralized; (3) NaOH-P (Pi and Po), extracted with 0.1 mol L^{-1} NaOH, combines with amorphous and some crystalline Fe and Al oxide and shows low availability to plants; (4) dil.HCl-Pi, extracted with 1.0 mol L^{-1} dilute HCl, is bound with Ca and will be utilized by plants after weathering; (5) conc.HCl-P (Pi and Po), extracted by concentrated HCl; and (6) residual-P, obtained by digestion with H_2SO_4 and H_2O_2 are hardly absorbed and utilized by plants because of their low solubility (Hou et al., 2016; Condron and Newman, 2011; Yang and Post, 2011; Tiessen and Moir, 1993, 2007; Frossard et al., 2000; Cross and Schlesinger, 1995; Hedley et al., 1982).

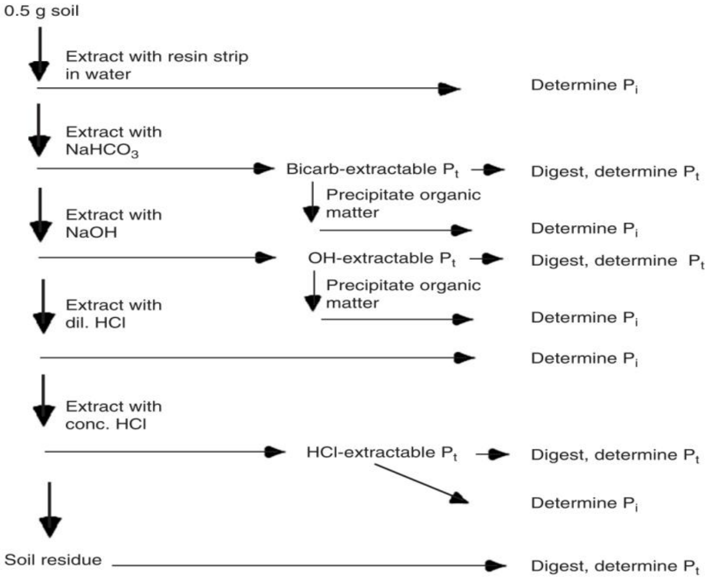


Figure 1-4 Sequential extraction procedure of soil P (Tiessen et al., 1984)

Synchronic-based X-ray absorption near-edge fine structure (P K-edge XANES): According to the unique absorption spectral characteristics of different phosphates, XANES was directly used to identify soil P fractions without damage and pretreatment in soil samples (Koch et al., 2018; Yan et al., 2018; Beauchemin et al., 2003b). This technology is mainly applied to the character the Pi molecular morphology (Liu et al., 2017, 2019; Toor et al., 2006). This is due to the lack of unique spectral characteristics of many Po compounds (Liu et al., 2018). The spectra of soil samples were compared with that in P standard samples, soil Pi fraction is quantified through least square fitting method (Ravel and Newville, 2005).

Bowman-Cole method (Bowman and Cole, 1978): This method divided the Po fractions into labile Po (extracted with 0.5 mol·L^{-1} $NaHCO_3$ (pH=8.5)), mid-labile Po (acid-soluble Po and alkali-soluble Pi), mid-stable Po (presented in nonprecipitated fulvic acid) and stable Po (present in precipitated humic acid). Labile P was easily absorbed by plants, while stable Po was hardly to be mineralized and couldn't be absorbed by plants.

Solution ^{31}P nuclear magnetic resonance (^{31}P-NMR spectroscopy) can accurately identify the peak value and the corresponding Po compounds to characterize soil Po fractions (Cade-Menun and Preston, 1996). Soil samples are extracted with 0.25 mol L^{-1} NaOH and 0.05 mol L^{-1} Na_2EDTA, which can remove some paramagnetic ions and degrade some organophosphorus compounds (OPCs) (Liu et al., 2019; Young et al., 2013; Doolette et al., 2009; McDowell et al., 2005). Generally, mononucleotides in orthophosphate monoesters are considered as degradation products of RNA, while α-glycerophosphate and β-glycerophosphate are considered as degradation products of phospholipid (Vestergren et al., 2012; Doolette et al., 2009; Turner et al., 2003). The conditions of soil extraction determine the success of the ^{31}P-NMR method (Cade-Menun and Liu, 2014). The soil samples state, selection of extractants, the extraction time and ratio of soil to water should be carefully considered in the same experimental analysis (McDowell and Koopmans, 2006; Lehmann et al., 2005; Cade-Menun and Preston, 1996). This is because the characteristics of P fraction vary under different conditions (Liu et al., 2018, 2014; Turner and Blackwell, 2013; Turner et al., 2012; Cade- Menun et al., 2010; Ding et al., 2010; Dou et al., 2009; Bünemann et al., 2008). Therefore, representative samples should be selected for scanning to obtain appropriate delay time and good spectra. For P-NMR profiles of soil samples, the chemical shifts of P compounds are generally between 25 and-25ppm (Fig. 1-5) with ^{31}P-NMR spectroscopy. The chemical shifts of phosphonates, orthophosphate phosphomonoester, orthophosphate phosphodiester, pyrophosphate and Polyphosphate are 25−7, 7−2.5, 2.5−4.4, -4−5, and -4.4 to-25 ppm, respectively (Cade-Menun, 2015). There exist great differences in the conclusions of Po fractions on the plant effectiveness (Jiang et al., 2014; Zhang and Li, 1998).

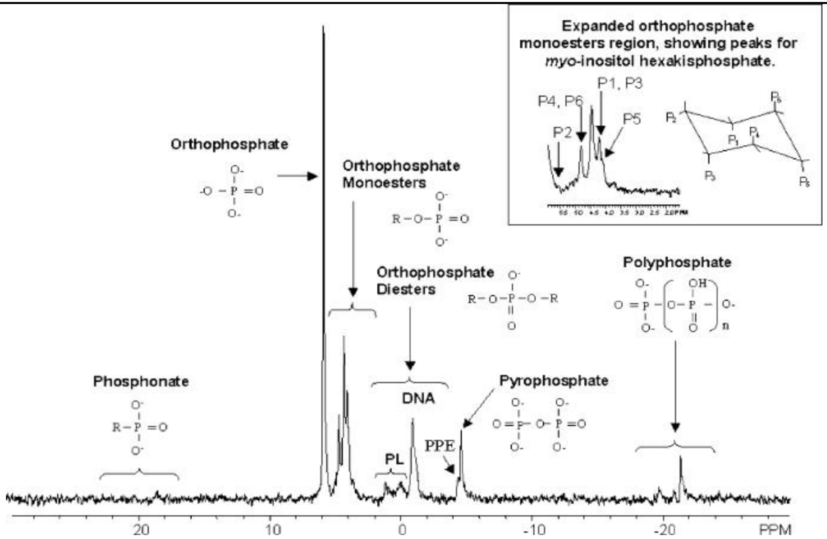


Figure 1-5 A solution ^{31}P-nuclear magnetic resonance (NMR) spectrum of a forest floor sample extracted with NaOH-EDTA (Cade-Menun, 2005)

Sequential extraction methods couldn't reflect the special fraction of Pi and Po (Condron and Newman, 2011; Negassa and Leinweber,2009). P K-edge XANES and ^{31}P-NMR spectroscopy are used in more and more studies to characterize the soil P fractions in the molecular level (Liu et al., 2015, 2020; Qin et al., 2020; Turner, 2004). However, until now, multiply techniques were used to comprehensively characterize the P fractions are few in the soil.

The application of P fertilizer shows significant direct effect on P fraction (Pizzeghello et al., 2014; Wang and Liang, 2014). Under long-term experiments, all P fraction contents decreased in soil without P fertilizers, while each P fraction increased in soil with P fertilizer (Zhang et al., 2006). Especially, the proportion of high active P fraction was higher in M treatment than that in NPK treatment (Yan et al., 2018; Shi et al., 2015). Under long-term P fertilizer input, the accumulate P were mainly Ca_2-P, Ca_8-P and Al-P with Jiang and Gu method in red soil, black soil and fluvo-aquic soil (Wang et al., 2019; Zhou and Zhang, 2005; Wang 2002). Combination of Hedley sequential method and P K-edge XANES, Yan et al. (2018) found that the proportion of Fe-P and inositol hexakisphosphate (IHP) significantly were higher and stable Ca-P was lower in M treatment than that in NPK treatment in a calcareous soil. Liu et al. (2019) pointed out that the proportion of brushite and deoxyribonucleic acid (DNA) were increased in alkaline soil with mineral P fertilizer and increased the P availability.

The soil physicochemical properties affected the transformation of soil P (Hou et al., 2016; Barrow, 2015; Vitousek et al., 2010; Tiessen and Moir, 2007). SOM, Mehlich-3 extractable iron (M3-Fe), and Al_o in black soil, pH, SOM, total nitrogen

(TN), M3-Ca and M3-Fe in calcareous soil showed significant effects on the variances of soil P fractions ($P < 0.05$), respectively (Wang et al., 2022; Yan et al., 2018). Many studies reported that SOM showed significant positive correlation with high active P fractions (Qin et al.,2020; Kopittke et al.,2018; McDowell et al., 2016). The low pH caused by manure input, and the organic acids from decomposition of SOM could increase in the solubility of stable Ca-P and the transformation of Ca-P to labile and moderately labile P (Yan et al., 2018). Moreover, SOM addition can promote mineralization of Po into high active Pi content (Sun et al., 2020).

Fertilization is main agricultural measure. It could directly provide P source, or indirectly increase available P through interaction with soil compounds (Liu et al., 2019; Barrow et al., 2015). Under different fertilizer regimes, the P availability is different. So how fertilization affect P availability? Moreover, many previous studies have clarified P formation process and its influence mechanism with single soil factor. The soil is complex, and the influence of comprehensive factors on the formation and availability of P species is unclear. Can quantitatively analyze the influence of these factors on P availability?

2.4 The characteristics of soil P adsorption and desorption and its availability

P sorption-desorption characteristics play important roles in controlling soil P behavior (Bolster et al., 2020). Adsorption can determine the phytoavailability of P, and desorption can cause the P loss risk from soil (Wang and Liang, 2014; Lair et al., 2009). The adsorption of soil P includes anion (HPO^{2-}/HPO^{-}) exchange adsorption and coordination adsorption (Alimi et al., 2006). Anion exchange adsorption is that phosphate is adsorbed on the surface of soil minerals or clay by replacing other adsorbed anions (mainly the electrostatic force). Coordination adsorption refers to the exchange of phosphate with hydroxide ion (-OH) on the surface of soil colloid to form ionic bond or covalent bond. Ion exchange adsorption shows weaker adsorption ability, and the phosphate adsorbed on the soil is more easily desorbed by other anions, in comparison with coordination adsorption.

The characteristics of P adsorption and desorption in soil reflect the P distribution in soil solid and liquid phase, indicating the ability of soil to absorb and release P from external sources (Lu et al., 2003). Langmuir and Freundlich equations are often used to quantitatively describe phosphate adsorption and desorption isotherms (Lair et al., 2009). Good fitness between the P adsorption and desorption curve and models have been shown in many studies (Wang et al., 2019; Yang et al., 2019; Wang et al., 2013). The maximum adsorption capacity (Q_{max}), adsorption constant (K), buffering capacity of soil P (MBC), readily desorbable P (RDP) and P sorption saturation (DPS) were calculated according to Langmuir equation to evaluate the characteristics of P adsorption and desorption.

P input, fertilizer regime and soil factors are the main factor affecting characteristics of P adsorption and desorption (Fang et al., 2017; Quesada et al., 2011). The value of

Q_{max} and MBC was decreased and RDP and DPS increased in soil with P fertilizers than that without P fertilizers. Significant difference was reported in NPKM treatment than that in NPK treatment because of high P input and partial replacement of chemical fertilizer by organic manure (Wang et al., 2019; Yan et al., 2018). Under the same P input, higher value of DPS and P desorption rate, and lower value of MBC and P immobilization amount was found in M treatment than that in NPK treatment, indicating the mechanism difference of P input and fertilizer regime on characteristics of P adsorption and desorption (Liu et al., 2021).

Soil property is another important factor affecting the characteristics of P adsorption and desorption (Fang et al., 2017; Gérard, 2016; Pizzeghello et al. 2016; Quesada et al. 2011). Various soil mineral compositions determined the adsorption capacity to P. The adsorption capacity of soil to P in montmorillonite and hydromica is higher than that in kaolinite. Moreover, clay content and SOM, pH and metallic oxide show significantly effect on the adsorption of phosphate. Generally, clay content is significant positive correlation with P adsorption. Zhang et al. (2018) analyzed five textural fluvo-aquic soils found that the major soil factors for the P adsorption were clay, silt fractions, SOM and Fe_d contents, for the P desorption was sand content. Wang et al (2019) use redundancy analysis (RDA) test showed that SOM and total P, were the main factors causing the difference of P adsorption desorption characteristic parameters under long-term fertilization in black soil in China. Yang et al. (2019) also proved the importance of SOM on the P adsorption desorption characteristic in black soil with an incubation period of 30 days. Therefore, SOM has been identified as an important factor affecting soil P availability (Yan et al., 2013). The addition of SOM can decrease the adsorption capacity of soil to P due to the decomposition products such as humic acid and small molecular organic acid (Kang et al., 2009; Laboski and Lamb, 2004). These products can interact with metallic oxides through competition in P adsorption sites or altering surface charges and cause phosphates to be electrostatically repelled, and then decrease P adsorption capacity (Chen et al., 2020; Guppy et al., 2005; Hinsinger, 2001; Redel et al., 2007; Zamuner et al., 2008; Antelo et al., 2007). Yang et al. (2019) also proved the importance of SOM on the P adsorption and desorption characteristic in black soil with an incubation period of 30 days. Meanwhile, the concentration, crystallinity and SSA of metallic oxides to phosphate decides the adsorption and desorption ability of soil to P and the availability of soil P (Schaefer et al., 2018; Fink et al., 2016; Barrón and Torrent, 1996). Soil pH is another important factor influencing soil P mobility and activity, the change of soil pH can affect the process of chemical fixation and precipitation/ dissolution of P (Simonsson et al., 2018). The increase of pH in acidic soil can release soil P fixed by Fe and Al oxides (Jing et al.,2013).

3. Scientific questions and objectives

Fertilizer is most important factor affecting P availability, what are the difference in P availability under different fertilization? P forms in soil directly determine the P availability, how does P forms change under long-term fertilization? Moreover, traditional method can only measure the availability of P form. Spectroscopy techniques can identify the structures of specific Pi and Po on molecular level. Until now, multiply techniques were used to comprehensively characterize the P form are few in the soil. The formation of P species is affected by soil properties, such as pH and SOM, metal oxides and so on. Many previous studies have clarified P formation process and its influence mechanism of single soil factor, but the soil is complex, so how do soil properties comprehensively affect P forms? In the soil profile, the soil properties are varied and the subsoil have huge P reserves, however, until now the study of P forms and P availability in the soil profile isn't clear, which is important to evaluate P leaching management. Based on these questions, in this study, we analyzed the characteristics of P availability (Olsen-P, total P, P forms, and P adsorption-desorption) under different fertilization regimes. The latest multifactor statistical analysis was used to quantitatively analyze the effect of soil properties on P availability and its relative contribution rate. The results will ascertain the chemical mechanism of organic-inorganic fertilizer application in increasing the availability of accumulated P, and provide a theoretical basis for the efficient utilization of accumulated P in black soil and the scientific application of P fertilizer.

4. Objective

P is one of the macroelements necessary for plant growth, soil is the main source of plant P, and application of P fertilizer is one of the key measures to achieve high and stable grain yield (Yang et al., 2015). The phenomenon of soil P accumulation caused by excessive application of P fertilizer is very common in the world, especially in China (MacDonald et al., 2011). The average accumulation amount of P in soil reached 700 kg P_2O_5 hm^{-2}, which increases the waste of limited phosphate rock resources and risk of water pollution (Yan et al., 2016; Xu et al., 2015; Zhou, 2015; Bai et al., 2013). Only about 2-10% of the accumulated P in the soil can be converted into available P, and most accumulated P is converted into the insoluble P form in the soil (Khan et al., 2018; Medinski et al., 2018). Therefore, studying on improvement of the availability of soil accumulated P and fertilizer P use efficiency is of great significance for rational utilization of accumulated P in soil and scientific application of P fertilizer.

Long-term fertilizer experiment is an important platform for soil fertility research (Xu et al., 2015). It is concerned by more and more researchers around the world because of comprehensive evolution of soil fertility. In the same long-term experiment, without difference in climate and planting system, formalized system of soil management makes soil characteristics develop in specific directions, thus forming soils with different fertility characteristics (Cao et al., 2012; Rasmussen et al.,1998). Using it as a material to study the effect of different fertilization on the P availability could provide scientific data with adequately strong explanatory power.

Northeast black soil region is a main grain producing area and commodity grain base, and plays an important role in the national food security strategy in China (Chu et al., 2010). Unreasonable development and utilization affect the supply capacity of soil nutrients, especially the availability of P in black soil. P fraction, the characteristics of P adsorption and desorption were the direct factors deciding the availability of soil P. Therefore, it is necessary to study soil P availability by comparing characteristics of P fraction, adsorption, and desorption under different long-term fertilization to provide scientific basis for rational utilization resources and improvement the utilization rate of P fertilizer in black soil.

In this study, a long-term experiment field in northeast China was conducted to study the effects of long-term different fertilization on P availability. The technology roadmap of this research was shown in the Fig. 1-6. Firstly, soil samples in different treatments and soil profiles were chosen to analyze the P fraction distribution in time scale and vertical scale to reveal the underlying morphology mechanism under different fertilization (chapter II and III). Secondly, evaluation the characteristics change of P adsorption and desorption under different fertilization (chapter IV). Moreover, soil properties were determined to achieve the main influence factors affecting P fraction and adsorption-desorption. All this will comprehensive expound the effect of different fertilization on P availability.

To expound on the above main objectives, the specific aims are as follows:

1. understand the evolution rule of soil total P, Olsen P and PAC under long-term fertilization.

2. comprehensively evaluate the P fractions under long-term different fertilization using multiple techniques (P K-edge XANES, solution ^{31}P-NMR and modified Hedley sequential extraction).

3. investigate the temporal and profile distribution characteristics of different P fractions and its response to P availability under long-term different fertilizer treatments.

4. investigate the characteristics of P adsorption and desorption in soil profile and its response to P availability under long-term different fertilizer treatments

5. identify the main soil factors affecting P fractions adsorption and desorption characteristics by principal components analysis (PCA) and redundancy analysis (RDA).

6. evaluate the environmental risk of P loss

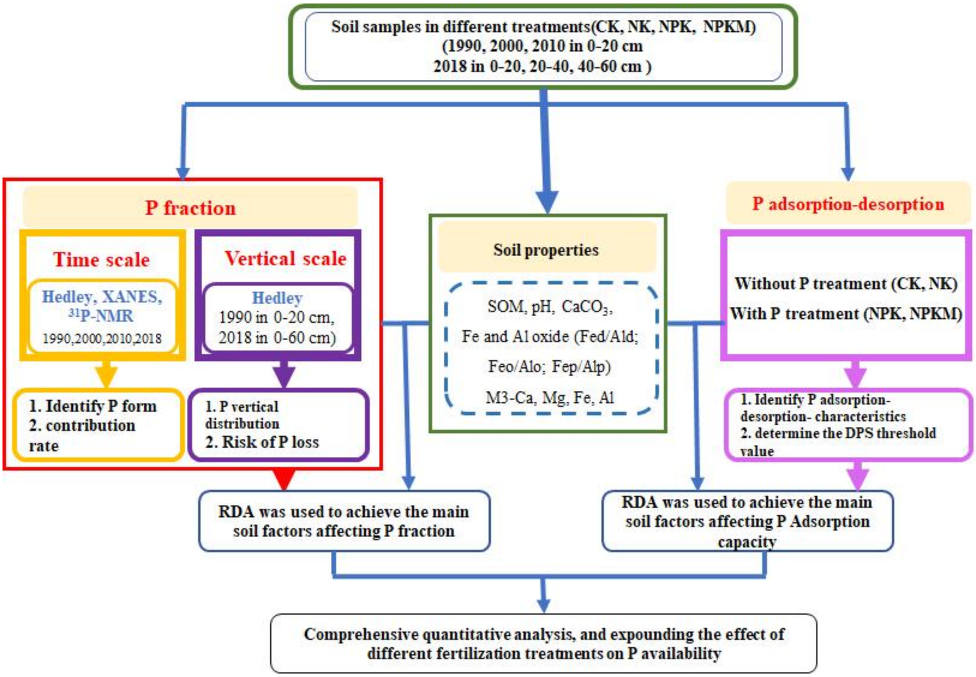


Figure 1-6 The technology route of this thesis

5. Overview of the chapters

This thesis was structured into the following 5 chapters:

Chapter I General introduction.

In this chapter, the general knowledge of the thesis and objectives were shown. We presented the difference of P availability under long-term fertilization as well as the effects of P fractions, P adsorption-desorption characteristics and soil properties, and pointed out the problems and knowledge gaps in this part.

Chapter II The phosphorus availability in black soil is determined by inorganic phosphorus fraction under long-term different phosphorus fertilization experiments

The objectives of this chapter were to clarify the effects of different fertilization regimes on soil P availability and its driving factors. In this study, a 29-year long-term experiment started in 1990 with a continuous maize monoculture was chosen. Three treatments including: no fertilizer (CK), chemical N, P, K fertilization (NPK), and NPK plus manure (NPKM) were investigated. Modified Hedley sequential extraction method, solution ^{31}P nuclear magnetic resonance (^{31}P-NMR) and P K-edge X-ray absorption near-edge (XANES) and soil properties were investigated.

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

The objectives of this chapter were to clarify the vertical distribution characteristics of different P fractions and the main soil factors affecting the P fractions under long-term fertilization. Four treatments (CK, NK, NPK, and NPKM) from a 29-year long-term experiment in black soil with maize cropping were involved. We analyzed soil P uptake and P balance, P fractions with modified Hedley sequential method, and soil properties in different soil layers.

Chapter IV Phosphorus adsorption and desorption characteristics as affected by long-term phosphorus application in black soil

The objectives of this chapter were to explore the difference characteristics of P adsorption and desorption, quantitatively explain its relationship with soil properties and determine the DPS threshold value in the soil without and with P fertilizers. The long-term field trial on black soil started in 1990 in Gongzhuling City, Jilin Province. Four treatments imposed were CK, NK, NPK, and NPKM. We analyzed soil physicochemical properties. Soil P adsorption-desorption characteristic parameters [maximum adsorption capacity (Q_m), adsorption constant (K_Q), maximum soil P buffering capacity (MBC), degree of P sorption saturation (DPS), maximum desorption capacity (D_m), and desorption ratio (D_r)] in different soil layers were determined using isothermal adsorption and desorption experiment.

Chapter V General discussion, conclusions, and perspective

In this chapter, the meaning, importance, and relevance of general results in the four main chapters were discussed. We presented the answers to the main questions, suggestions for the future research and the new knowledge for the future study.

Chapter II

The phosphorus availability in black soil is determined by inorganic phosphorus fraction under long-term different phosphorus fertilization experiments

From: Wang, Q., Zhang, N. Y., Chen, Y. H., Qin, Z. H., Jin, Y. W., Zhu, P., Peng, C., Colinet, G., Zhang, S. X., Liu, J. The phosphorus availability in black soil is determined by inorganic phosphorus fraction under long-term different phosphorus fertilization experiments. Agronomy, 2022, 12, 2364.

Abstract

Understanding the effects of a fertilization regime on the long-term accumulation and transformation of soil phosphorus (P) is essential for promoting the development of sustainable management of soil P. Based on a 29-year field experiment in Mollisol, the compositions and changes of P forms using a modified Hedley sequential extraction method, solution ^{31}P-NMR and P K-edge XANES and soil properties were investigated under continuous mono maize with and without manure (NPKM and NPK). Results showed a stronger positive related coefficient between soil total P and labile P, and mid-labile P fraction was found in NPKM than in NPK treatment. It indicated NPKM could improve the availability of soil accumulated P and reduce its transformation to stable P. Accumulated inorganic P (Pi) was dominated by aluminum phosphate (Al-P) and monobasic calcium phosphate monohydrate (MCP) for NPK treatment, Al-P, MCP, and tricalcium phosphate for NPKM treatment with XANES analysis, which contributed to the P availability in Mollisol. Moreover, the proportion of IHP with XANES and ratio of orthophosphate diesters to monoesters in NPK compared to NPKM indicated the higher Po lability with NPK treatment. Pi, especially $NaHCO_3$-Pi and NaOH-Pi, were the potential sources of resin-Pi. Soil organic matter (SOM), organic-bound iron, and alumina oxide (Fe_p+Al_p) showed significant influence on the transformation of P forms. Our research suggested that due to the rise in SOM and Fe_p+Al_p, the fertilization regime significantly increased most highly active soil P fractions, especially in NPKM treatment. This work gives new insight into sustainable P management, which benefits the reduction in soil P accumulation.

Keywords: P availability; P speciation; molecular speciation; solution NMR; P-XANES

1. Introduction

Phosphorus (P) fertilization is the key to meeting crops' growth needs and productivity (Qin et al., 2020; Medinski et al., 2018). Mineral P fertilizer application has been widely used in agronomic practice to ensure the sustainable development of agriculture over the past decades (Zhang, 2017). However, due to the low P use efficiency in the current season, excessive mineral P fertilizer input to increase crop yield has caused environmental risks, i.e., less soil P retainment and water eutrophication (MacDonald et al., 2011). Animal manure contains a high concentration of P (Cade-Menun, 2011). A combination of mineral P fertilizer with manure (NPKM) has gradually become a popularized fertilization practice (Wang et al., 2018, 2022; Liu et al., 2020). Specifically, higher content and proportion of plantavailable P easily absorbed by crops are observed in NPKM treatment than that in NPK treatment (Wang et al., 2018; Wu et al., 2017). Therefore, a thorough understanding of how the fertilization regime affects P availability by altering P transformation in the soil is essential to develop sustainable P management strategies.

