

# Kinetics of inorganic and organic phosphorus release influenced by low molecular weight organic acids in calcareous, neutral and acidic soils

Yongzhuang Wang<sup>1,2</sup>, Xin Chen<sup>1</sup>, Joann K. Whalen<sup>3</sup>, Yanhong Cao<sup>1,2</sup>, Zhi Quan<sup>1,2</sup>, Caiyan Lu<sup>1</sup>, and Yi Shi<sup>1\*</sup>

<sup>1</sup> State Key Laboratory of Forest and Soil Ecology, Institute of Applied Ecology, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang, 110164, China

<sup>2</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup> Department of Natural Resource Sciences, Macdonald Campus, McGill University, 21, 111 Lakeshore Road, Ste-Anne-de-Bellevue, QC, Canada H9X 3V9

## Abstract

Low molecular weight organic acids exuded by plants roots enhance inorganic  $P_i$  release into soil solution and thereby increases plant-available  $P_i$  in soils. Low molecular weight organic acids may also induce organic P ( $P_o$ ) release into soil solution, but kinetics of both  $P_i$  and  $P_o$  displacement from the soil matrix into soil solution of agricultural soils is poorly understood, and the mechanism for  $P_o$  release is not well explained. This study used kinetic experiments to determine the concentrations and release rates of  $P_i$  and  $P_o$  induced by oxalic acid, citric acid, and malic acid in calcareous, neutral and acidic soils. Kinetic data were well described by Elovich ( $r^2 = 0.801$ – $0.993$ ,  $P < 0.001$ ) and power functions models ( $r^2 = 0.721$ – $0.977$ ,  $P < 0.001$ ). Low molecular weight organic acids at  $10 \text{ mmol kg}^{-1}$  soil induced the exponential release of both  $P_i$  and  $P_o$ , which reached a plateau approx. 480–2,880 min after the start of the experiment. Cumulative  $P_o$  release induced by low molecular weight organic acids was ranked as oxalic acid ( $0.63$ – $3.17 \text{ mg kg}^{-1}$ ) > citric acid ( $0.61$ – $2.82 \text{ mg kg}^{-1}$ ) > malic acid ( $0.52$ – $1.76 \text{ mg kg}^{-1}$ ) and mainly resulted from the release of labile  $P_o$  ( $\text{NaHCO}_3\text{-}P_o$ ) regardless of soil type. By contrast, oxalic acid was most effective in enhancing  $P_i$  release from the  $\text{HCl-}P_i$  ( $\text{Ca-}P_i$ ) fraction of the calcareous soil, and citric acid was most effective in releasing  $P_i$  from the  $\text{NaOH-}P_i$  ( $\text{Fe/Al-}P_i$ ) fraction of the neutral and acidic soils. Therefore, the mechanism for the kinetics of  $P_o$  release induced by low molecular weight organic acids is ascribed to their ability to mobilize the labile  $P_o$  ( $\text{NaHCO}_3\text{-}P_o$ ) rather than their ability to chelate cations (*i.e.*,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) bound to  $P_o$  in soil.

**Key words:** citric acid / oxalic acid / malic acid / organic acid ligands / soil phosphorus fractions

Accepted April 30, 2015

## 1 Introduction

Phosphorus (P) deficiency limits crop production in most agricultural areas in China, mainly due to tight adsorption of P by Fe-, Al-oxides/hydroxides or Ca compounds in soil (Zhang et al., 2004; Verma et al., 2005; Xavier et al., 2009; Jalali and Tabar, 2011). Therefore, P fertilizer and/or manure are commonly added to soils to increase the availability of soil P to sustain crop P requirements and meet yield targets (Aulakh et al., 2003; Kuo et al., 2005). However, the P input from fertilizers and manures tends to accumulate, changing the concentration of P in soil solution and its association with soil minerals and organic matter (OM), due to the low P use efficiency (around 10–15% of applied fertilizer P) of most crops and the high P fixing capacity of soils (Boschetti et al., 2008; Zamuner et al., 2008; Chakraborty et al., 2011; Kang et al., 2011). Despite the fact that a large quantity of P is continuously supplied as soluble fertilizer, plant-available P content in soil solution is often very low ( $< 5 \text{ } \mu\text{mol L}^{-1}$ ). To overcome P deficiencies, plants also have evolved adaptive chemical process (*e.g.*, root-induced depletion/accumulation of P ions, acidification/alkalinization of rhizosphere, and exudation of organic acids/anions) and

alter their root structure to increase the mobility and bio-availability of P in the rhizosphere (Raghothama, 1999; Hinsinger, 2001; Zhang et al., 2004; Hinsinger et al., 2009; Makhani and Isaac, 2014). Among these strategies, exudation of low molecular weight organic acids from plant roots is considered to be one of the common and effective mechanisms mobilizing unavailable P in soil (Palomo et al., 2006; Chen et al., 2008).

