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Effects of mechanochemically activated phosphate rock on maize growth and phosphorus use

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Abstract: It is well known that mechanochemically activated phosphate rock (MAPR) could improve extractable phosphorus (P) (extracted in 2% citric acid) greatly in an ecological way. To evaluate the agronomic effectiveness of MAPR, we conducted a field experiment using spring maize in Luvisol (pH 6.47) soil in Northeast China for three consecutive years. Treatments consist of variation of P levels for substitution of triple superphosphate (TSP) (100% TSP, 10% MAPR, 20% MAPR, 50% MAPR, 100% MAPR). Compared with 100% TSP, all the combined applications of MAPR and TSP were as effective on straw yield. Treatments of 10% MAPR and 20% MAPR had similar effect on grain yield and P uptake, while 50% MAPR and 100% MAPR were significantly lower. For P partial nutrient productivity and apparent P recovery with the treatment of 20% MAPR had equal effectivity, likewise. For soil P_{Olsen}, treatment of 10% MAPR was equally operative, while 20% MAPR had the similar performance only in the last year (i.e. 2016). It is concluded that 10–20% of TSP can be effectively replaced by MAPR without affecting spring maize yield in soil with neutral pH.

Keywords: phosphorite; milling; fertiliser; corn production; phosphorus absorption

Phosphorus (P) is an essential but non-renewable natural resource that severely limits crop production. Substantial P is therefore added to maximise agricultural production to meet the increasing demand for food, which is inefficient and unattainable in the long term (Cordell et al. 2009). The exhaustion of the high-grade phosphate rock (PR) for water-soluble phosphate fertiliser (WSP), such as energy and acid consumption, discharge of waste residue, etc., is the major limitation of the use of WSP all over the world. Efficient use of low-medium grade (P < 12.22%) PR could be an alternative solution to alleviate the deficiency of WSP and scarcity of high-grade PR (Chien et al. 2010). Many PR producing countries, such as China, Africa and some areas of the United States have attempted to ground PR to the specified fineness, such as through a 2 mm sieve and apply it directly to the soils (Chien et al. 2010, Savini et al. 2016). However, it is not effective in most cases for its extremely low solubility in water (Hammond et

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al. 1989, Koppelaar and Weikard 2013), especially for the crops with a short growth period (Friesen et al. 1987).

In recent years, the mechanochemical method is widely applied to obtain nanomaterials with new properties. The mechanochemically activated phosphate rock (MAPR) has been paid more attention by researchers recently. It is characterised as a simple and ecologically clean way to increase the P solubility of PR with no flotation, sulfuric acid and wastes (Yaneva et al. 2009, Petkova et al. 2015, Fang et al. 2019). Compared with the inactivated PR, MAPR could improve the extractable P in citric acid (by 2–3 folds), which can be up-taken directly by plants (Yaneva et al. 2009, Fang et al. 2019). It is not only due to decreased particle size, but also on account of increased structural defects for the incorporation of CO_3^{2-} and formation of OH^- in the apatite structure of MARP (Yaneva et al. 2009, Fang et al. 2019). Compared with WSP, MAPR can continue provide available P for long periods and can also protect P from washing away by rain (Koleva and Petkova 2012).

Much research focused on the development of mechanochemical activation equipment and technologies, while the effects of MAPR on crop yield and its effect on soil P remains unclear. Especially, whether the use of MAPR from medium and low-grade PR (9.77%) to replace part of WSP in agricultural production is feasible? Therefore, this study aimed at assessing the effects of combined application of MAPR from low-grade PR and the WSP on maize yield, P uptake and soil available P, and verifying the optimum ratio of MAPR replace of P fertiliser in the test area.