Knowledge of existing soil P species is essential to the biogeochemical process of the P cycle and partly determinants the effectiveness of soil P on crop growth (Yang et al., 2021). The modified Hedley sequential method is widely used to characterize different inorganic P (Pi) and organic P (Po) fractions based on their solubility (Tiessen and Moir 2007; Hedley et al., 1982). Recently, advanced spectroscopy techniques, i.e., P Kedge XANES spectra and solution ^{31}PNMR spectroscopy, were utilized to identify the chemical forms and structures of specific Pi and Po fractions, respectively, on the molecular level (Liu et al., 2019, 2013). Professional and correct interpretation of data in spectroscopy techniques can provide a comprehensive and reliable understanding of soil P chemical nature when combined with the modified Hedley sequential method (Liu et al., 2019, 2015, 2013; Vogel et al. 2016; Toor et al., 2006). Meanwhile, a growing body of literature has shown the feasibility and advances of their integrated utilization in soil P speciation studies (Liu et al., 2018; Weyers et al., 2016; Abdala et al., 2015; Kizewski et al., 2011; Beauchemin et al., 2003). However, so far, studies on the difference in soil P forms under different long-term fertilization regimes using these advanced analytical techniques are few.

P availability is determined by P-existing species present in the soil (Liang et al., 2017). Solution Pi pool can be directly used by plants, while a large portion of P fractions interact with soil solid-phase. Structural equation modeling (SEM) enables quantitatively evaluating the importance of different P fractions transformations in regulating the availability of P in soil via a comparison between the observed covariance matrix and implicit covariance matrix in the current model (Hou et al., 2018, 2016). At present, the quantitative analysis of the transformation of P fractions by SEM is mainly focused on unfertilized or forest soil, highlighting the importance of Po fraction in soil P dynamics (Yang et al., 2021; Hou et al., 2016; Tiessen et al., 1984). With the continuous input of fertilizer P, more available P is accumulated in the form of Pi in the soil, influencing the transformation process of soil P (Yan et al., 2018; McDowell and Condron, 2012). So far, few pieces of research focus on direct and indirect quantitative effects of various P forms on P availability.

Changes in soil properties caused by fertilization affect soil P forms (Yang et al., 2019). Many studies have shown a positive correlation between soil organic matter (SOM) and highly active Pi components (Poblete-Grant et al., 2020; Qin et al., 2020; van der Bom et al., 2019). SOM could interact with metal oxides in many ways (competitive adsorption sites, cationic bridges, etc.) to form organomineral complexes (Poblete-Grant et al., 2020; Redel et al., 2016; Guppy et al., 2005). It can reduce the adsorption of metal oxides to P and increase the mineralization of Po and decomposition of Pi (Wang et al., 2019; Wang et al., 2015). Furthermore, soil pH is an essential influence factor on P fractions (Romany à and Rovira, 2009; Chang et al., 1991). The decrease in pH in calcareous soil can promote the conversion of stable crystalline Ca-P species to relatively soluble Ca-P and adsorbed P, and the increase in pH in neutral or acidic soils can reduce the adsorption of metal oxides to P (Nobile et al., 2020; Yan et al., 2018). Conversely, the opposite result about the positive correlation between soil pH and stable P is obtained in some calcareous soils (Liu et al. 2020; Kar et al., 2017). Therefore, understanding how soil properties affect the transformations of soil P fractions under a fertilization regime is very important to evaluate the sustainability of the fertilization regime and the long-term P speciation.

In northeast China, Mollisol (USDA Soil Taxonomy), rich in soil organic matter and P, is the most important major-producing region and commercial grain base (Yao et al., 2017; Soil Survey Staff, 2014). A long-term field trial in Mollisol provides important resources to investigate the influence of a fertilization regime on speciation and transformation of soil P, which cannot be achieved by a short-term experiment (Liu et al., 2020). In this study, two long-term fertilization treatments were selected, one with chemical fertilization (NPK) and the other with manure plus NPK (NPKM). We hypothesized that the concentration of Fe and Al oxides with high activity increases soil P availability in Mollisol because of the formation of mineral-C associations. The overall goal of the study is to clarify the effects of different fertilization regimes on soil P availability and its driving factors. The specific research objectives were to (1) comprehensively evaluate the P fractions under different fertilization measures using multiple techniques (P K-edge XANES, solution ^{31}P-NMR, and modified Hedley sequential extraction), (2) quantitatively analyze the contribution rate of P fractions to P availability in Mollisol via a structural equation model, and (3) identify the main influencing factors of P fractions by principal components analysis (PCA) and redundancy analysis (RDA).

2. Materials and methods

2.1 Study site and soil sampling

The long-term field trial, set up in 1989 in Gongzhuling, Jilin province, China (124◦4803400 E, 43◦3002300 N), belongs to the Chinese National Soil Fertility and Fertilizer Efficiency Monitoring Base of Mollisol. The monitoring base belongs to a temperate continental monsoon area with four distinct seasons, and the mean annual temperature and precipitation are 4–5 ◦C and 590.7 mm, respectively. The soil is classified as Mollisol in USDA Soil Taxonomy (Soil Survey Staff, 2014). The average properties at the start of the field trial are shown in Table 2-1.

Table 2-1 Physical and chemical properties of studied soil in the experiment in 1989.

Soil depth	pH	Bulk density	Soil organic matter	Total N	Total P	Total K	Olsen-P	Available K
cm		g cm^{-3}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
0-20	7.6	1.19	20	1.34	0.61	16.36	11.8	190

The following treatments were considered in this study: (1) unfertilized control plot (CK); (2) mineral N, P, K fertilizer (NPK) and NPK plus manure (NPKM). A total of 165 kg N ha^{-1} (urea), 36 kg P ha^{-1} (diammonium phosphate), and 68 kg K

ha^{-1} (potassium sulfate) were applied in the NPK treatment, and 50 kg N ha^{-1}, 36 kg P ha^{-1}, and 68 kg K ha^{-1} of the above-mentioned chemical fertilizers were applied in the NPKM treatment. The organic fertilizers were pig manure (1990–2004) and cattle manure (2005–2018), with 115 kg N ha^{-1}, 39 kg P ha^{-1}, and 77 kg K ha^{-1}. The cropping system was a continuous maize monoculture in this long-term field experiment. Details about the background information of the field trial and crop yields have been described by previous studies elsewhere (Wang et al. 2018; Liu et al., 2017). Each treatment plot covered 400 m^2 (57.18 × 7 m) in a randomized block design; three replications were considered for each treatment. In each replicate, five to seven topsoil samples (0–20 cm) were randomly sampled at “S” shaped distribution points after crop harvest in 1990, 1995, 2000, 2005, 2010, and 2018. The field-moist samples were gently broken apart, mixed thoroughly, air-dried, sieved to 2 mm, and stored for further analysis. Soil sample collected in the CK treatment in 1990 was treated as reference soil.

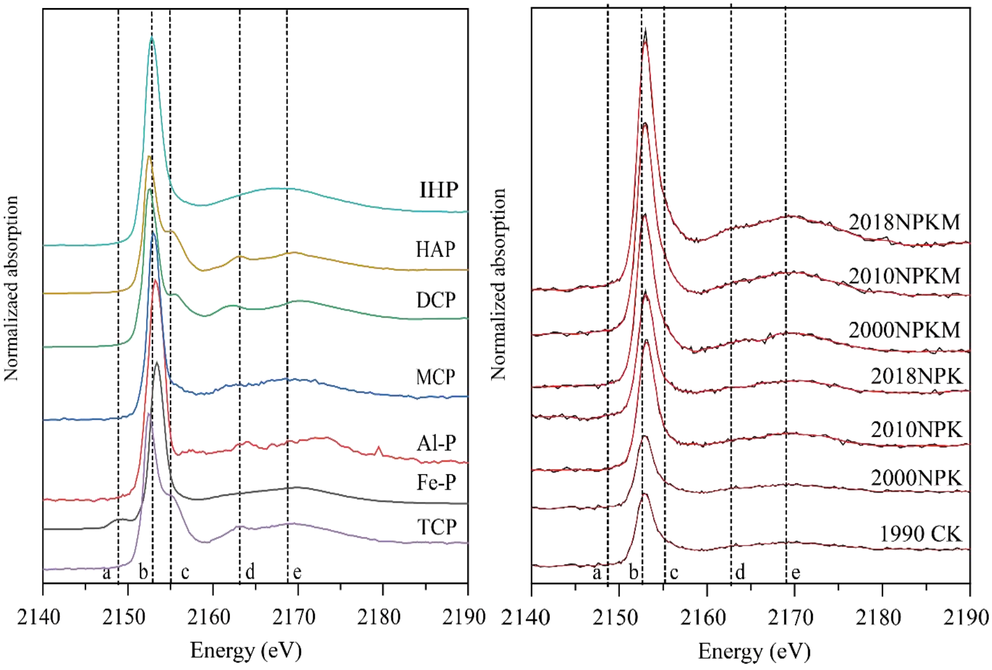
Vitriol acid–potassium dichromate oxidation was used to measure SOM content (Skjemstad and Baldock, 2007). Soil pH was determined from a 1:2.5 soil to distilled water (w/v) (Lu 1999). Crystalline iron and aluminum oxide (Fe_d and Al_d, respectively), amorphous Al and Fe oxide (Al_o and Fe_o, respectively), organic-bound iron and alumina oxide (Al_p and Fe_p, respectively) were extracted using $Na_2S_2O_4$-$Na_3C_6H_5O_7$-$NaHCO_3$ (DCB), 0.2 M ammonium oxalate (pH 3.0), and 0.1 M sodium pyrophosphate diphosphate (pH 10), respectively (Mehra and Jackson, 2013; Loveland and Digby, 1984; Mckeague et al., 1971). Then, those extracted Fe and Al oxides were determined by using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Lu, 1999). Mehlich-3 extracting solution (0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13 M HNO_3 + 0.001 M EDTA) was used to determine Ca (M3-Ca), Mg (M3-Mg), Fe (M3-Fe), and Al (M3-Al). All elements in the Mehlich-3 solutions were measured with ICP-OES (Mehlich, 2008).

2.2. Modified Hedley Sequential Fractionation

The modified Hedley sequential extraction method was chosen to distinguish different P fractions in collected soil. Briefly, 1.00 g soil sample was sequentially fractionated with the following extractants: (1) 2 resin strips + 30 mL deionized water to extract resin-P; (2) 0.5 M 30 mL $NaHCO_3$ (pH 8.5) solution to extract total and inorganic P on $NaHCO_3$ extract ($NaHCO_3$-Pt and $NaHCO_3$-Pi); (3) 0.1 M 30 mL NaOH to extract NaOH-Pt and NaOH-Pi; (4) 1 M 30 mL HCl to extract dil.HCl-Pi; (5) 10 mL concentrated HCl to extract conc.HCl-Pt and conc.HCl-Pi; (6) concentrated H_2SO_4-H_2O_2 to digest and extract the residual P at 360°C (Yang et al., 2021). All extract solutions were shaken and centrifuged. Each filtered supernatant was divided into two parts. One was directly used to determine the Pi fraction with colorimetric, and the other was digested with ammonium persulfate before being analyzed with molybdate colorimetry. The content of Po ($NaHCO_3$-Po, NaOH-Po, and conc.HCl-Po) was determined by the difference between Pt and Pi in each extract, respectively (Yang et al., 2021). Resin-P represented a soil soluble Pi pool, and $NaHCO_3$-Pi was thought to be released by ligand exchange with the bicarbonate ion (Yang and Post, 2011; Cross and Schlesinger, 1995). $NaHCO_3$-Po could be utilized after being mineralized (Bowman and Cole, 1978). NaOH-Pi fractions were considered to consist of Al_o/Fe_o and some Fe_d/Al_d (Yang et al., 2021). The dil.HCl-Pi was associated with calcium (Ca); it could be utilized by plants after weathering and release of primary mineral Ca-P (Yang and Post, 2011; Tiessen et al., 1984). Generally, labile P was thought to be the sum of resin-P, $NaHCO_3$-Pi, and $NaHCO_3$-Po; NaOH-Pi, NaOH-Po, and dil.HCl-Pi index mid-labile P , conc.HCl-Pi, conc.HCl-Po and residual P indicate a stable P pool which is in low availability (Condron and Newman, 2011; Tiessen and Moir, 2007; Hedley et al., 1983, 1984).

2.3 Synchrotron-based P K-edge XANES spectroscopy

Reference P standard and soil samples were analyzed using P K-edge XANES spectroscopy at the 4B7A soft X-ray beamline of the Beijing Synchrotron Radiation Facility , Beijing, China. The electron energy of the storage ring operated at 2.2 GeV , and the maximum beam current was 250 mA. After being air-dried, finely ground, and sieved (0.5 mm particle size), the soil samples were thinly spread over a P-free and double-sided carbon tape and then placed on a sample holder to collect XANES data (Schmieder et al., 2018). P standard samples were measured under total electron mode without self-absorption effects, P reference spectra were collected in partial fluorescence yield mode; in the meantime, multiple spectra for each sample were collected and averaged (Li et al., 2019; Yan et al., 2018). The spectra of P standards included iron phosphate dihydrate [Fe-P , $FePO_4{\cdot}2H_2O$], aluminum phosphate [Al-P, $AlPO_4$], dibasic calcium phosphate [DCP, $CaHPO_4{\cdot}2H_2O$], monobasic calcium phosphate monohydrate [MCP, $Ca(H_2PO_4)_2{\cdot}H_2O$], tricalcium phosphate [TCP , $Ca_3(PO_4)_2{\cdot}xH_2O$], hydroxyapatite [HAP, $Ca_5(PO_4)_3OH$], and inositol hexakisphosphate (IHP). The characteristic features of P K-edge XANES reference spectra of the calibrated P standards samples are shown in Fig. 2-1A. The characteristic post-white linke peak b and an oxygen resonance peak e were at 2152 eV and 2169 eV , respectively (Liu et al., 2018). Specifically, the pre-edge peak a (2148.0 eV) was the characteristic feature of Fe-associated P (Fe-P), the shoulder peak c (around 2155 eV) and peak d (approximately 2162.5 eV) were for Ca-associated P (Ca-P) (Toor et al., 2005; Zuo et al., 2015). All the XANES data, such as spectra averaging, background correction, and normalization, were analyzed with ATHENA (V ersion 0.9.26, Amazon Web Services, Inc., Seattle, WA, USA) (Ravel and Newville, 2005). The beamline energy was calibrated to 2149 eV (E0) using the first derivative peak of the $AlPO_4$ standard (Beauchemin et al., 2003). The improvement of the signal-to-noise ratio of spectra was realized through multiple scans for each sample. Linear combination fitting (LCF) of the sample spectra was conducted using the spectral region between −10 eV to 15 eV relative to E0 to identify the P species and estimate their proportions. The sum weights of all the P standards were forced to 1. The goodness-of-fit was assessed by the R-value and chi-squared values, and the P standards yielding the best fit were regarded as the most possible P speciation in the investigated soil samples.



(A) (B)

Figure 2-1 (A)The P K-edge XANES reference spectra of P standards; (B) The P K-edge XANES reference spectra of soil samples from long-term different P fertilization regime. The red lines represent the LCF for the studied soil sample spectra (B).

Note: The dashed lines indicate spectral features for different P compounds. (a) Fe-P (2148.0 eV), (b) absorption edge (white line) (2153 eV), (c)-(d) Ca-P (2155.0–2162.5 eV) (e) oxygen oscillation (2169.0 eV). Al-P, aluminum phosphate ($AlPO_4$), Fe-P, iron phsphate dihydrate [$FePO_4·2H_2O$], DCP, dibasic calcium phosphate ($CaHPO_4·2H_2O$), MCP, monobasic calcium phosphate monohydrate [$Ca(H_2PO_4)_2·H_2O$], TCP, tricalcium phosphate [$Ca_3(PO_4)_2·xH_2O$], HAP, hydroxyapatite, IHP, inositol hexaphosphate.

2.4 Solution ^{31}P-NMR spectroscopy

Solution ^{31}P-NMR was performed to classify the P composition of soil and manure samples based on the method described by Liu et al. (2020, 2019). Briefly, 3.00 g samples were extracted with 30 mL 0.25 M NaOH + 0.05 M Na_2-EDTA solution (16 h) at 20 °C, and centrifuged (5000 rpm, 30 min). After freeze-drying (−80 °C), the subsample was successively re-dissolved into 0.65 mL following solutions, D_2O, deionized water, and the extracting solution (0.25 M NaOH + 0.05 M Na_2EDTA), and 0.4 mL 10 M NaOH. Then, the solution was centrifuged and transferred into a 10-mm probe for NMR analysis. Solution ^{31}P-NMR spectra were obtained through a Bruker Avance 500 MHz spectrometer. NMR parameters were 90° pulse, 5 s relaxation delay, 0.68 s acquisition time, 20 °C, 2200–3500 scans, 12-Hz spinning, and no proton decoupling as described previously (Liu et al., 2020). Along with the peak of orthophosphate standardized at 6 ppm, the signals, and chemical shifts (ppm) were used to identify the P compounds according to the publications (Cade-Menun, 2015) and by spiking samples with reference standards (α− and β −glycerophosphate, myo-IHP, adenosine 5' monophosphate, and choline phosphate) (Liu et al., 2019). Generally, the degradations, including mononucleotides, α− and β −glycerophosphate, were considered diesters rather than monoesters (Schneider et al., 2016; Young et al., 2013). Signal areas were integrated with MestReNova (Version 11.0, Mestrelab Research, Spain).

2.4 Statistical analysis

The mean and standard error of soil P parameters and soil properties were reported. Analysis of variance (ANOVA) was used to analyze normality and homogeneity of measured variables. Redundancy analysis (RDA) to identify the dominant soil properties that could explain the changes in soil P fractions was performed using vegan package (Version 2.5–7) in R software (Version 1.3.1073, RStudio, USA). Structural equation modeling (SEM) was applied to explore the transformations of different P fractions, the lavaan package, along with the lavaan.survey package in R software Structural equation modeling (SEM) was applied to explore the transformations of different P fractions, the lavaan package (version 0.6–7) along with the lavaan.survey package (version 1.1.3.1) in R software (Version 1.3.1073, RStudio, USA) was used to analyze SEM. A chi−square test (χ^2) was carried out to investigate the overall goodness of fit and adequacy of the model. The P value > 0.05 indicated no statistical difference was found between covariance matrices produced by model fits and observed covariance matrices (Grace et al., 2010). In addition to the chi−square test, the comparative fit index (CFI) and standardized root mean square residual (SRMR) were used to validate the goodness of fit. The model fit index of CFI value > 0.95 and the SRMR value < 0.08 suggest a good fit (Rosseel, 2010).

3. Result

3.1 Soil total P and its relationship with P fraction using modified Hedley sequential method

Soil total P exhibited a linear decrease in CK treatment over time (K = −0.0024, R2 = 0.78*). Labile P and stable P, especially the P fraction of resin-P, NaHCO3-Po, NaOH-Pi, conc.HCl-Pi and conc.HCl-Po were the main depleted P pool, which showed a significantly positive relationship with total P in CK treatment (Fig. 2-2 and A1-A, D, G). Under P fertilization, soil total P significantly increased over time and positively related to labile P, mid-labile P, and stable P fractions (Fig. 2-2-A, C, D). Higher correlation coefficients between total P and labile P and mid-labile P were exhibited in NPKM treatment (K=277, R^2=0.96**; K=536, R^2=0.99**, respectively) than that in NPK treatment (K=115, R^2=0.96 **; K=491, R^2 =0.99**, respectively). Regardless of the P fertilization regime, the accumulated P in the soil was mainly transferred into the Pi fraction, accounting for 79.3–92.6%. Specifically, the transformation ratio of resin-P, $NaHCO_3$-Pi, and dil.HCl-Pi was higher; 0.84, 2.47, and 1.31 times in NPKM treatment than in NPK treatment (Fig. 2-S1).

The SEM revealed the P transformations in Mollisol (Fig. 2-3). This model reasonably fit our causal hypothesis (χ^2 = 7.27, P = 0.51, CFI = 1.00, RMSEA = 0.00, SRMR = 0.03), and could explain 96% of the variance. According to the result of SEM, Pi fractions showed the main influence on the resin-Pi. $NaHCO_3$-Pi and NaOH-Pi directly affected resin-Pi fraction with path coefficients of 0.72 and 0.35, respectively. Dil.HCl-Pi and stable P showed an indirect effect on resin-Pi by altering the concentration of NaOH-Pi or $NaHCO_3$-P.

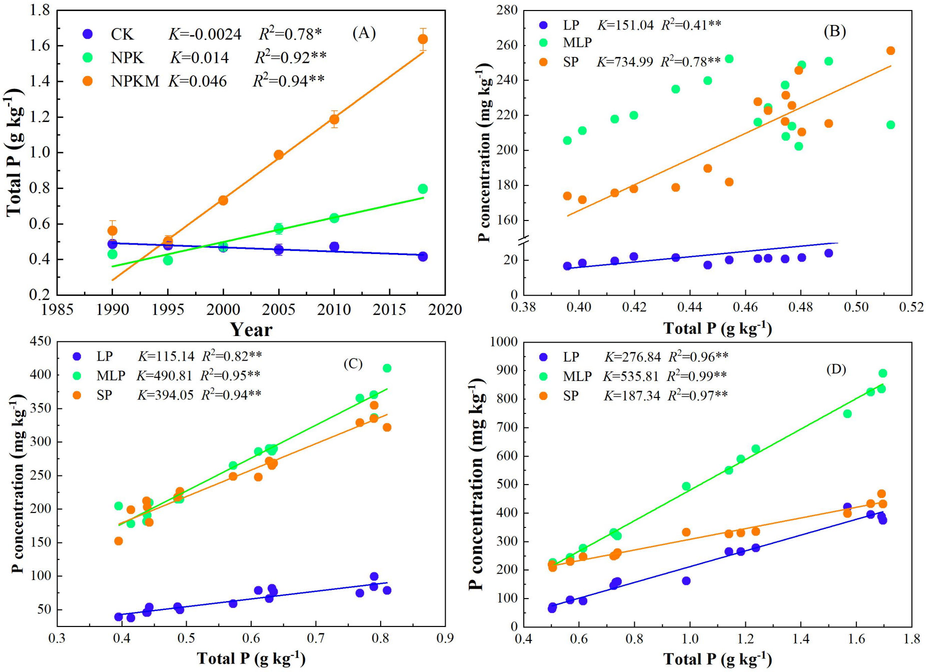


Figure 2-2 Total P content (A) and its relationship with P fraction in CK (B), NPK (C), and NPKM (D) treatments under long-term field trial in Mollisol.

Note: Fitted curves were: y = Kx + b. CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Total P, the sum content of each P fraction extracted by the Hedley sequential method. LP (labile P), the sum content of resin-P, $NaHCO_3$-Pi, and $NaHCO_3$-Po, MLP (Mid-labile P), the sum content of NaOH-Pi, NaOH-Po, and dil.HCl-Pi, SP (stable P), the sum content of conc.HCl-Pi, conc.HCl-Po and residual P . * and ** mean the relationship between total P and P fraction in $P < 0.05$, $P < 0.01$ level, respectively.

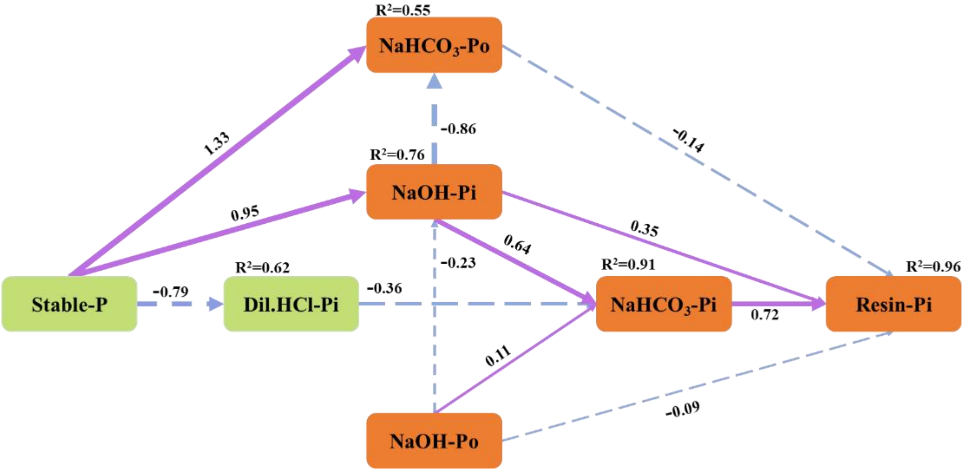


Figure 2-3 Structural equation model (SEM) exhibiting the transformation among different soil P fractions following fertilization regimes.

Note: The standardized path coefficients are marked on the arrows. Arrow width represents the strength of the path coefficient. The overall fit of the model: $\chi^2 = 7.27$, P = 0.51, CFI = 1.00 RMSEA = 0.00 SRMR = 0.03. Sum of conc.HCl-Pi, conc.HCl-Po and residual P indicate a stable P pool

3.2 P fraction using P Kedge-XANES

The characteristic features of P K-edge XANES spectra for P standard and soil samples are shown in Fig. 2-1. The soil samples' P speciation varied significantly in both P fertilization regimes. The XANES spectra LCF results showed that Ca-P, Fe-P, Al-P, and IHP fractions contributed 55–59, 21–29, 19–21% to soil total P for NPK and 71–77, 19–24, 7–15% to total P for NPKM treatments, respectively, in Mollisol (Table 2-2). The P speciation dominated as MCP (39.4%), Al-P (24.7%), IHP (18.8%), and TCP (14.0%) for NPK treatment, and TCP (43.0%), MCP (33.8%), and Al-P (24.2%) for NPKM treatment in 2018, respectively. A decreasing trend of HAP was detected in both treatments, with lower proportions in the NPKM than in the NPK in each cultivation year (Table 2-2).