It has been widely speculated that low molecular weight organic acids enhance the mobilization of soil inorganic P ( $P_i$ ) (Ström et al., 2002; Harold and Tabatabai, 2006; Taghipour and Jalali, 2013). Low molecular weight organic acids have the ability to: (1) directly promote the dissolution of sparingly soluble minerals containing  $P_i$ , (2) shift pH and chemical equilibria in soil solution, (3) alter the surface characteristics of mineral particles or occupy ligand exchange surfaces, (4) form complexes with ions of Fe, Al and Ca, thus blocking P adsorption sites on soil particles (Lan et al., 1995; Hocking, 2001; Ström et al., 2002; Chen et al., 2008). Moreover, low molecular weight organic acids may enhance the release of organic P ( $P_o$ ) bound to soil minerals (Fox, et al., 1990; Fox



\* Correspondence: Y. Shi; e-mail: shiyi@iae.ac.cn

and Comerford, 1992; Wei et al., 2010), but the mechanism for  $P_o$  release induced by low molecular weight organic acids is not well explained, especially for soils with contrasting physico-chemical properties (e.g., texture, pH, Fe-/Al-oxides, and Ca-carbonate), which may affect  $P_o$  release from soil. Though  $P_o$  needs to be mineralized prior to plant uptake, this process is facilitated once the  $P_o$  is in soil solution where it can be acted upon by phosphatases and the mineralized  $P_i$  is subsequently assimilated by plants (Xiao et al., 2006; Turner, 2008).

Both the concentration and rate of P release from solid to solution controls the lability of soil P, thus influencing P fertility of soils and P uptake by crops (McDowell and Sharpley, 2003; Shariatmadari et al., 2006). To fully assess the changes in P availability, the rate of P release must be considered. Kinetic experiment is an appropriate method to quantify the rate of P release from soil solid into solution phases (Sparks, 1995). Fox et al. (1990) reported that the kinetics of  $P_i$  release from Spodosols in the presence of low molecular weight organic acids (e.g., oxalic acid or formic acid) occurs in two phases: rapid release in the initial phase followed by a slower release, due to the ligand exchange or dissolution of metal-P compounds, respectively. The mode of organic acids loading (single vs. repeated sequential) affected the kinetic process but not the cumulative amount of  $P_i$  release (Fox and Comerford, 1992). The fast and slower rates of P release are related to the rapid desorption of surface labile P and slow dissolution of the crystalline P compounds (Toor and Bahl, 1999). Gerke (1994) also showed that the rate of  $P_i$  desorption was related to the release rate of Fe/Al, which is associated with P. However, Jalali and Zinli (2011) stated that the two phases of  $P_i$  release were characteristic of a diffusion-controlled process. McDowell and Sharpley (2003) and Nafiu (2009) also believed that the slow diffusion of P from inside of soil particles was possibly the rate limiting step in the kinetics of  $P_i$  release. Both diffusion and dissolution reactions are probably involved in the slower second phase of  $P_i$  release (Smet et al., 1998). While much research has been done on the kinetics of  $P_i$  release (Smet et al., 1998; Toor and Bahl, 1999; Nafiu, 2009; Jalali and Zinli, 2011), limited information is available on the impacts of low molecular weight organic acids on the kinetics of  $P_o$  release from soil solid phase (e.g.,  $P_o$  compounds bound to Fe/Al components). Low molecular weight organic acids enhance P release from labile P and crystalline P compounds (Ström et al., 2002; Harrold and Tabatabai, 2006; Wei et al., 2010), leading us to hypothesize that (1) low molecular weight organic acids will increase the rate of the kinetics of both  $P_i$  and  $P_o$  release. Of the low molecular weight organic acids, oxalic acid is generally the most effective reagent for enhancing  $P_i$  release from calcareous soils due to its ability to strongly chelate Ca in calcareous soils, while citric acid is the most effective in acidic soils where Fe and Al are the dominant cations generating surface charge on clays (Harrold and Tabatabai, 2006; Nwoke et al., 2008; Bais et al., 2006; Wei et al., 2010; Moradi et al., 2012). Since the release of  $P_o$  may share a similar mechanism with the release of  $P_i$ , which involves chelating the cations bound to  $P_o$  as well as  $P_i$ , thereby facilitating the release of  $P_i$  and  $P_o$  into soil solution, we further hypothesized that (2) oxalic acid will be the most effective reagent for increasing the rate of  $P_i$  and  $P_o$

