

# Periodic P fertilizer application is recommended for small-holder farmers in Northeast China: evidence from a 12-year study

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**Abstract** Phosphorus (P) fertilizer prices rose more than 150 % in the past two decades, thus periodic P fertilization (purchasing and applying superphosphate periodically) could be economically beneficial to small-holder farmers. Still, it is necessary to determine if periodic P fertilization could sustain corn production compared to annual P fertilization. Corn (*Zea mays* L.) obtains P for its growth and development from soil solution, which is replenished by soil P fractions associated with the soil minerals (inorganic P, Pi) and organic matter (organic P, Po). It is expected that P fertilization regimes (annual vs. periodic applications) will influence the concentration of soil P fractions contributing to corn P nutrition. The objective of the study was to evaluate soil Pi and Po fractions and P

uptake in corn agroecosystems of Northeast China under two fertilizer regimes: triple-superphosphate applied annually at 0, 25 or 75 kg P ha<sup>-1</sup>, or applied periodically (once every 6 years) as 150 or 450 kg P ha<sup>-1</sup>. During the two 6-year periods (1997–2002 and 2003–2008), both periodic and annual triple-superphosphate application significantly ( $P < 0.05$ ) increased the NaHCO<sub>3</sub>-Pi (93–453 %), NaOH-Pi (44–135 %) and HCl-Pi (11–45 %) fractions, thus sustaining crop P requirements. Although annual P fertilization gave 35 % more NaHCO<sub>3</sub>-Pi, 28 % more NaOH-Pi, 15 % greater HCl-Pi and 4 % more crop P uptake at the end of each 6-year period, there was no significant difference in corn yield. Therefore, periodic P application (once in 6 years) is recommended as an economical practice that could lower the cost of P fertilization for small-holder farmers producing corn in Northeast China.

**Keywords** Phosphorus fertilizer prices · Soil phosphorus fractions · Phosphorus uptake · Long term experiments

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## Introduction

Phosphorus (P) deficiency limits food production in Northeast China, where agricultural production is mostly the work of small-holder farmers (average farm size <2 ha and 800,000 small-holder farmers in the region). Soils in this region have low P

concentration in soil solution because P is strongly adsorbed by Fe and Al oxides/hydroxides and carbonates in soils. Small-holder farmers rely on P fertilizers like superphosphates, ammoniated phosphates. The P fertilizers are added to soils, singly or in combination with manures, to boost the soil P concentration to a level that could sustain crop P requirements and meet yield targets (Aulakh et al. 2003; Kuo et al. 2005). Because most crops have the low P use efficiency (around 10–15 % of applied fertilizer P), the P inputs from fertilizer and manure tend to accumulate in soils with high P fixing capacity, changing the concentration of P in soil solution and associated with soil minerals and organic matter (Zhang et al. 2004; Boschetti et al. 2008; Zamuner et al. 2008; Qin et al. 2010; Chakraborty et al. 2011; Kang et al. 2011). The sequential P fractionation of Hedley et al. (1982), later simplified by other researchers (Tiessen and Moir 1993; Guppy et al. 2000), is an appropriate method to quantify the effects of P fertilization practices on soil inorganic P (Pi) and organic P (Po) fractions since it identifies which soil P fractions are preferential sinks for P fertilizer inputs and whether these fractions are plant-available, thereby contributing to crop P uptake. This allows agronomists to adjust P fertilizer recommendations after considering historical build-up of plant-available P, consistent with the principle of sustainable nutrient management.

The way that P fertilization practices affect soil P fractions and P uptake by plants depends upon the type, rate and frequency of P fertilizer application, crop species and inherent soil properties (Saleque et al. 2004; Vu et al. 2010a). Sugihara et al. (2012) found that annual application of triple superphosphate at 50 kg P ha<sup>-1</sup> gradually increased soil Resin-, NaHCO<sub>3</sub>-, and NaOH-Pi fractions during a 4-year field experiment with corn grown on acidic, sandy soils in Tanzania. Although Lan et al. (2012) found that continuous application of triple superphosphate at 12 kg P ha<sup>-1</sup> to soils for 26 years increased both Po and Pi fractions, Verma et al. (2005) reported that 29 annual application of single superphosphate at 26–43 kg P ha<sup>-1</sup> for maize and 26–52 kg P ha<sup>-1</sup> for wheat grown on acidic silty clay loam soils in India significantly increased Pi fractions by twofold to threefold but increased Po fractions by <25 %. Up to 42 % of the P fertilizer input was retained through fixation with Fe and Al oxide, which indicates that NaOH-Pi acts as a sink for added superphosphate

fertilizer in soils containing more Fe and Al oxides than Ca carbonates. Crop P uptake also significantly increased with P fertilizer application in these studies, due to the greater P concentration in soil solution. Still, superphosphates did not appreciably accumulate in Po fractions, nor were they irreversibly fixed in residual P (Guo et al. 2000; Boschetti et al. 2008; Vu et al. 2008; Jalali and Ranjbar 2010). Based on these research findings, we hypothesize that (1) triple superphosphate application will increase crop P uptake and the concentration of labile and moderately labile Pi fractions, but not change the concentration of Po and residual P fractions, and (2) added triple superphosphate will accumulate preferentially in the NaOH-Pi fraction in soil where Fe and Al oxides control P fixation.