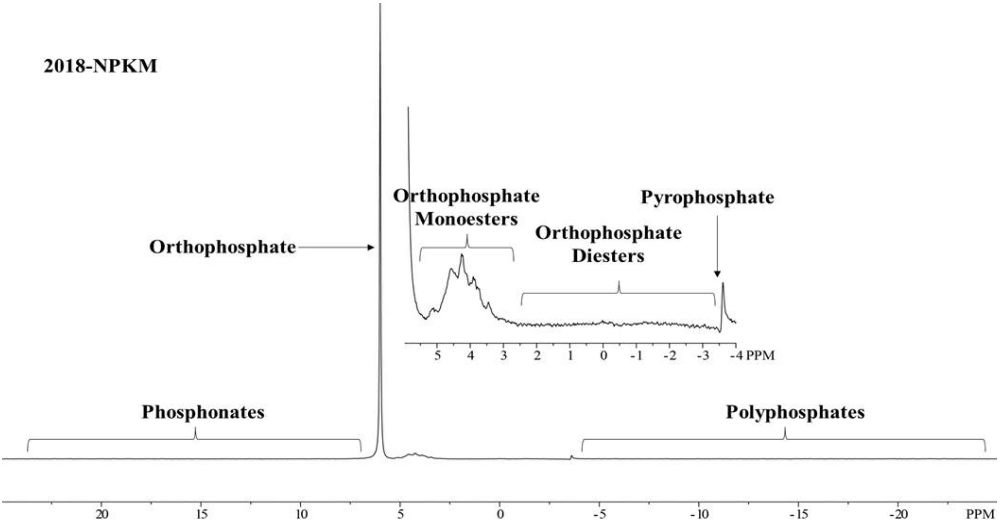
Table 2-2 The linear fitting of P fractions with P K-edge XANES in the studied soil under long-term field trial in Mollisol.

Year	Treatment	Linear combination fitting							
		HAP	Al-P	IHP	MCP	TCP	Fe-P	Ca-P	Goodness of fit
		Proportion (%)				*Proportion (%)*			R factor
1990	CK	42.1±0.2a		10.3±1.4c			42.4±1.3	42.1	0.0125
2000	NPK	21.5±2.2b	21.1±0.7bc	19.9±0.9a	36.6±0.2b			58.1	0.0143
	NPKM	17.9±1.1bc	23.6±2.0bc	14.8±1.4b	27.7±1.4d	25.8±1.0b		71.4	0.0055
2010	NPK	18.7±0.5bc	28.9±1.1a	20.8±1.8a	35.9±0.3b			54.6	0.007
	NPKM	15.9±0.1c	19.0±0.4c	10.8±0.6c	33.4±0.1c	25.7±0.2b		75	0.0061
2018	NPK	5.4±0.8d	24.7±0.5ab	18.8±0.2a	39.4±0.1a	14.0±1.1c		58.8	0.0073
	NPKM		24.2±0.7ab	7.2±0.6c	33.8±0.6c	43.0±0.6a		76.8	0.0038

CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Al-P, aluminum phosphate ($AlPO_4$), Fe-P, iron phosphate dihydrate [$FePO_4 \cdot 2H_2O$], DCP, dibasic calcium phosphate ($CaHPO_4 \cdot 2H_2O$), MCP, monobasic calcium phosphate monohydrate [$Ca(H_2PO_4)_2 \cdot H_2O$], TCP, tricalcium phosphate [$Ca_3(PO_4)_2 \cdot xH_2O$], HAP, hydroxyapatite, IHP, inositol hexaphosphate. Data are mean ± SE (n = 3). The lowercase letter indicates the significant difference in soil properties in the same column ($p < 0.05$).

3.3 Soil P fraction using ^{31}P-NMR

The ^{31}P-NMR fraction extracted by NaOH-EDTA and the chemical shifts associated with P fractions of studied soil samples is shown in Fig. 2-4. The recovery rate of the NaOH-EDTA extraction for ^{31}P-NMR was 26.7–62.7% of the total P in this experiment (Table 2-3). The application of P fertilizer significantly improved the proportion of soil Pi fractions, especially in orthophosphate, with the proportion 28.6–47.3% higher in NPKM treatment than in NPK treatment (Table 2-A1). Orthophosphate monoesters, accounting for 20.0–49.2%, were dominated by the stereoisomers of IHP (e.g., myo-IHP, scyllo-IHP, and neo-IHP), α and β -glycerophosphate, mononucleotides, choline phosphate, and glucose 6-phosphate in both P fertilization regimes. By correcting the degradation products, the proportion of orthophosphate monoester and orthophosphate diester was 19.0–53.3% for NPK and 1.55–8.25% for NPKM, respectively. A decreasing trend in the proportion of orthophosphate monoester and orthophosphate diester was exhibited in both P fertilization treatments from 1990 to 2018.



f1 (ppm)   f1 (ppm)

Figure 2-4 Solution ^{31}P NMR spectra in the studied soil under long-−term field trial in Mollisol.

Note: The inserted spectra were used to show more information about the region from 6 ppm to −−4 ppm. CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018).

Table 2-3 The proportion of P fraction with NaOH-EDTA extractions of the studied soil under long-term field trial in Mollisol.

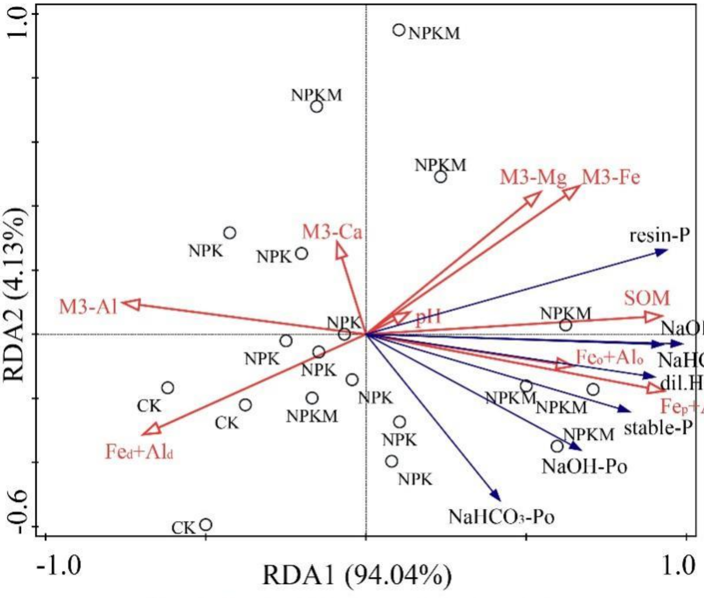
Year	Treatment	NaOH-EDTA extraction				
		Recovery (%)	Pi	Po	total IHP	Mono
1990	CK	40.1	37.9	62.1	5.57	57.6
2000	NPK	33.7	48.1	51.9	6.44	46.9
	NPKM	27.6	64.7	35.3	6.28	34.2
2010	NPK	46.9	48	52	4.29	49.2
	NPKM	26.7	67.7	32.3	3.19	30.8
2018	NPK	62.7	62.9	37.1	4.31	35.2
	NPKM	54.5	79.4	20.6	1.83	20
Year	Treatment	Di	D:M	cMono	cDi	cD:cM
1990	CK	2.81	0.05	53.3	7.09	0.13
2000	NPK	1.26	0.03	39.9	8.25	0.21
	NPKM	1.06	0.03	31	4.17	0.13
2010	NPK	2.08	0.04	46.2	5.13	0.11
	NPKM	0.95	0.03	29	2.73	0.09
2018	NPK	0.86	0.02	33.1	2.96	0.09
	NPKM	0.51	0.03	19	1.55	0.08

CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Pi, inorganic P; Po, organic P; total IHP, the total of inositol hexakisphosphate; Mono, orthophosphate monoester; Di, orthophosphate diesters; D:M, the ratio of orthophosphate diesters to orthophosphate monoester; C denotes a correction for degradation products.

3.4 Soil properties and its relationship with P fraction

Regardless of the duration, when compared to CK in 1990, a lower pH value was observed in NPK treatment, while NPKM treatment could maintain soil pH and reduce acidification (Table 2-4). Compared to CK treatment, the content of SOM, Fe_p+Al_p and Fe_o+Al_o showed a significant increasing trend, whereas Fe_d+Al_d decreased in both fertilizer treatments, especially in NPKM treatment. In comparison with NPK treatment, the content of SOM, M3-Mg, Fe_p+Al_p and Fe_o+Al_o was significantly increased, and the content of M3-Ca and M3-Al was decreased in NPKM treatment in 2018, respectively. Compared with NPK treatment, increased content of M3-Mg and M3-Ca but decreased content of M3-Al and M3-Fe in NPKM treatment indicated that plants showed different utilization choices of nutrient elements after different fertilization treatments.

The most closely correlated soil properties were SOM and different Fe-Al oxides for P fractions (Table 2-A2). Moreover, the PCA indicated that the above-mentioned soil properties exhibited the most importance in the variance between both treatments (Fig. 2-A3). The redundancy analysis (RDA) test indicated that soil properties could explain 98.2% of soil P fraction variation across the P fertilization regime (Fig. 2-5). Soil SOM and Fe_p+Al_p explaining 51.8%, and 9.64%, respectively, were the major factors ($P < 0.01$) (Fig. 2-5) and exhibited positive correlation with each P fraction ($R^2 = 0.46–0.93$ *) (Table 2-S2).



SOM: 51.82%, $P<0.001$; Fe_p+Al_p: 9.64%, $P<0.008$

Figure 2-5 Correlation between soil properties and P fraction contents under long-term different fertilization regimes with redundancy analysis (RDA) triplots.

Note: SOM, soil organic matter; Fe_d+Al_d were the sum of free iron (Fe) and aluminum (Al) oxide; Fe_o+Al_o were the sum of amorphous Fe and Al oxides; Fe_p+Al_p were the sum of humus complex Fe and Al oxides. M3-Mg, M3-Fe, and M3-Al were Mg, Fe and Al extracted by Mehlich-3 extraction. Stable P, sum P pool of conc.HCl-Pi, conc.HCl-Po, and residual P.

Table 2-4 Soil properties of collected samples in black soil

Year	Treatment	pH	SOM	M3-Ca	M3-Mg	M3-Al	M3-Fe	Fe_d+Al_d	Fe_p+Al_p	Fe_o+Al_o
			g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	$g\cdot kg^{-1}$	g kg^{-1}	g kg^{-1}
1990	CK	7.40±0.3a	21.5±0.2d	4.55±0.04b	0.35±0.00e	1.20±0.01b	0.22±0.01b	12.12±0.04a	0.65±0.01e	5.88±0.04g
2000	NPK	6.03±0.1c	28.5±1.8c	3.82±0.05d	0.41±0.01d	1.30±0.02a	0.25±0.00a	11.26±0.09c	0.80±0.03d	7.49±0.02d
	NPKM	7.10±0.1a	32.8±2b	4.62±0.04a	0.45±0.01c	1.15±0.02b	0.26±0.01a	11.28±0.08c	0.82±0.02cd	6.61±0.01f
2010	NPK	6.73±0.1b	26.9±0.4c	3.83±0.04d	0.41±0.01d	1.35±0.02a	0.25±0.01a	11.58±0.10b	1.04±0.02b	8.22±0.06b
	NPKM	7.21±0.02a	41.0±2a	4.57±0.18b	0.54±0.00a	1.04±0.02c	0.24±0.01a	10.74±0.05d	0.86±0.02c	7.78±0.03c
2018	NPK	6.11±0.2c	26.7±0.1c	4.17±0.01c	0.28±0.01f	1.18±0.03b	0.25±0.00a	10.62±0.09d	1.04±0.02b	6.84±0.01e
	NPKM	7.36±0.04a	40.3±1.9a	3.89±0.01d	0.47±0.00b	1.04±0.03c	0.24±0.01a	10.78±0.11d	1.19±0.01a	8.45±0.10a

CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). SOM, soil organic matter; M3-Ca, M3-Mg, M3-Fe, and M3-Al were Ca, Mg, Fe_d+Al_d were the sum of free iron (Fe) and aluminum (Al) oxide; Fe_o+Al_o were the sum of amorphous Fe and Al oxides; Fe_p+Al_p were the sum of humus complex Fe and Al oxides. Data are mean ± SE (n = 3). The lowercase letter indicates the significant difference in soil properties in the same column ($P < 0.05$).

4. Discussion

4.1 Effect of fertilization on the P fractions with multiple techniques

Regardless of the fertilization regime, the stronger related coefficient in each Pi fraction than that in the Po fraction relative to total P indicated that P accumulated in the soil was mainly transformed into the Pi fraction (Fig. 2-A1). Moreover, the related coefficient between resin-P, $NaHCO_3$-Pi, dil.HCl-Pi, and total P increased in soils treated with P fertilizer when compared with that in CK treatment, which indicated large of the increased accumulated P was plant-available, especially in the manure-amended treatment.

The distribution and transformation process of soil P species under different fertilization regimes could be comprehensively evaluated by the combined application of the Hedley sequential method and techniques of P-XANES and ^{31}P-NMR (Liu et al., 2019; Koch et al., 2018). Results showed that fertilization significantly increased the Pi accumulation in soil; specifically, the proportion of orthophosphate dominated by Al-P and Ca-P increased (Table 2-2). In addition to the direct input of inorganic phosphate fertilizer, a large number of inorganic P pools in manure was another main reason for the increase in soil Pi content (Sato et al., 2005). The added organic fertilizer was pig and cattle manure in this studied soil, which contained 48.6% and 91.6% orthophosphate, respectively (Table 2-S1). P-XANES results showed that long-term P fertilizers application resulted in a dominance of Ca-P , especially in the NPKM (Table 2-2). The formation of the Ca phosphates was the result of enrichment with Ca and P via manure, and many studies suggested that manure was rich in considerable amounts of Ca-P (Güngör et al., 2007; Toor et al., 2005; Sharpley and Moyer 2000). Furthermore, the proportion of HAP decreased or even could not be detected in NPKM treatment over the cultivation (Table 2-2). Similar results were obtained in gray desert soil and alkaline soil; TCP rather than HAP was the main accumulated Pi fraction in soil under long-term P fertilization, especially in the soil treated with organic fertilizer (Liu et al., 2020, 2015; Yan et al., 2018). The possible reason was that presence of organic acids in manure could inhibit the crystallization and formation of HAP through stabilizing amorphous calcium phosphate (ACP) and delaying its subsequent transformation to thermodynamically more stable phases (Ge et al., 2020; Sato et al., 2005). In addition, Mg showed an inhibitory effect on the Ca-P crystallization (Nair et al., 2003). In this study, the content of M3-Mg in the soil increased significantly in NPKM treatment, which may be another reason for the less stable Ca-P (Yan et al., 2018). Lower pH value was the main factor controlling for the decrease in HAP in NPK treatment compared to NPKM treatment (Table 2-4). The solubility of HAP showed a negative correlation with soil pH (Shen et al., 2011). Once the highly active orthophosphate was released into the soil by HAP, Fe/Al-P could be formatted due to the high affinity of orthophosphate to Fe and Al (Hydr) oxides and might subsequently be retained in the soil as reserves. NaOH-Pi was dominated by Al-P (21.1% for NPK and 19.0% for NPKM) under P fertilization (Table 2-2). A similar result had been reported in previous studies that Al-P specie was considered as an effective source of Pi-solubilized with higher content than that of Fe-P-solubilized in Mollisol (Yang et al., 2019; Liu et al., 2017; Shen et al., 2002).

The soil Po content accounted for 20.6–62.1% with the ^{31}P-NMR method (Table 2-3). Similar results were observed in the same area by Liu et al. Liu et al. (2017). However, the proportion of IHP determined by ^{31}P-NMR was lower than that by P-XANES spectral analysis (Table 2-2 and 2-3). The possible reason was that the recovery rate of ^{31}P-NMR was 20–60%, while the XANES spectrum detected the entire soil sample; meanwhile, it is difficult to detect various Po species by XANES (Cade-Menun et al., 2015; Prietzel et al., 2013). These results indicated that a good consistency would be shown between ^{31}P-NMR and P-XANES in the determination of samples containing a high concentration of IHP (Liu et al., 2020; Weyers et al., 2016; Prietzel et al., 2013). The ^{31}P-NMR results showed that a lower proportion of Po in NPKM treatment was detected in 2018 than in 2000 (Table 2-3). The main reason was that the organic fertilizer was changed from pig manure (1990–2005) to cattle manure (2005–2018), reducing the input of phosphate and the accumulation of Po in soil.

4.2 Transformation of soil P fractions

The transformation of solid-phase P speciation critically determines the bioavailability of soil P (Fan et al., 2019; Yang and Post 2011). Our model revealed that soluble Pi (resin-Pi) was mainly affected by highly active Pi fractions (such as $NaHCO_3$-Pi, NaOH-Pi), and stable P showed an indirect effect on resin-Pi through a transformation in Mollisol. Similar results had been verified on some unfertilized soils around the world by Hou et al. (2016) and Tiessen et al. (1984). In fact, previous studies had confirmed that the Pi fraction was important to soil P dynamics and was considered the primary source of available P in fertilized soil (Liu et al., 2020; Qin et al., 2020; Chen et al., 2019). In our study, the Pi fraction in fertilizer-treated soil accounted for 83.8–92.2% of Pt, and more than 60% of soil P was converted into a labile and mid-labile Pi fraction and accumulated in the soil (Fig. 2-1 and 2-S1).

$NaHCO_3$-Pi showed a greater direct effect on resin-Pi than other P fractions. As a short-term and plant-available P fraction, $NaHCO_3$-Pi showed a strong correlation with resin-P and could quickly supplement the available P sources for plants when resin-Pi was depleted in soil (Tiessen and Moir, 2007; Frossard et al., 2000). NaOH-Pi was mainly related to Fe_o and Al_o in soil, and it took a longer time to transform into plant-available P fractions by desorption or dissolution in comparison with $NaHCO_3$-Pi (Tiessen and Moir, 2007). NaOH-Pi showed a direct positive influence on resin-Pi (Fig. 3), which is opposite to the results obtained in unfertilized soil by Hou et al. (2016) and Tiessen et al. (1984). The reason is that the increased negatively charged functional groups in SOM could interact with Fe and Al (hydr) oxides, promoting the desorption of P on the surface of Fe and Al (hydr) oxides (Wang et al. 2019; Fink et al., 2016; Hinsiger et al., 2011). Hence, when resin-Pi in soil solution was exhausted, it could be immediately replenished by $NaHCO_3$-Pi and NaOH-Pi. The possible reason for $NaHCO_3$-Po and NaOH-Po showing negative and little total influence on resin-Pi in comparison to Pi was that mineralization limited the transformation of these Po fractions to resin-Pi (Bünemann, 2008).

4.3 Effects of soil property on soil P fractions

Fertilization affects soil P status through changing soil properties such as SOM, mineral composition, pH, and so on (Spohn, 2020; Hou et al., 2018; Redel et al., 2016). SOM and Fe_p+Al_p were the main factors regulating the changes of P fractions (Fig. 2-5). Fe/Al oxide exhibited great absorbability to phosphate because of the large amount of positive charge (Guo et al., 2007). In this research, the change in the content of Fe/Al oxides and their correlation with SOM suggested that SOM could promote the transformation of Fe/Al oxides from crystalline to poorly crystalline (Table 2-4 and Fig. 2-s2) (Abdala et al., 2015; Guo et al., 2007). The transformation progresses decreased the P maximum buffering capacity and promoted the P desorption in the soil and improved the level of high active P fractions (Table 2-A2) (Wang et al., 2019, 2022; Fink et al.,2016; Redel et al., 2016). The possible reason was that the high content of SOM in the soil could interact with soil Fe and Al oxides in many ways (competitive adsorption sites, changing surface charge, cationic bridge, etc.) and increase the surface sites and charges, decomposition product from SOM competed with phosphate in the soil solution for adsorption sites, weakening the adsorption of soil to P (Wang et al., 2022; Kang et al., 2009). Moreover, phosphate could form chemisorbed inner-sphere and outer-sphere complexes on the surface of Fe/Al oxides through ligand exchange reaction and electrostatic interaction and change the P adsorption by Fe and Al minerals (Ma et al., 2021; Chitrakar et al., 2006; Luengo et al., 2006). In addition, our results indicated that the transformation ratio of NaOH-Po in NPK was higher than that in NPKM treatment (Fig. 2-S1). It was partly due to the influence of soil pH value. The adsorption capacity of Fe and Al (hydr) oxides to Po showed a negative relationship with soil pH (Hinsinger, 2001).

5. Conclusion

A stronger positive related coefficient between soil total P and labile P and mid-labile fractions was found in the NPKM treatment compared to NPK treatment, which highlighted the positive effect of manure amendment on the soil P availability in this experimental field. This increment might be caused by the sufficient input of P fertilizer and higher SOM and Fe_p+Al_p content in NPKM treatment, which resulted in the accumulation of labile P and mid-labile P pool, especially the proportion of Al-P, MCP, and TCP. A combination of modified Hedley extraction, P-XANES, and P-^{31}NMR comprehensively indicated the soil P dynamics under P fertilization. Specifically, the available P pool was contributed by Al-P and MCP in

NPK treatment and Al-P, MCP, and TCP in the NPKM treatment with P K-edge XANES. Meanwhile, a higher related coefficient with Hedley extraction proportion of IHP measured with P K-edge XANES and the ratio of orthophosphate diesters to monoesters was found in NPK treatment than in NPKM treatment indicated that mineral P fertilizer could facilitate the accumulation of soil Po, which showed higher soil Po lability. The structural equation model revealed that resin-P was positively and directly decided by $NaHCO_3$-Pi and NaOH-Pi, and indirectivity affected by dil.HCl-Pi and stable P. This research revealed the changes and transformations in various soil P fractions under fertilization regimes and their chemical-associated mechanism in Mollisol. Meanwhile, these results give insight into the knowledge of optimizing fertilization regimes by the combination of chemical fertilizer with manure. However, the appropriate application amount of manure must be considered carefully to lower accumulation and subsequent loss of soil P, which could pose an adverse risk to the water environment.

6. Acknowledgement

We thank all the staff for their valuable work at Jilin Academy of Agricultural Sciences associated with the long-term Monitoring Network of Soil Fertility and Fertilizer Effects in China and Agro-Environmental NMR Microstructure Lab, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences. This research was supported by the National Natural Science Foundation of China (41977103 and 41471249) and the Reform and Development Fund of the Beijing Academy of Agriculture and Forestry Sciences, China (YZS201905).

7. Supplementary Figures and Tables

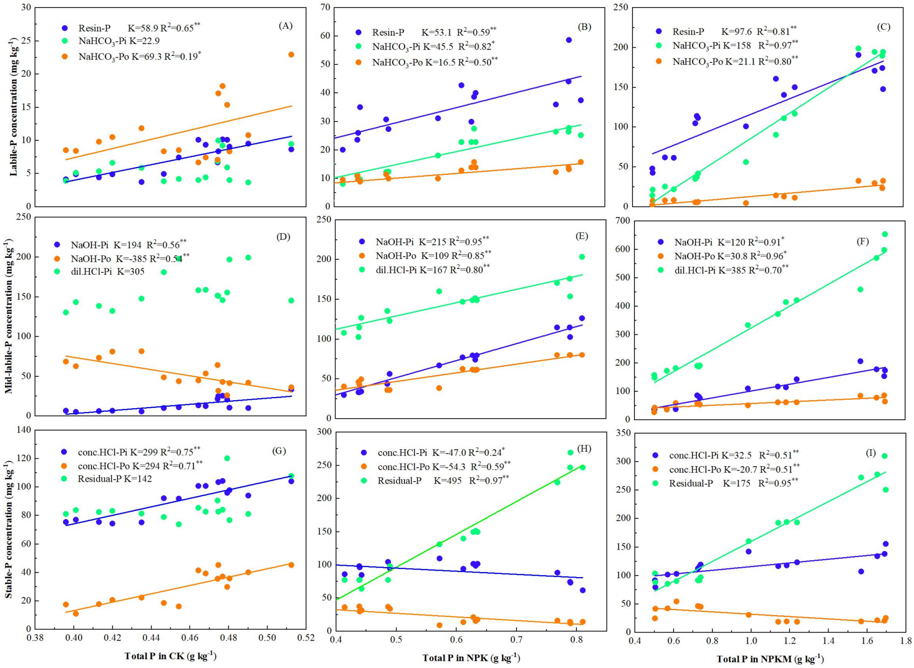


Figure 2-S1 The correlation between total P and each P fraction in CK (A, D, G), NPK (B, E, H) and NPKM (C, F, I) treatments under long−term experiment.

Note: Fitted curves were: $y = Kx + b$. CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Total P, the sum content of each P fraction extracted by the Hedley sequential method. * and ** mean the relationship between total P and P fraction in $P < 0.05$, $P < 0.01$ level, respectively.