release into soil solution of calcareous soils, while citric acid will be the most effective in acidic soils.

The ability of low molecular weight organic acids to chelate with Ca, Fe, and Al can be inferred from the decrease in levels of soluble forms of these cations in soil solutions (Ström et al., 2005; Wang et al., 2012), but a direct way to measure how chelation of Ca, Fe, and Al by low molecular weight organic acid affects  $P_i$  and  $P_o$  release is to measure soil P fractions. Soil contains various  $P_i$  and  $P_o$  fractions including soil soluble and exchangeable P (NaHCO<sub>3</sub> extracted  $P_i$  and  $P_o$ ), Fe/Al-bound P (NaOH extracted  $P_i$  and  $P_o$ ), Ca-bound P (HCl extracted  $P_i$ ), and residual P (Hedley et al., 1982; Jalali and Ranjbar, 2010). As chelating agents, low molecular weight organic acids can displace P from Fe/Al-P and/or Ca- $P_i$  compounds in soils (Hinsinger, 2001; Jones, 1998), which changes the proportion of the Ca-bound  $P_i$  (HCl extracted  $P_i$ ) and the Fe/Al-bound P (NaOH extracted P) fractions. Additionally, other possible mechanisms for  $P_o$  release from soil (e.g., desorption or dissolution of soil labile  $P_o$ ) can also be inferred from the changes in labile  $P_o$  fraction. Therefore, measuring the concentrations of the soil  $P_o$  fractions after kinetic experiment is a direct way to determine the  $P_o$  pools acted upon by low molecular weight organic acids, and to deduce mechanisms. McDowell and Sharpley (2003) used P fractionation to determine the presences of P forms relevant to the kinetics of  $P_i$  release. Taghipour and Jalali (2013) also suggested that the release of  $P_i$  induced by low molecular weight organic acids at 10 mmol L<sup>-1</sup> was mainly from the Ca- $P_i$  (HCl extracted  $P_i$ ) fraction due to chelation of Ca<sup>2+</sup> by organic acids in their calcareous soils. Because  $P_o$  is associated with organo-mineral complexes, the release of  $P_o$  by low molecular weight organic acids could be due to chelating effects of organic acid ligand cations (e.g., Fe and Al on clay surfaces) that bind  $P_o$ , we hypothesized that (3) the release of  $P_o$  will result from mobilizing the Fe/Al-  $P_o$  (NaOH extracted  $P_o$ ).

The objective of this study was to study the impact of three common low molecular weight organic acids (oxalic acid, citric acid, and malic acid) on the kinetics of  $P_i$  and  $P_o$  release in calcareous, neutral, and acidic soils. In addition, the mechanism for  $P_o$  release were inferred by analyzing the difference in soil  $P_o$  fractions after kinetic experiments.

## 2 Material and methods

### 2.1 Soils and organic acids

Surface layers (0–20 cm) of three soils were collected from three Experimental Stations of Ecology (Chinese Academy of Sciences): Luancheng (37°53'N, 114°40'E), Shenyang (41°31'N, 123°24'E), and Taoyuan (28°56'N, 111°26'E), respectively. The mean annual precipitation and temperature for the three climatic regions are 530 mm and 12.2°C, 650 mm and 7.5°C, and 1440 mm and 16.5°C, respectively. Each of the tested soils was a major soil type for agricultural production in their respective regions, where P fertilizer was applied every year to prevent P deficiency of the wheat (Luancheng), corn (Shenyang), and rice (Taoyuan). All soil samples were air-dried and ground to pass through a 2-mm

sieve before use. Selected chemical and physical properties are shown in Table 1.

