



Phosphorus transformation response to soil properties changes induced by manure application in a calcareous soil



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ABSTRACT

Management of phosphorus (P) loss in soils with heavy manure application requires improved understanding of the transformation characteristics of soil P. Influences of manure application on the forms and sorption-desorption characteristics of P in surface (0–30 cm) and subsurface (30–60 cm) layer of a calcareous soil were investigated in a six-year field trial in comparison to chemical fertilizer application. Hedley fractionation and P K-edge X-ray absorption near-edge structure spectroscopy were used to determine the soil P forms. Manure (M) and chemical fertilizer (F) treatments resulted in P accumulation in two soil depths, but the total P accumulation in surface soil with M treatment was significantly lower than F treatment with similar P surplus. Compared to control, M and F treatments were significantly increased the proportion of labile P at both depths. In surface soil, M treatment significantly decreased stable Ca-associated P proportion and increased Fe-associated P and inositol hexakisphosphate proportions. The accumulation and transformation of P in M treatment distinctly decreased P sorption maximum, sorption coefficient and buffer capacity, and increased the degree of P saturation and P desorption relative to F treatment. The soil properties of pH, organic carbon (OC), total nitrogen (TN), Mehlich-3 extractable Ca and Fe, and phytase in surface soil and pH, OC, TN, Mehlich-3 extractable Ca and dehydrogenase in subsurface soil had significant effects on the compositions of soil P ($P < 0.05$), respectively. Lowered pH due to manure application mainly contributed to P transformation and release in the calcareous soil.

1. Introduction

Globally, soil phosphorus (P) accumulation is typically related to intensive livestock production (Kronvang et al., 2009; Rubæk et al., 2013). In general, the soils receiving heavy manure inputs have P build-up to levels that far exceed the agronomic optimum P requirement for satisfactory crop production (Dou et al., 2009). A soil with high manure application has less capacity to retain P (Sims et al., 1998; Sharpley et al., 2001), posing a higher risk for environmental pollution compared to a soil receiving less or no manure (Jiao et al., 2007; Yan et al., 2016). Hence, information on the chemical composition and the sorption-desorption characteristics of P in manured soils is essential to improve understanding of P transformation and transport in the agroecosystem.

Manure application affects the soil P status, either directly by adding P compounds in terms of manure, or indirectly by changing other soil properties such as pH, organic carbon (OC) etc., which in turn can favor P transformation and affect soil P mobility and loss. A significant increase in inorganic P (Pi) and a shift in the relative sizes of

the different Pi forms were observed in manured soil (Sato et al., 2005; Xue et al., 2013; Yan et al., 2016). Both sequential extraction and P K-edge X-Ray absorption near-edge structure (XANES) spectroscopy methods indicated the increase in the proportion of calcium-associated P (Ca-P) in the total P (Pt) pool in soils with the history of long-term manure application versus those with no or limited application. It is attributed to high P and Ca in manure (Sharpley and Moyer, 2000), and the role of increased pH in acidic or neutral soils due to manure application in forming various Ca-P (Sato et al., 2005). However, calcareous soil originally contains high Ca and the calcareous properties are important in controlling soil P forms because calcium carbonate (CaCO₃) minerals fix P via adsorption or mineral precipitation (Leytem and Mikkelsen, 2005; Weyers et al., 2016). Manure application can lower soil pH in highly calcareous or alkaline soils (Chang et al., 1991; Romanyà and Rovira, 2009; Weyers et al., 2016), suggesting the occurrence of different soil P transformation in response to manure application in those soils, e.g., the precipitation and solubility of Ca-P.

Variable effects (i.e., both significant and non-significant changes)

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Table 1

Mean annual N, P and K input, crop P removal and P surplus under different fertilization treatments in vegetable protected field from 2008 to 2014.

Treatments [†]	N input		P input		K input		Yield (Mg ha ⁻¹ yr ⁻¹)	Crop P removal	P surplus [§]
	OM [‡]	CF	OM	CF	OM	CF			
	(kg ha ⁻¹ yr ⁻¹)								
C	0	0	0	0	0	0	51	20	-20
F	0	1007	0	209	0	403	126	50	160
M	1008	0	220	0	420	0	128	51	169

[†] C (control), no fertilization; F, chemical fertilizer application; M, organic manure application.[‡] OM, organic manure; CF, chemical fertilizer.[§] P surplus = P input – P removal by crops.

of manure application on organic P (Po) content were observed in soil (Koopmans et al., 2007; Keller et al., 2012; Annaheim et al., 2015; Yan et al., 2016). Generally, increases in Po content in response to the manure occurred when the addition of P was sufficient and OC increased after application. Further, manure contains a variety of organic compounds, including high proportion of inositol hexakisphosphate (IHP; phytic acid) with high stability. However, some researchers reported that the contents of IHP were not significantly different between manured and un-manured soils, even in heavy manured soil (Dou et al., 2009; Doolette et al., 2010). The high mineralization and subsequent downward movement of P might be the contributing factors (Dou et al., 2009). Generally, the mineralization of Po decreased at a lower pH (Beek and van Riemsdijk, 1982; Condron and Goh, 1989; Song et al., 2011), facilitating a rapid microbial degradation in calcareous soils (Doolette et al., 2011). However, the lowered pH due to manure application may contribute to the accumulation of Po (e.g., IHP) in calcareous soil.