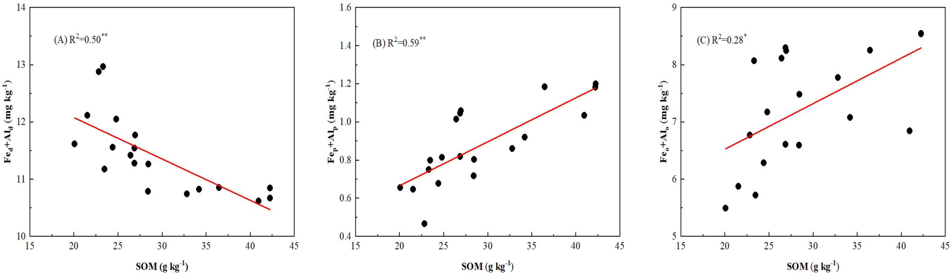


Figure 2-S2 The relationship between SOM and $Fe_d + Al_d$ (**A**), $Fe_p + Al_p$ (**B**), and $Fe_o + Al_o$ (**C**) under long-term field trial.

Note: Fitted curves were: y = Kx + b. SOM, soil organic matter; Fe_d and Al_d, crystalline iron and aluminum oxide; Al_o and Fe_o, amorphous Al and Fe oxide; Al_p and Fe_p, organic−bound iron and alumina oxide. * and ** mean the relationship between total P and P fraction in $P < 0.05$, $P < 0.01$ level, respectively. * and ** mean the relationship between total P and P fraction in $P<0.05$, $P<0.01$ level, respectively.

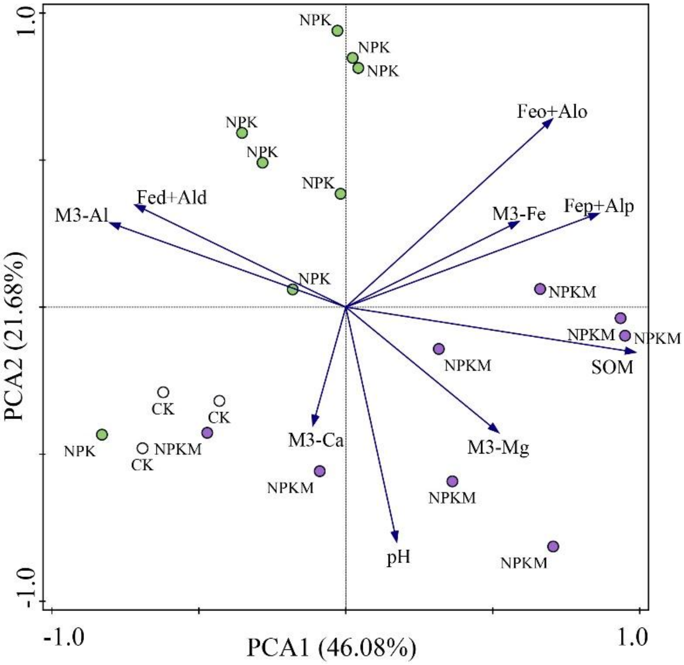


Figure 2-S3 Correlation between soil properties under long−term different fertilization regimes with principal components analysis (PCA).

Note: The sum of the first two principal components (PC) of the soil properties accounted for 67.8% of the variance. CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Loadings for PC1 were dominated by SOM (0.47), M3−Fe (0.33), M3−Mg (0.27), M3−Al (−0.39), Fed + Ald (−0.38), Fep + Alp (0.44), whereas, loadings for PC2 were dominated by pH (−0.63), Feo + Alo (0.38) and M3−Ca (−0.39). SOM, soil organic matter; Fe_d and Al_d, crystalline iron and aluminum oxide; Al_o and Fe_o, amorphous Al and Fe oxide; Al_p and Fe_p, organic−bound iron and alumina oxide. M3−Ca, M3−Mg, M3−Fe, and M3−Al were Ca, Mg, Fe, and Al extracted by Mehlich−3 extraction.

Table 2-S1 The proportion of P fraction determined by integration of P−NMR signals of the studied soil under long−term field trial in Mollisol.

Year	Treatment	Ortho	Pyro	Poly	Phos	scyllo-IHP	myo-IHP	neo-IHP	α-Glycb
1990	CK	33.3	1.81	2.83	1.70	0.94	3.40	1.23	1.33
2000	NPK	47.2	0.92	0.01	3.73	0.76	4.66	1.03	3.31
	NPKM	63.0	1.26	0.41	0.09	0.44	5.69	0.15	1.02
2010	NPK	44.4	2.41	1.19	0.70	0.66	3.45	0.19	0.56
	NPKM	65.4	1.54	0.77	0.55	0.43	1.83	0.93	0.20
2018	NPK	60.1	2.73	0.08	1.05	0.49	2.46	1.37	0.61
	NPKM	77.3	1.25	0.82	0.08	0.36	1.39	0.08	0.10
	Pig manure	44.5	0.41	0.41	7.19		14.8		
	Cow manure	87.6	0.09	0.32	2.51				0.41

Year	Treatment	β-Glyc	Nucl	Pchol	G6P	Mono1	Mono2	Mono3	OrthDi
1990	CK	1.56	1.39	0.92		0.10	43.60	2.95	2.81
2000	NPK	1.55	2.13	0.71	1.84	1.13	23.80	5.55	1.26
	NPKM	1.20	0.91	0.35	0.25	0.78	19.88	3.53	1.06
2010	NPK	1.75	0.74	0.98	0.45	1.88	33.54	5.04	2.08
	NPKM	0.99	0.60	0.26	0.23	0.80	21.45	3.11	0.95
2018	NPK	0.80	0.70	0.49	0.12	0.29	27.51	0.36	0.86
	NPKM	0.49	0.44	0.21	0.22	0.73	15.26	0.72	0.51
	Pig manure		12.2		2.53	8.90	6.39	2.38	

	Cow manure	1.89	0.30			3.58	1.63	0.19	1.53

Orthophosphate, Ortho; pyrophosphate, Pyro; polyphosphate, Poly; phosphonates, Phos; myo−inositol hexakisphosphate, myo−IHP; scyllo−inositol hexakisphosphate, Scyllo−IHP; neo−inositol hexakisphosphate, neo−IHP; α and β glycerophosphate, (α−glyc and β−glyc, respectively); mononucleotides, Nucl; choline phosphate, Pchol; glucose 6−phosphate, G6P; orthophosphate monoesters, regions 1, 2, and 3 (Mono1, Mono2, and Mono3, respectively); and orthophosphate diesters (OthDi). CK, no fertilizer input; NPK treatment, applying N, P, K fertilizer; NPKM treatment, applying NPK and manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018).

Table 2-S2 Relationship between soil properties and P fraction

	Resin-P	$NaHCO_3$-Pi	$NaHCO_3$-Po	NaOH-Pi	NaOH-Po	dil.HCl-Pi	Stable-P
SOM	0.930^{**}	0.883^{**}	0.462^{*}	0.825^{**}	0.507^{*}	0.916^{**}	0.801^{**}
pH	0.353	0.357	0.214	-0.003	-0.190	0.404	0.117
Fe_d+Al_d	-0.703^{**}	-0.559^{*}	-0.180	-0.559^{*}	-0.410	-0.564^{*}	-0.530^{*}
Fe_p+Al_p	0.790^{**}	0.788^{**}	0.537^{*}	0.944^{**}	0.824^{**}	0.755^{**}	0.854^{**}
Fe_o+Al_o	0.522^{*}	0.542^{*}	0.385	0.721^{**}	0.627^{**}	0.514^{*}	0.641^{**}
M3-Ca	-0.039	-0.188	-0.262	-0.105	-0.199	-0.083	-0.069
M3-Mg	0.645^{**}	0.563^{*}	0.137	0.418	-0.037	0.553^{*}	0.249
M3-Al	-0.772^{**}	-0.748^{**}	-0.458^{*}	-0.686^{**}	-0.483^{*}	-0.826^{**}	-0.754^{**}
M3-Fe	0.548^{*}	0.341	0.063	0.616^{**}	0.429	0.284	0.465^{*}

SOM, soil organic matter; Fe_d+Al_d were the sum of free iron (Fe) and aluminum (Al) oxide; Fe_o+Al_o were the sum of amorphous Fe and Al oxides; Fe_p+Al_p were the sum of humus complex Fe and Al oxides; M3−Ca, M3−Mg, M3−Fe, and M3−Al were Ca, Mg, Fe, and Al extracted by Mehlich−3 extraction. * and ** mean the relationship between soil properties and P fraction in $P > 0.05$, $P < 0.01$ level, respectively.

Chapter III

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

From Wang, Q., Qin, Z. H., Zhang, W. W., Chen, Y. H., Zhu, P., Peng, C., Wang, L., Zhang, S. X., Colinet, G., 2022. Effect of long-term fertilization on phosphorus fractions in different soil layers and their quantitative relationships with soil properties. Journal of Integrative Agriculture, 21, 9, 2720-2733.

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 (M3-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.

Keywords: long-term experiment, phosphorus fractions, soil profile, phosphorus availability, black soil

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 (Bauke et al., 2018; Ayaga et al., 2006). 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} (Zhan et al., 2015; Zhang et al., 2014). 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 (Chen and Graedel, 2016;

Li et al., 2015). 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 (Glaesner et al., 2019; Stutter et al., 2012; Olson et al., 2010; Castoldi et al., 2009). 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 (Kautz et al., 2012; Godlinski et al., 2004). 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 (McDowell et al., 2016; Annaheim et al., 2015; Ahlgren et al., 2013). 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 (van der Bom et al., 2019; Yan et al., 2016; Bünemann et al., 2008). 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 (Nobile et al., 2020; Yan et al., 2018; Whalen et al., 2000), and altered the availability of P (Sharpley et al., 2004; McDowell and Sharpley, 2003). 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 (Yan et al., 2018; EichlerLöbermann et al., 2007; Sharpley et al., 2004; McDowell and Sharpley, 2003; Whalen et al., 2000). 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 (Sowers et al., 2018; Kramer and Chadwick, 2018; Fink et al., 2016). 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 (Wang et al., 2021; Yan et al., 2018; Mundus et al., 2017). 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 3-1 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 3-2. 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 m^2 (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.

Table 3-1 Physical and chemical properties of studied soil in the experiment 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
40-64	7.5	1.33	6.3	0.58	0.44	15.94	3.14	185

Table 3-2 Mean annual nitrogen (N), phosphorus (P) and potassium (K) inputs under four long-term fertilization treatments in black soil

Treatment¹⁾	Inorganic fertilizer (kg ha^{-1}) ²⁾			Organic fertilizer (kg ha^{-1})		
	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).

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 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 (Carter and Gregorich, 2007; Sui et al., 1999; Hedley et al., 1982). 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_2SO_4-H_2O_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-μm 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 (Martin et al., 1999; Murphy and Riley, 1962). 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 (Yang and Post, 2011; Carter and Gregorich, 2007; Motavalli and Miles, 2002), 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 (Hou et al., 2016; Yang and Post, 2011; Cross and Schlesinger, 1995). 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 (Condron and Newman, 2011; Hedley et al., 1982).

2.4 Calculations

The P uptake and P balance are calculated as follows:

$$\text{P uptake (kg ha}^{-1}\text{)} = \text{Crop yield (kg ha}^{-1}\text{)} \times \text{Crop P content (\%)} + \text{Straw yield (kg ha}^{-1}\text{)} \times \text{Straw P content (\%)} \quad (1)$$

$$\text{P balance} = \text{P input} - \text{P uptake} \quad (2)$$

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})/(T otal 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):

$$y_1 = a_1x + b_1 x < T \quad (4)$$

$$y_1 = a_1x + b_1 x \geq T \quad (5)$$

where a_1, a_1, b_1, and b_1 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 P uptake and crop yield (Table 3-3). 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.

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

	Treatment1)	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 ($P<0.05$).

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 3-3), 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 $CaCl_2$-P, further, $CaCl_2$-P increased rapidly when Olsen-P was greater than 50.6 mg kg^{-1} (Fig. 3-1).

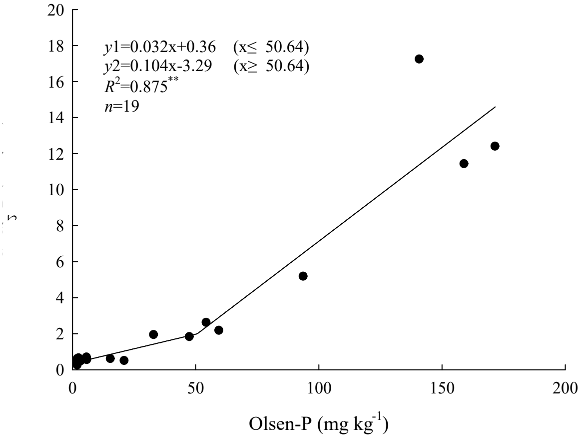


Figure 3-1 The change point between soil Olsen-P and $CaCl_2$-P for black soil at Gongzhuling. **, $P<0.01$.

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. 3-2-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. 3-2-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 were 1.7 and 1.3 times those for the 40–60 cm soil depth ($P<0.05$) (Fig. 3-2-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.

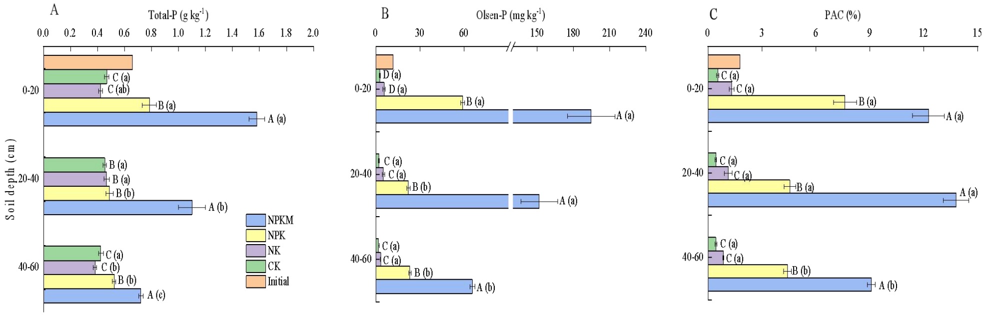


Figure 3-2 Total P and Olsen-P concentrations, and phosphorus activation coefficient (PAC) values in 1990 (initial) and in 2018 under long-term different fertilization treatments.

Note: 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).

3.4 P fractions in the 0–60 cm soil profile

The concentrations of labile-P and partially labile-P in the 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. 3-3-A and B). The concentrations of labile-P and partially labile-P in the NPKM treatment were 2.2–4.8 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. 3-3). 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. 3-4). 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 with P fertilizer in each soil depth, especially in the NPKM treatment (Fig. 3-4-A, B and D and Fig. 3-S1). 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. 3-4-A, B and F and Fig.3-S1). In the 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. 3-4-B, D, E, F and I).

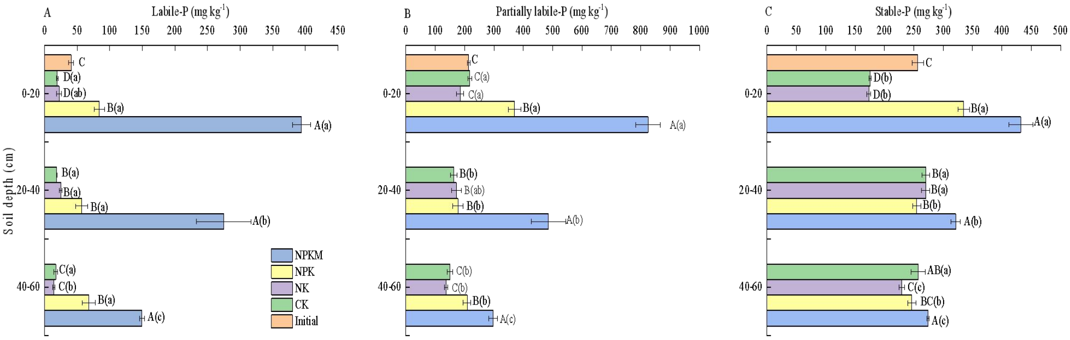


Figure 3-3 Concentrations of labile P, partially labile P, and stable P in 1990 (initial) and in 2018 under different long-term fertilization treatments.

Note: 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).

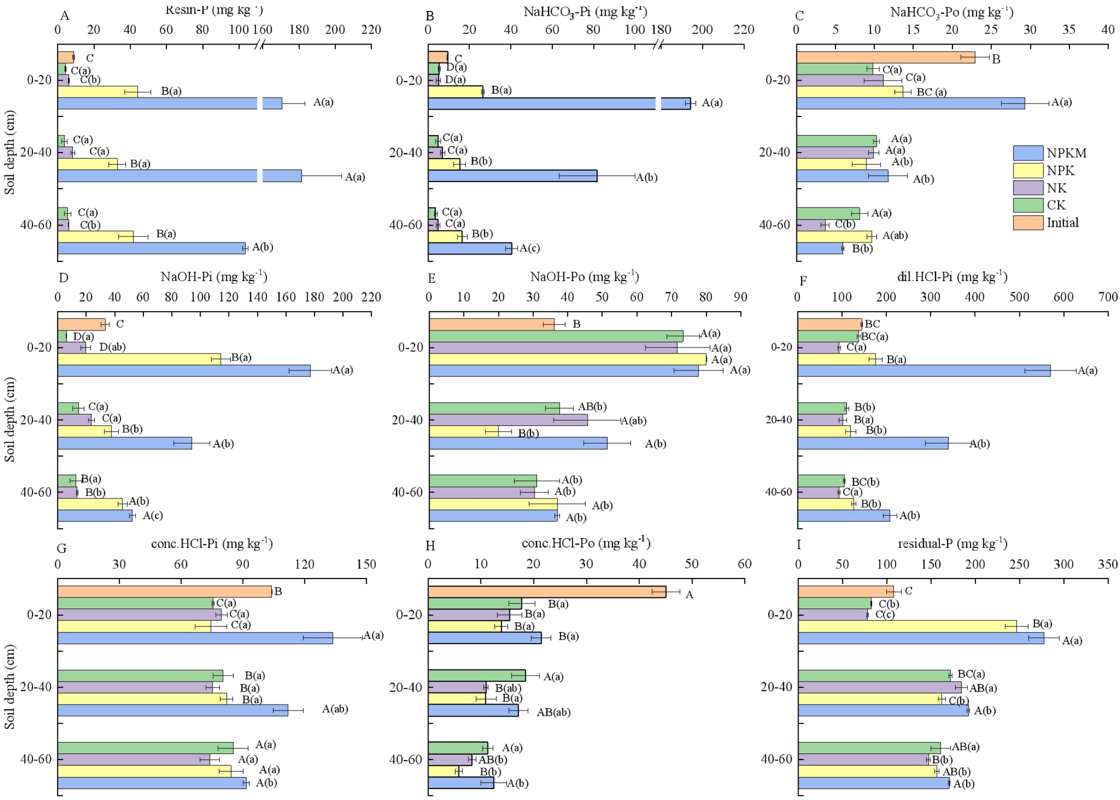


Figure 3-4 Concentrations of each P fraction in 1990 (initial) and in 2018 under different long-term fertilization treatments.

Note: 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).

3.5 Soil properties in the 0–60 cm soil profile

Different long-term fertilization treatments had a distinct impact on soil properties (Table 3-4). 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 profiles. With increasing soil depth, a significant decrease 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 3-4).

Table 3-4 Soil properties^1 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 ($g\ kg^{-1}$)	$CaCO_3$ ($g\ kg^{-1}$)	M3-Ca ($g\ kg^{-1}$)	M3-Mg ($g\ kg^{-1}$)	M3-Al ($g\ kg^{-1}$)	M3-Fe ($g\ kg^{-1}$)
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
	CK	7.66±0.1 Aa$^{3)}$	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
	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
	NPK	6.11±0.2 Bb	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
	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
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
	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
	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
	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
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
	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
	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
	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
Soil depth		*	**	**	**	NS	*	**
fertilization		**	**	**	**	**	*	**
Soil depth×fertilization		**	**	**	**	NS	**	**
Soil depth cm	Treatment$^{2)}$	Fed ($g\ kg^{-1}$)	Ald ($g\ kg^{-1}$)	Feo ($g\ kg^{-1}$)	Alo ($g\ kg^{-1}$)	Fep ($g\ kg^{-1}$)	Alp ($g\ kg^{-1}$)	

0–20	Initial	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	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	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	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	9.12±0.06 Ca	1.66±0.02 Cb	4.36±0.08 Aa	4.09±0.01 Aa	0.48±0.01 Aa	0.71±0.01 Aa
20–40	CK	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	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	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	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	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	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	9.56±0.08 Cb	2.17±0.03 Aab	3.40±0.2 ABb	3.48±0.08 Bb	0.20±0.02 Ab	0.60±0.03 Ab
	NPKM	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
fertilization		**	**	**	**	**	**
Soil depth×fertilization		**	**	**	NS	**	NS

1) SOM, soil organic matter; Fed, free iron oxide; Ald, free aluminum oxide; Feo and Alo, amorphous Fe and Al oxides; Fep and Alp, 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). *—P<0.05; **—P<0.01; NS—No significant difference.

3.6 Influence of soil properties on P fractions

SOM, Fe_o, Al_o, Fe_p, and Al_p showed strong positive correlation with highly active P fractions (resin-P, $NaHCO_3$-Pi, $NaHCO_3$-Po, NaOH-Pi and dil.HCl-Pi), whereas, Fe_d, Al_d, and $CaCO_3$ showed a negative correlation with these P fractions at each soil depth (Fig. 3-S2). 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. 3-5). SOM, M3-Fe, and Al_p at 0–20 cm, Fe_d and pH at 20–40 cm, and $CaCO_3$, 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 $CaCO_3$ (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 (Table 3-S1).

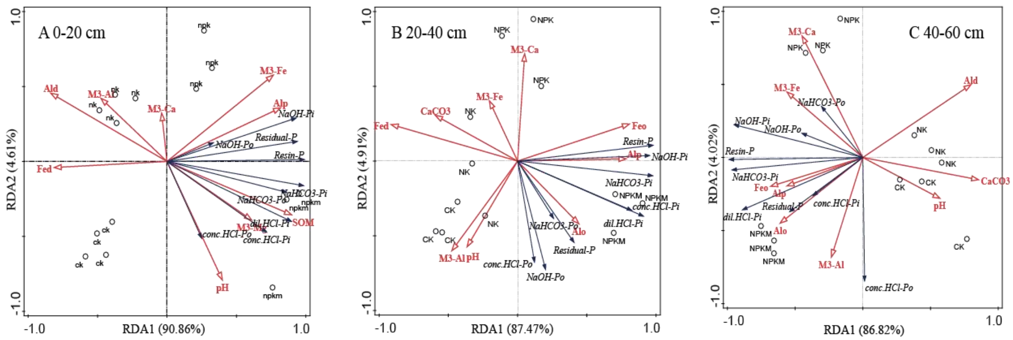


Figure 3-5 Redundancy analysis (RDA) triplots showing the relationship between soil properties and P fractions under different longterm fertilization treatments in 2018.

Note: 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).

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 (Qin et al., 2020; Zhang, 2014). 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 3-3 and Fig. 3-2). 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 3-3). A possible reason for this is that N and K addition may increase plant P uptake and root biomass (Schleuss et al., 2020; Wang et al., 2018; Liu et al., 2017; Yuan and Chen, 2012). 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 three periods (Table 3-3). 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. 3-1). 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 (Qin et al., 2020; Zhang et al., 2019; Pizzeghello et al., 2014). Labile and partially labile Pi (resin-P, $NaHCO_3$-Pi, NaOH-Pi, and dil.HCl-Pi) were the main P fractions increased by NPKM treatment (Fig. 3-3). These Pi fractions are mainly water soluble or colloidal P with strong mobility, and are easily leached into the water (Liu, 2013; Heathwaite et al., 2005).

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 (Nobile et al., 2020; Pizzeghello et al., 2016). 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 $NaHCO_3$-Pi via ligand exchange and mineralization of $NaHCO_3$-Po (Yang and Post, 2011; Carter and Gregorich, 2007; Frossard et al., 2000). 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. 3-4). 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. 2-4; Fig. 3-S1). These results suggest that mineral P addition enriched the plantavailable 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 (Yang et al., 2019; Liu et al., 2017). 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 (Fig. 3-S1), 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 (Liu et al., 2020; Sato et al., 2005).

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 (Yan et al., 2013, 2018; Pizzeghello et al., 2011). Most previous studies have focused on investigation of the influence of a single soil property on the P fractions in soil (Fan et al., 2019; Xu et al., 2018). 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 Alp, caused by fertilization, were the main factors influencing P fractions in the 0–20 cm soil depth (Table 3-4), 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 (Fig. 3-S2). 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 (Abdala et al., 2015; Guo et al., 2007; Celi et al., 2003). 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 (Yan et al., 2014; Celi et al., 1999, 2003, 2020). 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 (Wang et al., 2017; Barrow et al., 2015; Li et al., 2013). In our study, the concentration of NaOH-Pi in soil 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 (Zamuner et al., 2008; Antelo et al., 2007; Redel et al., 2007; Bayon et al., 2006; von Wandruszka, 2006). Soil mineral components and pH were the main factors influencing the P fractions in the subsoil (Fig. 3-S3). The concentrations of $CaCO_3$, Fe_d and Al_d in soil with P fertilizers were lower than in the CK treatment, which increased P availability because of their negative relationships with labile and partially labile Pi in subsoil (Fig. 3-S2).

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 Alp 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.

6. Acknowledgement

We thank all staff for their valuable work associated with the National Soil Fertility and Fertilizer Effects Long term Monitoring Network in China. This research was supported by the National Natural Science Foundation of China (41977103 and 41471249), and the Reform and Development Fund of Beijing Academy of Agriculture and Forestry Sciences, China (YZS201905).