The organic acids selected for this study were oxalic acid, citric acid, and malic acid because of their widespread natural occurrence in soils. Each organic acid was applied at a concentration of 10 mmol kg<sup>-1</sup> soil. This concentration was chosen by considering the rhizosphere values of these organic acids reported by Jones (1998) and Li et al. (2010), and the values of carboxylic acids in soil extracts (Strobel, 2001). Wei et al. (2010), Jalali and Zinli (2011) and Jalali and Tabar (2011) used 10 mmol kg<sup>-1</sup> soil of organic acids to determine the impacts of organic acids on the release of P<sub>o</sub> from forest soils and the kinetics of P<sub>i</sub> release from calcareous soils, respectively. In addition, Gerke et al. (2000) reported that below a concentration of around 10 mmol kg<sup>-1</sup> soil the P solubility was not markedly increased by the addition of citric acid. Thus, this concentration should be sufficient and suitable to enhance P mobilization and explore related mechanisms based upon abiotic mineral studies.

## 2.2 Kinetic experiments

The experiment used a completely randomized design to evaluate the three soils (calcareous, neutral, and acidic) subjected to four treatments (water, oxalic acid, citric acid, and malic acid) and kinetic evaluation at 11 time points, with three replicates for each time point giving a total of 396 experimental units. Soil (2 g) was placed in 50 mL centrifuge tubes, and then 20 mL of deionized water (control) or 20 mL of organic acid solution, containing 10 mmol kg<sup>-1</sup> soil of oxalic acid, citric acid or malic acid, were added to each tube. Two drops of toluene were added to inhibit microbial activity prior to cap the tubes. It should be noted that this sterilization method may have the potential disadvantage of altering soil physical and

chemical properties (i.e., increasing pH and cation exchange capacity) for the duration of the equilibration phase (Lotrario et al., 1995). The suspensions were shaken on an end-to-end shaker (200-cycles min<sup>-1</sup> at 25 ± 1°C) for 5, 10, 15, 30, 60, 120, 240, 480, 960, 1,440 or 2,880 min, centrifuged at 12,000 × g for 10 min and filtered through Whatman filter paper (No. 42). The P<sub>i</sub> concentration in a 10 mL aliquot of the extract was determined by the malachite-green method (Ohno and Zibilske, 1991; Guppy et al., 2000). Total P content in a second 10 mL of extract was quantified by digestion with 0.6 g 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> in autoclave (103.4 K Pa, 121°C) for 60 min. The concentration of organic P in the solution was the difference between total P and inorganic P. Soil was collected from centrifuge tubes that were shaken for 2,880 min, rinsed and dried (40°C for 72 h) for subsequent P fractionation analysis. We prepared 72 extra centrifuge tubes (triplicates) for each soil type and treatment to evaluate the pH values of extracts before the kinetic experiment and at 2,880 min with a glass electrode.

The cumulative P<sub>i</sub> and P<sub>o</sub> released into soil solution was plotted against time for each soil and different kinetic models were fitted to the data. The P<sub>i</sub> and P<sub>o</sub> release with time was fitted using the following equations:

$$\text{First order } \ln Q_t = B - k_1 t, \quad (1)$$

$$\text{Second order } 1/Q_t = B + k_2 t, \quad (2)$$

$$\text{Elovich equation } Q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t, \quad (3)$$

$$\text{Power function equation } \ln Q_t = \ln a + b \ln t, \quad (4)$$

$$\text{Parabolic diffusion model } Q_t = A + R t^{1/2}, \quad (5)$$

**Table 1:** Some physical and chemical properties of the three soils studied from Experimental Stations of Ecology, Chinese Academy of Sciences.