Although the frequency of P fertilizer application is important, there is limited information on how periodic P fertilizer applications (i.e., once in a while, not every year) will affect the dynamics of soil P fractions and crop P uptake. It is not unusual for agricultural producers to apply P fertilizer periodically. During the establishment of perennial crops, producers often add large quantities of P fertilizer in the root zone, expecting this P input to sustain crop production for many years. For example, asparagus plantations received 68 kg P ha<sup>-1</sup> from triple superphosphate at planting and an additional 40 kg P ha<sup>-1</sup> in the first two production years, which raised the soil P saturation from 16.2 % P/Al to 25.3 % P/Al within three years and was expected to support asparagus production for 20 years (Sommerville and Whalen 2005). Rock phosphate, the raw material for all mineral P fertilizers, is a non-renewable resource (Smil 2000; Cordell et al. 2009) and global P demand is forecast to increase by around 3–4 % annually (Maene 2007). Consequently, P fertilizer prices have increased by more than 150 % in the past two decades (Zhao et al. 2010; USDA Economic Research Service 2013), leading small-holder farmers to consider the economic advantages of purchasing and applying P fertilizer periodically, rather than every year, on their annual crops. Small-holder farmers who take advantage of a discounted price or sale to buy more P fertilizer are going to apply it to their agricultural fields in the year it is purchased (1) to save on labor costs, and (2) because they lack fertilizer storage facilities. However, when the P input from superphosphate fertilizer is higher than P uptake by crops, the excess P will gradually

accumulate in soil as Fe-P, Al-P or Ca-bound P forms, decreasing P availability to the crop (Boschetti et al. 2008; Gichangi et al. 2009). These P fixation reactions occur within days of the dissolution of superphosphate fertilizer granules (Vu et al. 2010b), meaning that periodic application of superphosphate will result in greater P fixation and lower P use efficiency of crops than annual application of superphosphate. Further, we hypothesize that annual P fertilizer application will cause a greater increase in soil labile ( $\text{NaHCO}_3\text{-Pi}$ ) and moderately labile P ( $\text{NaOH-}$  and  $\text{HCl-Pi}$ ) fractions than periodic P fertilizer application, with greater crop P uptake predicted from annual than periodic P fertilizer application (once in 6 years).

The objective of the study was to evaluate soil Pi and Po fractions and P uptake in corn agroecosystems of Northeast China under two fertilizer regimes: triple-superphosphate applied annually at 0, 25 or 75 kg P ha<sup>-1</sup>, or applied periodically (once every 6 years) as 150 or 450 kg P ha<sup>-1</sup>. The duration of the experiment was 12-year.

## Materials and methods

### Experimental site characteristics

The long-term field experiment started in 1997 at the Shenyang Experimental Station of Ecology (41°31'N, 123°24'E), Chinese Academy of Sciences, China. The climate is temperate semi-humid continental monsoon, characterized by warm-wet summer and dry-cold winter. The mean annual temperature is 7–8 °C, the corn heat units cumulated during the growing season are 3100–3400, frost-free period is 147–164 days and annual precipitation is 650–700 mm. The tested soil is a silt loam meadow burozem (Hapli-Udic Cambisols in Chinese soil taxonomy, corresponding to Inceptisols in US soil taxonomy), which is a major soil type for agricultural production in Northeast China, covering more than 4 million hectares. Initial soil properties before establishment of the experiment are shown in Table 1. The annual crop was corn (*Zea mays* L. cv Fuyou 1) grown in a no-till system for the duration of the experiment (Zhao et al. 2010).

Microplots (1 m × 1 m) were designated in a randomized complete block design that included five P fertilizer treatments with three replications per treatment. There was a 1 m buffer area between each

**Table 1** Soil physical and chemical properties of a silt loam meadow burpzem (Inceptisol) under corn production at the Shenyang Experiment Station of Ecology, Northeast China

	Total N (g kg <sup>-1</sup> )	Total P (g kg <sup>-1</sup> )	Organic C (g kg <sup>-1</sup> )	Olsen-P (mg kg <sup>-1</sup> )	Available K (mg kg <sup>-1</sup> )	pH 1:2.5H <sub>2</sub> O	Soil texture (%)	Available micronutrients <sup>a</sup> (mg kg <sup>-1</sup> )					
								Sand			Clay	Fe	Mn
1.01		0.41	10.65	7.0	103.5	7.02	14.7	60.4	24.9	35.4	72.5	2.9	1.6
Soil P fractions (mg kg <sup>-1</sup> )													
NaHCO <sub>3</sub> -Pi	NaHCO <sub>3</sub> -Po	NaOH-Pi	NaOH-Po	HCl-Pi	Residual P	Fe <sub>d</sub> <sup>b</sup> (g kg <sup>-1</sup> )	Al <sub>d</sub> <sup>b</sup> (g kg <sup>-1</sup> )	Fe <sub>o</sub> <sup>b</sup> (g kg <sup>-1</sup> )	Al <sub>o</sub> <sup>b</sup> (g kg <sup>-1</sup> )	CaCO <sub>3</sub> (g kg <sup>-1</sup> )	P adsorption maxima <sup>c</sup> (mg kg <sup>-1</sup> )		
12.2	23.6	58.5	24.7	103.6	188.8	13.56	9.21	3.27	0.21	7.29	574.7		

<sup>a</sup> Soil available micronutrients were DTPA (diethylene triamine pentacetate acid)-extractable Fe, Mn, Zn and Cu

<sup>b</sup> Fe<sub>d</sub> and Al<sub>d</sub> were dithionite-citrate-bicarbonate-extractable Fe and Al, respectively, and Fe<sub>o</sub> and Al<sub>o</sub> were oxalate-extractable Fe and Al, respectively

<sup>c</sup> P adsorption maxima was calculated by the linear form of Langmuir adsorption isotherms after shaking soil with a range of equilibrating P solutions (1:15 soil/solution ratio, 0–50 mg P L<sup>-1</sup>)

micro-plot. The five treatments were P0 (0 kg P ha<sup>-1</sup> annually), P25 (25 kg P ha<sup>-1</sup> annually), P25\* (150 kg P ha<sup>-1</sup> once every 6 years), P75 (75 kg P ha<sup>-1</sup> annually) and P75\* (450 kg P ha<sup>-1</sup> once every 6 years). The P fertilizer [triple superphosphate containing 45 % P<sub>2</sub>O<sub>5</sub> (0–45–0) and 15 % Ca, broadcast uniformly across the plot] was the main influential factor. To avoid nutrient deficiency, all plots received 150 kg N ha<sup>-1</sup> (urea, broadcast uniformly across the plot) each year as basal fertilizer. Other nutrients in soil were at the adequate range and thus were not applied. The field study occurred in two 6-year periods (1997–2002 and 2003–2008).