7. Supplementary Figures and Tables

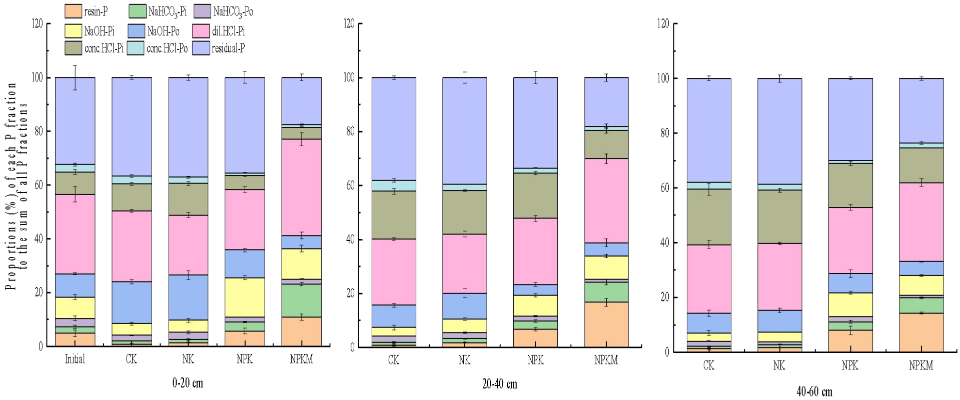


Figure 3-S1 Proportions (%) of each P fraction to the sum of all P fractions in black soil samples collected in 1990 (initial) and in 2018 under long-term different fertilization treatments.

Note: 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). 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.

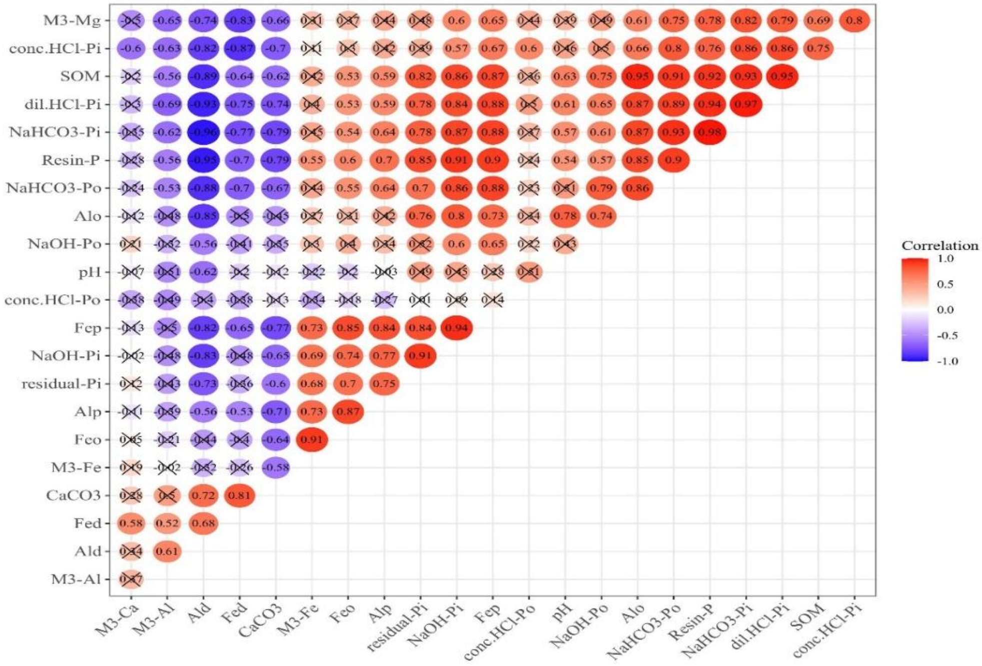


Figure 3-S2 (1) Correlation between soil properties and P fraction in 0–20 cm.

Note: SOM, soil organic matter; Fe_d and Al_d, free Fe and Al oxide; Fe_o and Al_o, amorphous Fe and Al oxide; Fe_p and Al_p, humus complex Fe and Al oxide; M3-Ca, M3-Mg, M3-Fe and M3-Al were Ca, Mg, Fe and Al extracted by Mehlich-3 extraction. “×” means no significant difference between parameters.

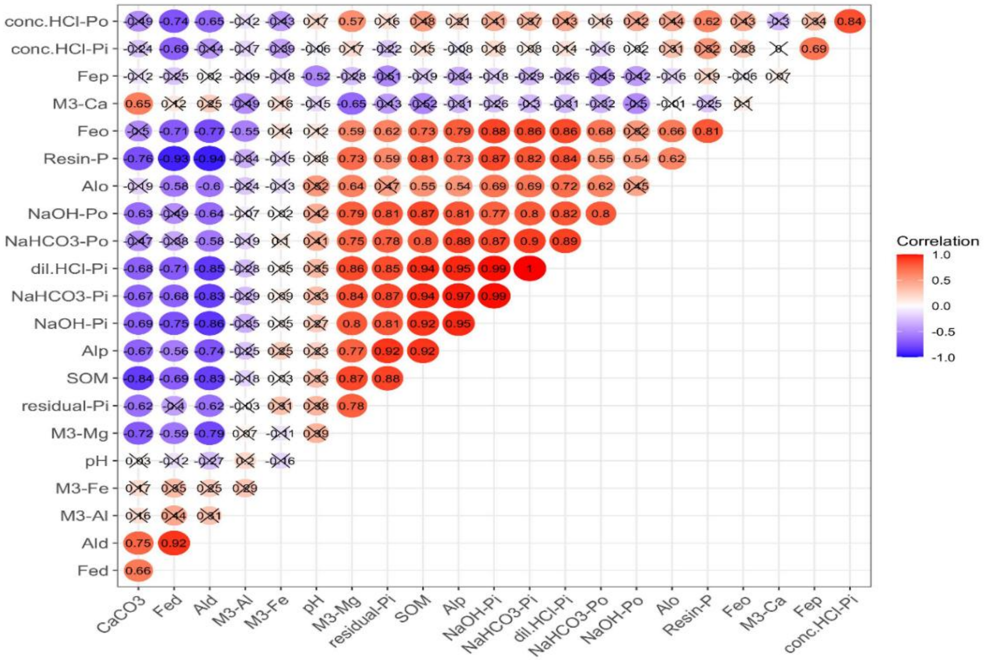


Figure 3-S2 (2) Correlation between soil properties and P fraction in 20–40 cm.

Note: SOM, soil organic matter; Fe_d and Al_d, free Fe and Al oxide; Fe_o and Al_o, amorphous Fe and Al oxide; Fe_p and Al_p, humus complex Fe and Al oxide; M3-Ca, M3-Mg, M3-Fe and M3-Al were Ca, Mg, Fe and Al extracted by Mehlich-3 extraction. “×” means no significant difference between parameters.

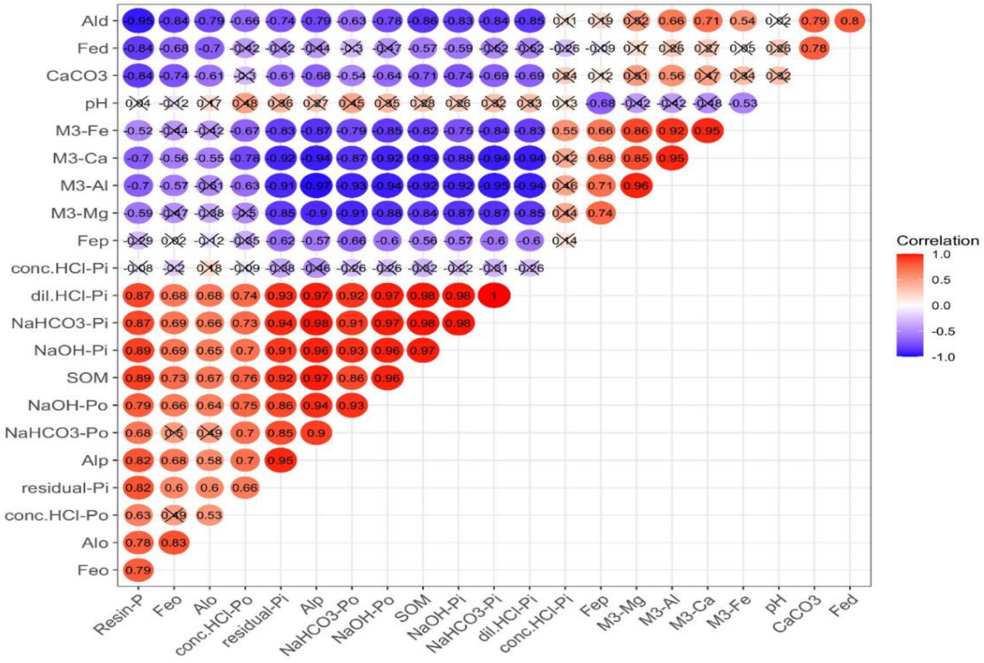


Figure 3-S2 (3) Correlation between soil properties and P fraction in 40–60 cm.

Note: SOM, soil organic matter; Fe_d and Al_d, free Fe and Al oxide; Fe_o and Al_o, amorphous Fe and Al oxide; Fe_p and Al_p, humus complex Fe and Al oxide; M3-Ca, M3-Mg, M3-Fe and M3-Al were Ca, Mg, Fe and Al extracted by Mehlich-3 extraction. “×” means no significant difference between parameters.

Table 3-S1 Comprehensive interpretation rate of phosphorus fraction by soil properties

Soil depth	Properties	Explains %	P
0-20 cm	SOM[1)]	73.8	0.002
	M3-Fe	16.7	0.002
	Alp	1.8	0.048
20-40 cm	Fed	73.2	0.002
	pH	12.4	0.004
40-60 cm	$CaCO_3$	63.7	0.004
	Ald	10.5	0.024
	M3-Ca	10.1	0.036

1) SOM, soil organic matter; Fe_d, free Fe_2O_3; Al_d, free Al_2O_3; Al_p, humus complex Al oxide; M3-Ca, M3-Mg, M3-Fe and M3-Al were Ca, Mg, Fe and Al extracted by Mehlich-3 extraction.

Chapter IV

Phosphorus adsorption and desorption characteristics as affected by long-term phosphorus application in black soil

From Wang, Q., Chen, Y. H., Zhang, N. Y., Qin, Z. H., Jin, Y. W., Zhu, P., Peng, C., Colinet, G., Zhang, S. X. 2022. Phosphorus adsorption and desorption characteristic and its difference mechanism under long-term without and with phosphorus application treatments in black soil. Journal of Plant Nutrition and Fertilizers. 28, 0, 1–14 (in Chinese)

Abstract

Comparison of P adsorption-desorption characteristics in long-term soil with and without P fertilizer can provide a theoretical basis for P management in black soils. The long-term field trial on black soil started in 1990 in Gongzhuling City, Jilin Province. The four treatments were no fertilizer (CK treatment), nitrogen (N) and potassium (K) fertilizers (NK treatment), N, P, K fertilizers (NPK treatment), and NPK plus manure (NPKM treatment). We analyzed soil physicochemical properties. Soil P adsorption-desorption characteristic parameters [maximum adsorption capacity (Q_m), adsorption constant (K_Q), maximum soil P buffering capacity (MBC), degree of P sorption saturation (DPS), maximum desorption capacity (D_m), and desorption ratio (D_r)] in different soil layers were determined using isothermal adsorption and desorption experiment. The adsorbed and desorbed P increased initially and stabilized with increasing P concentration in the equilibrium solution. Compared to the untreated soil, the adsorbed P decreased, and desorbed P increased in the soil with P fertilizers. Compared to the untreated soil, Q_m and MBC decreased by 4.94%−63.46% and 15.90%−75.18%, while D_r increased by 8.52%−474.0% in the 0−60 cm soil profile. Notably, the most significant changes were recorded in the NPKM treatment. The long-term P input increased total P and soil organic matter (SOM) by 34.40%−145.5% and 12.77%−50.07%, decreased the free iron and aluminum oxide (Fe_d+Al_d) by 5.14%−11.35%, respectively, in different soil layers compared to soil without P fertilizers. SOM, Fe_d+Al_d, and total P in soil without P fertilizers, as well as Fe_d+Al_d, organic-bound iron and alumina oxide (Fe_p+Al_p), pH, and SOM in the soil with P fertilizers were the main factors influencing the differences in the characteristic parameters of P adsorption and desorption. The main factors explained 77.59% and 90.62% of the total variation in the soil without and with P fertilizers, respectively ($P < 0.05$). The correlation between Olsen-P and DPS showed that the DPS threshold value for environmental purposes was about 8%. The $DPS_{M\text{-}P}$ (calculated by Mehlich-3 extractable P, Fe, and Al) and $DPS_{O\text{-}P}$ (calculated by Olsen-P and Q_m) ranged from 7.77% to 25.96% and 17.24% to 24.75%, respectively, in 0−60 cm soil profile in NPKM treatment, which far exceeded the threshold, increasing the risk of P loss. Our research suggests that long-term exogenous P input decreases adsorbed P and increases desorbed P, respectively. SOM and Fe_d+Al_d are the main drivers of P adsorption and desorption characteristics in soil without P fertilizers. In the soil with combined P fertilizer, especially NPKM, Fe_d+Al_d, Fe_p+Al_p, SOM, and pH were the main factors affecting the P adsorption and desorption characteristics.

Key words: black soil; long-term fertilization; phosphorus adsorption-desorption; phosphorus loss potential

1. Introduction

Phosphorus (P) is an essential nutrient element for plant growth and affects the production and quality of crops (Liu et al., 2017). In most farmlands of China, long-term excessive fertilization has caused large accumulation of soil P, resulting in P loss and water eutrophication (Van et al., 2017). Meanwhile, P is deficient in some farmlands when little P fertilizer is applied to soil, which greatly restricts the crop yield (Wang et al., 2013). The soill P supply and buffer capacity, and P adsorption behavior of soil to P are used to evaluate P environmental effect (Wang and Liang, 2014; Lair et al., 2009; Laboski and Lamb, 2004; McDowell et al., 2002). Hence, information on the sorption-desorption characteristics of P in soil is essential to improve P availability and assess the risk of P environmental loss.

The adsorption isotherms are used to characterize soil P adsorption-desorption process (Xia et al., 2008). Langmuir equation has been developed to quantitatively fit the P adsorption-desorption isotherms (Lair et al., 2009). Parameters, obtained from the equation, such as the maximum adsorption capacity (Q_m), the maximum desorption capacity (D_m) and the maximum buffering capacity (MBC), are often used to evaluate the mobility of soil P and P loss risk. Soil P level has been considered as direct factor affecting the adsorption–desorption characteristics of soil P (Xia et al., 2009). When soil with low P concentration, there existed large number of soil P high-energy adsorption sites and strong P adsorption binding energy. High energy adsorption is the main adsorption pattern, with higher Q_m and MBC values and lower D_m (Liu et al., 2021). With the continuous P input, the high-energy adsorption sites were gradually saturated. Low-energy adsorption is the main adsorption pattern with lower Q_m and MBC values and higher D_m than when soil P is deficient (Wang et al., 2019; Zhang et al., 2019). In addition to P input, soil properties, such as soil organic matter (SOM), pH, metal oxides, soil clay content, etc., are the main factors affecting the adsorption-desorption characteristics of soil P (Yang et al., 2019; Xu et al., 2014). The increase of clay and silt could promote the adsorption capacity of soil to P (Zhang et al., 2019, Nwoke et al., 2003). Chen et al. (2010) found that the MBC and soil P adsorption capacity increased with the increase of clay content in different textures of cotton field soils. Abdala et al (2015) found that amorphous Fe and Al (hydr)oxides counteract the inhibition of P adsorption by SOM through creating additional P adsorption sites. Therefore, it was important to identify the factors affecting P adsorption-desorption characteristics to reduce the adsorption of soil to P and improve the availability of P. Current studies about the effect of soil properties on P adsorption-desorption characteristics focused on integrating different treatments as a whole (Zhang et al., 2019; Wang et al., 2018; Yan et al., 2018). However, the responses and mechanisms of P adsorption-desorption characteristics without and with P fertilizers to soil properties were completely different. Few studies focused on this phenomenon. The adsorption and desorption behavior determined P mobility (Dari et al., 2018; Kleinman et al., 2002). Comprehensively consideration soil P level and P retention capacity, degree of P adsorption (DPS) was often used to evaluate the capacity of P migration and leaching loss (Sharpley et al., 2020; Breeuwsma et al., 1992). When the DPS value was lower than the threshold value, the P was easily absorbed and fixed by the soil colloid, reducing the transformation of P in the soil (Dou et al., 2009). When DPS exceeded threshold value, retention capacity of soil to P decreased, causing P leaching and water pollution (Liu et al., 2007). Therefore, it was important to study the P adsorption-desorption characteristics in soil profile and determine the environmental threshold value of soil DPS to reduce the risk of P loss.

Black soil was one of the most important grains producing areas and commercial grain bases with high quality of soil fertility and structure in Northeast China (Wang et al., 2019). In recent years, unreasonable P fertilizer input and P management, soil P content varied greatly. Some areas showed a large amount of P accumulation, even the phenomenon of P loss. Understanding P adsorption-desorption characteristics in different soil layers under different fertilization is critical for predicting the long-term P accumulation and release dynamics. This will improve P availability and reduce P loss risk. This research based on a 29-year long-term fertilization experiments in black soil, which provided a platform to evaluate sustainable agricultural management systems (Bhattacharyya et al. 2015). The objectives of this researches were to: (1) explore the difference in characteristics of P adsorption and desorption; (2) quantitatively explain its relationship with soil properties; (3) determine the DPS threshold value in the soil without and with P fertilizers. This study will provide scientific support to improve P availability and reduce agricultural non-point source pollution in black soil.

2. Materials and methods

2.1 Site description

This experiment, built in 1989, was carried out on the national soil fertility and fertilizer effects long-term monitoring network in Gongzhuling City, Jilin Province, China (124°48′34″E, 43°30′23″N). The soil was classified as a Mollisol in USDA Soil Taxonomy (Soil Survey Staff, 2014). The monitoring station belonged to the continental monsoon climate of medium latitudes, with four distinct seasons. The average annual temperature and precipitation were 4−5 °C and 590.7 mm, respectively. The growing season of crops was mainly concentrated in April to September, and the annual accumulated temperature was 2800 °C.

2.2 Fertilization treatments and cropping practices

Soil samples were collected in three soil depths (0–20, 20–40, and 40–60 cm) after crop harvesting under four different treatments in 2018. No fertilization (CK), inorganic nitrogen (N), potassium (K) fertilizers (NK), inorganic N, P, K fertilizers (NPK), NPK plus manure (NPKM). The amount of N (urea) and K (potassium sulfate) in NK and NPK treatments were N: 165 $kg\cdot ha^{-1}$, K: 68 $kg\cdot ha^{-1}$, respectively, and amount of P (diammonium phosphate) in NPK treatment was 36 $kg\cdot ha^{-1}$. In NPKM treatment, the amount in chemical fertilizer were N: 50 $kg\cdot ha^{-1}$, P: 36 $kg\cdot ha^{-1}$ and K: 68 $kg\cdot ha^{-1}$, respectively, and the amount in organic fertilizer (cattle manure) were N: 115 $kg\cdot ha^{-1}$, P: 39 $kg\cdot ha^{-1}$ and K: 77 $kg\cdot ha^{-1}$, respectively. The whole dose of cattle manure and chemical fertilizer (P and K, and one-third of N fertilizer) were applied as base fertilizer before sowing of the crop, and the remaining two-thirds of N fertilizer was applied to the soil 10 cm below the topsoil before jointing stage. Randomized block design with an area of 400 m^2 (57.18 m×7m) and three replications were considered for each field experiment. Continuous maize monoculture was the main cropping pattern, which was sown in late April and harvested in late September. The experimental area was managed in a conventional manner. After the autumn corn harvest in 2018, "S"-shaped sampling method was used to collect soil samples. The soil samples were mixed, air-dried, and sieved for analysis and determination. The basic physical and chemical properties of the soil were shown in Table 3-1.

2.3 Soil sample analyses

The potassium dichromate oxidation-outer heating method, H_2SO_4-$HClO_4$ heating digestion method and $NaHCO_3$ extraction method were used to measure SOM, total P, Olsen-P, respectively (Lu, 1999). Soil pH was decided in electrical potential method of 1:2.5 soil/distilled water (w/v). $Na_2S_2O_4$-$Na_3C_6H_5O_7$-$NaHCO_3$ (DCB), 0.2 mol L^{-1} ammonium oxalate (pH=3), and 0.1 mol L^{-1} sodium pyrophosphate diphosphate (pH=10) was used to extract free Fe and Al oxide (Fe_d and Al_d), amorphous Fe and Al oxide (Fe_o and Al_o), and humus complexed Fe and Al oxide (Fe_p and Al_p), respectively, and were then determined with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Lu 1999). Nitrogen adsorption method was used to measure soil specific surface area (Lu 1999). The content of Mehlich 3-Ca (M3-Ca), M3-Mg, M3-Fe, M3-Al and M3-P were extracted with Mehlich-3 extractant (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), and then measured with ICP-OES (Mehlich 2008).

2.4 Phosphate adsorption and desorption

1.00 g air-dried soil through 2 mm sieve was added to a 50 mL equilibration tube, and add sufficient 0.01 mol L^{-1} 25 mL NaCl (pH=7) solution containing 0, 5, 10, 20, 40, 80, 120 mg P L^{-1} KH_2PO_4, to give a soil/solution ratio of 1:25. Three drops of chloroform were added to restrain the microbial activity. And then the tubes were placed on end-over-end shaker at 150 r/min for 1 h at 25±1°C. The contents of tubes were centrifuged at 4000 rpm for 10 min and then filtered through a 0.45 μm membrane filter after equilibrium for 24 h. The P concentration in the equilibrium solution was measured with the ascorbic acid– molybdophosphate blue method. The amounts of P adsorption were the difference between the initial concentration of P added and the P concentration in the equilibrium solution. 20 mL of saturated NaCl solution at pH 7.0 was added to the tubes to wash the solution two times at the end of the adsorption experiment and the supernatant had been removed. Then 25 mL 0.01 mol L^{-1} NaCl solution at pH 7.0 was added to determine the P desorption amount after shaking, equilibrium, centrifuging. The amount of P in the solutions was considered as desorbed P (Kovar et al., 2009).

2.5 Calculations

Langmuir adsorption equation (Yang et al., 2019): $C/Q = 1/(K_Q \times Q_m) + C/Q_m$; C was the P concentration in the equilibrium solution (mol L^{-1}); Q ($mg \cdot kg^{-1}$) was the amount of P adsorbed to soil at the P concentration in the equilibrium solution; Q_m ($mg \cdot kg^{-1}$) was the maximum adsorption capacity; K_Q ($L \cdot mg^{-1}$) was adsorption constant and related to binding strength of P; MBC ($L \cdot kg^{-1}$) was the comprehensive parameter of Q_m and K_Q and called maximum buffering capacity of soil P; $MBC = K_Q \times Q_m$. D_r, The desorption ratio.

Langmuir desorption equation (Wang et al., 2011): $C/D = 1/(K_D \times D_m) + C/D_m$; D ($mg \cdot kg^{-1}$) was the amount of P desorbed from soil at the P concentration in the equilibrium solution; K_D ($L \cdot mg^{-1}$) was desorption constant and related to desorbing strength; D_m ($mg \cdot kg^{-1}$) was maximum desorption capacity, the desorption ratio (D_r) was the ratio of D_m to Q_m.

Degree of P sorption saturation (DPS) was calculated as follows (Wang et al., 2011; Jalali and Jalali, 2016).

$DPS_{O\text{-}P} = \text{Olsen-P}/(\text{Olsen-P} + Q_m) \times 100\%$

$DPS_{M\text{-}P} = (\text{M3-P}/31)/(\text{M3-Fe}/56 + \text{M3-Al}/27) \times 100\%$

2.6 Statistical analysis

All statistical data was analyzed in average. One way analysis of variance (ANOVA) and Duncan test were used to determine the significant difference in the P adsorption-desorption characteristics and soil properties in different soil layers under long-term different experiments. Pair-sample T-test was used to compare the difference of soil properties between soil without and with P fertilizers at the same soil layer. The “Psych”, “Vegan” package in R software were used to quantitative analysis the relationship between soil properties and P adsorption-desorption characteristics. The figure of P adsorption-desorption curves and soil properties were performed with Origin 9.0.

3. Results

3.1 The characteristics of P adsorption and desorption in soil without and with P fertilizers

The P adsorption and desorption isotherms were shown in Fig. 4-1. The amount of P adsorption and desorption increased rapidly when the P concentration increased to 20 $mg \cdot L^{-1}$, and then slowly increased as the P concentration was higher than 20 $mg \cdot L^{-1}$. In the same soil depth, the order of soil P adsorption capacity was CK＞NK＞NPK＞NPKM. Moreover, the capacity of P adsorption in CK and NK was higher than that in NPK and NPKM treatments. For the same treatment, the amount of P adsorption decreased with the increase of the soil layer (Fig. 4-1 (a-c)). On the contrary, in the same soil depth, the order of P desorption capacity was NPKM > NPK > NK > CK. The P desorption amount in soil with P fertilizers was higher than that in the soil without P fertilizers, especially in 0-20 cm soil depth (Fig. 4-1 (d-f)).

