

CHANGES OF SOIL PHOSPHORUS FRACTIONS IN PARENT MATERIAL OF A MOLLISOL AT THE EARLY PEDOGENIC STAGE IN NORTHEAST CHINA

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(Received 8th Nov 2019; accepted 30th Jan 2020)

Abstract. Fertility degradation of Mollisols affects world food security. Understanding the degradation mechanisms of Mollisols is essential in order to restore the soils' productivity. A long-term field experiment was conducted to assess soil phosphorus (P) concentrations and fractions in a Mollisol at its early development stage under different cropping systems in Northeast China. Parent material (PM) and mature Mollisol (OM) were used for comparison. Organic P (Po) concentrations under natural fallow (Pnat), alfalfa (*Medicago sativa* L.) (Palf) and soybean-maize (S-M) rotation without fertilizer application (PCS-F) increased by 68-74% after 10 years. S-M rotation with mineral fertilizer (PCS + F), organic matter amendment (PCS + F + OM), or crop straw return (PCS + F + BM) increased Po concentrations by 74.1-108 mg kg⁻¹, which is equivalent to 33% of total Po in the OM; and increased Ca₂-P, Ca₈-P, Al-P and Fe-P concentrations by 0.9-1.3, 7.1-8.8, 2.1-2.7 and 1.6-1.7 times, respectively. 67% of the applied fertilizer P was transformed to Pi for the treatments with chemical fertilizer. The results indicate that return of crop residue combined with chemical fertilizers enhances the accumulation of P in soils at their early development stage, which has important implications for the fertility restoration of a Mollisol in Northeast China and elsewhere in the world.

Keywords: soil development, natural fallow, long-term restoration experiment, organic phosphorus, inorganic phosphorus

Introduction

Phosphorus (P) is one of the essential elements for crop growth and development. Over 80% of P absorbed by crops comes from a soil reserve (Fageria et al., 2008) and applied fertilizer P reverts to less available forms in the soil (Han et al., 2005a, b). Therefore, the fractions and availability of soil P, and the transformation and availability of applied fertilizer P have received much attention in agronomic research (Milic et al., 2019; Sun et al., 2019). Soil P fractions include inorganic P (Ca₂-P, Ca₈-P, Al-P, Fe-P, O-P, Ca₁₀-P) and organic P (labile organic P, moderately labile organic P, moderately stable organic P and highly stable organic P). Generally, organic P (Po) accounts for 30-65% of the total P in soils (Pätzold et al., 2013; Jin et al., 2013), while organic P in Mollisol accounts for 42-69% of total P (Song et al., 2007), which can be attributed to the relatively high organic matter contents (Hou et al., 2014). Crops directly utilize inorganic P (Pi) in soil solution (generally orthophosphates), which is in dynamic equilibrium with phosphate minerals and surface adsorbed P in soil (Xiang et al., 2004). With the advancement of soil development, Po fractions become dominant and P availability is more closely related to the activity of soil microorganisms (van der

Bom et al., 2019; Richardson et al., 2011). Generally, plant available P comes from the pools of Fe-P, Al-P, moderately labile organic P (MLOP) and labile organic P (LOP) in acid soil; while from the pools of Ca₂-P, Ca₈-P, LOP and MLOP in alkaline soil (Li et al., 2005). Therefore, Po fractions play an important role in P supply, especially in soils with relatively high organic matter content (Vanden Nest et al., 2016; Nobile et al., 2020).

The development and utilization of a Mollisol in Northeast China underwent both natural virgin stages through the stages of cultivation without fertilizer application, cultivation with organic matter application, and cultivation with the combination of organic matter and inorganic fertilizers. The impacts of different cropping systems and agricultural practices on the content and fractions of P in Mollisol have been reported (Song et al., 2007). Mollisol was fertile in nature and could sustain P supply under both natural and agricultural production systems. Excessive applications of chemical P fertilizers increased both available and unavailable P fractions (Song et al., 2007). However, the soils in Northeast China suffered from severe erosion as a result of intensive agricultural practices, which has caused 60% loss of soil organic matter content (Miao et al., 2019). In some extreme cases, soil erosion has removed the surface layer, with exposed parent material (C horizon). It is important to understand P transformations in soil during the period from parent material to current stage.