#### Sampling and sample analysis

All above-ground plant material in each micro-plot was collected every year at harvest, and divided into stem, cobs and grain. Plant components were dried to constant mass (75 °C for 24 h, then 105 °C for the next 48 h), and then the biomass was determined. Although these drying conditions should not affect plant tissue P concentrations because P is not volatile, it could reduce plant tissue N concentrations due to NH<sub>3</sub> loss from protein denaturation and we recommend that plant components be dried to constant mass at 60–70 °C if N analysis is to be done. Subsamples of plant materials were ground to pass a 1-mm screen, and the P content was determined by the following procedure: the sample (0.5 g) was digested with H<sub>2</sub>SO<sub>4</sub> (5 ml) and HNO<sub>3</sub> (10 drops) at 360 °C for 4 h, and then the solution was diluted to 100 ml. The concentration of P in the digests was determined colorimetrically with the molybdate-blue method (Murphy and Riley 1962) using a UV-721 spectrophotometer at 700 nm. Crop P uptake (kg P ha<sup>-1</sup>) was calculated by multiplying the P concentration (g P kg<sup>-1</sup>) by the plant biomass (kg ha<sup>-1</sup>). Mean P use efficiency under the two P fertilizer regimes was calculated from the 12-year averaged values of P uptake of corn, according to the computing method of Srivastava et al. (2013), where:

Mean P use efficiency (%)

$$= \frac{(\text{Mean P uptake under treatments} - \text{Mean P uptake under control}) \times 100}{\text{Mean P fertilizer dose}}$$

Surface (0–20 cm) soil samples were collected annually after corn harvest, using a composite soil sampling method with 4 soil cores taken from each micro-plot. Soil samples were air-dried, ground to pass a 2 mm sieve and preserved for analysis. Subsamples of the tested soil were ground to pass a 0.15 mm sieve for the analysis of soil P fractions, according to the procedures of Hedley et al. (1982) and Kang et al. (2011). Briefly, soil (0.5 g) was weighed into a 50 ml centrifuge tube and the fractions extracted were (1) labile P (NaHCO<sub>3</sub>-P), soil extracted with 30 ml 0.5 M NaHCO<sub>3</sub> (pH 8.5) for 16 h; (2) Fe- and Al-bound P (NaOH-P), residue from the first fraction extracted with 30 ml 0.1 M NaOH for 16 h; (3) Ca-bound P (HCl-P), residue from second fraction extracted with 1.0 M HCl for 16 h; (4) residual P (Res-P), residue from the last fraction digested with H<sub>2</sub>SO<sub>4</sub>-HClO<sub>4</sub> at 360 °C. The extracted Pi collected at each step was analyzed colorimetrically with the Murphy and Riley (1962) method, which involved adding ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] with ascorbic acid to each extract after adjusting the extract pH to 4.4. After 30 min color development at 25 °C, the absorbance of P in the solution was measured at 700 nm with a UV-721 spectrophotometer. Total P in the NaHCO<sub>3</sub> and NaOH extracts was determined by digesting in autoclave (103.4 K Pa, 121 °C) with 0.3 g acidified potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and 10 ml 0.9 M H<sub>2</sub>SO<sub>4</sub> (Wei et al. 2010). The Po concentration in the NaHCO<sub>3</sub> and NaOH fractions was calculated as the difference between total and inorganic P.

#### Statistical analysis

All data on soil P fractions and crop P uptake were subject to the normality test before analysis of variance (ANOVA) using SAS statistical package (SAS 9.13). One-way ANOVA was used to detect significant differences in each P fraction among the P fertilizer treatments (P0, P25, P25\*, P75, P75\*) at each sampling year (1997–2008). Least significant

difference (LSD) was conducted only when the analysis of variance was significant at  $P < 0.05$ . Pearson correlation analysis was used to explore the relationship between soil P fractions and P uptake by plants. In all cases, differences were considered statistically significant at  $P < 0.05$ .

## Results

### Dynamics of soil P fractions

#### *Pi fractions*

In this soil, the dominant Pi fraction was HCl-Pi (21–27 % of total P), followed by NaOH-Pi (8–24 % of total P) and  $\text{NaHCO}_3$ -Pi (2–14 % of total P). Without P fertilization, the  $\text{NaHCO}_3$ -, NaOH- and HCl-Pi fractions decreased with time by 17.6 %, 38.1 % ( $P < 0.01$ ) and 14.1 % ( $P < 0.05$ ) after 12 years of continuous corn monoculture. Long term P fertilization increased the soil P concentrations by 11.4–55.3 mg kg<sup>-1</sup> for  $\text{NaHCO}_3$ -Pi, 25.9–78.7 mg kg<sup>-1</sup> for NaOH-Pi, 10.1–47.3 mg kg<sup>-1</sup> for HCl-Pi (Fig. 1). Most of the added P entered the NaOH-Pi fraction (equivalent to 33–39 % of P fertilizer input), followed by HCl-Pi (equivalent to 15–22 % of P fertilizer applied) and  $\text{NaHCO}_3$ -Pi (equivalent to 6–19 % of P fertilizer applied) at the end of each 6-year period. The concentration of soil Pi fractions varied temporally due to P fertilization regimes (Fig. 2). Greater concentrations of the Pi fractions (NaHCO<sub>3</sub>-, NaOH- and HCl-Pi) were induced with periodic P fertilization (once every 6 years) than annual P application during the first 3 or 4 years of each 6-year period. During the last half of each 6-year period, soil Pi fractions were larger with annual P fertilization than periodic P fertilization regimes (Fig. 2). Overall, the concentration of labile Pi fractions were greater with the periodic P fertilization than annual P fertilization, showing on average 26.3–51.2 % larger  $\text{NaHCO}_3$ -Pi fraction, 7.6–15.9 % more NaOH-Pi fraction and 7.8–10.4 % more HCl-Pi during the 12-year.