Site	Soil	Total N	Total P	Organic C	Available P	pH (H <sub>2</sub> O)	Soil texture / %			Bulk density	
		/ g kg <sup>-1</sup>	/ g kg <sup>-1</sup>	/ g kg <sup>-1</sup>	/ mg kg <sup>-1</sup>	1:2.5	sand	silt	clay	g cm <sup>-3</sup>	
Luancheng	Calcareous	1.17	0.89	13.92	4.5	8.24	32.5	48.8	18.7	1.32	
Shenyang	Neutral	1.11	0.37	10.65	7.2	7.02	14.7	60.4	24.9	1.11	
Taoyuan	Acidic	0.89	0.49	4.37	3.9	4.72	12.1	44.6	44.3	1.19	
Site	P fractions / mg kg <sup>-1</sup>						Fe <sub>d</sub> <sup>e</sup>	Al <sub>d</sub> <sup>e</sup>	Fe <sub>o</sub> <sup>e</sup>	Al <sub>o</sub> <sup>e</sup>	CaCO <sub>3</sub>
	NaHCO <sub>3</sub> -P <sub>i</sub> <sup>a</sup>	NaHCO <sub>3</sub> -P <sub>o</sub> <sup>a</sup>	NaOH-P <sub>i</sub> <sup>b</sup>	NaOH-P <sub>o</sub> <sup>b</sup>	HCl-P <sub>i</sub> <sup>c</sup>	Residual P <sup>d</sup>	/ g kg <sup>-1</sup>				
Luancheng	9.1	10.8	8.3	48.1	482.6	291.4	6.56	1.21	1.27	–	98.24
Shenyang	12.2	23.6	58.5	49.7	103.6	188.8	13.56	9.21	3.27	0.21	11.18
Taoyuan	8.2	14.3	105.1	26.7	6.5	306.1	50.08	9.61	3.41	5.56	–

<sup>a</sup>NaHCO<sub>3</sub>-P<sub>i</sub> was soil soluble and exchangeable inorganic P<sub>i</sub>, and NaHCO<sub>3</sub>-P<sub>o</sub> was comprised of P<sub>o</sub> in the soil solution and P<sub>o</sub> that sorbed on the soil surface.

<sup>b</sup>NaOH-P<sub>i</sub> and P<sub>o</sub> were P<sub>i</sub> and P<sub>o</sub> compounds held more strongly by chemisorption to Fe and Al components of soil surface.

<sup>c</sup>HCl-P<sub>i</sub>, soil Ca bound inorganic P.

<sup>d</sup>Residual P, soil resistant inorganic and organic P.

<sup>e</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.

where  $Q_t$  ( $\text{mg P kg}^{-1}$ ) is the amount of P released at time  $t$ ,  $A$  ( $\text{mg P kg}^{-1}$ ),  $\alpha$  ( $\text{mg P kg}^{-1} \text{ min}^{-1}$ ),  $a$  [ $(\text{mg P kg}^{-1} \text{ min}^{-1})^b$ ], and  $A$  ( $\text{mg P kg}^{-1}$ ) are initial P release (rate),  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  [ $(\text{mg P kg}^{-1})^{-1}$ ] are the first- and second-order rate constant,  $\beta$  [ $(\text{mg P kg}^{-1})^{-1}$ ],  $b$  [ $(\text{mg P kg}^{-1})^{-1}$ ] and  $R$  [ $(\text{mg P kg}^{-1})^{-0.5}$ ] are P-release rate constants. Each kinetic model was tested by coefficient of determination ( $r^2$ ) and the standard error of estimate (S.E.) was calculated from:

$$\text{SE} = [\sum (Q_t - Q_t')^2 / (n - 2)]^{1/2}, \quad (6)$$

where  $Q_t$  and  $Q_t'$  are the measured and predicted amounts of released P at time  $t$ , respectively, and  $n$  is the number of measurements.

### 2.3 Soil P fractions

For each soil, bulk soil that represented the original P chemistry and soil that was subjected to treatments (water, oxalic acid, citric acid, and malic acid) by shaking 2,880 min in the kinetic experiment was subjected to sequential P fractionation using the Hedley et al. (1982) procedure modified by Kang et al. (2011). A representative soil sample (0.5 g) was weighed into a 50 mL centrifuge tube and P fractions were determined as follows: (1) labile P ( $\text{NaHCO}_3\text{-P}$ ), soil extracted with 30 mL 0.5 M  $\text{NaHCO}_3$  (pH = 8.5) for 16 h; (2) Fe- and Al-bound P ( $\text{NaOH-P}$ ), residue from the first fraction extracted with 30 mL 0.1 M NaOH for 16 h; (3) Ca-bound P ( $\text{HCl-P}$ ), residue from second fraction extracted with 1.0 M HCl for 16 h; (4) residual P ( $\text{Res-P}$ ), residue from the last fraction digested with  $\text{H}_2\text{SO}_4\text{-HClO}_4$  at 360°C. Extracted  $P_i$  collected at each step was analyzed colorimetrically with the molybdate-blue method. Total P of  $\text{NaHCO}_3$  and NaOH extracts was determined by digesting in autoclave (103.4 kPa, 121°C) with acidified K-persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ). The  $P_o$  in  $\text{NaHCO}_3$  and NaOH fractions was calculated as the difference between total P and  $P_i$ .