MATERIAL AND METHODS

Preparation of mechanochemically activated rock phosphate. The composition of PR (from Yichang, China) contained: 9.77% P, 2.28% F, 31.91% Ca, 1.07% Na, 0.05% S, 3.50% Si and 1.52% Mg. The PR was prepared with the jaw crusher and passed through a 2 mm sieve as raw material for MAPR. Then it was ground in an eccentric vibration mill (Jiaxing, China) with the capacity of 0.5 t/h and a maximum amplitude of 20 mm. The median particle size D50 and specific surface area of initial PR and MAPR varied from 53.91 μm and 12.42 μm, 111.0 m^2/kg to 340.2 m^2/kg, respectively (Figure 1). The extractable P contents (in 2% citric acid) of initial PR (through 2 mm sieve) and MAPR were 3.9% and 11.92%, respectively.

Field study. The study was conducted in the research fields of the Academy of Dalian Agricultural

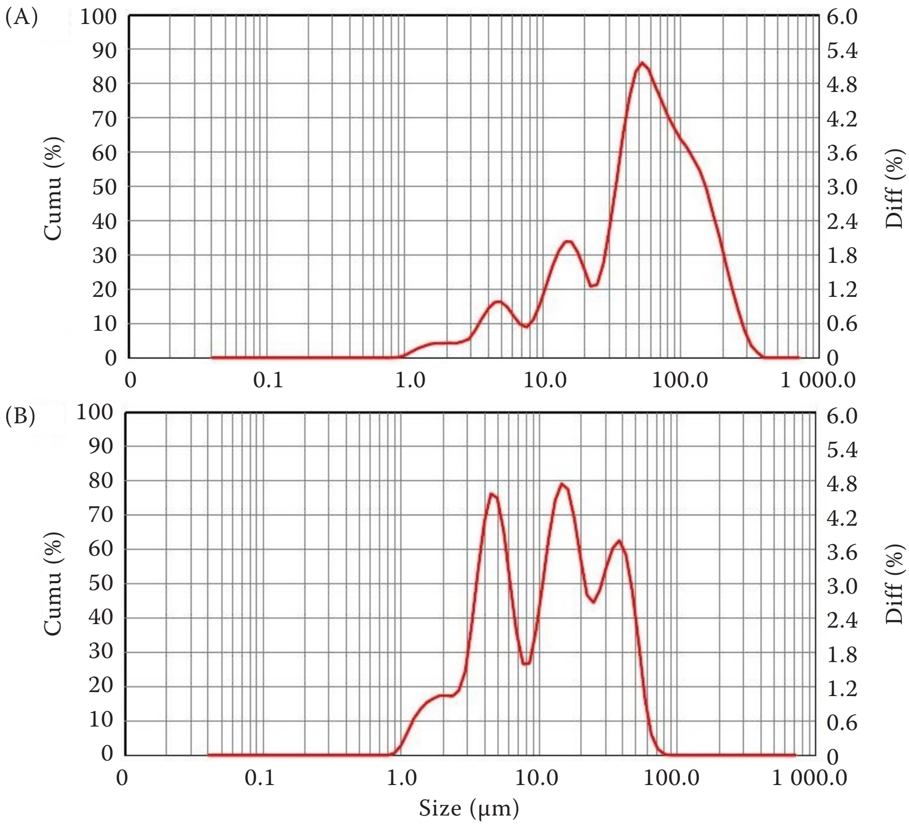

Figure 1. Particle size distribution of (A) the initial phosphate rock and (B) mechanically activated phosphate rock

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Sciences, China (38.95'N, 121.57'E, 96.8 m a.s.l.), with the mean annual precipitation and temperature of 389, 558, 540 mm and 11.4, 11.3, 11.1 °C, respectively from 2014 to 2016. The total sunshine and frost-free period in the whole year were 2 500–2 800 h and 198–211 days. The tested soil (Luvisol, sandy loam): pH 6.47; P_{Olsen} 23.45 mg/kg; P_{tot} 1.02 g/kg; N_{tot} 1.10 g/kg. The tested P fertilisers were MAPR with 9.77% P and triple superphosphate (TSP) with 20.08% P. The N and K fertilisers were urea (46% N) and potassium sulfate (K_2SO_4, 20.74% K), respectively. The pure amounts of N, P and K fertiliser applied in the field were 230, 39.29, 20.91 kg/ha, respectively. The experiment was a completely random block with a unit plot size of 38.6 m^2 (10.72 m × 3.6 m), replicated three times. Treatments included: no fertilisers (N0P0K0), no P fertiliser (NP0K), 100% TSP, 10% MAPR, 20% MAPR, 50% MAPR, and 100% MAPR (Table 1). The N fertiliser was applied at a ratio of 3:7 at the sowing and elongation stage of maize, respectively. The P and K fertilisers were one-time applied as the basal fertiliser.