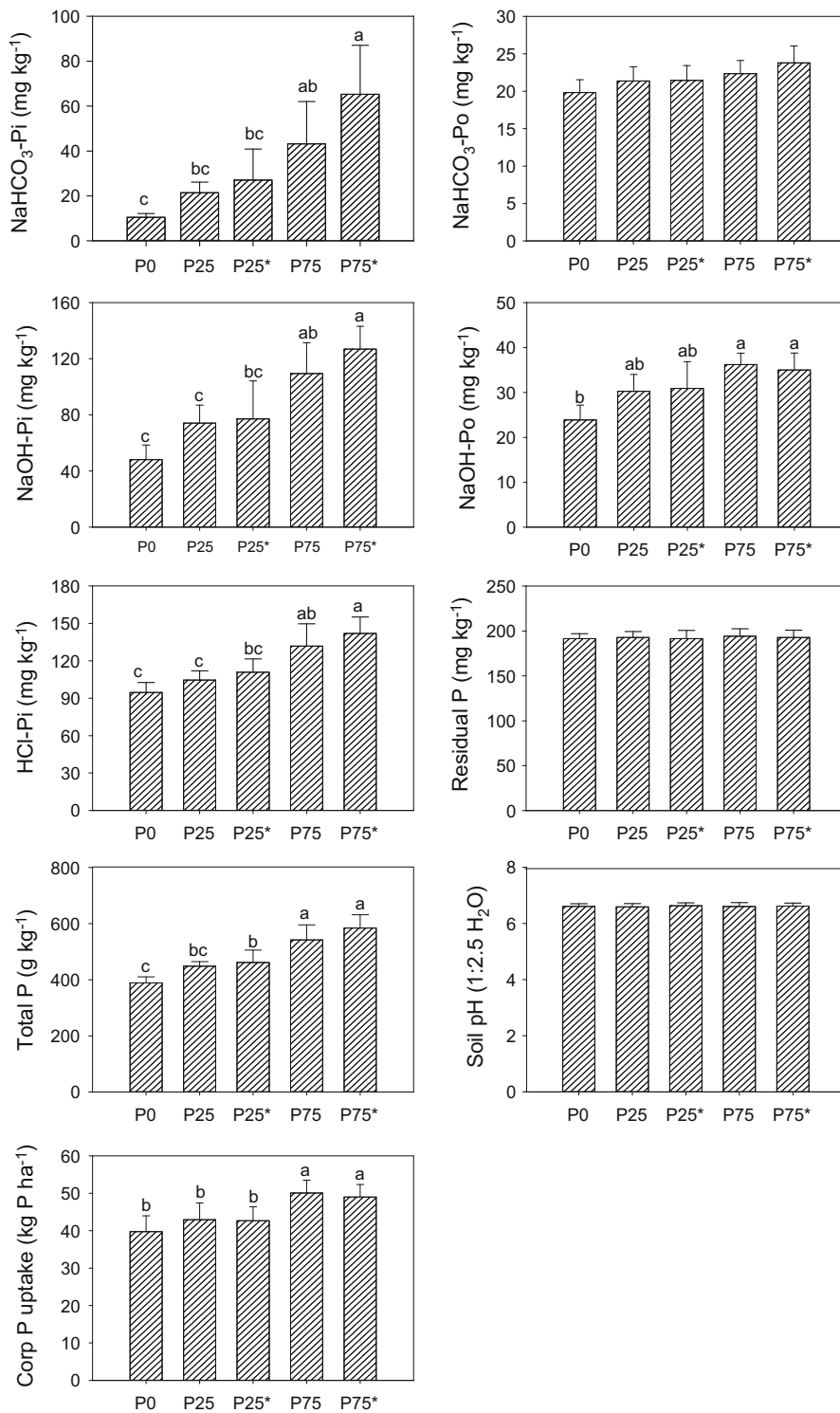
#### *Po and residual P fractions*

Without P fertilization, the  $\text{NaHCO}_3$ -Po and NaOH-Po decreased by 1.6 and 5.1 mg kg<sup>-1</sup> after the first 6-year period, and by 4.9 and 5.4 mg kg<sup>-1</sup> by the end of the

second 6-year period (Fig. 3). Twelve years of triple superphosphate fertilization increased the  $\text{NaHCO}_3$ -Po fraction by 7.7–19.2 %, but there was no significant difference among P fertilizer treatments in 9 of the 12 years. Greater gains with triple superphosphate fertilization occurred in the NaOH-Po fraction, which increased by 26.6–51.7 % with P fertilization and showed a significantly greater ( $P < 0.05$ ) NaOH-Po concentration with periodic P fertilization than annual P application in year 1, but no effect of P fertilizer regime from years 2 to 6 (Fig. 3). By year 6, there was a lower NaOH-Po concentration in the P25 and the P25\* treatments than the P75 and P75\* treatments. Residual P concentration ranged from 181.4 to 208.5 mg kg<sup>-1</sup> and the temporal dynamics of this fraction were not influenced by P fertilization rate and application frequency (Fig. 3). Overall, the recovery of P using sequential P fractionation method in our study was >96 % and no significant difference was observed between the sum of the fractions and the total soil P content.

