Long-term rotation fertilization has differential effects on soil phosphorus

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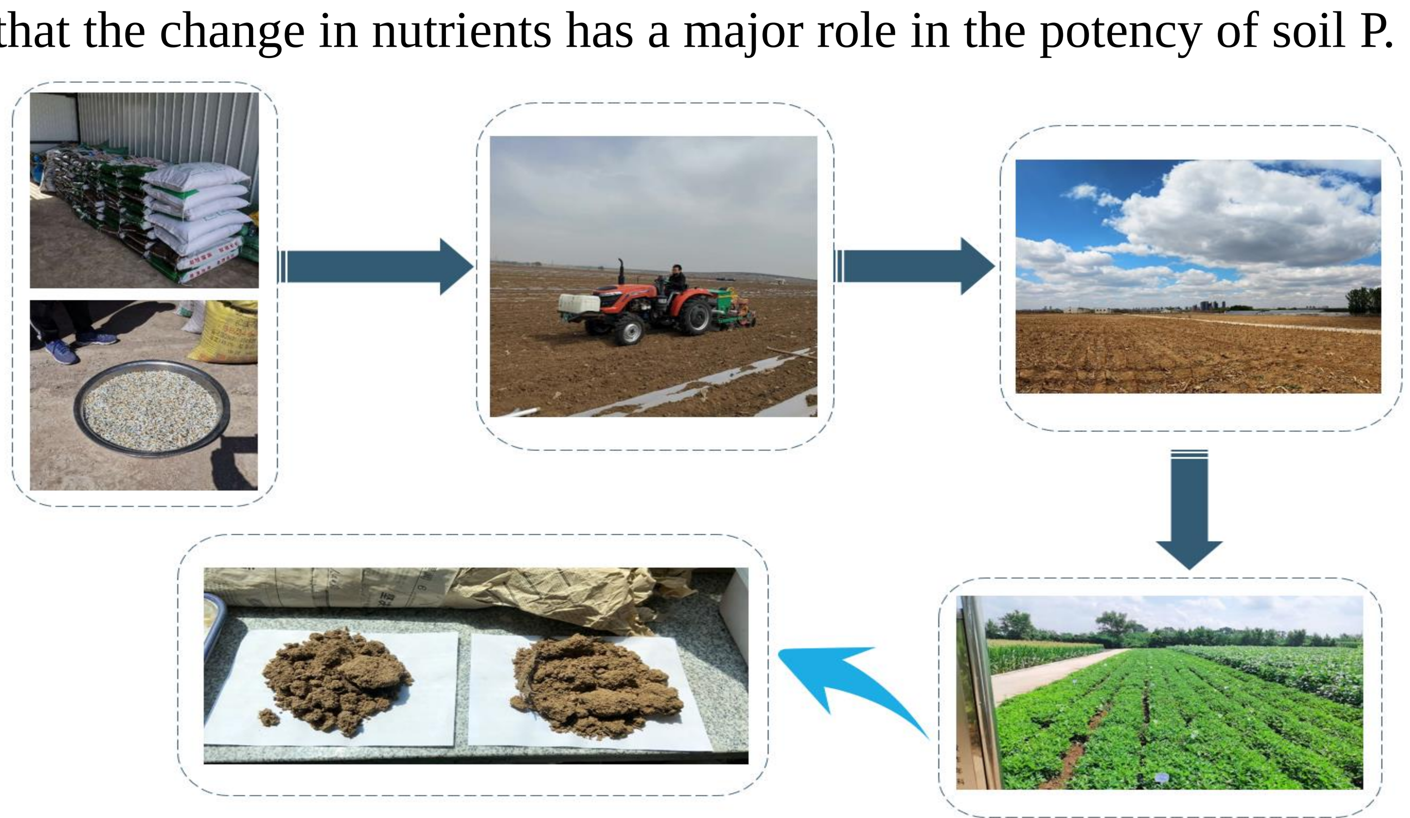
Introduction

The increase in soil phosphorus (P) content was observed in recent years as a result of increased P fertilizer application owing to its positive effect on crop yields and low P fertilizer prices (Xu et al. 2008). However, excessive fertilization has become a serious issue that causes environmental pollution (Gao et al. 2006). Additionally, animal manure has begun to accumulate in large quantities owing to high animal populations. In an attempt to improve P efficiency, some places use crop straw and animal manure in large quantities, leading to soil pollution and other problems (Li et al. 2015). Therefore, reducing the use of mineral P fertilizer and partially supplementing it with an organic fertilizer such as manure could be beneficial to the environment if done correctly. To achieve this goal, it is necessary to understand the forms of P in soil and how they are affected by long-term fertilization strategies.