### 2.4 Statistical analysis

Linear forms of the kinetic equations (1–5) were fitted to the kinetic experimental data, separately for each soil. Least-square-regression analysis was used to ascertain the model that best described P-release kinetics for each soil studied. Soil P fraction data were subject to the normality and homogeneity tests before analysis of variance (ANOVA) using SAS statistical package (SAS 9.13). Significant differences ( $P < 0.05$ ) in the concentration of each P fraction before and after shaking with each treatment solution (water, oxalic acid, citric acid, and malic acid) was evaluated with one-way analysis of variance (ANOVA) for each soil studied. Least significant difference (LSD) was conducted only when the analysis of variance was significant at  $P < 0.05$ .

## 3 Results

### 3.1 Soil properties

The three soils were calcareous (pH 8.24), neutral (pH 7.02), and acidic soil (pH 4.72), having a low available P status (3.9 to 7.2  $\text{mg kg}^{-1}$ ; Table 1). The  $\text{HCl-P}_i$  (Ca-P) concentration

and Ca-carbonate equivalent were greatest in the calcareous soil, and lowest in the acidic soil, while the  $\text{NaOH-P}_i$  (Fe, Al-P) fraction and Fe-/Al-oxides concentrations were the greatest in the acidic soil and the lowest in the calcareous soil. Soil textures were sandy loam, silty loam, and silty clay for the calcareous, neutral and acidic soils, respectively.

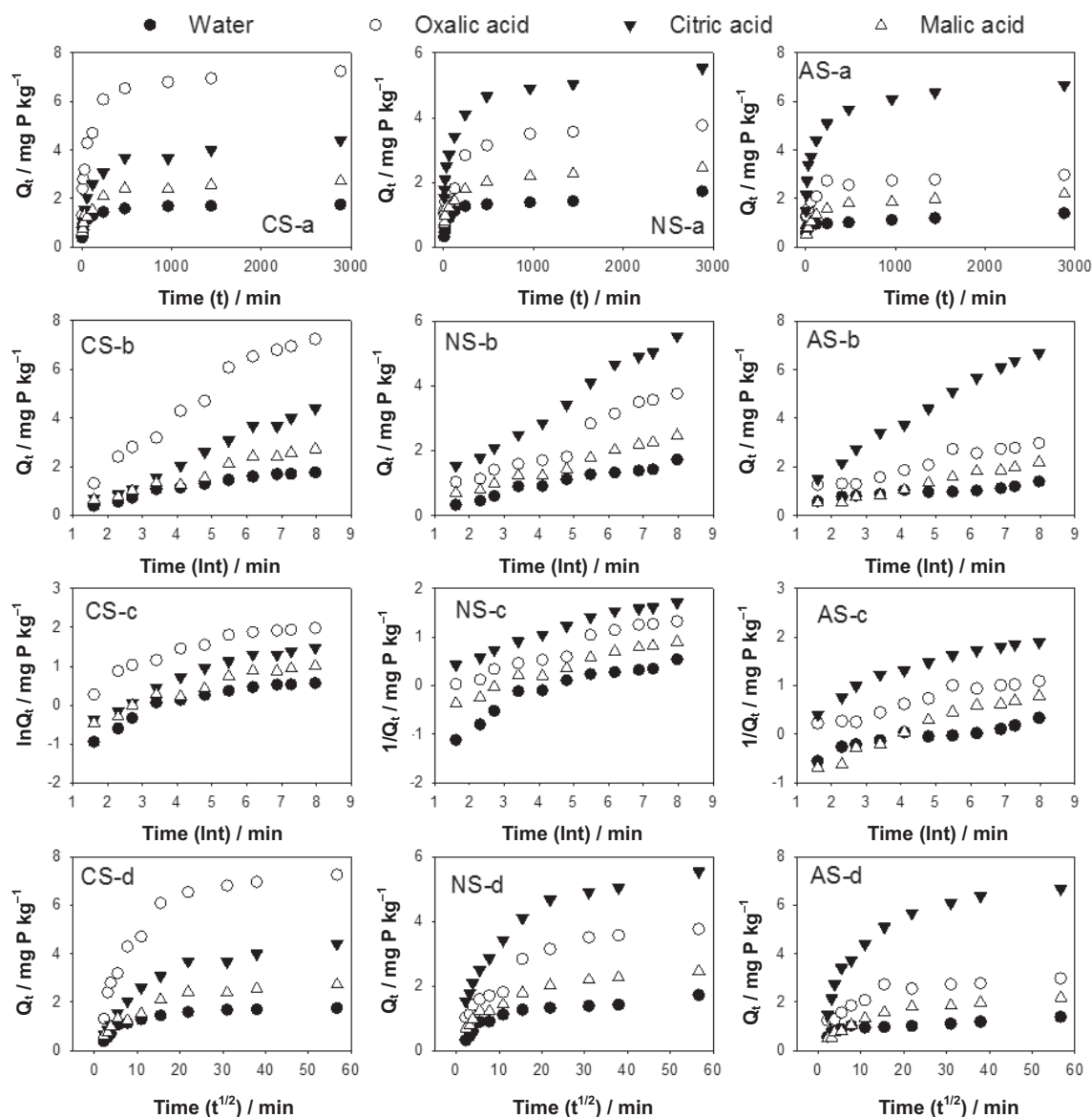
### 3.2 Kinetics of $P_i$ and $P_o$ release