### Dynamics of crop P uptake

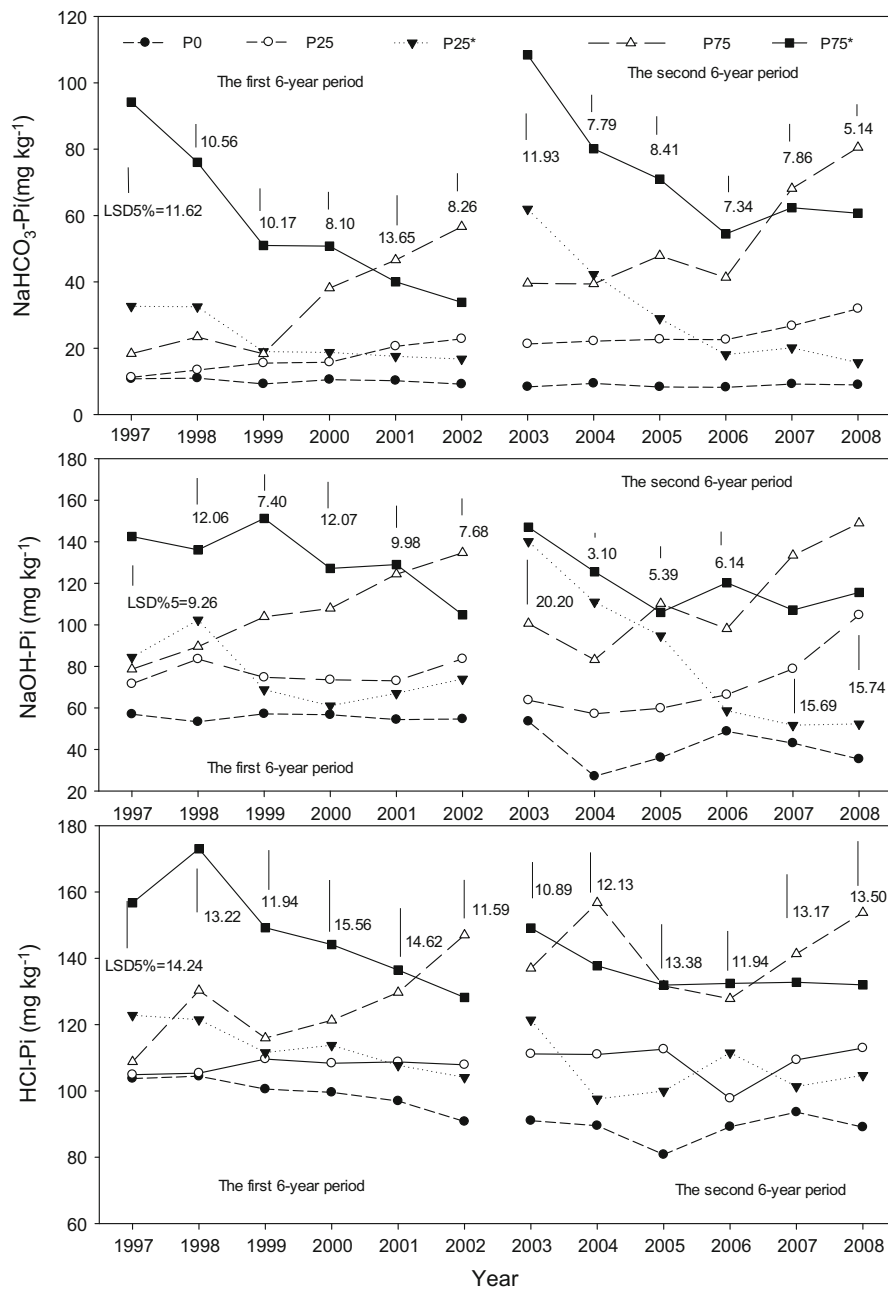
Twelve years of triple superphosphate application slightly ( $P > 0.05$ ) increased crop biomass above the control, but no differences were found between periodic and annual P fertilization (Table 3). The low P inputs in the P0, P25 and P25\* treatments were less than annual crop P removal, so P budgets were negative in these micro-plots, but they were positive in the P75 and P75\* treatments that received more P fertilizer than could be used by the crop each year. There were also no significant differences in P budgets between periodic and annual P fertilization. In contrast, the 12-year average corn P uptake increased by 7.6 %, when triple superphosphate was applied at 25 kg P ha<sup>-1</sup> and averaged 24.7 % ( $P < 0.05$ ) with 75 kg P ha<sup>-1</sup>, regardless of whether the P fertilizer was applied periodically (once in 6 years) or annually (Fig. 1). During the two 6-year periods, periodic P fertilization (once every 6 years) induced a higher ( $P < 0.05$ ) crop P uptake than that of annual P application at the beginning of each 6-year period, but opposite situation occurred at the end of each 6-year period (Fig. 4). Over the 12-year trial period, crop P uptake varied from 23.1 to 83.1 kg P ha<sup>-1</sup> and the mean P use efficiency was 12.5 % when P fertilizer was applied periodically (once 6 year), which was not



**Fig. 1** The 12-year average contents of various P fractions, crop P uptake and soil pH as affected by different P management: P0 (0 kg P ha<sup>-1</sup> annually), P25 (25 kg P ha<sup>-1</sup> annually), P25\* (150 kg P ha<sup>-1</sup> once every 6 years), P75

(75 kg P ha<sup>-1</sup> annually) and P75\* (450 kg P ha<sup>-1</sup> once every 6 years). Bars indicate the standard errors; the different letters indicate significance of treatments at the 5 % level