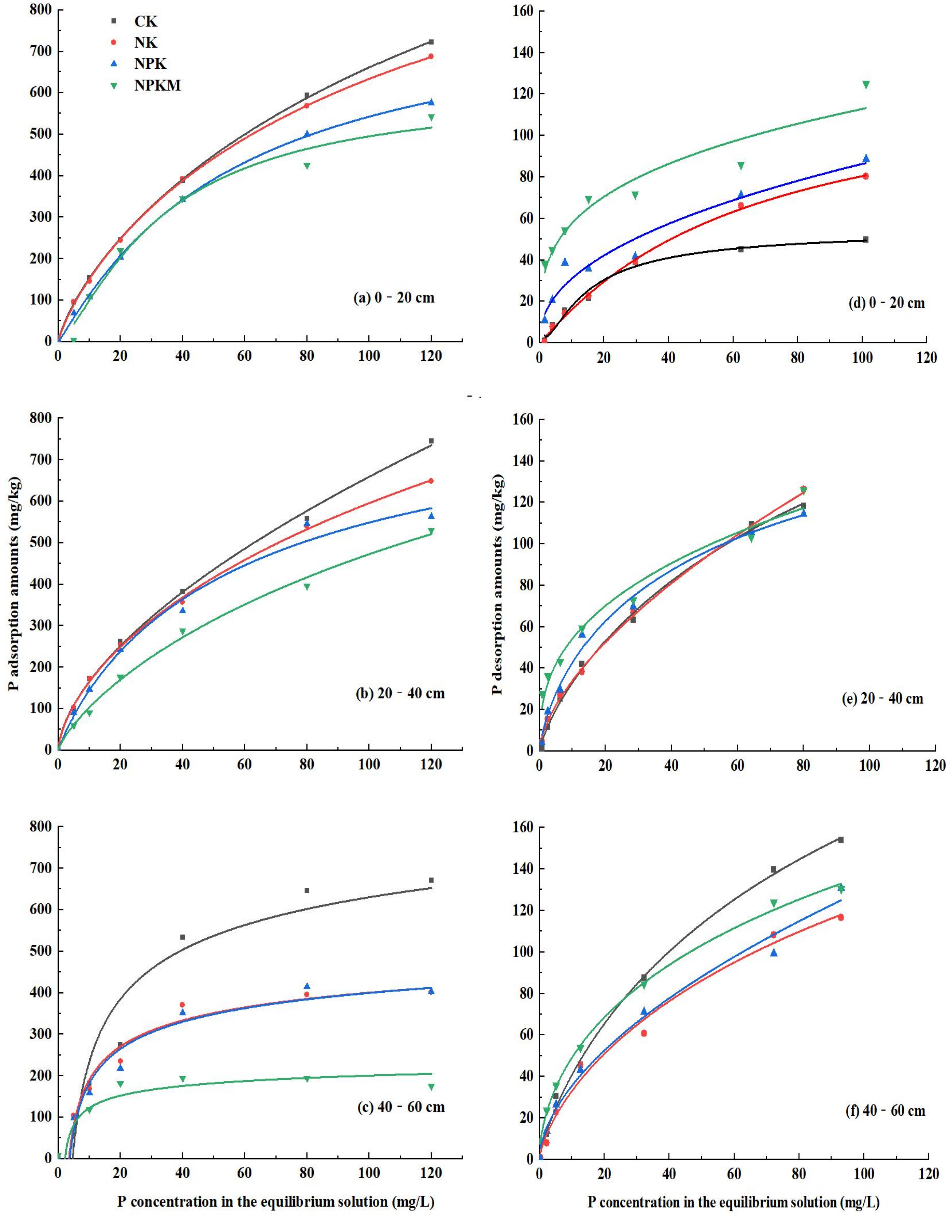


Figure 4-1 Phosphate isothermal adsorption-desorption curves in three soil depths of black soil without and with P fertilizers under long-term experiment

Note: CK—No fertilizer input; NK—Applying N and K fertilizer; NPK—Appling NPK fertilizer; NPKM—Applying NPK and manure.

Langmuir equation fitted well the P adsorption and desorption isotherms, the regression coefficients ranged from 0.8368 to 0.9969 and 0.8938 to 0.9955, respectively ($P<0.01$) (Table 4-1 (a)).

The parameters of P adsorption-desorption were determined by Langmuir equations (Table 4-1 (b)). The maximum P adsorption capacity (Q_m) reflected the number of P adsorption sites per unit weight of soil, and was used to evaluate the adsorption capacity of soil to P (Yan et al., 2013; Hiradate and Uchida, 2004). The Q_m ranged from 192.3 to 815.8 $mg \cdot kg^{-1}$ in black soil. In the same soil depth, compared to CK and NK treatment, the Q_m significantly was decreased by 4.94%-63.46% in NPK and NPKM treatment. And the Q_m values in 0-20 cm and 20-40 cm were 27.54% and 31.82% lower in NPKM treatment than that in NPK treatment, respectively. Significant decrease trend was shown in the Q_m content with increasing soil depth, with the contents in the 40–60 cm being 35.49%-73.17% lower compared with that in the 0–20 cm. The P bonding energy (K_Q) reflected the affinity of soil to P. The higher K_Q value, the stronger P adsorption capacity (Wang and Liang, 2014). Compared to soil without P fertilizers, the K_Q value was decreased by 33.33%-66.67% in 0-20 cm and 14.29%-42.86% in 20-40 cm, respectively, in soil with P fertilizers. Compared to NPK, the K_Q value was decreased by 50.00%, 33.33% and 18.52% in each soil depth in NPKM, respectively. MBC value was combined with Q_m and K_Q value, high MBC value indicates that more P will be adsorbed (Wang et al., 2002). The MBC value was decreased by 15.90%-75.18% in the NPK and NPKM treatments than that in the CK and NK treatments. Especially, the MBC value is lower 12.39%-52.58% in NPKM than that in NPK. DPS was based on the saturation of soil P adsorption sites to determine P release (intensity factor) and soil P level (capacity factor) (Dari et al., 2018; Kleinman and Sharpley, 2002; Breeuwsma et al., 1992). DPS was used to character soil P fixation capacity and the risk of P loss (Nair et al., 2020; Sharpley, 2020; Vadas et al., 2005). Two calculation methods showed that $DPS_{M\text{-}P}$ and $DPS_{O\text{-}P}$ ranged from 0.12% to 25.96% and 0.49% to 24.75%, respectively. In the same soil depth, the values of $DPS_{M\text{-}P}$ and $DPS_{O\text{-}P}$ increased significantly with the increase amount of P fertilizers. NPKM treatment showed the highest DPS value than other treatments, and the value was 1.97-4.92 times and 2.60-5.43 times higher than that in NPK treatment, respectively. With the increase of soil depth, the $DPS_{M\text{-}P}$ value significantly decreased, and $DPS_{M\text{-}P}$ value in different treatments decreased 49.30%-70.08% in 40-60 cm than that in 0-20 cm (Table 4-1(b)).

D_m was defined as the content of P that can be desorbed when the adsorption site of P on the adsorbent was saturated. D_m reflected the maximum content of P available to the crop. D_r reflected the desorption degree of P, and the higher the D_r value, the stronger desorption capacity of P (Yang et al., 2019; Wang and Liang, 2014). The D_m showed opposite trend to that in Q_m. In 0-20 cm soil depth, the D_m value was higher in the soil with P fertilizers than that in the soil without P fertilizer, and the D_m value was increased by 32.72%-414% in NPKM treatment in comparison with other treatments. The D_r value in 0-60 cm profile in the soil with P fertilizers was higher than that in the soil without P fertilizers, with an increase rate of 8.52%-474.0%. In each soil depth, NPKM treatment showed the highest D_r value than other treatments, and the value was 34.27%-91.32% higher than that in NPK treatment (Table 4-1 (b)).

Table 4-1 (a) Phosphate adsorption and desorption equations and parameters of black soil with and without P fertilizers in three soil depths

		Adsorption equation		Desorption equation	
Depth (cm)	Treatment	$C/Q = C/Q_m + 1/K_QQ_m$	R^2	$C/D = C/D_m + 1/K_DD_m$	R^2
0-20	CK	$C/Q=0.0012Q+0.0195$	0.9466^{**}	$C/D=0.0303D+0.2813$	0.9651^{**}
	NK	$C/Q=0.0013Q+0.0217$	0.9675^{**}	$C/D=0.0142D+0.3411$	0.9295^{**}
	NPK	$C/Q=0.0014Q+0.0521$	0.9798^{**}	$C/D=0.0107D+0.1446$	0.9249^{**}
	NPKM	$C/Q=0.0020Q+0.0521$	0.8368^{**}	$C/D=0.0059D+0.126$	0.8215^{**}
20-40	CK	$C/Q=0.0013Q+0.0187$	0.9446^{**}	$C/D=0.008D+0.1068$	0.9182^{**}
	NK	$C/Q=0.0014Q+0.0201$	0.9660^{**}	$C/D=0.0087D+0.0856$	0.8938^{**}
	NPK	$C/Q=0.0015Q+0.0239$	0.9657^{**}	$C/D=0.0079D+0.0845$	0.9955^{**}
	NPKM	$C/Q=0.0022Q+0.0123$	0.9581^{**}	$C/D=0.007D+0.097$	0.9462^{**}
40-60	CK	$C/Q=0.0013Q+0.0123$	0.9866^{**}	$C/D=0.0057D+0.0806$	0.9947^{**}
	NK	$C/Q=0.0023Q+0.0128$	0.9969^{**}	$C/D=0.0061D+0.1599$	0.9807^{**}
	NPK	$C/Q=0.0038Q+0.0149$	0.8454^{**}	$C/D=0.006D+0.1425$	0.9280^{**}
	NPKM	$C/Q=0.0049Q+0.0218$	0.9855^{**}	$C/D=0.0063D+0.1111$	0.9733^{**}

Table 4-1 (b) Phosphate adsorption and desorption equations and parameters of black soil with and without P fertilizers in three soil depths

Depth (cm)	Treatment	Q_m mg kg^{-1}	K_Q L mg^{-1}	MBC L kg^{-1}	DPS_{M-P} %	DPS_{O-P} %	D_m mg kg^{-1}	D_r %
0-20	CK	815.85±46.62Aa	0.06±0.006Ba	51.41±4.15Ba	0.24±0.04Ac	0.49±0.19Ac	35.48±2.59Cc	4.34±0.06Cc

	NK	753.97±39.68Aa	0.06±0.01Ba	45.98±4.97Ba	0.69±0.22Ac	0.88±0.18Ac	72.86±1.26Cb	9.73±0.64Cb
	NPK	716.73±29.63Aa	0.04±0.001Cb	19.19±8.31Cb	6.76±0.46Ab	6.87±1.13Ab	92.66±8.16Cb	13.02±1.45Cb
	NPKM	519.35±23.17Ab	0.02±0.001Cc	12.76±1.25Cc	25.96±1.70Aa	24.75±2.48Aa	128.22±8.61Ba	24.91±2.76Ba
P fertilization effect		*	**	**	*	*	**	**
20-40	CK	769.23±18.31Aa	0.07±0.008Ba	53.48±1.70Ba	0.21±0.02ABb	0.50±0.21Ab	121.89±1.93Bab	16.24±0.19Bb
	NK	714.29±14.47Aa	0.07±0.006Ba	49.75±2.16Bb	0.41±0.03Ab	0.92±0.26Ab	115.95±5.72Bb	16.67±0.63Bb
	NPK	666.67±3.43Aa	0.06±0.006a	41.84±0.42Bb	3.32±0.31Bb	2.68±0.44Bb	120.79±3.47Bab	18.09±0.76Bb
	NPKM	454.54±9.54Ab	0.04±0.003Bb	19.84±0.54Bc	19.66±4.90Aa	17.24±3.29Aa	134.78±4.91ABa	24.29±0.77Ba
P fertilization effect		**	**	**	*	*	NS	*
40-60	CK	526.32±5.68Ba	0.19±0.009Aa	98.04±4.18Aa	0.12±0.02Bc	0.51±0.14Ac	165.53±5.01Aa	30.95±1.19Ac
	NK	434.78±4.39Ba	0.18±0.004Aa	78.13±1.83Aa	0.25±0.05Ac	0.83±0.07Ac	152.95±5.83Aa	35.38±0.57Ac
	NPK	192.31±9.19Bb	0.27±0.003Aa	52.36±1.84Ab	2.61±0.49Bb	5.62±0.68Ab	162.14±4.36Aa	48.38±0.83Ab
	NPKM	204.08±3.56Bb	0.22±0.007Aa	45.87±1.35Ac	7.77±0.95Ba	23.19±1.50Aa	157.97±6.99Aa	80.25±3.83Aa
P fertilization effect		**	NS	**	**	*	NS	**

Note: Q_m—Maximum P adsorption capacity; K_Q—P adsorption constant; MBC—P maximum buffering capacity; D_m—P maximum desorption capacity; K_D—P desorption constant; DPS_{M-P}— Degree of P sorption saturation calculated with Mehlich-3 extracted P, Fe and Al; DPS_{O-P}— Degree of P sorption saturation calculated with Olsen-P and D_m; D_r— The P desorption ratio. Data followed by different lowercase letters indicate significant difference among treatments in the same soil depth, and followed by different uppercase letters indicate significant difference among soil depths of the same treatment ($P < 0.05$); P fertilization effect was defined as the T-test between the average values of NPK and NPKM and that of CK and NK treatment, *—$P < 0.05$，**—$P < 0.01$.

3.2 Soil properties

Compared to the soil without P fertilizers, the content of total P and SOM increased by 34.30%-145% and 12.77%-50.07%, Fe_d+Al_d decreased by 5.14%-11.35%, respectively, in the soil with P fertilizers ($P<0.05$, Fig. 4-2). The content of Fe_o+Al_o and Fe_p+Al_p increased by 13.06%-18.22% and 20.66%-32.15%, respectively, in the P fertilizer treatments, compared to that without P fertilizer treatments, in 0-20 and 20-40 cm. Meanwhile, P application significantly increased the content of M3-Fe in 0-20 cm and 40-60 cm, M3-Al and M3-Ca in 40-60 cm. For the soil without P fertilizers, the contents of SOM, M3-Al and M3-Fe decreased by 27.10%, 7.71% and 20.50%, respectively, and Fe_d+Al_d increased by 4.70% in 40-60 cm than that in 0-20 cm ($P<0.05$). For the soil with P fertilizers, the content of total P, SOM, Fe_o+Al_o, Fe_p+Al_p, M3-Al and M3-Fe in 40-60 cm were lower 48.51%, 10.52%, 24.40%, 2.11% and 16.33%, respectively, than that in 0-20 cm.

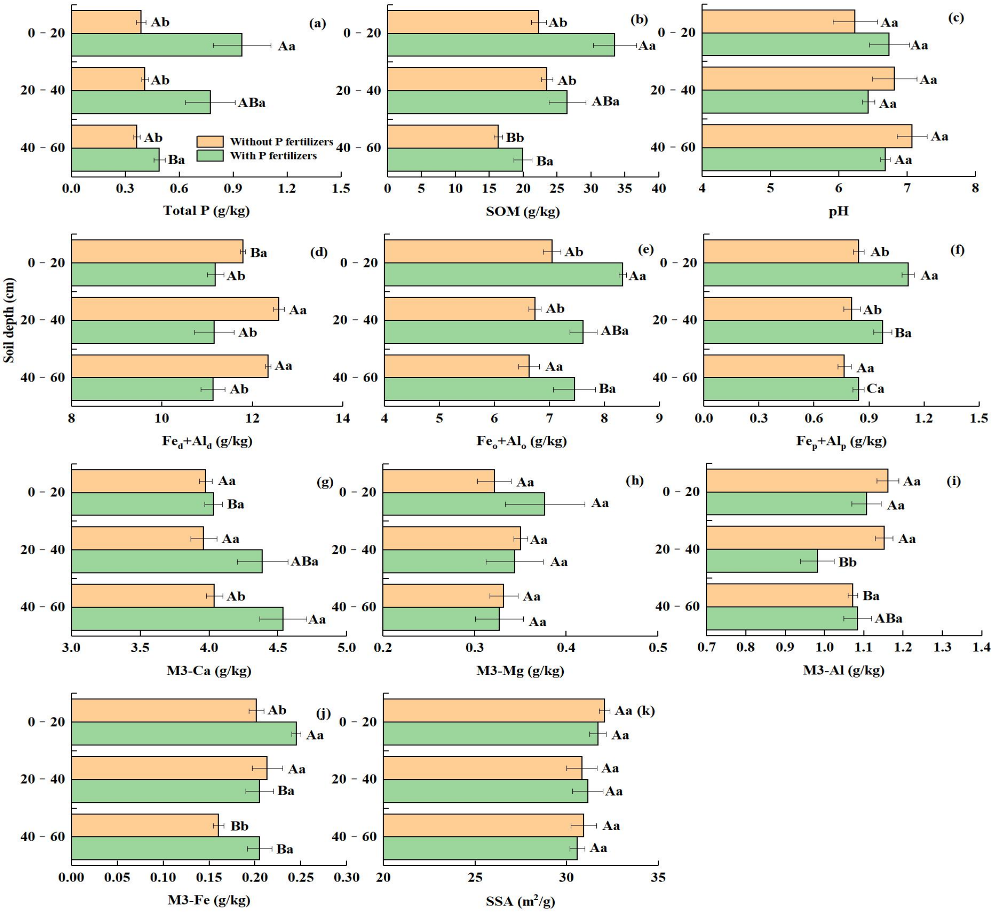


Figure 4-2 Soil properties in three soil depths of black soil without and with P fertilizers under long-term experiment

Note: The data for statistics was the average of CK and NK, and that of NPK and NPKM; SOM−Soil organic matter; $Fe_d + Al_d$ were the sum of free iron and aluminum oxide; $Fe_o + Al_o$ were the sum of amorphous Fe and Al oxides; $Fe_p + Al_p$ were the sum of humus complex Fe and Al oxides; M3-Ca, M3-Mg, M3-Fe and M3-Al were the Ca, Mg, Fe and Al extracted by Mehlich-3 solution, respectively. SSA−Soil specific surface area. Different uppercase letters beside the bars indicate significant difference among soil depths of the same treatment, and lowercase letters indicate significant difference among treatments in the same soil depth ($P < 0.05$).

3.3 Relationship between soil properties and characteristic parameters of P adsorption-desorption

In the soil without P fertilizer, total P was significantly negatively correlated with $DPS_{O\text{-}P}$ and positively correlated with Q_m. SOM, M3-Al and M3-Fe showed significantly positive correlation with Q_m, and negatively correlation with K, MBC and D_r (Fig. 4-3a). $DPS_{M\text{-}P}$ showed negative correlation with pH, and positive correlation with Fe_o+Al_o and Fe_p+Al_p ($P < 0.05$). Significantly positive correlation was found between SOM and M3-Fe, Fe_p+Al_p and M3-Fe. Significantly negative correlation was found between Fe_d+Al_d and Fe_o+Al_o, Fe_p+Al_p and pH. RDA result showed that soil properties could explain 77.59% of the total variance in the P adsorption and desorption characteristics. SOM, Fe_d+Al_d and total P were the main factors, and the explanation rates were 36.73%, 16.55% and 13.38%, respectively (Fig. 4-4).

In the soil with P fertilizers, soil properties showed significant effects on the $DPS_{M\text{-}P}$, $DPS_{O\text{-}P}$ and MBC (Fig. 4-3b). Total P, SOM, Fe_p+Al_p, pH and M3-Mg showed a significant positive correlation with $DPS_{M\text{-}P}$ and $DPS_{O\text{-}P}$, and significant negative correlation with MBC. In addition, Fe_p+Al_p was negatively correlated with K_Q, D_m and D_r, Fe_o+Al_o was positively correlated with $DPS_{M\text{-}P}$ and $DPS_{O\text{-}P}$, and Fe_d+Al_d and M3-Ca were negatively correlated with $DPS_{M\text{-}P}$ and $DPS_{O\text{-}P}$ ($P<0.01$). There existed extremely significant positive correlation between total P and SOM, which were significantly negatively correlated with Fe_d+Al_d and M3-Ca, and positively correlated with Fe_o+Al_o, Fe_p+Al_p, pH and M3-Mg ($P<0.05$). Fe_d+Al_d was significantly negatively correlated with Fe_p+Al_p and M3-Mg, and positively correlated with M3-Ca and M3-Fe ($P<0.05$). There existed extremely significant positive correlation between Fe_o+Al_o and Fe_p+Al_p, which were negatively correlated with M3-Ca and positively correlated with M3-Mg. RDA result showed that soil properties could explain 90.62% of the total variance in the P adsorption and desorption characteristics. Fe_d+Al_d, Fe_p+Al_p, pH and SOM were the main factors, and the explanation rates were 33.94%, 28.57%, 5.89% and 3.28%, respectively (Fig. 4-4).

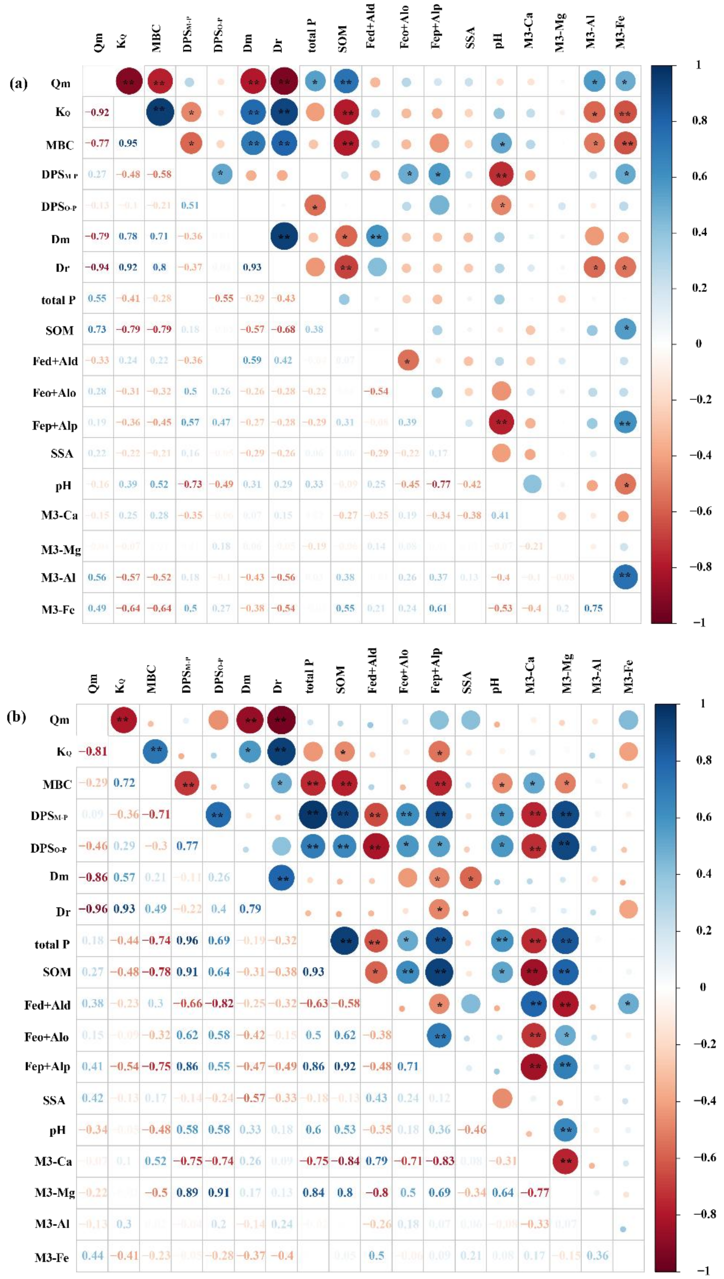


Figure 4-3 The relationship between soil properties and P adsorption and desorption characteristics of black soil without and with P fertilizers under long-term experiment

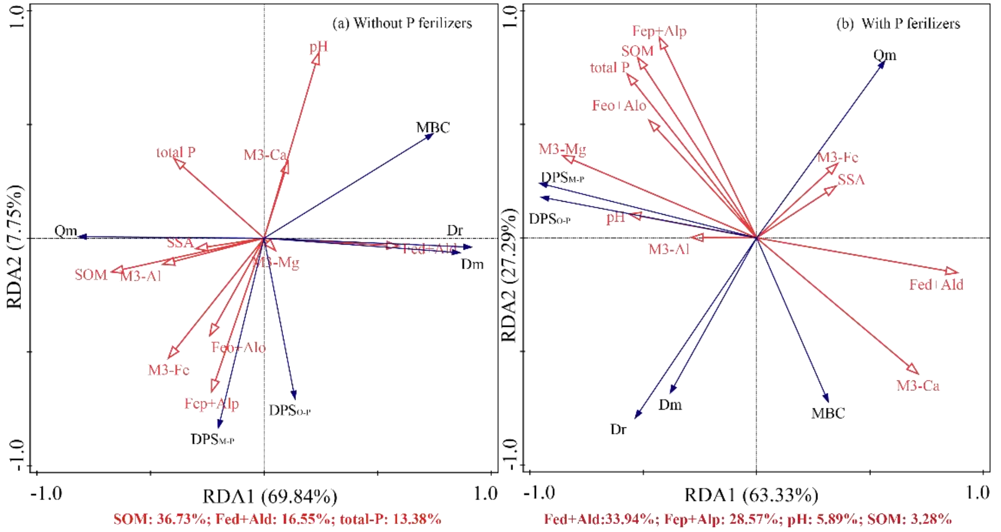


Figure 4-4 Effect of the P adsorption and desorption characteristics to soil properties of black soil without and with P fertilizers under long-term experiment

4. Discussion

4.1 The characteristics of P adsorption-desorption in the black soil without and with P fertilizers

The P adsorption capacity in different treatments increased rapidly at first, and then gradually tended to slow down (Fig. 4-1). It was similar to the results studied by Liu et al (2021) in yellow soil, Yang et al. (2019) in black soil, Zhang et al. (2019) in fluvo-aquic soil. The possible reason was that the adsorption process of P was multistage kinetic process, which was affected by the adsorption capacity and residence time of solid phase (Bhadha et al., 2012). Under low P concentration in equilibrium solution, chemical adsorption dominated the adsorption process, and ion exchange and ligand exchange were the main mechanisms for its high adsorption rate (Lai and Lam, 2009). Under high P concentration in the equilibrium solution, the available adsorption sites of soil P were gradually saturated, the P in the solution was fixed by soil in the form of physical-chemical adsorption (Wang and Liang, 2014; Lai and Lam, 2009). The P desorption amount was lower than that P adsorption amount in each treatment, indicating that the P adsorbed in soil can be desorbed and re-released into soil solution to a certain extent (Yang et al., 2019). The P desorption amount increased along with the increase of P concentration in soil equilibrium solution (Fig. 4-1). The possible reason was that under low P concentration in equilibrium solution, P was adsorbed to the high bond energy site of soil colloid and showed strong binding capacity. With the increase of P concentration in soil equilibrium solution, the binding energy of soil to P gradually decreased, the adsorbed-P was easy to be desorbed, and the amount of P desorption increased gradually (Qian et al., 2012).