The restoration of degraded soil has been undertaken at a large-scale and proven to be successful in terms of above-ground ecosystem properties. However, it still lacks understanding regarding soil development in relation to vegetation changes (Griffiths et al., 2008; Harris, 2009), which could be attributed to the fact that it takes a long time to build a high level of soil fertility under natural conditions (Harrison et al., 2008). Anthropogenic activities can accelerate the pedogenic process as indicated by a significant increase in soil organic matter content with all the treatments including no fertilizer, chemical fertilizer and chemical fertilizer plus organic residue amendments during the first eight years of soil development from parent material (You et al., 2017). The inputs of crop residue and manure changed the distribution of carbon (C) density fraction and humic substances. High organic matter input first caused an increase in labile C pool, followed by stable C fractions (You et al., 2014). Soil microbial activity increased with tillage and organic amendment at the early pedogenic stage of parent material, as evidenced by an increase in soil microbial biomass-C and total PLFAs, as compared to the parent material (Li et al., 2014). The soil food web was quickly developed with fertility restoration practices (Li et al., 2016). However, information was limited about P transformations at the initial stage of soil development from the parent material.

Prior studies have focused on the impact of different vegetation types and agricultural practices on P fractionation in mature Mollisol, with much less attention being paid to young soils. Lu et al. (2015) reported that fertilizer P applied in Mollisol was transformed to Al-P and Fe-P, with less than 20% being accumulated as Po. Few reports are available about the effects of cropping systems (or vegetation types) and related agricultural practices on the changes of P fractions in the initial stages of soil development. Accordingly, a field experiment was established in 2004 to examine soil development from parent material (C horizon) of a Mollisol. To simulate the effects of cropping systems and agricultural practices on P fractions at the early development stage of soil, it was hypothesized that application of exogenous P including chemical fertilizer P and P in organic amendment can enhance the accumulation of P in parent

material, which can reach relatively high levels within a short term. The objectives of this study were to: (1) identify P fractions in parent material and; (2) determine the effect of cropping systems and agricultural practices on P fraction in the initial stage of soil development.

Materials and methods

Site description and soil sampling

The long-term restoration experiment was located in the center of the Mollisol' area in Northeast China at the State Key Experimental Station of Agroecology, Chinese Academy of Sciences, Hailun, Heilongjiang province (47°26'N, 126°38'S). The Mollisol was derived from the sedimentary material of loamy loess parent material (Xiong et al., 1987). Typical soil profiles consist of A-AB-BC-C horizons (A, 0-60 cm; AB, 60-115 cm; BC, 115-150 cm; C, > 170 cm depth). The depth to bedrock is > 20 m. Soil classification is Pachic Haploborolls (fine-silty, mixed, superactive, mesic Pachic Ultic Haploxeroll) according to the USDA Soil Taxonomy (Soil Survey Staff, 2014). The climate in the region is typical temperate continental monsoon, characterized by cold winters and hot summer; with the mean annual temperature of 2.2 °C. The average total annual precipitation is 550 mm, with approximately 358 mm occurring from June to August.

The long-term restoration experiment started in June 2004 with 24 enclosed plots (each plot measured 1.4 m long, 1.0 m wide and 0.8 m deep). The enclosures consisted of cement strips (0.2 m wide and 0.8 m deep) that protruded 0.1 m above the ground. These enclosures were refilled with parent material taken from the 2 m depth (C horizon) below surface near the experimental station. The parent material had a semi-blocky structure. Nylon mesh with 75 µm openings was placed on the parent material at 0.8 m depth to prevent root penetration, but it allowed water and nutrient exchange. The parent material contained 4.79 g C and 0.41 g N kg⁻¹ soil, had a pH of 6.88 (soil: DI water 1:2.5), bulk density of 1.35 g cm⁻³, 420 g kg⁻¹ clay (< 0.002 mm) and 356 g kg⁻¹ silt (0.02-0.002 mm). The dominant clay minerals were vermiculite, chlorite and illite (*Fig. 1*).

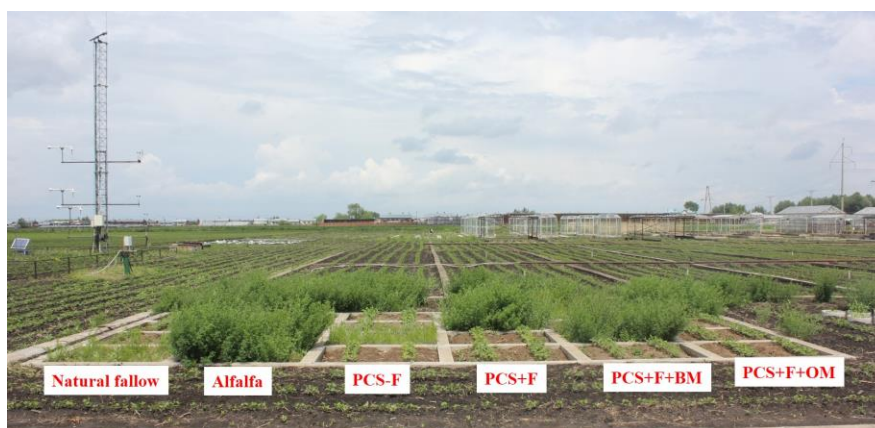


Figure 1. The experimental plots in the field

The following six treatments were assigned to the 24 plots with the parent materials as a randomized block design with four replications: natural fallow without weed