Plant sampling and analysis. All the above-ground parts of each plot were harvested at maturity. Ten plants were randomly harvested from each plot with maize straw and grain separated, air-dried for two weeks and weighed to calculate dry matter yield (DM). Then oven-dried at 70 °C, ground, through a 2 mm sieve for chemical analysis. Phosphorus uptake in maize straw and grain were assayed after sulfuric acid digestion by spectrophotometer (UV1100II, Techcomp Co., Ltd, Shanghai, China) and calculated according to Eq. (1):

$$P_{uptake}\ (kg/ha) = \frac{P_x \times DM}{1000000} \qquad (1)$$

P_x – P content in different plant tissue (mg/kg); DM – dry matter yield (kg/ha).

P partial nutrient productivity (P_{pnp}) was calculated using Eq. (2):

$$P_{pnp}\ (kg/kg) = \frac{Y}{TP} \qquad (2)$$

Y – grain yield (kg/ha); TP – total P initially applied *via* fertiliser (kg P/ha).

The apparent P recovery (P_{rec}) was calculated according to Eq. (3) (Begum et al. 2004):

$$P_{rec}\ (\%) = \frac{(P_i - P_0)}{TP} \times 100 \qquad (3)$$

P_i – phosphorus uptake of the treated plot (kg/ha); P_0 – phosphorus uptake of the control plot without P fertiliser (kg/ha); TP – total P initially applied *via* fertiliser (kg P/ha).

Soil sampling and analysis. After harvesting, soil samples (five soil cores) were collected and analysed according to standard procedures. Soil P_{Olsen} was extracted using 0.5 mol/L $NaHCO_3$ at a pH of 8.5, P in the filtrate was determined calorimetrically by the molybdate method.

Statistical method. The comparisons among the treatments and cultivation years were performed using a one-way ANOVA Duncan multiple ranges test at a 5% level of probability by SPSS 16.0 (Chicago, USA).

RESULTS AND DISCUSSION

Maize straw and grain yield treated at all P treatments ranged from 7 032.26 to 9 371.72 kg/ha and 9 238 to 9 632 kg/ha from 2014 to 2016, respectively. It showed an obvious trend of escalation (Figures 2 and 3). Compared with 100% TSP, all the combined applications of MAPR and TSP were equally effective, for straw yield (Figure 2). Both treatments of 10% MAPR and 20% MAPR had equal effectivity, while

Table 1. The dosage of N, P and K fertilisers applied in the field study

Treatment	Urea (N, kg/ha)	Triple superphosphate (P, kg/ha)	Mechanochemically activated phosphate rock (P, kg/ha)	Potassium sulfate (K, kg/ha)
N0P0K0	0	0	0	0
NP0K	230	0	0	20.91
100% TSP	230	39.29	0	20.91
10% MAPR	230	3.93	35.36	20.91
20% MAPR	230	7.86	31.43	20.91
50% MAPR	230	19.645	19.645	20.91
100% MAPR	230	0	39.29	20.91

N0P0K0 – no fertilisers; NP0K – no P fertiliser; TSP – triple superphosphate; MAPR – mechanochemically activated phosphate rock