Materials and Methods

In this study, a long-term site-based experiment was conducted which was established in 1979 in Shenyang Agricultural University (41° 48'N, 123° 33'E), China, and could be confirmed that the change in nutrients has a major role in the potency of soil P.



Results

Forty years of N application decreased soil pH, but the addition of manure can slow down this phenomenon. Long-term application of manure can significantly increase the contents of total P, Olsen-P, inorganic P, and organic P; besides, it was extremely increased the rates of P activation coefficient. There was a significant positive correlation between total P and available P, inorganic P, and organic P. The spectrum of all treatments had the highest content is orthophosphate. According to the ^{31}P NMR peak and its integral strength, the mineral forms of P at the chemical shift are orthophosphate, with an abundance of 15.4–477.2 mg/kg. ^{31}P NMR spectra showed that orthophosphate and monoesters (mineral forms of P) were the main samples. Phytic acid is the most easily detected component of all processed phosphate monoesters. It may be that phytic acid originated from plants, especially seeds. Orthophosphate content increased when the inorganic P components were increased. Orthophosphate has an high correlation with Ca2-P, Al-P, and O-P. Fertilization can extremely increase organic P components and phosphate monoester contents. As a whole, the phosphate monoester in the soil is high correlated to the MLOP and HROP.

Correlation between soil P and P components in different fertility soils.

Table 1. Results of analysis of Pearson's correlation (P-values) for inorganic phosphorus (P) and organic P with total P, available P, and P activation coefficient on different fertilisers

Treatment	Item	Inorganic P						Organic P			
		Ca_2-P	Ca_8-P	Al-P	Fe-P	O-P	Ca_{10}-P	LOP	MLOP	MROP	HROP
CK0	TP	0.90**	0.96**	0.76*	0.73*	0.69*	0.69*	0.85**	0.97**	0.68*	0.61*
	AP	0.70*	0.82**	0.85**	0.84**	0.59*	0.62*	0.97**	0.88**	0.79*	0.64*
	PAC	−0.64*	−0.84**	−0.71*	−0.58*	−0.33	−0.30	−0.94**	−0.73*	−0.59*	−0.51*
CK	TP	0.97**	0.97**	0.96**	0.95**	0.86**	0.75*	0.91**	0.75*	0.87**	0.95**
	AP	0.95**	0.95**	0.90**	0.95**	0.87**	0.83**	0.96**	0.80**	0.90**	0.97**
	PAC	0.92**	0.92**	0.88**	0.94**	0.90**	0.88**	0.94**	0.82**	0.93**	0.97**
NPK	TP	0.97**	0.94**	0.82**	0.95**	0.94**	0.90**	0.97**	0.97**	0.96**	0.97**
	AP	0.91**	0.86**	0.80**	0.88**	0.87**	0.87**	0.95**	0.98**	0.84**	0.86**
	PAC	−0.77*	−0.90**	−0.70*	−0.89**	−0.82**	−0.70*	−0.80**	−0.76*	−0.94**	−0.92**
M1NPK	TP	0.85**	0.97**	0.89**	0.79*	0.80**	0.57*	0.86**	0.89**	0.76*	0.87**
	AP	0.83**	0.71*	0.89**	0.92**	0.94**	0.98**	0.85**	0.90**	0.97**	0.76*
	PAC	−0.71*	−0.89**	−0.69*	−0.63*	−0.56*	−0.29	−0.75*	−0.73*	−0.52*	−0.82**
M2NPK	TP	0.87**	0.89**	0.85**	0.85**	0.87**	0.92**	0.95**	0.93**	0.85**	0.95**
	AP	0.82**	0.97**	0.97**	0.98**	0.61*	0.89**	0.91**	0.70*	0.64*	0.86**
	PAC	−0.77**	−0.71*	−0.59*	−0.60*	−0.96**	−0.73*	−0.82**	−0.90**	−0.92**	−0.90**

r-value was shown. *P < 0.05; **P < 0.01. Indicating significance (P < 0.05; Person coefficient). The inorganic P of the soil sample was determined by a sequential fractionation method developed (Jiang and Gu 1989, Samadi and Gilkes