In the soil without P fertilizers, P adsorption amount and Q_m were lower in NK than that in CK (Fig. 4-1). Q_m showed a significantly positive correlation with total P, SOM, M3-Fe and M3-Al (Fig. 4-3a). Previous studies showed that compared to CK, NK decreased the content of SOM, and showed little effect on total P, M3-Fe and M3-Al (Wang et al., 2022). As the main factor affecting P adsorption-desorption characteristics (Fig. 4-4a), the decrease of SOM content was the possible reason for the decrease of Q_m in the NK (Yang et al., 2019; Wang and Liang, 2014). Moreover, P adsorption amount and Q_m was lower in the 40-60 cm than that in 0-20 cm (Fig. 4-1 and Table 4-2 (b)). The possible reason was that the decreased adsorption sites due to the decrease of SOM, M3-Fe and M3-Al, reduced the adsorption of soil to P (Wang et al., 2022). In the same soil depth, P adsorption amount, Q_m, K_Q and MBC were decreased, D_m and D_r were increased in NPK and NPKM than that in CK and NK, similar results were also found in the gray desert soil and calcareous soil. It indicated that long-term P fertilizer application could reduce adsorption capacity of soil to P, increase the desorption capacity and improve soil P availability (Wang et al., 2013). However, Liu et al. (2021) found that application of chemical P fertilizer increased the adsorption sites and binding energy of soil P in the yellow soil. Lin et al. (2011) found that the Q_m and P adsorption sites increased in NPKM when compared to that in NK and NPK, indicating that the influencing factors of P adsorption and desorption are complex and its influence mechanism needed to be further studied.

4.2 Effects of soil properties on P adsorption-desorption characteristics in black soil without and with P fertilizers

P level, SOM and metal oxides are important factors affecting P adsorption-desorption characteristics (Sun et al., 2020; Yang et al., 2019; Wang et al., 2019; Zhang et al., 2019). In this study, SOM was significantly positively correlated with Q_m and negatively correlated with D_m in CK and NK (Fig. 4-3a). This was similar to the results obtained by Yang et al. (2019) through incubation experiments in black soil. The results showed increase of SOM significantly increased the Q_m value and decreased the D_m value when soil total P was low. These results indicated that when soil P was deficiency, the increase of SOM could increase the adsorption sites of P and storage capacity of soil (Zhou and Zhu, 2003). The possible reason was that SOM was a medium for P-fixing, and it could enhance the activity of Fe/Al oxides through dissolution and increase the adsorption capacity of soil to P (Mamo et al., 2005; Hu et al., 1993). The result of this study verified this view that there was positive relationship between SOM and M3-Fe in CK and NK. Decreased Q_m and increased D_m and D_r values in NPK and NPKM indicated that long-term P input could reduce adsorption of soil to P, increase the P desorption capacity and improve P utilization (Yang et al., 2019). RDA analysis showed that Fe_d+Al_d and Fe_p+Al_p were the main factors affecting the characteristics of P adsorption and desorption, followed by pH and SOM in NPK and NPKM (Fig. 4-4). Kang et al. (2009) found that although there was significant correlation between SOM and Q_m, SOM showed indirect effect on Q_m through the interaction with Fe/Al oxides (Gan and Xu, 1994;

Xia and Roy, 2000). In this study, P fertilizers significantly affected the transformation of Fe/Al oxides, reducing the physical and chemical adsorption potential of soil colloid to P.

4.3 P management in black soil

The research results showed P fertilizer could significantly decrease the adsorption capacity of soil to P and increase P availability. However, it easily increased the risk of environmental pollution (Xue, 2013). Generally, DPS value=25% was defined as the threshold value for P loss purpose (Schoumans and Groenendijk, 2000). The DPS threshold value ranges in different soils. For example, the DPS threshold value exceeded 8% in red soil and 10% in yellow soil could cause the P loss risk (Liu et al., 2021; Wang, 2004; Liu et al., 2001). In this study, two methods were used to calculate the soil DPS value, which showed significantly correlation with Olsen-P ($P<0.01$) ($R^2=0.7888^{**}$ and 0.9756^{**}) (Fig. 4-5). The critical value of Olsen-P loss in black soil determined in previous studies was 50.64 mg kg^{-1} (Wang et al., 2022), and according to the value, the $\text{DPS}_{\text{O-P}}$ and $\text{DPS}_{\text{M-P}}$ were 8.82% and 7.48%, respectively. Therefore, it was believed that when the DPS value of black soil was about 8%, there existed high risk of soil P loss. DPS value was affected by Olsen-P, Q_m and Fe/Al oxide, which was directly determined by fertilization. Therefore, rational P input and the ratio of chemical fertilizer and manure should be deeply considered to regulate P supply and reduce the risk of P loss in black soil.

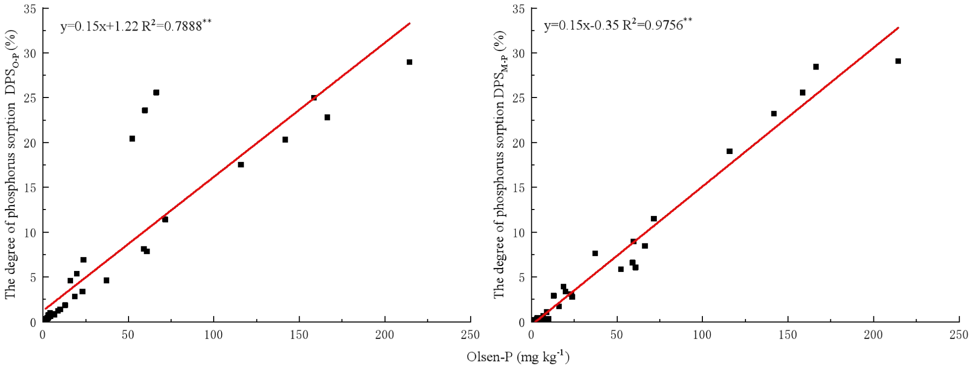


Figure 4-5 The relationship of the degree of P sorption saturation ($\text{DPS}_{\text{O-P}}$, $\text{DPS}_{\text{M-P}}$) with Olsen-P of soil.

Note: $\text{DPS}_{\text{M-P}}$ and $\text{DPS}_{\text{O-P}}$ was the degree of P sorption saturation calculated by Mehlich-3 extractable P and Olsen-P, respectively.

5. Conclusion

Long-term P put significantly decreased the adsorption, increase the desorption of soil to P and improve the P availability by reducing the Q_m and MBC, and increasing the D_m. Higher effectiveness was found in NPKM than NPK. According to RDA analysis, SOM, Fe_d+Al_d and total P in soil without P fertilizers, and Fe_d+Al_d, Fe_p+Al_p, pH and SOM in soil with P fertilizers, respectively, were the main factors affecting characteristic parameters of P adsorption and desorption.

6. Acknowledgement

This research was supported by the National Natural Science Foundation of China (41977103), and National Key Research and Development Program of China (2021YFD1500205).

Chapter V

General discussion, conclusions, and perspective

1. General discussion

1.1 Effects of long-term different fertilizer treatments on total P, Olsen-P and transport of P in soil profile

Olsen-P is an important indicator of soil P supply capacity. The Olsen-P level decides the crop yield and is affected by fertilization, soil physical and chemical properties, climate and so on. In this study, compared to initial value, the Olsen-P content was lower in no P treatments (CK and NK), and higher in P fertilizer treatments (NPK and NPKM) under long-term experiment. Similar result that Olsen-P content decreased under long-term without P fertilizers in falvo-aquic soil, alkaline soil, purplish soil, lou soil and red soil (Zhang et al., 2022; Zhang et al., 2021; Fan et al., 2018, Shen et al., 2014a). In the soil without P fertilizer, parent material was the main source of total P, and P depletion was mainly due to crop uptake. Although the P stored in the soil could be partially mineralized as Olsen-P every year, it wasn’t enough to meet the needs of crops, and the Olsen-P content gradually decreased (Qu et al., 2008; Tang et al., 2008). In addition, natural factors such as precipitation, soil erosion, etc. could cause P loss, thereby reduced the content of Olsen-P. The decrease in Olsen-P content was lower in NK treatment than that in CK treatment (Table 3-3), which was similar to the findings of many long-term experiments (Wei et al., 2017; Wang et al., 2010). The possible reasons were that: (1) the synergistic uptake of crop to P due to the utilization of by crop promoted the conversion of insoluble P form to high active P form and increased the Olsen-P content. The results showed that compared to CK, no significant difference was found for total P content , but proportion of P species with higher activity increased in NK in 2018, supporting the conclusion (Fig. 3-S1). (2) In NK, due to the long-term application of urea, which increased the concentration of soil H^+, the lower soil pH promoted the dissolution of insoluble phosphate, thus supplementing Olsen-P content. (3) In addition, low pH in NK could promote the acid phosphatase activity, which would mineralize Po form to available P, thereby slowing the decline of Olsen-P. No P fertilizer was input in CK and NK, the total P didn’t decrease in 20-40 and 40-60 cm soil depth in comparison with initial value, the possible reason was that the soil P mineralization could maintain the total P content in subsoil.

The Olsen-P content increased under long-term P fertilizer treatments, especially in NPKM (Table 3-3), which might be affected by the accumulation of soil P (Huang et al., 2016; Shen 2014; Sun et al., 2009; Xu et al., 2000). Moreover, the organic acid generated during the decomposition of the organic fertilizer could activate soil P and reduce the adsorption and fixation capacity of soil to P then increase the content of soluble P in the soil (Qi et al., 2012). However, Liu et al (2019) found that Olsen-P increase rate was higher in NPK than that in NPKM in the yellow soil. The possible reason was that the addition of organic fertilizers to soil aggravated the reduction process under waterlogged conditions, increasing the fixation of P by Fe/Al oxides and weakening the improvement of soil properties by organic fertilizer (Yang et al., 2004; Zhang et al., 1998).

In NPKM, a lot of amount P was trapped in the 0-20 cm soil profile due to the soil P adsorption, while the content of total P and Olsen-P decreased in 20-40 and 40-60 cm soil profile (Fig. 3-2). Although most P was retained in the topsoil, parts of it leached to subsoil because of over application of P fertilizer (Milic et al., 2019). Liu et al. (2019) found that dissolved Pi and Po were the main P forms in the profile leachate after one-year excessive application of P fertilizer in paddy soil. In our study, resin-P, $NaHCO_3$-Pi, NaOH-Pi and dil.HCl-Pi were the mainly increased P fractions in 20-40 and 40-60 cm in NPKM, which contributed the P availability and increased the risk of soil P loss. Moreover, the increased degree of P saturation and reduced adsorption capacity due to the excessive P fertilizer application caused the P downward migration (Pizzeghello et al., 2016). Furtherly, the results achieved herein showed that, the DPS value and Olsen-P content had exceeded the critical value for environmental purpose in 40-60 cm in NPKM treatment (Fig. 3-1, Fig. 4-5), which presented a potential risk of P loss to groundwater, more and more P will migrate to the water with progress of experiment if no change was made in NPKM.

1.2 Effects of long-term different fertilizer treatments on P species

The modified Hedley sequential extraction method is widely used to character the different Pi and Po fractions based on their solubility (Tiessen and Moir, 1993; Hedley et al.,1982). P K-edge XANES and solution ^{31}P-NMR spectroscopy are used to speciate Pi and Po at the molecular level, respectively (Liu et al., 2020, 2015 2013, Toor et al., 2006). The results showed that the Pi fraction was the main soil P species under different fertilizer treatments, which indicated that Pi was the sensitive P source affecting the P supply capacity of black soil (Zhang et al. 2018). The P K-edge XANES and ^{31}P-NMR showed that orthophosphate, especially, Ca-P and Fe-P was the main Pi fraction for the initial soil in this experiment (Table 2-2 and 2-3). When soil with P fertilizers, the proportion of P fraction was changed, Pi was dominated by Al-P and monobasic calcium phosphate monohydrate (MCP) for NPK, Al-P and MCP and tricalcium phosphate (TCP) for NPKM, indicating fertilization regime could affect P composition in the soil.

P fractions extracted with Hedley methods showed different P availability. Resin-P is a kind of soil solid Pi in equilibrium with soil solution, can be immediately and directly utilized by plants and is the most active P fraction (Shi et al., 2013; Yang and Post, 2011; Tiessen et al., 1984). $NaHCO_3$-Pi is adsorbed on the surface of soil particles with high effectiveness and can be released by ligand exchange with HCO_3^-, so it is easy to be absorbed and utilized by crops. NaOH-Pi is combined with amorphous and some crystalline Fe, Al compounds and clay particles by chemisorption, with low availability to plants (Bunemann, 2008; Tiessen and Moir, 2007; Zhang et al., 2004; Cross and Schlesinger, 1995). Dil.HCl-P is primary mineral P pool and bound with calcium (Ca), which can be utilized by plants after released by weathering (Yang and Post, 2011; Cross and Schlesinger, 1995). Conc.HCl-P and residual-P are low solubility and least available to plants (Condron and Newman, 2011; Tiessen and Moir, 1993; Hedley et al., 1982).

When soil P was deficient, stable P can be considered as a P pool. Daroub et al. (2001) found that long-term cultivated crops could promote the transformation of stable-P into high active P. Guo et al (2008) also proved when soil Olsen-P level was low, stable Pi would become the main P source for crops growth. Zhan (2015) showed that after long-term without P fertilizer, the content of conc.HCl-Pi and residual-P in CK and NK significantly decreased in black soil, indicating that extreme P deficiency (synergistic absorption of P caused by the application of nitrogen fertilizer) improved the transformation of stable P to active P fraction. In this research, the proportion of $NaHCO_3$-Po and conc.HCl-Po decreased in CK and NK when compared to that in initial year, mineralization was the main reason in variance of P fractions (Nziguheba and Bünemann, 2005; Addiscott and Thomas, 2000; Hedley et al., 1982; Adepetu and Corey, 1976). The occurrence of Po mineralization was related to the environmental condition of the soil and the quality of organic residues (Xavier et al., 2009). However, the content and proportion of NaOH-Po increased in CK and NK after 29-year experiment in comparison with that in initial year (Fig 3-S1). It was related to the increase of amorphous and organic-bound Fe/Al oxides in CK and NK, which significantly positively correlated with NaOH-Po (Table 3-4) and promoted its adsorption of NaOH-Po. No manure was applied in CK and NK since 1989, the main sources of Po in the soil were crops, including roots and crop residues and P fixation by soil microorganisms (Condron and Tiessen, 2005), which promoted the transformation of Pi to Po and were the possible reasons for the increase in NaOH-Po. Moreover, the increased proportion of total inositol phosphate, which was easily adsorbed and fixed by soil Fe and Al oxides and showed significant positive relationship with NaOH-Po in CK and NK treatment (data weren't shown), was another reason for the increase of NaOH-Po (Giaveno et al., 2010). Soil microorganism was the main body of mineralization, and it was also the "source" of C, N, P, S and other substances (Oberson and Joner, 2005). When the soil P was deficient, the soil microorganism itself was lack of energy, competed with crops to absorb soil nutrients, and the mineralization was weakened, which decreased the Pi fraction and increased the proportion of Po fraction. Compared to CK, NK increased the proportion of high active Pi fraction to sum of P fractions (resin-P, $NaHCO_3$-Pi, and NaOH-Pi) in each soil layer studied. In 0-20cm soil layer, the decrease of Ca-P (dil.HCl-Pi) was the main source of the increase of high active Pi. In 20-40 and 40-60 cm soil layers, the transformation of stable Pi and the mineralization of Po were the main reasons for the increase of the proportion of Pi with higher activity. The possible reason was that long-term application of N and K fertilizer could reduce the content of soil pH and $CaCO_3$, and promote the efficient use of P in maize, increasing the release of stable P.

After long-term application of P fertilizer, compared to CK, except for the fractions of P utilized by crops, the excess P accumulated in the soil and transformed into different P fractions (resin-P, $NaHCO_3$-P (Pi+Po), NaOH-P (Pi+Po), dil.HCl-Pi and residual-P). The resin-P and $NaHCO_3$-Pi increased after long-term P fertilization, similar results were also found in clay loam soil and vertisol (Shi et al., 2013; Singh et al., 2001). The accumulation of $NaHCO_3$-Pi in the NPKM was significantly higher than that in the NPK, the possible reason was that the content of SOM was significantly increased, reducing the adsorption of P by interaction with mineral oxides, and improving the transformation of stable P and mid-labile P to high active P fraction. Similar results were also found by Singh (2001) and Reddy (1999) that the application of cattle manure could significantly replenish $NaHCO_3$-Pi.

The increased rate of resin-Pi, $NaHCO_3$-P, dil.HCl-Pi was higher, residual-P was lower in NPKM than that in NPK, which indicated that NPKM could promote the transformation of total P to high active P species. Dil.HCl-Pi showed greatest increase rate when compared to other P fractions in NPKM. Specifically, the result of XANES (Table 2-2) showed that Ca-P, especially MCP and TCP, were the main increased P fractions. The possible reason was that high content of calcium and P in manure was the main source of Ca-P in NPKM treatment (Güngör et al., 2007; Toor et al., 2006; Sharpley and Moyer 2000), and the presence of organic acids in manure could inhibit formation of HAP. Higher increase rate in NaOH-Pi and Al-P was found in NPK than that in NPKM (Fig.3-S1 and Table 2-1). Weand et al. (2010) reported that there was a significant positive relationship between NaOH-P and soil Al^{3+}, Fe^{3+} concentration. In this research, soil pH decreased and the M3-Al concentrations was significantly higher in NPK than that in NPKM, increasing the adsorption of P to form mid-labile P fraction, and increase the proportion of NaOH-Pi (Abdala et al., 2018; Chen et al., 2018). The possible reason for the low increase rate in NPKM were that SOM could interact with Fe and Al through cation bridge, decreasing the concentration of soil metal ions and its fixation of P (Fink et al., 2016). Long-term application of P fertilizer increased the content of $NaHCO_3$-Po and NaOH-Po, but the transformation rate of total P to Po and proportion of Po to sum of P fraction were lower than that of Pi (Fig. 2-S1, Table 2-S1). Many reports had shown that long-term application of manure made a great contribution to the accumulation of Pi, but had no significant effect on Po, which lead to a decrease in the proportion of Po to the total P (Yan, 2015; Keller et al., 2012; Sharpley et al., 2004). The application of P fertilizer significantly decreased the proportion of orthophosphate diester after correction of degradation products, and some studies showed that the dominant component of soil microbial biomass P was orthophosphate diester (Condron and Tiessen, 2005). Therefore, we speculated that P fertilizer could promote the transformation of Po to Pi by increasing the biological mineralization process of microorganisms.

1.3 Effects of long-term different fertilizer treatments on P adsorption-desorption characteristics and its correlation with P fractions

Soil P adsorption-desorption is an important part for the absorption, utilization, and fixation of P fertilizers into the soil, which determines the cycle of P in the biological environment (Xiong and Mahmood, 2010). Significant difference of soil P balance, total-P and Olsen-P were found in different treatments, soil colloids showed different immobilization and fixation for phosphate ions (Guo, 2005). Under long-term no P input, the content of total P was low, sufficient adsorption sites of P on the soil colloid were exhibited, and bidentate coordination was the main binding mode between phosphate and colloid (An et al., 2013). For CK and NK, soil P was depletion due to long-term no P input and P uptake by crop, and high Q_m and low D_m

were obtained. Moreover, due to the low Olsen-P and M3-P (data not displayed), low DPS value was determined in soil without P fertilizer. P fertilizer could cause the characteristics change of P adsorption and desorption (Pizzeghello et al., 2014; Yan et al., 2013). After the application of P fertilizer, the content of total P in the soil gradually increased, the P adsorption sites on the soil colloid were gradually saturated, and monodentate coordination was the main binding mode between phosphate and colloid (Zhan, 2016; An et al., 2013; Abdala et al., 2012). Soil P desorption is the reverse of the adsorption process, which is more closely related to soil P availability. The readily desorbale P in soil is considered as generally the P adsorbed on the soil solid particles (calcium carbonate, Fe/Al oxide) (Heidari et al. 2017; Guedes et al. 2016).

Compared with CK and NK, long-term P application reduced the P adsorption site and binding energy and increased the P desorption capacity and improve the P availability, especially in NPKM. Vu et al. (2008) also found that Qm and MBC were decreased after long-term application of P fertilizer. It indicated that characteristics of P adsorption-desorption was affected by both P application input and fertilizer regime. Similar results were obtained in yellow soil, red soil, and gray desert soil, the researchers found that there existed significant difference under different treatments, the adsorption capacity of soil to P increased under without P fertilizer and the desorption of P increased after P application (Wang et al., 2013; Qi et al., 2012; Wang et al., 2010).

Information on the P fractions and P adsorption-desorption characteristics is important to understand the transformation in the agroecosystem (Yan et al., 2018). RDA result showed that P adsorption-desorption characteristics could explain 69.29% of the total variance in the P fraction parameters, and MBC (49.6%) and D_m (17.8%) were the main factors that contributed to the observed differences in the P fractions (Fig. 5-1). Compared to CK and NK, MBC and Q_m value decreased and increased D_m and D_r value increased in NPK and NPKM (Table 4-1). Correlation analysis showed that MBC showed a highly significant negative correlation with all P fractions except conc.HCl-Po, indicating that the input of P fertilizer could promote the desorption of P from soil. Moreover, the significantly positive relationship between D_m or D_r and P fractions in the soil with P fertilizers indicated that the P desorbed into the soil was easily to form different P fractions, especially resin-P, $NaHCO_3$-Pi, NaOH-Pi, and residual-P (R^2=0.801-0.908**). Zhan (2015) also in black soil found that MBC showed negative correlation and RDP showed positive correlation with available P efficiency, indicating the change of P adsorption-desorption characteristics could affect the P availability through changing P fractions in soil.

The characteristics of P adsorption-desorption and P fractions were affected by P input, fertilizations, and soil properties (Jalali and Jalali, 2016; Daly et al., 2015; Börling et al., 2001). The concentration of soil P, caused by P fertilizer, determine the adsorption pattern of soil to P, which affects the P desorption amounts (Xia et al., 2008). The change of soil properties, caused by P input and fertilization measures, affected the adsorption way of metal oxides to P and change the P fractions in the soil (Fink et al., 2016). Yan et al (2018) found that manure treatment could decrease pH, increased organic carbon (OC), total nitrogen (TN) in calcareous soil, which decreased the soil maximum buffer capacity, increased the content of H_2O-Pi, NaOH-Pi and improved P availability.

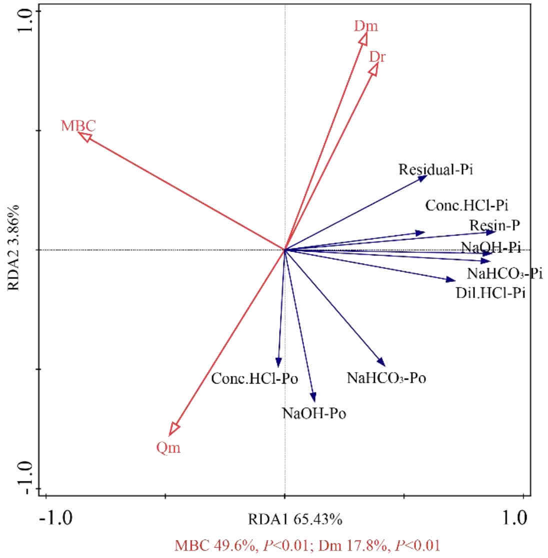


Figure 5-1 Redundancy analysis (RDA) triplots showing the relationship between P adsorption-desorption characteristics and P fractions under different long-term fertilization treatments in black soil

1.4 Driving factors of phosphorus activation coefficient

Soil P existed in various forms and can be transformed under certain conditions (Sharpley et al., 2000). P forms were the most direct and important factors affecting P availability (Wang et al., 2014). The Boosting Regression Tree (BRT) results showed that compared to other factors, P fractions (50.71%), including $NaHCO_3$-Pi, resin-P, NaOH-Pi, and dil.HCl-Pi, were the most important variables affecting PAC value. This result supported the topic in second chapter that P availability in black soil was determined by Pi fractions. Meanwhile, significantly positive correlation was found between PAC and each P forms (Fig. 5-2). Similar results were found in red soil and fluvo-aquic soil that PAC showed significant correlation with high active Pi fraction extracted with Hedley method (Wu et al., 2017). It indicated that these P fractions could easily transform to biologically available P (De Schrijver et al., 2012). The SEM result indicated resin-P was mainly, positively, and directly influenced by $NaHCO_3$-Pi and NaOH-Pi (Fig. 2-2). Therefore, the more content of resin-P, $NaHCO_3$-Pi and NaOH-Pi, the higher value of PAC. Ca-P was main Pi fraction in black soil (Table 2-1). Dil.HCl-Pi was bound with Ca and could be utilized by plants after weathering (Cross and Schlesinger, 1995). Soil with fertilizer, especially manure could significantly increase the content and proportion of dil.HCl-Pi, which could increase resin-P content by affecting $NaHCO_3$-Pi.