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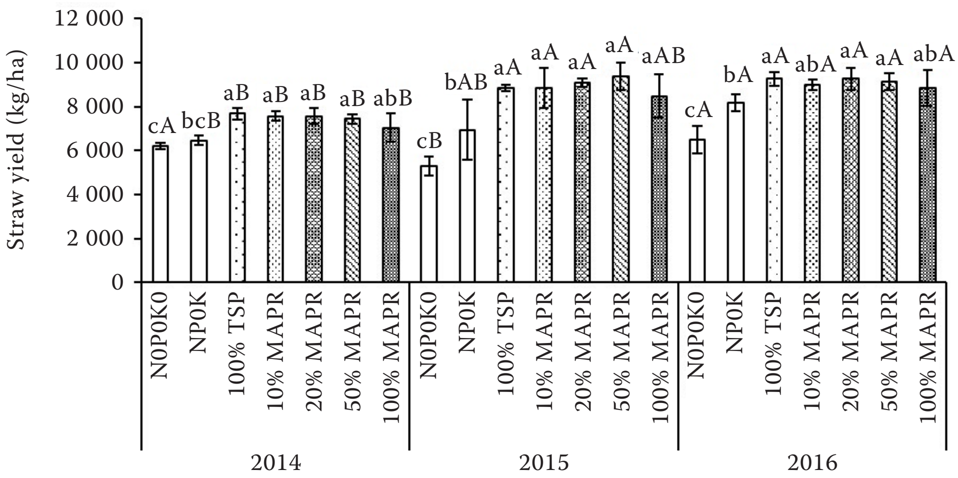

Figure 2. The straw yield of maize under combined application of mechanically activated phosphate rock (MAPR) and water-soluble phosphate fertiliser (WSP). Lowercase letters indicate significant differences between different applications in the same year, and uppercase letters indicate significant differences between different years in the same treatments (P < 0.05; Duncan's test). N0P0K0 – no fertilisers; NP0K – no P fertiliser; TSP – triple superphosphate

that of 50% MAPR and 100% MAPR were significantly lower for grain yield (P < 0.05) (Figure 3). The straw and grain yield with the treatment of 20% MAPR showed an increase by 2.84% and 3.89% (the highest), respectively, at the spring maize maturity (130 days after sowing) in a neutral soil (pH 6.47) in our study, whereas the dry-matter yield of maize 30 days after transplanting with granulated Florida PR and monoammonium phosphate with P ratio = 1:1 had a decrease (no significant) by 6.9% in acidic soil (pH 4.8) in the greenhouse experiment, compared with WSP treatment alone (Chen 2019). It is also in accordance with the results of the combined application of partially acidulated phosphate rocks with WSP (single superphosphate, SSP) at a ratio of 1:1 of acidic and near-neutral soil (Menon and Chien 1990). With the increasing rate of MAPR and WSP up to more than 1:1 (50% MAPR), it agrees with the