control (vegetation consisted mainly of *Leymus chinensi*, *Poa annua* L. and *Equisetum tataricus*) (Pnat), N-fixing alfalfa (*Medicago sativa* L.) (Palf) and four Soybean (S)-Maize (M) rotation: (i) S-M without mineral fertilizer and biomass removed (PCS-F), (ii) S-M with mineral fertilizer and biomass removed (PCS + F), (iii) S-M with mineral fertilizer and partial return of residue as a soybean powder-maize straw mixture (PCS + F + OM) and (iv) S-M with mineral fertilizer and all biomass incorporated (PCS + F + BM) (Table 1 and 2). The biomass in each plot of Pnat and Palf treatments was left in the fields as mulch. In P + F-OM, 2250 kg ha⁻¹ ground soybean seeds that had been baked at 200 °C and 4500 kg ha⁻¹ chopped (20-50 mm long pieces) maize straw were incorporated into the soil at the same time as the other residue return treatments. The C content in the soybean powder and maize straw was equivalent to the C content of a typical organic manure application and return of maize straw C in this region (Qiao et al., 2014). In the PCS + F + BM treatment, the biomass of each year's crop was incorporated into the field, but the maize grain and soybeans were pulverized as above. The fertilizer sources were diammonium phosphate and potassium sulphate, applied at 54, 60, and 54 kg N, P and K ha⁻¹ year⁻¹, respectively, for soybean and maize. An additional 140 kg N ha⁻¹ year⁻¹ was applied as urea at the V8 stage of maize growth. The parent material was tilled to 20 cm depth with a spade to incorporate the chopped crop residue, and ridges (70 cm wide and 25 cm high) were made after applying the organic amendments. The first crop of rotation was soybean. The crop densities were 70000 and 270000 plants ha⁻¹ for maize and soybean, respectively. The varieties of soybean and maize were Dongsheng 7 and Haiyu 6, respectively. The crops were sown in rows in May and harvested in October. At harvest, the above-ground biomass in each plot was cut and weighed, and subsamples were oven-dried at 60 °C to determine the dry weight of grain and non-grain biomass.

Table 1. The list of abbreviations for field treatments

Field treatments	Natural fallow	Alfalfa	Parent material	Mineral fertilizer	Biomass	The mixture of soybean powder-maize straw
Abbreviations	Pnat	Palf	PCS	F	BM	OM

Table 2. Experimental treatments (i.e. crop rotations, inputs of plant material and mineral fertilizer, tillage) in the 10 years field experiments

Field treatments	Cropping systems ^a	Organic incorporation ^b	Mineral fertilizer input ^c	Tillage ^d
Pnat	Natural fallow	Litter and roots	None	No
Palf	Alfalfa	Litter and roots	None	No
PCS-F	Crop rotation	Roots	None	Yes
PCS + F	Crop rotation	Roots	NPK	Yes
PCS + F + BM	Crop rotation	All crop straw, seeds and roots	NPK	Yes
PCS + F + OM	Crop rotation	Roots, and amended soybean seeds and maize straw	NPK	Yes

^aCrop rotation is the rotation of soybean and maize in different years since 2004

^bThe amendment rates in PCS + F + OM were 2250 kg hm⁻¹ of baked soybean powder and 4500 kg hm⁻¹ of maize straw mixed homogeneously. The C:N ratios were 7.4:1 in soybean seeds, 33.5 in maize, 63.3:1 in maize straw and 59.1 in soybean straw

^cDiammonium phosphate was source of N and P and applied at a rate of 300 kg hm⁻¹ yr⁻¹; Potassium sulfate (K) was applied at a rate of 120 kg hm⁻¹ yr⁻¹

^dTillage was performed manually down to 20 cm with ridges made in October after harvest

Soil samples at the surface layer (0-20 cm) were collected from the six treatments in all four replications after harvest in October 2013. Composite soil samples, consisting of four random subsamples, were removed with a spade from the ridge and furrow locations and mixed thoroughly. The soil surface layer (0-20 cm) of each treatment was air-dried after removing all visible roots and plant fragments and sieved through a 2 mm or 0.25 mm sieve. The samples of parent material (PM) were taken below 2 m depth in 2004. Mature Mollisol (OM) was sampled from the A horizon (0-20 cm) from an adjacent experimental field, which had been cropped to a maize and soybean rotation since 1993 and received only mineral N (120 g kg⁻¹, urea) and P (51.8 g kg⁻¹, diammonium phosphate) fertilizers for maize and N (20.3 g kg⁻¹, urea) and P (51.8 g kg⁻¹ diammonium phosphate) fertilizers for soybean. All aboveground biomass had been removed from field of the mature Mollisol and soil tillage had been manually conducted to the 20 cm depth using a spade.