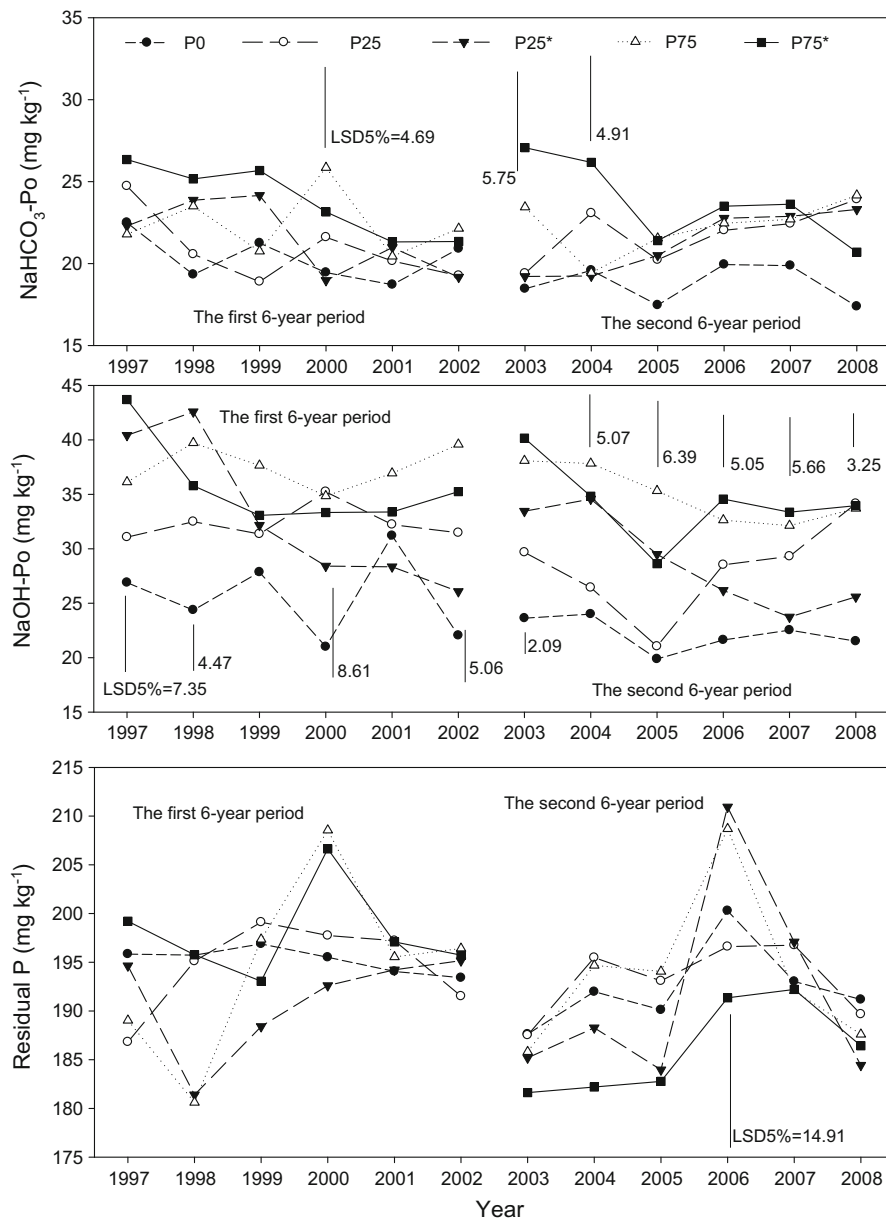


**Fig. 2** Soil Pi fractions in the 0–20 cm soil layer from 1997 to 2008 as influenced by different P fertilization regimes: P0 (0 kg P ha<sup>-1</sup> annually), P25 (25 kg P ha<sup>-1</sup> annually), P25\* (150 kg P ha<sup>-1</sup> once every 6 years), P75 (75 kg P ha<sup>-1</sup>

annually) and P75\* (450 kg P ha<sup>-1</sup> once every 6 years). Each data point is the mean of three replications. The vertical bars, which are inserted in the years when the treatment effects are significant, represent the 5 % LSD

significantly different ( $P > 0.05$ ) from the crop P uptake (18.4–74.2 kg P ha<sup>-1</sup>) and the mean P use efficiency (12.8 %) when P fertilizer was applied annually. Corn P uptake was positively correlated

( $P < 0.05$ ) with the NaHCO<sub>3</sub>-Pi, NaOH-Pi and HCl-Pi fractions, with larger coefficients indicating stronger relationships between corn P uptake and NaHCO<sub>3</sub>-Pi > HCl-Pi > NaOH-Pi (Table 2).



**Fig. 3** Soil Po and residual P fractions in the 0–20 cm soil layer from 1997 to 2008 as influenced by different P fertilization regimes: P0 ( $0 \text{ kg P ha}^{-1}$  annually), P25 ( $25 \text{ kg P ha}^{-1}$  annually), P25\* ( $150 \text{ kg P ha}^{-1}$  once every 6 years), P75

( $75 \text{ kg P ha}^{-1}$  annually) and P75\* ( $450 \text{ kg P ha}^{-1}$  once every 6 years). Each data point is the mean of three replications. The vertical bars, which are inserted in the years when the treatment effects are significant, represent the 5 % LSD

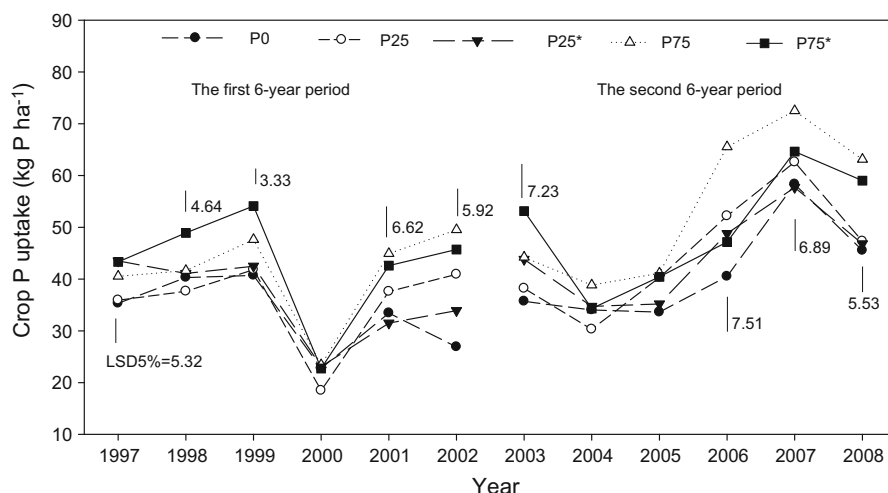
## Discussion

### Effects of P fertilization regimes on soil P fractions

The decrease in  $\text{NaHCO}_3\text{-Pi}$  with time in unfertilized microplots indicated continuous depletion of plant-

available P by corn uptake over the 12-year field trial. The  $\text{NaHCO}_3\text{-Pi}$  fraction is considered to be plant-available and is the basis for the Olsen P soil test (Hedley et al. 1982). But the reduction of the  $\text{NaHCO}_3\text{-Pi}$  concentration with no P fertilization was 7 times less than P removal through crop P uptake in