Soil properties explained 29.17% variation of PAC and were the second important influencing factors. Especially, Fe_o+Al_o, Fe_d+Al_d, and Fe_p+Al_p (total contribution rate was 19.97%) were the main variables affecting the change of PAC. The RDA results showed that Fe/Al oxides have important effect on P forms and P adsorption-desorption characteristics, which affected P availability under long-term fertilizer treatments (Fig. 3-5 and 4-4). Pearson correlation analysis showed that there was significant negative correlation between Fe_d+Al_d oxides and properties except for MBC and Q_m, and opposite trends were found in Fe_o+Al_o and Fe_p+Al_p (Table 5-1). Fe/Al oxide exhibited great absorbability to phosphate because of large amount of positive charge (Guo, 2007). In our results, the content of Fe_d+Al_d oxides decreased and Fe_o+Al_o and Fe_p+Al_p increased after P fertilization, indicating the transformation of free Fe/Al oxides to amorphous and organic-bound Fe/Al oxides. The transformation progresses decreased the absorbability of soil to P and increased the content of high active P fractions and improved the P availability. The possible reasons were that the input of fertilizer or manure could increase the SOM content, and the negatively charged functional groups in organic substances could alter P adsorption through interaction with Fe/Al oxides such as cation bridges, changing surface charges; competition for adsorption sites or change the surface charge of Fe/Al oxides and lead toelectostatic repulsion (Hinsiger et al., 2011; Antelo et al., 2007; Borggaard et al., 2005; Guppy et al., 2005; Hinsinger, 2001).

The input of exogenous P showed important effect on the PAC value. In this study, compared with the initial year, the PAC value in CK and NK decreased, while the PAC value significantly increased under long-term P fertilizer treatment, and the PAC value was greater than 2% (Fig. 3-2). The direct reason for this phenomenon is that the difference of P input in these treatments. Under soil P deficiency, adsorption of available P by crops from the soil decreases the content of available P, causing a decreasing trend in PAC value (Lu et al., 2017). When soil P is surplus, the change of soil properties caused by fertilizer could interact with mineral oxide in soil then promote the transformation of stable P form to high active P form, and increase the PAC value (Chen et al., 2009; Zhang et al., 2008).

In this part, BRT instead of SEM was used to obtain the driving factors of PAC by integrating all the variables.BRT uses classification algorithm to build a large number of decision trees and output the mean prediction as a single tree (Liaw and Wiener, 2002; Breiman, 2001). The result obtained from the algorithm is more accurate than any single classifier making up the ensemble (Dietterich, 2002). BRT emphasizes relatively significant factors by comparing their relative importance in the model and also investigate their influence patterns (Elith et al., 2008). SEM is a confirmatory factor analysis. Theoretical knowledege, causal assumptions and hypotheses should be as support before runtime. It emphasizes the causal relationship between the variables (Grace et al., 2010). Combination the two methods can clarify the chemical mechanism of affecting PAC. This is also the work we need to do in the future.

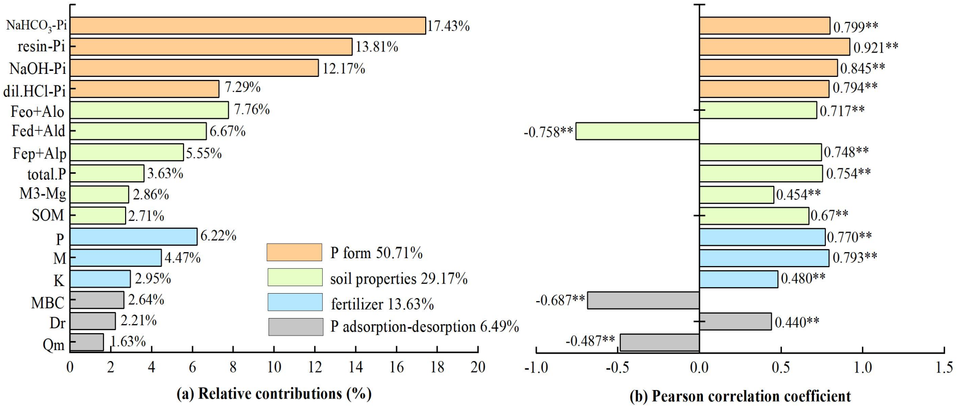


Figure 5-2 The relative influence (%) of individual and total edaphic factors for the boosted regression tree (BRT) of phosphorus activation coefficient (a). Pearson correlation between phosphorus activation coefficient and different factors (b).

Note: P form: resin-P, $NaHCO_3$-Pi, NaOH-Pi, dil.HCl-Pi, conc.HCl-Pi, residual Pi; soil properties: total.P, SOM, M3-Mg, $CaCO_3$, Fe_d+Al_d, Fe_o+Al_o, Fe_p+Al_p; fertilizer input: phosphorus (P) input, nitrogen (N) input, and potassium (K) input, manure (M) were pig manure (1990–2004) and cattle manure (2005–2018). P adsorption-desorption characteristics: Q_m, maximum adsorption capacity; MBC, maximum buffering capacity of soil; D_m, maximum desorption capacity; Dr, the ratio between Q_m and D_m.

Table 5-1 Pearson correlation between Fe/Al oxide and different factors

	Fe_d+Al_d	Fe_o+Al_o	Fe_p+Al_p
resin-P	-0.780^{**}	0.584^{**}	0.734^{**}
$NaHCO_3$-Pi	-0.586^{**}	0.558^{**}	0.741^{**}
NaOH-Pi	-0.589^{**}	0.621^{**}	0.781^{**}
dil.HCl-Pi	-0.615^{**}	0.505^{**}	0.674^{**}
Olsen-P	-0.673^{**}	0.622^{**}	0.781^{**}
Total-P	-0.650^{**}	0.369^{**}	0.625^{**}
Fe_o+Al_o	-0.388**		0.709**
Fe_p+Al_p	-0.546**	0.709**	
SOM	-0.572^{**}	0.445^{**}	0.627^{**}
MBC	0.608**	-0.617**	-0.715**
Qm	0.416^{**}	-0.183	-0.046
Dr	-0.386^{*}	0.156	-0.067
P	-0.617^{**}	0.500^{**}	0.512^{**}
K	-0.339^{**}	0.405^{**}	0.530^{**}
M	-0.802^{**}	0.411^{**}	0.538^{**}

Note: P form: resin-P, $NaHCO_3$-Pi, NaOH-Pi, dil.HCl-Pi, conc.HCl-Pi, residual-Pi; soil properties: total.P, SOM, M3-Mg, $CaCO_3$, Fe_d+Al_d, Fe_o+Al_o, Fe_p+Al_p; fertilizer input: phosphorus (P) input, nitrogen (N) input, and potassium (K) input, manure (M) were pig manure (1990–2004) and cattle manure (2005–2018). Q_m, maximum adsorption capacity; MBC, maximum buffering capacity of soil; Dr, the ratio between Q_m and D_m; D_m, maximum desorption capacity.

1.5 Influencing factors of degree of soil P sorption saturation and its environmental risk indication

Excessive use of chemical P fertilizer or organic fertilizer can greatly increase the content of soil P, increasing the risk of P loss and resulting in a lot of serious agricultural eco-environmental problems (Withers et al., 2019; Osterholz et al., 2020). The degree of soil P sorption saturation is used as indicator to evaluate environmental risk of soil P. The higher DPS value, the fewer sorption sites to combine additional P, enhancing the potential to release P to surface runoff or leaching water (Nair et al., 2020; Sharpley et al, 2020a; Vadas et al., 2005). In this research, DPS=8% was considered as the critical value for environmental purpose. According to the result of BRT, P fractions contributed the most (48.71%) to the variance of DPS, followed by soil properties (39.28%) and fertilizer (12.01%). All these factors in the model showed significantly correlation with DPS. The input of exogenous P directly increased the soil total-P content, and partial accumulated P would be transformed to high active P (Osterholz et al., 2020). This process would increase the available P content and DPS value. Wu (2018) pointed out that the change of DPS, calculated with Q_m and Olsen-P, was decided by resin-Pi, $NaHCO_3$-Pi and $NaHCO_3$-Po in black soil, red soil and fluvo-aquic soil, respectively, which supported our results. Moreover, fertilization could change the soil properties and affect DPS value (Pizzeghello et al., 2011). Significantly positive correlation between SOM, Fe_o+Al_o, Fe_p+Al_p and DPS indicating that complexation between Fe/Al oxides and SOM could promote DPS (Sharlpey et al., 2020b; Campos et al., 2018). Zou et al (2011) also reported that DPS showed significant relationship with SOM in paddy soil. In this study, the DPS value in NPKM treatment had far exceeded the critical value in 0-60 cm, easily causing risk of P loss. Compared to NPK treatment, soil treated with NPKM treatment showed higher transformation rate of total-P to high active Pi fractions and DPS value, indicating high environmental risk. Therefore, rational P input and manure management is particularly important in NPKM treatment. Composting and then returning manure to the field is an important way in manure application in field; the addition of metal oxides, such as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ to the compost could reduce the P release and decrease the risk of P leaching under manure treatment (Eigenberg et al., 2009; Sikora and Enkiri, 2005). In the face of shortage of P resources and environmental pollution, based on local climate and crops demand, the input of chemical fertilizer and manure should be strictly controlled, rational P nutrient management measure are implemented to reduce the environmental nutrient loss and realize the sustainable development of agriculture.

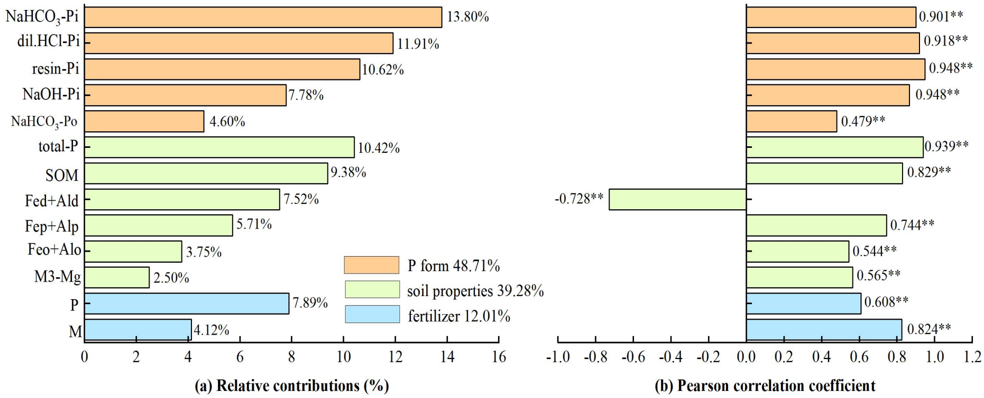


Figure 5-3 The relative influence (%) of individual and total edaphic factors for the boosted regression tree (BRT) of degree of soil P sorption saturation (a). Pearson correlation between degree of soil P sorption saturation and different factors (b).

Note: P form: resin-P, $NaHCO_3$-Pi, NaOH-Pi, dil.HCl-Pi, conc.HCl-Pi, residual-Pi; soil properties: total P, SOM, M3-Mg, $CaCO_3$, Fe_d+Al_d, Fe_o+Al_o, Fe_p+Al_p; fertilizer phosphorus (P) input, manure (M) were pig manure (1990–2004) and cattle manure (2005–2018).

1.6 The accumulation of soil P and its migration in the soil profile in NPKM

In agricultural production, unreasonable disposal of agricultural waste (crop straw, manure, etc.) caused great losses of reusable resources and posed serious risks to the environment (Osterholz et al., 2020; Withers et al., 2019). Partial replacement of chemical fertilizer by organic materials can reduce the overuse of chemical fertilizer, alleviate the problem of improper disposal of organic waste (Bi et al, 2020; Huang et al, 2020). In this study, the Olsen-P and DPS value exceeded the environmental threshold in NPKM. High P input increased soil P pool in NPKM, which directly increased soil P accumulation and cause P loss risk. Moreover , the amount and fractions of P in the soil decided the soil P mobility and its environmental risk (Condron et al, 2005; Pierzynski et al., 2005). In this study, compared to NPK, high content and proportion of high active P fractions and DPS value were found in NPKM (Fig.3-4 and Table 4-1). Pi, especially Ca-P, was main fractions of accumulated P (Fig.3-4). It showed that the dissolution and release of Ca-P in the soil profile was an important mechanism for the transformation of Pi. The change of soil properties affected soil P fractions. Moreover, the input of manure promoted the transformation and mobility of P fractions by changing soil physical and chemical properties. NPKM significantly increased the SOM, M3-Mg, Fe_o, Al_o, Fe_p, Al_p contents, decreased the Fe_d, Al_d in the soil profile when compared to other treatments. The interaction of soil properties and P fractions increased the solubility of Ca-P and decomposition of $CaCO_3$, and promote the release of Pi. This was the main reason to promote the movement of P in the soil profile. In conclusion, excessive input of P fertilizer and manure increased soil P accumulation and P mobility in NPKM. Therefore, rational amount of organic fertilizer, regular soil nutrient monitoring should be considered to minimize the risk of P loss in NPKM.

1.7 Soil P management in agricultural soil

Generally, when the Olsen-P content exceeds the critical value for high crop yield, the negative environmental consequences caused by further application of P fertilizer is far greater than the economic benefits (Hart et al., 2004). Increasing P utilization rate is the key to improve utilization rate of P fertilizer and reduce environmental risks. The main ways to improve P utilization rate are: (1) soil P resource should be fully considered for P input in farmland and balanced fertilization to solve the problem of insufficient and excessive P application. When soil P is large surplus (Olsen-P content > environmental threshold), properly control P fertilizer input, maintain soil fertility, and change the focus of work from "fertilizing soil" to "efficient agricultural production". When soil is small surplus (agronomic threshold < Olsen-P content < environmental threshold), stable P fertilizer application could improve the P utilization rate in current season. Therefore, the application of P fertilizer and Olsen-P content can meet the needs of high and stable crops yield without causing environmental problems. For areas with P deficiency and low soil Olsen-P, it’s necessary to appropriately increase P input and improve soil fertility to achieve efficient and high-yield agriculture. (2) Precise P nutrient management. For the soil and rotation system in different regions, proper type of P fertilizer, correct application time, reasonable application amount and correct application method should be considered to improve the utilization rate of P fertilizer in the current season. (3) Full utilization of organic fertilizer can reduce the input of chemical fertilizer, and promote the conversion of stable P pool to soluble P through input of organic carbon and its interaction with soil properties

2. General conclusion

Present study showed that P availability were significantly affected by long-term fertilization regimes. To reveal the underlying mechanism of P availability, in this paper, soil samples in different fertilization regimes (CK, NK, NPK and NPKM) and soil profiles were selected in a long-term field experiment in black soil (Gongzhuling) in Northeastern of China. Characteristics of P fraction and adsorption-desorption in time scale and vertical scale were determined to evaluate the P availability and P loss risk. Soil properties were determined to achieve the main influence factors affecting P fraction, P adsorption-desorption via RDA model. This would comprehensively expound the effect of different fertilization on P availability.

Under long-term without P application, crop yields were decreased and soil P was deficient. Compared to initial value, the content of total-P and Olsen-P decreased by 29.02%-35.85% and 47.37%-76.11%, respectively. Specially, the resin-P, $NaHCO_3$-P (Pi and Po), NaOH-Pi, conc.HCl-P (Pi and Po) and residual-P were the main decreased P pool in CK and NK treatment. Meanwhile, the decreased pH caused by chemical N, K fertilizer promoted the dissolution and transformation of dil.HCl-Pi and decreased its content in NK treatment. P application could increase soil fertility and crop yield, there was no significant difference between NPK and NPKM treatment for crop yield, which indicated that when the soil Olsen-P content exceeded the agronomic critical value of soil Olsen-P, P was no longer the limiting factor for crop grows. Meanwhile, the soil P was in balance or surplus with P fertilizers, the content of total-P and Olsen-P increased by 0.19-1.40 and 4.52-17.25 times than initial value, and the PAC value in NPKM treatment was 1.61 times in NPK treatment, increasing the P availability. Accumulated P in the soil was mostly converted to Pi fractions, including resin-P, $NaHCO_3$-P (Pi and Po), NaOH-P (Pi and Po), dil.HCl-Pi and residual-P, and the proportion of resin-P, $NaHCO_3$-Pi and NaOH-Pi significantly increased when compared to initial value. Especially, due to the large amount of Ca in the manure, the content and proportion of dil.HCl-Pi significantly increased in NPKM treatment than other treatments and initial value. The results of ^{31}P-NMR and P K-edge XANES spectroscopy showed that accumulated inorganic P were dominated by aluminum phosphate (Al-P) and monobasic calcium phosphate monohydrate (MCP) for NPK treatment, Al-P and MCP and tricalcium phosphate (TCP) for NPKM treatment. Meanwhile, the organic P (Po) was comprised of phosphate monoester and phosphate diester in black soil with ^{31}P-NMR analysis.

The relationship between Olsen-P and $CaCl_2$-P showed that environmental threshold in soil Olsen-P was 50.6 mg kg^{-1}, and the DPS value, determined by Olsen-P, was 8% for environmental purpose. The Olsen-P content and DPS value far exceeded the threshold in NPKM treatment in 0-60 cm soil profile, respectively, increasing the risk of P runoff. The BRT result showed that labile and mid-labile Pi (resin-P, $NaHCO_3$-Pi, NaOH-Pi and dil.HCl-Pi), soil properties (total-P, SOM and Fe/Al oxides) and fertilization were the main influencing factors to DPS. The increased SOM caused by fertilization could interact with metal oxides in soil and change the adsorption pattern of metal oxides to P, increasing the high active P fractions and DPS value.

Distribution of P in the soil profile differed because of difference in soil properties. Dil.HCl-Pi and stable-Pi were the main P fractions in the black soil. With the input of mineral fertilizer and manure, the content and proportion of resin-Pi, $NaHCO_3$-Pi and NaOH-Pi to sum of P fractions increased, and SOM, M3-Fe, and Al_p, caused by fertilization, were the main influencing factors in the 0–20 cm surface soils. Due to the excessive P input, high active P fractions, such as resin-P, $NaHCO_3$-Pi, NaOH-Pi and dil.HCl-Pi were moved to deeper soil layer (20-60 cm). In these soil layers, soil mineral components, such as Fe_d, Al_d, $CaCO_3$ and so on, were the main factors influencing the difference of P fractions in the subsoil.

The characteristics of P adsorption-desorption were affected by fertilization regimes and soil properties. Fertilization reduced the adsorption of soil to P and increased the P desorption amount. Specific performance as follows: the values of Q_m and MBC were decreased, and D_r and D_m increased in the treatment with P fertilizers than that in the treatment without P fertilizers. In the treatment without P fertilizers, SOM, Fe_d+Al_d and total-P were the main factors influencing the differences in P adsorption and desorption characteristic parameters. With the increase of P input and improvement of soil fertility, mineral components, e.g., Fe_d+Al_d, Fe_p+Al_p were the main factors influencing the differences in P adsorption and desorption characteristic parameters.

The BRT result showed that P forms (50.71%), soil properties (29.17%), fertilizer (13.63%) and P adsorption-desorption characteristics (6.49%) affected the PAC in black soil. P forms were the most important factors affecting PAC. SEM result showed that $NaHCO_3$-Pi and NaOH-Pi, were the potential sources of resin-Pi and decided the soil P availability. Input amount and regimes of fertilizer could change the soil properties and its binding mode with P, affecting soil P fractions and its availability.

In conclusion, P fertilizer application could increase crop yield, but it affected soil P form distribution, transformation, and migration to a certain degree. Therefore, in agricultural production, it is necessary to pay more attention to the transformation of soil P form and its environmental risks when considering the effect of P input and fertilizer regime on the crop yield.

3. Innovations

Based on the 29-year different fertilizer experiments, this research comprehensively evaluated the P availability from the aspects of P forms, P adsorption-desorption and soil properties in black soil under different treatments. Meanwhile, this research comprehensively clarified the importance of SOM (37-74%) and Al/Fe oxides (62-74%) on the P form and adsorption-desorption.

Based on long-term field experiment, multiple techniques (modified Hedley sequential extraction methods, P-XANES, and solution ^{31}P NMR spectroscopy) to comprehensively clarify that the P forms with fertilizer are mainly Ca-P (TCP, MCP) and Al-P for Pi and IHP for Po, Structural equation model analysis was used to evaluate the availability of different P fractions. resin-P is mainly directly affected by MCP ($NaHCO_3$-Pi) and Al-P (NaOH-Pi) with modified Hedley method and XANES.

4. Perspectives

Based on these results in our study, the following points are proposed to better understand the mechanism for improving P availability.

(1) Existing forms of soil Pi are relatively complex. Some phosphates are combined with Fe or Al oxide and difficult to be characterized by simple compounds. Some synthetic standard samples of adsorbed phosphates should be used to characterize the P forms in detail. The Po forms showed significant difference in different treatments. The transformation of soil Po is also affected by phytic acid, activities of soil microorganisms, especially bacteria and protozoa and soil phosphate activities. Therefore, further study should pay more attention to the soil phosphate activity, microbial biomass, and microbial community structure, etc..

Combination of Hedley sequential extraction method and ^{31}P-NMR, will be used to comprehensively evaluate the change characteristics of Po species and reveal the turnover process of Po under different fertilizer treatments.

(2) The result in this research showed that the Olsen-P content in NPKM in the 0-60 cm soil layer had exceeded the environmental threshold, increasing the P loss risk. The amount and time for reducing the input of P fertilizer need to be further studied and determined. Moreover, an indoor simulating experiment should be conducted to evaluate the chemical mechanism to P leaching loss.

(3) The results showed that SOM and Fe and Al oxides (such as Fe_d+Al_d and Fe_p+Al_p) were the main factors affecting P fractions and adsorption-desorption characteristics. Meanwhile, SOM showed significant relationship with Fe and Al oxides. However, the interaction mechanism between SOM (content, functional group structure) and Fe and Al oxides (type and forms) and its effect on P availability are not clear, which need further in-depth study. Moreover, multivariate analysis (BRT and SEM) is required to quantify the contribution rate of the factors involved and clarify the chemical mechanism on the P availability.

Chapter VI

References and appendix

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Appendix

1. Publications

(1) **Wang, Q.,** Qin, Z.H., Zhang W.W., Chen, Y.H., Zhu, P., Peng, C., Wang, L., Zhang, S.X., Colinet, G. Effect of long-term fertilization on phosphorus fractions in different soil layers and their quantitative relationships with soil properties. Journal of Integrative Agriculture. 2022

(2) **Wang, Q.,** Zhang, N. Y., Chen, Y. H., Qin, Z. H., Jin, Y. W., Zhu, P., Peng, C., Colinet, G., Zhang, S. X., Liu, J. The phosphorus availability in black soil is determined by inorganic phosphorus fraction under long-term different phosphorus fertilization experiments. Agronomy. 2022

(3) **Wang, Q.,** Chen, Y.H., Zhang, N.Y., Qin, Z.H., Jin, Y.W., Zhu, P., Peng, C., Colinet, G., Zhang, S.X. Phosphorus adsorption and desorption characteristic and its difference mechanism under long-term without and with phosphorus application treatments in black soil. Journal of Plant Nutrition and Fertilizers. (In Chinese with English abstract)

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

(5) **Wang, Q.,** Zhan, X.Y., Zhang, S.X., Peng, C., Gao, H. J., Zhang, X.Z., Zhu, P., Colinet, G. Increment of soil phosphorus pool and activation coefficient through long-term combination of NPK fertilizers with manures in black soil. Journal of Plant Nutrition and Fertilizers. 2018 (In Chinese with English abstract)

(6) Zhang, N.Y., **Wang, Q.,** Zhang, X. Y., Wu, Q.H., Huang, S. M., Zhu, P., Yang, X.Y., Zhang, S.X. Characteristics of inorganic phosphorus fractions and their relationship with soil properties in three northern soils. Journal of Integrative Agriculture. 2022

(7) Zhang W.W., **Wang, Q.,** Wu, Q. H., Zhang, S.X., Zhu, P., Peng, C., Huang, S. M., Wang, B.R., Zhang, H.M. The response of soil Olsen-P to the P budgets of three typical cropland soil types under long-term fertilization. PLoS One. 2020

(8) Ibrahim, K., **Wang, Q.,** Wang, L., Zhang, W.W., Peng, C., Zhang, S.X. Determining the optimum level of soil Olsen phosphorus and phosphorus fertilizer application for high phosphorus-use efficiency in Zea mays L. in black soil. Sustainability. 2021

(9) Gao, X., Peng, Y.T., Guo, L.L., **Wang, Q.,** Guan, C.Y., Yang, F., Chen, Q. Arsenic adsorption on layered double hydroxides biochars and their amended red and calcareous soils. Journal of Environmental Management 2020

(10) Qin, Z.H., **Wang, Q.,** Zhang, N.Y., Jin, Y.W., Zhang, S.X. Characteristics of phosphorus fractions above and below different available phosphorus thresholds in black soil and the response of phosphorus fractions to soil chemical properties. Scientia Agricultura Sinica. 2022 (In Chinese with English abstract)

(11) Huang, G.J., **Wang, Q.,** Zhang, Q., Yang, Z.P., Wang, B. Improving effects of different carbon and sulphur-containing amendments on inland soda saline soil. Soil and Fertilizer Sciences in China. 2020 (In Chinese with English abstract)

(12) Development and efficient use of phosphorus in China. 2020 China Agricultural Science and Technology Press

2. Presentations

(1) Evolution characteristics and morphological mechanism of available phosphorus in black soil (2017 Modernizing soil Phosphorus Fertility Recommendations and Managing Impacts, Beijing, 06/11/2017, Oral Presentation)

(2) Phosphorus forms characteristics and its relationship with soil properties under long-term different fertilization experiments in black soil (2019 Soil science society of China, Hunan, 06/11/2019, Oral Presentation)