Soil sample analysis

The soil samples were air-dried and sieved through a 2-mm sieve for the laboratory experiment. Total P (T-P) in soil samples was determined by digesting soil in a tri-acid mixture (HNO₃, HClO₄, and H₂SO₄ at a 3:1:1 ratio) and P concentration in the digested samples determined calorimetrically using the vanado-molybdate-yellow color method (Jackson, 1973). Soil total organic P was determined after the soil was combusted at 550 °C and extracted with 4 M H₂SO₄ (Anderson, 1960). Available P was analyzed with the colorimetric molybdenum method following extraction with 0.5 M NaHCO₃ (Olsen et al., 1957).

Organic P fractions

Soil organic P (Po) was separated into four fractions using a modified sequential extraction procedure developed by Bowman et al. (1978) and modified by Fan et al. (1990). A flow diagram for the Po fraction procedure is given in *Figure 2*. Highly stable organic P (HSOP) was determined by subtracting the moderately stable organic P (MSOP) from the stable organic P.

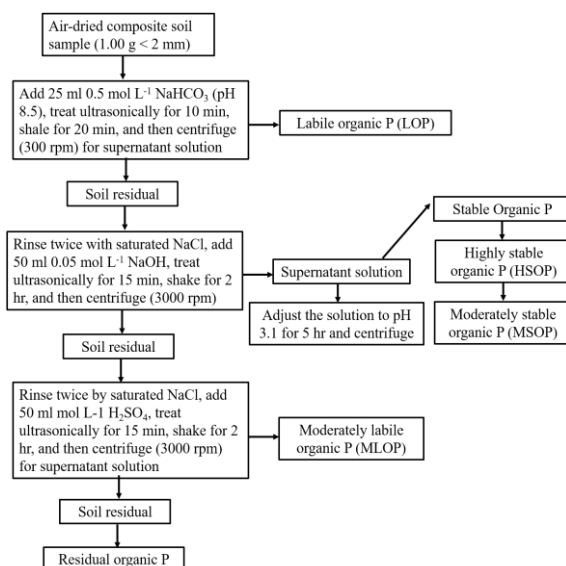


Figure 2. Scheme of sequential extraction of organic P in a Mollisol (Yang et al., 2006)

Inorganic P fractions

Inorganic P fractions were measured according to the fractionation scheme of Jiang et al. (1989) modified from the method described by Chang et al. (1957) and Hedley et al. (1982). Briefly, the fractionation involved a sequential extraction with (1) 0.25 M NaHCO₃ (pH 7.5) to extract Ca₂-P, (2) 0.5 M CH₃COONH₄ (pH 4.2) to extract Ca₈-P, (3) 0.5 M NH₄F (pH 8.2) to remove Al-P, (4) 0.1 M NaOH-0.1 M Na₂CO₃ to obtain Fe-P, (5) 0.3 M sodium citrate-Na₂S₂O₄-0.5 M NaOH to obtain the occluded P and (6) 0.5 M H₂SO₄ to extract Ca₁₀-P. These fractions were designated as NaHCO₃-soluble P (Ca₂-P), NH₄Ac-soluble P (Ca₈-P), NH₄F-soluble P (Al-P), NaOH-NaCO₃-soluble P (Fe-P), occluded P (O-P), and H₂SO₄-soluble P (Ca₁₀-P).

Statistical analysis

The analysis of variance (ANOVA) was performed using the SPSS (version 16, IBM SPSS Statistics, Somers, NY) to determine the significant difference between the treatments. Standard errors were calculated for mean values of determinations. The multiple comparison test was performed using Fisher's (protected) Least Significant Difference (LSD) at the 0.05 significant level. A principal component analysis (PCA) of the soil phosphorus fractions for all the field treatments, mature Mollisol and parent material was generated using CANOCO 5.0 software (written by Cajo J. F. ter Braak and Peter Smilauer, <http://www.canoco5.com>).