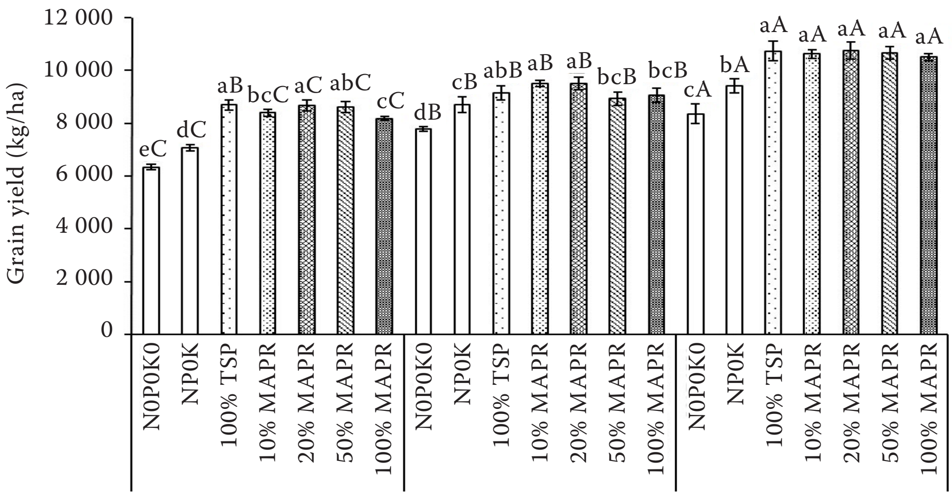

Figure 3. Grain yield of maize under combined application of mechanically activated phosphate rock (MAPR) and water-soluble phosphate fertiliser (WSP). Lowercase letters indicate significant differences between different applications in the same year, and uppercase letters indicate significant differences between different years in the same treatments (P < 0.05; Duncan's test). N0P0K0 – no fertilisers; NP0K – no P fertiliser; TSP – triple superphosphate

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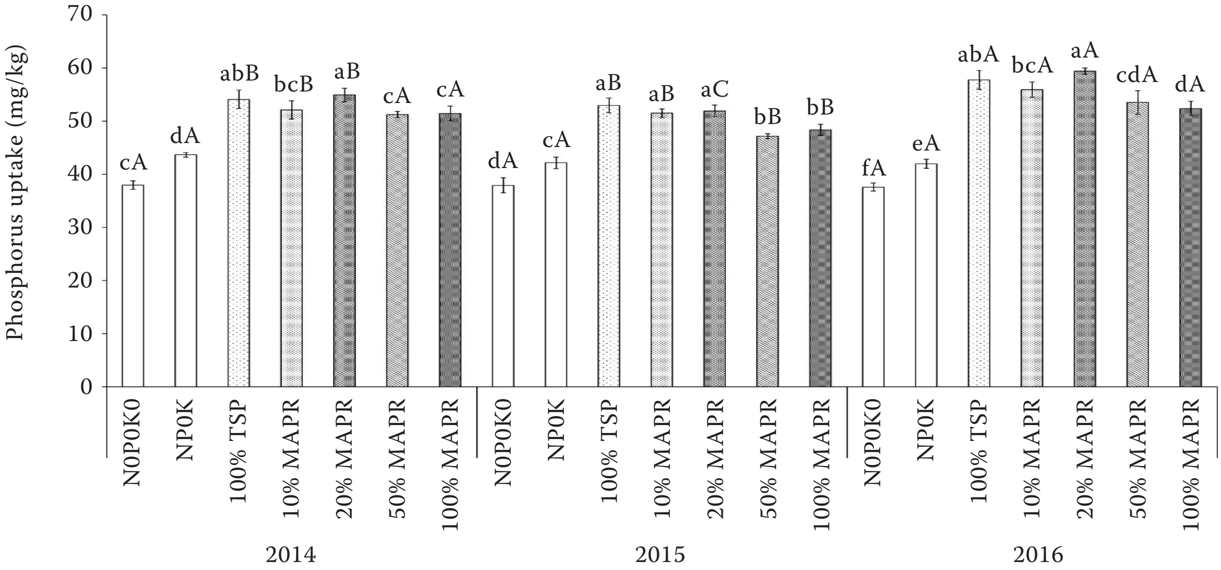

Figure 4. Phosphorus uptake of maize under combined application of mechanically activated phosphate rock (MAPR) and water-soluble phosphate fertiliser (WSP). Lowercase letters indicate significant differences between different applications in the same year, and uppercase letters indicate significant differences between different years in the same treatments ($P < 0.05$; Duncan's test). N0P0K0 – no fertilisers; NP0K – no P fertiliser; TSP – triple superphosphate

earlier findings (Monrawee et al. 2013). The cause of the combined application of PR and WSP has a good effect on maize maybe for the starter effect of WSP, which can promote the development of the root system with more organic acids in the early stage of maize (Chien 2019). In addition, it may be due to the drastically reduced particle size and increased specific surface area of MAPR, increasing the contact surfaces between roots and P fertilisers, conducive to P uptake by crops.