**Fig. 4** Corn P uptake during the 12-year trial periods with different P fertilization regimes: P0 (0 kg P ha<sup>-1</sup> annually), P25 (25 kg P ha<sup>-1</sup> annually), P25\* (150 kg P ha<sup>-1</sup> once every 6 years), P75 (75 kg P ha<sup>-1</sup> annually) and P75\* (450 kg P ha<sup>-1</sup>

once every 6 years). Each data point is the mean of three replications. The vertical bars, which are inserted in the years when the treatment effects are significant, represent the 5 % LSD

**Table 2** Pearson correlation coefficients (*r*) of soil various P fractions and crop P uptake. Data were pooled among fertilizer treatments and sampling year (*n* = 72)

Variable	NaHCO <sub>3</sub> -Pi	NaHCO <sub>3</sub> -Po	NaOH-Pi	NaOH-Po	HCl-Pi	Residual P	Corn P uptake
NaHCO <sub>3</sub> -Pi	1.000						
NaHCO <sub>3</sub> -Po	0.594**	1.000					
NaOH-Pi	0.877**	0.565**	1.000				
NaOH-Po	0.609**	0.527**	0.748**	1.000			
HCl-Pi	0.839**	0.579**	0.849**	0.702**	1.000		
Residual P	-0.257*	-0.101	0.169	0.058	0.247	1.000	
Corn P uptake	0.307*	0.115	0.242*	0.131	0.331*	-0.051	1.000

\* Significant at *P* < 0.05; \*\* significant at *P* < 0.01

**Table 3** Corn biomass and P budget under different P fertilization practice from 1997 to 2008

Treatments	P input (kg P ha <sup>-1</sup> )	Corn biomass (t ha <sup>-1</sup> )		P output as corn uptake (kg ha <sup>-1</sup> )		P budget (kg P ha <sup>-1</sup> )
		Grain	Stem + cobs	Grain	Stem + cobs	
P0 <sup>a</sup>	0	10.8	9.7	316.8	130.1	-446.9
P25 <sup>b</sup>	300	10.8	10.1	337.4	145.8	-177.2
P25* <sup>c</sup>	300	11.1	9.1	347.2	134.4	-181.6
P75 <sup>d</sup>	900	11.2	9.8	424.2	158.5	317.3
P75* <sup>e</sup>	900	10.9	10.4	395.1	170.8	334.1

<sup>a</sup> P0, 0 kg P ha<sup>-1</sup> annually

<sup>b</sup> P25, 25 kg P ha<sup>-1</sup> annually

<sup>c</sup> P25\*, 150 kg P ha<sup>-1</sup> once every 6 years

<sup>d</sup> P75, 75 kg P ha<sup>-1</sup> annually

<sup>e</sup> P75\*, 450 kg P ha<sup>-1</sup> once every 6 years

this study, suggesting that an equilibrium between the  $\text{NaHCO}_3$ -Pi and other P fractions (Schmidt et al. 1997), such that P desorbed from other inorganic P fractions or mineralized from organic P compounds (Vandekar et al. 2009) sustained the  $\text{NaHCO}_3$ -Pi concentration when no P fertilizer was added. For instance, moderately labile Pi pools (including NaOH- and HCl-P fractions) were considered to buffer the  $\text{NaHCO}_3$ -Pi, for not only can they absorb excess Pi from the  $\text{NaHCO}_3$  fraction (Kuo et al. 2005; Jalali and Tabar 2011), but the moderately labile Pi pools can be converted back into the  $\text{NaHCO}_3$ -Pi fraction (Richter et al. 2006). Our study provides evidence that the equilibrium in the  $\text{NaHCO}_3$ -Pi fraction in microplots without P fertilization was sustained by Pi dissolution and desorption from the NaOH- and HCl-Pi fractions, since the mean P concentrations in these fractions declined by 38.1 and 14.1 %, respectively, after 12 years. Although mineralization of organic P compounds associated with the  $\text{NaHCO}_3$ -Po and NaOH-Po fractions may contribute to the plant-available  $\text{NaHCO}_3$ -Pi fraction, and maintained the level of labile Pi in a P deficient soils (Beck and Sanchez 1994), there is scant evidence for this phenomena in the present study. During the 12 year field study, the combined reduction in the  $\text{NaHCO}_3$ -Po (on average,  $3.8 \text{ mg kg}^{-1}$ ) and NaOH-Po (an average of  $1.9 \text{ mg kg}^{-1}$ ) concentrations were less than the decline in the mean concentration of NaOH-Pi plus HCl-Pi ( $19.2 \text{ mg kg}^{-1}$ ). This supports our conclusion that the supply of  $\text{NaHCO}_3$ -Pi in unfertilized microplots was mainly from Pi fractions rather than Po fractions.

As hypothesized, there was a greater increase in  $\text{NaHCO}_3$ -Pi, NaOH- and HCl-Pi concentrations with annual P fertilizer application than periodic P fertilizer application. Long term P fertilization (P25, P25\*, P75 and P75\*) significantly increased all Pi fractions and the incremental gains in Pi fractions increased with the P application rate. The concentrations of  $\text{NaHCO}_3$ -, NaOH- and HCl-Pi fractions were significantly higher ( $P < 0.05$ ) with annual P application than periodic P application at the end of each 6-year period, indicating that annual P fertilization can sustain higher levels of these Pi fractions. However, Shen (1998) suggested that the critical value of soil available P ( $\text{NaHCO}_3$ -Pi) for food production is  $10.0 \text{ mg kg}^{-1}$  for this region. Since P fertilization practices in this study maintained a minimal  $\text{NaHCO}_3$ -Pi concentration of  $15.7 \text{ mg kg}^{-1}$  with periodic (once

every 6 years) applications and  $11.3 \text{ mg kg}^{-1}$  with annual P application, it is clear that either of these fertilizer regimes would meet the critical level required for corn production in this area. Agricultural producers should then consider the fertilizer regime that is most sensible from an economic perspective.