Results

Total P and Olsen P

Compared to parent material (PM), total P in unfertilized soils (Pnat, Palf and PCS-F) did not significantly increase ($P > 0.05$), but Olsen P did ($P < 0.05$) (Fig. 3). For the treatments with mineral fertilizers and organic matter amendment (PCS + F, PCS + F + OM and PCS + F + BM), total P concentrations increased by 282.1-330.6 mg kg⁻¹ (Fig. 3), which was equivalent to the total P concentration in the OM. Olsen P concentrations increased by 93.3-114.9 mg kg⁻¹ (Fig. 3), which was higher than that in the OM, indicating that application of chemical fertilizers and organic amendment enhanced P accumulation in soil after the initial 10 years of treatments from parent material.

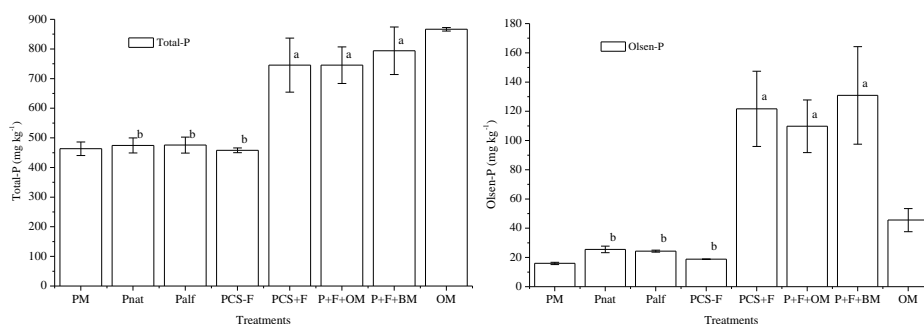


Figure 3. The contents of total P and Olsen P in parent material of soil formation, parent material and mature Mollisol. (Pnat, natural fallow (grasses); Palf, alfalfa; PCS-F, unfertilized soybean-maize (S-M) control; PCS + F, chemical fertilizer S-M; PCS + F + OM, organic amendment plus chemical fertilizer S-M; PCS + F + BM, chemical fertilizer and all crop biomass returned S-M. Values followed by different letters differ significantly at $P < 0.05$)

Organic and inorganic P

Total organic and inorganic P

Compared to PM, the treatments without chemical fertilizers (Pnat, Palf and PCS-F) increased organic P (Po) but decreased inorganic P (Pi) (Fig. 4). However, the treatments with chemical fertilizers and organic amendment (PCS + F, PCS + F + OM and PCS + F + BM) significantly increased Pi concentrations with the highest value of 586.8 mg kg⁻¹ occurred to the PCS + F treatment, which was higher than that in OM (348.7 mg kg⁻¹) (Fig. 4). The Po concentrations in all the field treatments increased by 68.2-138%, as compared to PM, and the highest value (186.2 mg kg⁻¹) was observed in the PCS + BM treatment, which was 39.4% of Po in the OM. OM had a similar Pi concentration as the PM, but had more Po (Fig. 4). The percentages of Po in the total P were lower in PM than OM, which were 57.4%, 18.2% and 20.6 - 31.9%, respectively for OM, PM and all the tested soil. The percentages of Po in the total P within Pnat, Palf and PCS-F treatments was higher than those in the PCS + F, PCS + F + OM and PCS + F + BM treatments (Fig. 4).

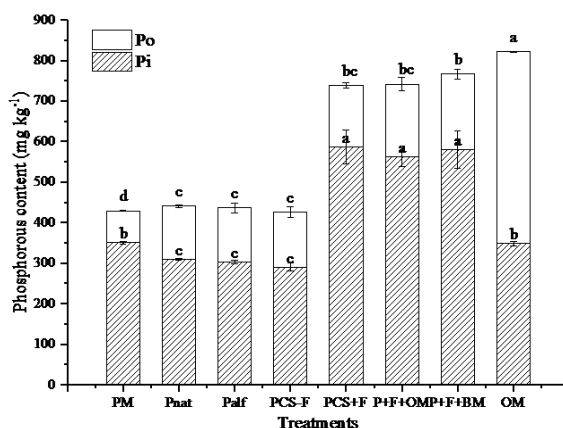


Figure 4. The concentrations of organic p and inorganic P in parent material of soil formation, parent material and mature Mollisol. (Pnat, natural fallow (grasses); Palf, alfalfa; PCS-F, unfertilized soybean-maize (S-M) control; PCS + F, chemical fertilizer S-M; PCS + F + OM, organic amendment plus chemical fertilizer S-M; PCS + F + BM, chemical fertilizer and all crop biomass returned S-M; Po, organic P; Pi, inorganic P; PM, parent material; OM, mature Mollisol. Values followed by different letters differ significantly at P < 0.05)