Phosphorus uptake of maize treated with all P treatments ranged from 50.63 to 55.41 kg/ha for three years, which showed an upward trend yearly (Figure 4). Phosphorus uptake of maize with the treatments of 10% MAPR and 20% MAPR were equally effective as that of 100% TSP ($P < 0.05$), while that of 50% MAPR and 100% MAPR were significantly lower. This is consistent with the results of McLay et al. (2000). Compared with the limited effectiveness of the initial PR for its extremely low solubility

Table 2. Phosphate partial nutrient productivity (P_{pnp}) and apparent phosphorus recovery (P_{rec}) of maize under combined application of mechanically activated phosphate rock and water-soluble phosphate fertiliser

Treatment	P_{pnp} (kg/kg)			P_{rec} (%)		
	2014	2015	2016	2014	2015	2016
N0P0K0	161.15 ± 2.56^{fC}	197.92 ± 2.25^{dB}	212.51 ± 9.57^{cA}	–	–	–
NP0K	180.15 ± 3.04^{eC}	221.28 ± 7.48^{cB}	239.49 ± 7.02^{bA}	–	–	–
100% TSP	221.20 ± 4.81^{aB}	232.75 ± 6.95^{abB}	272.98 ± 9.43^{aA}	12.49 ± 4.39^{abB}	14.45 ± 3.63^{aB}	25.48 ± 3.92^{abA}
10% MAPR	213.48 ± 3.09^{cdC}	241.81 ± 2.73^{aB}	270.34 ± 4.12^{aA}	6.95 ± 2.59 ^{bB}	10.78 ± 2.59^{abB}	20.19 ± 3.64^{bcA}
20% MAPR	220.84 ± 5.17^{bC}	240.96 ± 4.68^{aB}	273.64 ± 8.41^{aA}	14.84 ± 3.31^{aB}	13.04 ± 2.28^{aB}	29.25 ± 2.24^{aA}
50% MAPR	219.23 ± 5.49^{bcB}	227.09 ± 6.38^{bcB}	271.00 ± 5.93^{aA}	7.30 ± 2.06 ^{bB}	4.45 ± 0.86^{cB}	17.99 ± 4.13^{cA}
100% MAPR	208.12 ± 1.63^{dC}	230.20 ± 6.63^{bcB}	267.05 ± 3.57^{aA}	9.09 ± 2.72 ^{abB}	6.60 ± 2.47^{bcB}	15.26 ± 3.37^{cA}

Lowercase letters indicate significant differences between different applications in the same year, and uppercase letters indicate significant differences between different years in the same treatments ($P < 0.05$; Duncan's test). N0P0K0 – no fertilisers; NP0K – no P fertiliser; TSP – triple superphosphate; MAPR – mechanically activated phosphate rock

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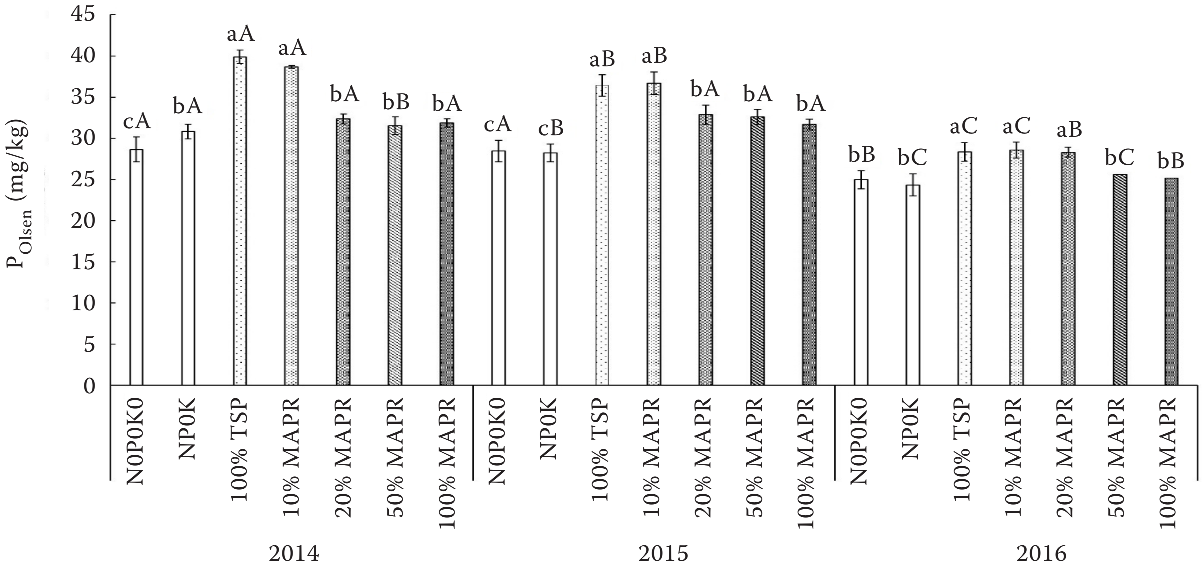