The P concentrations in the NaOH- and HCl-Pi fractions were equivalent to 33–39 and 15–22 % of the applied P fertilizer, respectively, owing to the higher contents of Fe-, Al-oxides than  $\text{CaCO}_3$  in the croplands of this region (Table 1). This indicated that soil moderately labile Pi, especially the NaOH-Pi, acted as a sink of the applied P fertilizer in this region. Soil pH could affect the transformation of P fertilizer into soil Pi fractions, but there was no significant change in soil pH values, initially pH 6.6–6.8 and between pH 6.4–6.7 by the end of the study, that could be attributed to the P fertilizer regimes (data not shown). Fertilization increased Po fractions by  $1.7$ – $12.4 \text{ mg P kg}^{-1}$  soil, obviously less than Pi fractions ( $10.9$ – $78.2 \text{ mg P kg}^{-1}$  soil). This could be attributed to the fact that most of the applied P was immediately adsorbed by soil Fe-, Al-oxides/hydroxides and  $\text{CaCO}_3$  in this soil, and thus transformed into various Pi fractions (Beck and Sanchez 1994; Motavalli and Miles 2002; Aulakh et al. 2003). The increases in Po fractions may result from higher immobilization of Pi by microbial activity and complexation of Pi with soil organic matter than the mineralization of Po fractions (Negassa and Leinweber 2009; Yin and Liang 2013), but these transformations were relatively minor compared to P adsorption and fixation reactions.

The residual P changed little in all P fertilization regimes studied, indicating that long-term P fertilizer applications had little influences on this P fraction. Similar results were also found in previous studies (Boschetti et al. 2008; Lan et al. 2012). This could be explained by that the residual P was the most difficultly extractable part of soil P, and it remains unavailable to plants for years and has little impact on soil fertility (De Schrijver et al. 2012).

#### Effects of P fertilization regimes on crop P uptake

Corn P uptake was also greater at the first 3 or 4 years of each 6-year period but lower in 5th and 6th years following periodic P fertilizer application than with annual P application. The similarity in temporal

patterns of P uptake and soil Pi fractions during each 6-year period resulted in a positive and significant correlation between P uptake and soil Pi fractions, indicating that crop P uptake was likely derived from the Pi fractions ( $\text{NaHCO}_3$ -,  $\text{NaOH}$ - and  $\text{HCl}$ -Pi). Since annual P application is more conducive to the buildup of  $\text{NaHCO}_3$ -Pi and moderately labile Pi ( $\text{NaOH}$ - and  $\text{HCl}$ -Pi) fractions, this is further evidence that higher crop P uptake with annual P application resulted from uptake of Pi fractions. Therefore, annual P fertilization is recommended to sustain soil P fertility and will be beneficial to crops that require higher crop P uptake to meet yield targets. However, since corn yields and the mean P use efficiency were not enhanced by higher crop P uptake, there is no economic gain from annual P fertilization and it could be more expensive in the longer-term because P fertilizer has to be purchased and applied every year, which implies annual costs for labor and machinery use. From this perspective, periodic P application (once in 6 years) is better for agricultural producers growing corn due to the insignificant difference in crop biomass and the ability of periodic P fertilizer applications to sustain crop P requirements. We previously observed that periodic P fertilizer application induced lower water-soluble P concentrations and higher P adsorption capacities at the end of each 6-year period than annual P fertilization (Wang et al. 2014a). Thus, the silty loam soils in our study area do not show appreciable build-up of water-soluble with periodic P fertilization that could pose an agroenvironmental risk (i.e., non-point source P pollution). On the other hand, soil available micronutrients (DTPA-extractable Zn, Fe, Mn and Cu) were always sufficient to meet crop need with periodic P application during the 12-year period (Wang et al. 2014b), indicating that P-Zn antagonism, which is reported for plants that received high P fertilizer applications, did not occur in this study. Considering the cultivation practices on small land-holdings, soil and climatic conditions in Northeast China, periodic P fertilizer application (once in 6 years) could be recommended to local small-holder farmers.

## Conclusion

The Hapli-Udic Cambisols (Inceptisols) of Northeast China are soils of major agricultural importance for

corn production on more than 4 million hectares. When unfertilized, the plant-available P ( $\text{NaHCO}_3$ -Pi) supply in such soil is sustained by reserves of moderately labile Pi ( $\text{NaOH}$ - and  $\text{HCl}$ -Pi fractions), with a minor contribution from moderately labile Po fractions. Increasing rates of triple superphosphate boosts crop P uptake and replenishes the Pi fractions. Annual applications of P fertilizer resulted in a constant buildup of Pi fractions ( $\text{NaHCO}_3$ -,  $\text{NaOH}$ - and  $\text{HCl}$ -Pi), whereas periodic P fertilization (once every 6 years) produced a greater concentrations of the Pi fractions, on average, over the 12-year study. Both periodic (once in 6 years) and annual P fertilization could sustain crop P requirements and produced equivalent crop biomass when fertilized with the same amount of P during a 6-year period. Under the soil conditions in our study region, periodic P application (once every 6 years) is recommended for local small-holder farmers as an economic practice that could lower the cost of P fertilization for corn. This conclusion is valid for soils having sufficient K and micronutrient reserves to sustain crop production, where P is a major limiting nutrient. We advise that any P fertilization strategy (annual or periodic P fertilization) can impact micronutrient availability and uptake, which needs to be evaluated on a site-specific basis.

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