Application of manure is known to affect the chemical reactions that control P sorption and desorption between the soil solution and solid phases. The P sorption is mainly controlled by iron (Fe) and aluminum (Al) oxides and clay minerals in acidic soils (Dari et al., 2015), and CaCO₃ and clay minerals in neutral and calcareous soils (Pizzeghello et al., 2011; Pizzeghello et al., 2014). The low-molecular-weight organic acids and soluble humic and fulvic acids released during the decomposition of organic residues may reduce the sorption of added P by competing for binding sites on soil colloids (Bhatti et al., 1998; Haynes and Mokolobate, 2001). Furthermore, the change in soil pH due to manure application can affect the P sorption. In acidic soil, increased pH and lowered extractable Al can decrease the soil P sorption capacity (Cong and Merckx, 2005; Xavier et al., 2009). Conversely, lowering pH may promote the solubility of CaCO₃ and can possibly induce leaching loss of Ca ion, which in turn affect P sorption in calcareous soil.

It is crucial to understand the forms and sorption-desorption characteristics of P in manured calcareous soils to predict long-term P accumulation and release dynamics. We hypothesized the different responses of soil properties to manure application (e.g., lowered pH) will result in different soil P accumulation and transformation characteristic in calcareous soil such as the decrease in stable Ca-P (i.e., more crystalline Ca-P) formation. The overall objective of this study was to determine the impact of continuous manure application on accumulation, distribution, and release of soil P in a six-year field trial in the vegetable protected field. The specific objectives of the study were to (i) determine changes in different P forms and sorption-desorption characteristic using the P K-edge XANES spectroscopy and modified Hedley methods, (ii) explain variation in soil P accumulation and transformation in terms of contributing soil factors.

2. Materials and methods

2.1. Experimental site and treatments

The study was conducted in a vegetable protected field located in agricultural experiment station of Daxing District, Beijing, China (E 116° 33', N 39° 73') since August 2008. The soil is classified as Inceptisols in US soil taxonomy with 23.2% sand, 59.5% silt, and 17.3% clay in surface soil (0–30 cm), and 11.0% sand, 64.6% silt, and 24.4% clay in subsurface soil (30–60 cm), respectively. Soil had 8.5 g C kg⁻¹ of OC, 0.9 g N kg⁻¹ of total N (TN), 670 mg P kg⁻¹ of Pt, 13.9 mg P kg⁻¹ of Olsen P and 42.4 g kg⁻¹ of CaCO₃ for surface soil, and the corresponding values of 6.1 g C kg⁻¹, 0.8 g N kg⁻¹, 513 mg P kg⁻¹, 4.6 mg P kg⁻¹ and 49.7 g kg⁻¹ for subsurface soil. Details of the site, soil, crop establishment and management are given in the supplementary material (SM). Three treatments were investigated in current experiments: (1) no fertilization (C; control), (2) chemical fertilizer application (F) and (3) organic manure application (M). The organic manure used in this experiment was composted chicken manure (pH of 7.96). It has 20.1 g N kg⁻¹, 7.9 g P kg⁻¹ and 14.8 g K kg⁻¹. Urea (46% N), diammonium phosphate (18% N and 20% P) and potassium sulfate (50% K) were used as chemical fertilizers. The F and M treatments had similar nutrient inputs (Table 1). The plot size was 68.2 m² (11 m × 6.2 m). A randomized block design was followed with three replicates. Soil samples were taken from 0 to 60 cm depth with 30 cm increments in June 2014 and June 2016, respectively (details in SM).

2.2. Soil analyses

The soil pH was measured in distilled water with soil: solution ratio of 1:2.5. The CaCO₃ was determined by acid neutralization (Richards, 1954). The OC was determined using dichromate redox titration method (Skjemstad and Baldock, 2007). The TN was measured using the CN analyzer (Vario Macro CN, Elementar Analysensysteme GmbH, Germany). The Pt was determined with H₂SO₄-HClO₄ digestion followed by the colorimetric method using ascorbic acid (Bao, 2010). The Po was determined by the ignition method (O'Halloran and Cade-Menun, 2007). Soil Pi was calculated as the difference between Pt and Po. Soil samples were extracted with Mehlich-3 extracting solution (0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.13 M HNO₃ + 0.001 M EDTA) by shaking for 5 min at a 1:10 soil to solution ratio to determine P (M3-P), Ca (M3-Ca), Mg (M3-Mg), Fe (M3-Fe), and Al (M3-Al) (Mehlich, 1984). All elements in the Mehlich-3 solutions were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 7300 V, USA). The concentration of Olsen-P in the soil solution was measured by the ascorbic acid method with 0.5 M NaHCO₃ (soil: solution ratio of 1:20) (Olsen et al., 1954). The microbial biomass C (MBC) and N (MBN) were analyzed with the chloroform fumigation-extraction method (Vance et al., 1987) and measured using CN analyzer (Vario Macro CN, Elementar Analysensysteme GmbH, Germany). The phytase, alkaline phosphatase

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