Figure 5. Soil P_{Olsen} after maize harvest under combined application of mechanochemically activated phosphate rock (MAPR) and water-soluble phosphate fertiliser (WSP). Lowercase letters indicate significant differences between different applications in the same year, and uppercase letters indicate significant differences between different years in the same treatments (P < 0.05; Duncan's test). N0P0K0 – no fertilisers; NP0K – no P fertiliser; TSP – triple superphosphate

and reactivity (Hammond et al. 1989, Koppelaar and Weikard 2013), the extractable P content of MAPR largely increased by 2 folds (Yaneva et al. 2009). Hence, the application of MAPR can increase the available P concentration (soil P_{Olsen}) around the root system.

The P_{pnp} and P_{rec} of maize treated with all P treatments ranged from 208.12 to 273.64 kg/kg, 4.45% to 29.25% from 2014 to 2016 (Table 2), respectively. Both for P_{pnp} and P_{rec}, the treatments of 10% MAPR and 20% MAPR (except 10% MAPR in 2014) had equal effectivity for the three years, compared with 100% TSP (P < 0.05). It was in accordance with the results of the combined application of 50% Kodjari PR and 50% TSP that led to the equal effects on sorghum yields and P uptake in ferric Lixisol (Bonzi et al. 2011). Initial PR has little effect on promoting plant growth, due to the negligible amount of WSP during short periods of crop growth, especially in neutral (pH 6.5) or even high pH soil (McLay et al. 2000). It can drastically improve the reactivity and solubility of PR by mechanochemical activation (Yaneva et al. 2009), and increase the P efficiency distinctly.

In 2014 and 2015, soil P_{Olsen} for treatment with 10% MAPR were equally effective, compared with 100% TSP (P < 0.05). With the increase of the substitution P with the amount of MAPR, soil P_{Olsen} was significantly lower. In 2016, soil P_{Olsen} with the treatments of 10% MAPR and 20% MAPR had equal effectivity (P < 0.05) (Figure 5). After three years of continuous combined application of MAPR and WSP, the soil available P after maize harvest was comparable to that of TSP alone, confined to 20–40 mg/kg considered to be within the optimum available P content required by crops (Li et al. 2011). Plant phosphorus uptake and the redistribution of dissolved P may explain why the available P measured at harvest in the combined application treatments were not the highest. Low soil pH is generally favourable for PR dissolution, but not in neutral or alkaline soils (Hagin and Harrison 1993). Therefore, further verification is required.

In conclusion, in a neutral Luvisol, the combined application treated with 10% MAPR and 20% MAPR had equal effectivity as 100% TSP in increasing maize yield, phosphorus uptake and P efficiency, although it could not increase the soil available P significantly. Therefore, it is a feasible solution with 10–20% substitution of MAPR for WSP fertiliser on spring maize in the northeast of China for nearly neutral soil (pH 6.47). It is of great significance to partially replace WSP fertiliser with MAP for alleviating the P resource crisis and sustainable development of agriculture in China. Further studies are needed to establish the performance of MAPR at the selected ratio of MAPR/TSP for different soil pH and climatic zone.

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