320 mg P kg⁻¹ was applied to the soil as diammonium phosphate every year during the 10 years of the experiment in the treatments with chemical fertilizers (PCS + F, PCS + F + OM and PCS + F + BM) (Table 2). Compared to PM, total P concentrations in the treatments with chemical fertilizers increased by 282.1-330.6 mg kg⁻¹, which was comparable to the amount of P applied in fertilizers (Fig. 4). The different total P concentrations among treatments could be attributed to the removal of P in aboveground biomass, which possibly caused P loss in the PCS + F treatment. Total P concentrations in the PCS + BM treatment reached the highest value of 330.6 mg kg⁻¹ (Fig. 3), which is higher than the total P input via fertilization. This can be attributed to biomass decomposition including aboveground and root biomass (Fig. 3). This indicates that most of the applied P accumulated in the top 0-20 cm of soil depth. This increased in

total P was made up of the increase of 211.1-235.9 mg kg⁻¹ of Pi and 74.1-108.0 mg kg⁻¹ of Po over the 10-year period of the experiment (Fig. 4). Compared to PM, available P in the PCS + F, PCS + F + OM and PCS + F + BM treatments increased by 93.8-114.9 mg kg⁻¹, indicating that approximately 33% of the applied fertilizer P accumulated in the Olsen P pool (Fig. 4).

Phosphorus fractions

The total P concentrations in soil increased after the initial 10 years of experiment regardless of treatments, whilst vegetation types and agricultural practices showed different effects on Pi fractions (Table 3). There was an increase mainly in the concentrations of LOP and MLOP. Compared with the LOP of PM without P fertilizers, the highest concentration of LOP was found in the PCS + F + OM treatment, which accounted for approximately 25% of the amount in OM (Table 3). MLOP concentrations in all the tested soils increased by 2.9-5.3 times, with the highest value in the PCS + BM treatment, which was similar to that in OM (Table 3). Treatments with P fertilization increased MSOP by 15.3-62.2%, and this accounted for approximately 33% of the MSOP in the OM (Table 3). The PCS-F and PCS + F treatments decreased the contents of HSOP, but the rest of treatments did not affect HSOP concentrations. The HSOP concentrations in all the tested soil were much lower than that in OM (Table 3).

Table 3. The contents of different P fractions in parent material under treatments, parent material and mature Mollisol

Treatments	Organic P (mg kg ⁻¹)				Inorganic P (mg kg ⁻¹)					
	LOP	MLOP	MSOP	SOP	Ca ₂ -P	Ca ₈ -P	Al-P	Fe-P	O-P	Ca ₁₀ -P
PM	0.0 e	19.4 d	34.5 d	24.3 c	15.0 c	4.6 c	20.4 b	94.0 b	80.9 ab	135.9 a
Pnat	0.45 de	75.0 c	32.6 d	23.4 c	6.8 d	13.4 c	5.9 c	114.8 b	60.4 bc	108.2 b
Palf	0.97 cd	79.4 c	31.3 d	21.6 c	4.4 d	8.4 c	1.4 c	118.7 b	66.2 bc	109.5 b
PCS-F	1.68 c	90.9 bc	38.5 cd	5.1 d	3.0 d	7.0 c	5.7 c	104.8 b	65.2 bc	104.8 b
PCS + F	0.91 cd	98.1 abc	49.3 bc	4.0 d	32.1 b	37.1 a	76.5 a	253.8 a	80.1 ab	107.2 b
P + F + OM	4.00 b	96.3 abc	56.0 b	23.4 c	28.3 b	37.5 a	63.7 a	241.4 a	87.2 a	103.9 b
P + F + BM	1.45 c	116.4 ab	39.8 cd	28.6 b	34.3 b	45.1 a	67.9 a	252.4 a	77.0 ab	103.4 b
OM	16.7 a	122.1 a	149.6 a	184.2 a	42.2 a	26.1 b	55.7 a	122.9 b	44.2 c	57.6 c

Pnat, natural fallow (grasses); Palf, alfalfa; PCS-F, unfertilized soybean-maize (S-M) control; PCS + F, chemical fertilizer S-M; PCS + F + OM, organic amendment plus chemical fertilizer S-M; PCS + F + BM, chemical fertilizer and all crop biomass returned S-M; PM, parent material; OM, mature Mollisol; LOP, labile organic P; MLOP, moderate labile P; MSOP, moderate stable organic P; SOP, stable organic P; Ca₂-P, NaHCO₃-soluble P; Ca₈-P, NH₄Ac-soluble P, Al-P NH₄F-soluble P; Fe-P, NaOH-NaCO₃-soluble P; O-P, occluded P; Ca₁₀-P, H₂SO₄-soluble P. Values followed by different letters at same column differ significantly at P < 0.05