Table 2. Concentrations of phosphorus (P) compound classes (mg/kg) by solution ^{31}P NMR (nuclear magnetic resonance) spectroscopy

Treatment	Orthophosphate	Pyrophosphate	Monoester	Diester	Phosphonates	M:D	c Monoester	c Diester	c M/D
CK0	77.0	5.0	65.9	2.6	0.0	25.8	48.5	20.0	2.4
CK	15.4	7.0	49.5	0.6	0.0	86.1	35.2	14.9	2.4
NPK	73.4	2.3	79.6	3.1	0.2	25.7	57.7	25.0	2.3
M1NPK	346.2	7.7	138.5	7.0	3.5	19.8	98.9	46.6	2.1
M2NPK	477.2	15.6	190.4	6.7	6.7	28.4	136.9	60.2	2.3

c Monoester, c Diester – phosphate monoester and diester, respectively, denote the correction for degradation products; M:D – monoester:diester ratio; c M:D – monoester:diester ratio, corrected for degradation products.

Identification of forms of P in soil by 31P NMR

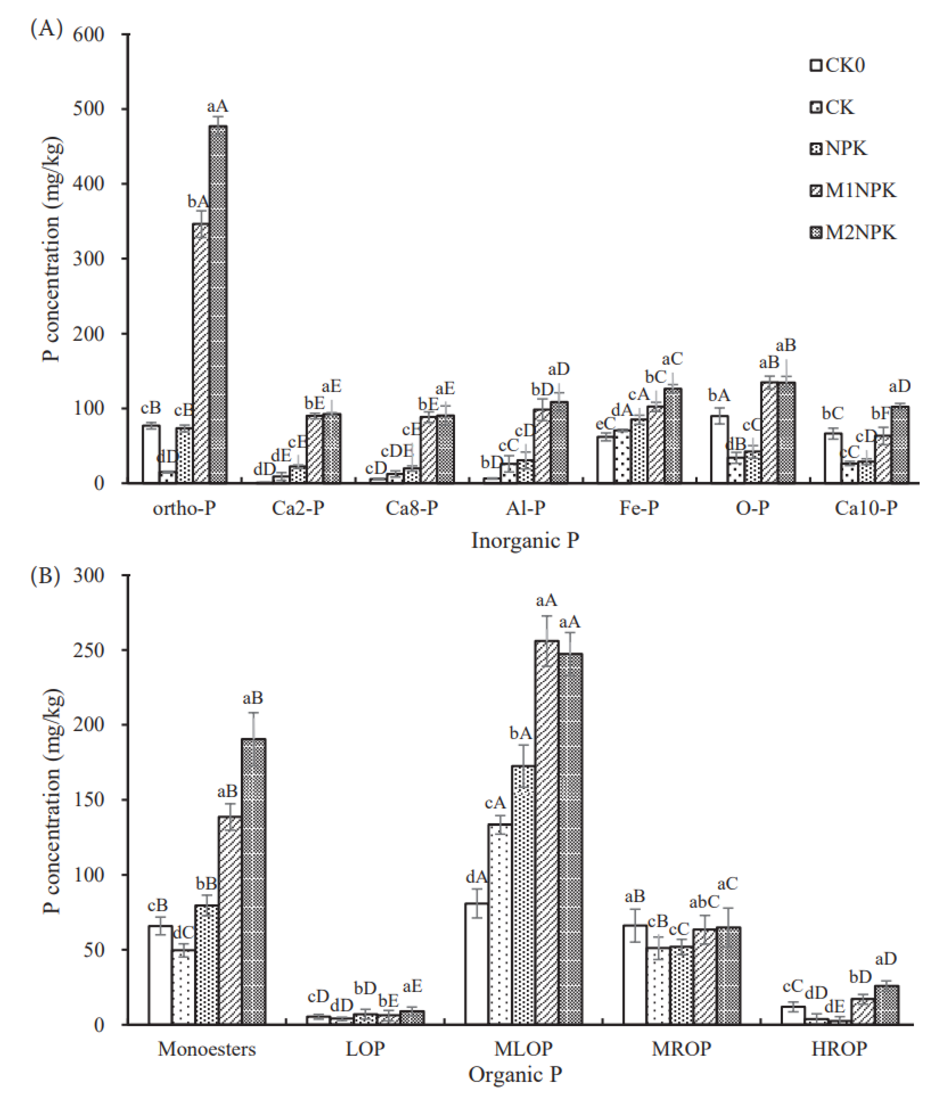


Figure 1. The response of (A) inorganic phosphorus (P) and (B) organic P. Values were means ± standard deviation (n = 3). Values with different uppercase letters within different treatments and different lowercase letters within different P forms indicated statistically significantly different at P < 0.05 level. Ca_2-P – $NaHCO_3$-soluble P; Ca_8-P – NH_4Ac-soluble P; Al-P – NH_4F-soluble P; Fe-P – $NaOH$-Na_2CO_3-soluble P; O-P – occluded-P; Ca_{10}-P – H_2SO_4-soluble P. LOP – labile organic P; MLOP – moderately labile organic P; MROP – moderately resistant organic P; HROP – highly resistant organic P. CK0 – soil before planting in 1979; CK – unfertilised control in 2018; NPK – NPK mineral fertiliser; M1NPK – NPK mineral fertiliser plus low pig manure; M2NPK – NPK mineral fertiliser plus high pig manure