In contrast with PM, the treatments without fertilization (Pnat, Palf and PCS-F) decreased the concentrations of Ca₂-P, Al-P and Ca₁₀-P and increased the concentrations of Ca₈-P and Fe-P, whereas the treatments with fertilization (PCS + F, PCS + F + OM and PCS + F + BM) significantly increased the Pi fractions except for Ca₁₀-P and O-P (Table 3). The concentrations of Ca₂-P, Ca₈-P, Al-P, and Fe-P increased by 0.9-1.3, 7.1-8.8, 2.1-2.7 and 1.6-1.7 times (Table 3). The concentrations of Ca₂-P,

Ca₈-P, Al-P, and Fe-P in OM were much higher than those in PM, but the concentrations of O-P and Ca₁₀-P in OM was lower than those in PM (Table 3).

Pedogenic process of parent material under Mollisol

Principal component analysis demonstrated that a large difference was found between OM and PM (Fig. 4), parent material with the field treatments had developed into mature Mollisol over the 10-year period of the experiment. Compared with the treatments without fertilizers (Pnat, Palf and PCS-F), the soils receiving fertilized treatments were closer to mature Moillisol (Fig. 5). Inorganic P concentrations in the soils treated with chemical fertilizers (PCS + F + BM, PCS + F + OM and PCS + F) were similar to the Pi in the OM, but a large difference in Po concentration exists between PM and OM (Fig. 5).

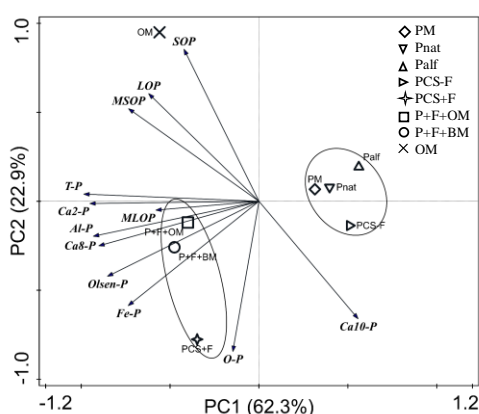


Figure 5. The first two principal components (PC1 and PC2) of soil phosphorus fractions for all the field treatments, mature Mollisol and parent material. (Pnat, natural fallow (grasses); Palf, alfalfa; PCS-F, unfertilized soybean-maize (S-M) control; PCS + F, chemical fertilizer S-M; PCS + F + OM, organic amendment plus chemical fertilizer S-M; PCS + F + BM, chemical fertilizer and all crop biomass returned S-M)

Discussion

Changes in different P fractions

Most P was present as calcium phosphates at the early pedogenic stage of rock, and vegetation occurrence converted Pi to Po in soil (Lu, 1980). In the parent material of Mollisol, the Pi concentration was 78.2 mg kg⁻¹, which accounted for 16.55% of that in mature Mollisol (Fig. 4). The unfertilized treatments (Pnat, Palf and PCS-F) did not increase total P, but increased Po to 131.5-136.1 mg kg⁻¹, accounting for 27.8-28.8% of Po in OM (Fig. 4), which is consistent with the organic carbon change measured by You et al. (2017), who reported that organic carbon increased by 7-60% in the same site. Soil organic carbon gradually increased in the parent material after vegetation occurrence, which resulted in an increase in Po, but a decrease in Pi concentration of a similar amount, indicating the transformation of Pi to Po during soil development from parent material. Specifically, Ca₂-P, Al-P, O-P and Ca₁₀-P were transformed to LOP and MLOP (Table 3), indicating that plants absorbed Pi and returned Po in residues to soil.

The Pnat and Palf treatments demonstrated a similar effect on the transformation of P fractions, which differed from the PCS-F treatment (Table 3) where SOC was only

derived from root and litter. This resulted in a relatively low Po concentration with a decrease in HSOP in the PCS-F treatment. Perroni et al. (2014) has documented that Alfalfa growth resulted in an increase in Po in a desert scrub soil in Mexico. Parent material used in the present study had a low SOC (4.8 g kg^{-1}) in this study, and the field treatments rapidly increased SOC (You et al., 2017) and subsequently Po in the soil. However, Alfalfa did not show any advantage in the accumulation of Po fractions in the parent material.

A mature Mollisol had been cultivated for hundreds of years, underwent no fertilization stage, farmyard manure stage and chemical fertilization stage. The accumulation of Po increased during soil development and utilization. However, the accumulation of Po concentration became steady at a certain level without the application of inorganic P fertilizers (Song et al., 2011). The transformation of Pi to Po occurred at a lower rate in the treatments without fertilizers where Po accumulation per year accounted for 1% of that in the mature Mollisol (Table 3). Apparently, external P inputs could accelerate the accumulation of Po in soil under field conditions.

Effects of fertilizer application on P fractions

In this study we attempted to accelerate P formation in the parent material by adding P fertilizers to contrast with the natural soil development process. P fertilizer applied to soil was mainly presented as Pi in the plant-available fractions in parent material under the imposed cropping systems and agricultural practices (Table 3). The rate of Po accumulation in the treated parent material was relatively slow, but approximately 33% of the fertilizer P was transformed to Po. Total P concentration in the treated parent material was close to that in the mature Mollisol, which may be attributed to the application of P fertilizers over the 10-year of the experiment (Fig. 4). Soil development in the Mollisol parent material was accelerated by P fertilization based on the result of PCA (Fig. 5), whilst soil development in the vegetation restoration contexts may take hundreds of years to accomplish this level of fertility (Harrison et al., 2008). Po accumulation was as high as 40% in the mature Mollisol, which is an evidence of the acceleration of soil development in the parent material used in this study.

Reddy et al. (2000) found that soil P fractionation was affected by soil type and fertilization practices, and the application of cattle manure increased the concentration of Po, activated fixed Pi in soil, and thus enhanced uptake of P by crops. Application of chemical fertilizers, straw and animal manure increased Pi concentration in the soils of Northwest China (Wei et al., 2011). Chemical fertilizers and organic manure also affected P sorption capacity in a Mollisol (Song et al., 2007). The long-term experiment with a Mollisol showed that chemical fertilizers (N and P), and the combination of chemical fertilizers with pig manure increased both total P and Olsen P, dominantly in the forms of $\text{Ca}_2\text{-P}$, $\text{Ca}_8\text{-P}$ and Al-P , but no significant increase in Po was noted (Song et al., 2011). Similar results were obtained in present study. P fertilization enhanced Pi accumulation in the treated parent material, which resulted in a significant increase in Pi with the treatments of PCS + F, PCS + F + OM and PCS + F + BM.

The concentrations of Pi showed a decreasing order of PCS + F + AM, PCS + F + OM > PCS + F > Pnat, Palf, PCS-F. The highest value reached 186.2 mg kg^{-1} , accounting for 39.4% of that in the mature Mollisol (Fig. 4). Accumulated Po in the parent material was mainly derived from crop residues, and a higher rate of organic amendment resulted in more accumulation of Po in soil.

Long-term field experiments have documented that organic amendment significantly increased the concentration of Olsen P and reduced soil adsorption capacity for P (Motavalli et al., 2002; Allen et al., 2006). Low molecular weight organic substances in organic amendment reduced the adsorption capacity of variable charge minerals for P by competition for adsorbing sites (Guppy et al., 2005). There was no significant difference in the total P and Olsen P concentrations between chemical fertilizers alone and the combination of chemical fertilizers and organic amendment. Applied fertilizer P was mainly presented in the Olsen P pools in the treated parent material. Compared with chemical fertilizer treatment alone (PCS + F), the treatments of chemical fertilizers with organic amendment (PCS + F + OM and PCS + F + BM) had no significant difference in Pi and Po concentrations or the Po : total P ratio.

Conclusions

The long-term field experiment was established in 2004 to determine the impact of cropping systems and agricultural practices on soil P concentration and fractionation during the first 10 years of soil development from parent material of a Mollisol. Po and Pi concentrations were 78.9 and 350.9 mg kg⁻¹ in parent material, and 472.6 and 348.7 mg kg⁻¹ in mature Mollisol. The treatments without chemical fertilizers (Pnat, Palf and PCS-F) enhanced P transformation from Ca₂-P, Al-P, O-P, Ca₁₀-P to Po in PM. The treatments with chemical fertilizers (PCS + F, PCS + F + OM and PCS + F + BM) increased total P concentration in PM to a level similar to that in OM, Po by 74.1-108 mg kg⁻¹, accounting for 20.6-31.9% of in the total P, lower than that in the Mollisol. The results from the present study indicate that agricultural practices with fertilizer application can enhance the accumulation of P during soil development from parent materials of a Mollisol in semi-arid and semi-humid climatic regions in a relatively short period. This information has important implications in the restoration of degraded Mollisols. The further studies are warranted to detect the mechanisms of P transformation during the process of fertility restoration.

Acknowledgement. The study was supported by the National Basic Research Program of China (No. 2016YFD0300806, 2016YFD0200309 and 2017YFD0300605), the Natural Science Foundation of China (NSFC) (41771327, 41671299 and 41807085), China Agriculture Research System (CARS04), Applied Technology Research and Development Program of Heilongjiang (GY2017ZB006). We are grateful to Zheli He for his modification for the manuscript.

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