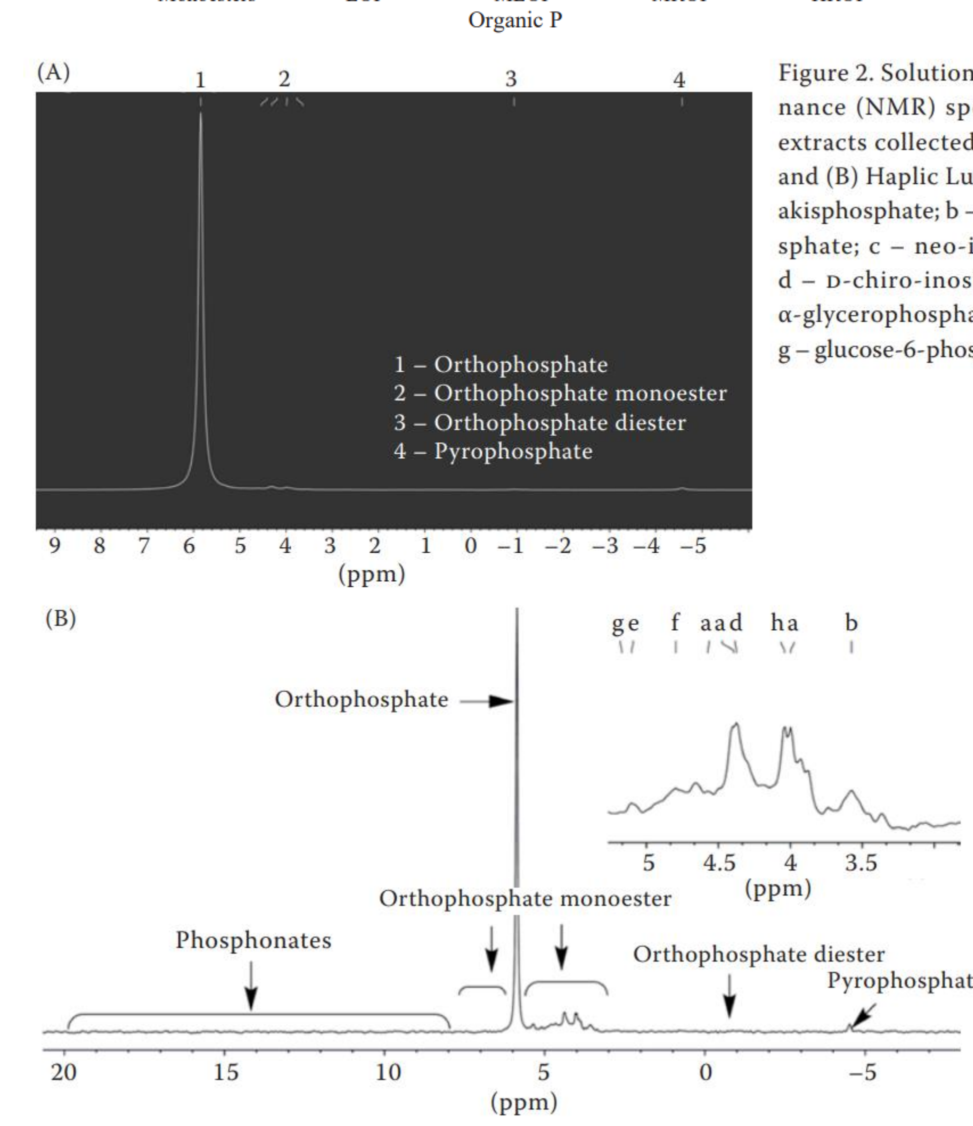


Figure 2. Solution ^{31}P nuclear magnetic resonance (NMR) spectra of NaOH-EDTA soil extracts collected from (A) manure fertiliser and (B) Haplic Luvisol. a – myo-inositol hexakisphosphate; b – scyllo-inositol hexakisphosphate; c – neo-inositol hexakisphosphate; d – D-chiro-inositol hexakisphosphate; e – α-glycerophosphate; f – β-glycerophosphate; g – glucose-6-phosphate; h – choline phosphate

The effects of different fertilization soils on the components changes of inorganic P and organic P.

Table 3. Correlations orthophosphate (ortho-P) with inorganic phosphorus (P) of different fertiliser treatments

Inorganic P	Significance Ortho-P	Marginal means for treatments (mg/kg)				
		CK0	CK	NPK	M1NPK	M2NPK
Ca_2-P	*	0.90	9.06	22.17	89.89	92.62
Ca_8-P	**	5.81	12.31	19.57	88.28	90.56
Al-P	*	6.43	25.93	30.45	98.31	108.82
Fe-P	ns	62.03	70.59	84.98	102.09	126.28
O-P	*	90.01	34.08	41.99	134.76	134.47
Ca_{10}-P	ns	66.40	26.40	28.67	63.16	102.44

Table 4. Correlations phosphate monoester (monoesters) with organic phosphorus (P) of different fertiliser treatments

Organic P	Significance Monoesters	Marginal means for treatments (mg/kg)				
		CK0	CK	NPK	M1NPK	M2NPK
LOP	ns	5.32	3.84	6.95	6.07	8.86
MLOP	**	80.88	133.35	172.48	255.95	247.32
MROP	ns	66.13	50.94	51.85	63.45	64.92
HROP	*	11.85	3.42	2.27	16.98	25.78

ns – not significant; *P < 0.05; **P < 0.01 indicating significance (P < 0.05; Person coefficient).

Discussion and Conclusion

The results show that the main P compounds were orthophosphate and phosphate monoester. The combination of a high amount of manure and NPK fertilizers can increase the content of orthophosphate that can be absorbed and utilized by crops, the orthophosphate was 477.2 mg/kg, and phosphate monoester was 190.4 mg/kg. The long-term addition of nitrogen fertilizer significantly reduced the pH value of soil, and the addition of manure slowed down the trend of pH reduction. Furthermore, manure in combination with NPK fertilizer, can extremely increase the total P extracted by NaOH-EDTA by changing soil pH. The $NaHCO_3$-soluble P (Ca_2-P), NH4Ac-soluble P (Ca_8-P), NH_4F-soluble P (Al-P), and occluded-P (O-P) were positively correlated with orthophosphate, while middle stable and high stable organic P was positively correlated with monophosphate.

Acknowledgments

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