Comparison of coefficients of determination ( $r^2$ ) and the standard errors of estimate (S.E.) for kinetic models indicated that kinetics of  $P_i$  and  $P_o$  release by low molecular weight organic acids in the three soils were better fitted with the Elovich ( $r^2 = 0.801\text{--}0.993$ ;  $P < 0.001$ ; S.E. = 0.05–0.37), power function ( $r^2 = 0.721\text{--}0.977$ ;  $P < 0.001$ ; S.E. = 0.03–0.20), and Parabolic diffusion models ( $r^2 = 0.427\text{--}0.831$ ;  $P < 0.05$ ; S.E. = 0.05–1.17) than the first- ( $r^2 = 0.325\text{--}0.572$ ; S.E. = 0.06–0.52) and second-order models ( $r^2 = 0.226\text{--}0.487$ ; S.E. = 0.04–0.59) (Table 2). The kinetics of both  $P_i$  and  $P_o$  release was initially rapid, followed by a slower reaction (Fig. 1: CS-a, NS-a, AS-a; Fig. 2: CS-a, NS-a, AS-a). A single straight line nearly covering the entire course of reaction time was only obtained when the soil P release data for each soil were plotted according to the Elovich and power function equations (Fig. 1: CS-b/c, NS-b/c, AS-b/c; Fig. 2: CS-b/c, NS-b/c, AS-b/c). These results indicated that Elovich and power function models were the most suitable to describe and compare the kinetics of P release of the three different soils. Overall, the kinetic parameters, obtained from Elovich ( $\alpha$ ,  $\beta$ ) and power function ( $a$ ,  $b$ ) models were higher when soils were treated with low molecular weight organic acids than with water (Table 3).

Organic acids generated more  $P_o$  release than water in the three soils, and there was a consistent trend of greater  $P_o$  release in soil-solution mixtures induced by oxalic acid (0.63–3.17  $\text{mg P}_o \text{ kg}^{-1}$ ) than by citric acid (0.61–2.82  $\text{mg P}_o \text{ kg}^{-1}$ ) or malic acid (0.52–1.76  $\text{mg P}_o \text{ kg}^{-1}$ ). Cumulative  $P_i$  release from soil induced by water ranged from 0.32 to 1.75  $\text{mg P}_i \text{ kg}^{-1}$  for the three soils, while  $P_i$  release from soil induced by oxalic acid, citric acid, and malic acid ranged from 0.64 to 7.25  $\text{mg kg}^{-1}$ , 0.64 to 6.67  $\text{mg kg}^{-1}$  and 0.50 to 2.18  $\text{mg P}_i \text{ kg}^{-1}$ , respectively. The type of organic acid affects  $P_i$  release and the impact on  $P_i$  release in soil-solution mixtures was ranked as oxalic acid > citric acid > malic acid for the calcareous soil, and citric acid > oxalic acid > malic acid for the neutral and acidic soils. The pH values of the soil-low molecular weight organic acids mixed solution could be ranked as malic acid > citric acid > oxalic acid at the beginning and at the end of the kinetic experiments (Table 4).

### 3.3 Soil P fractions

In the calcareous soil, treatment with low molecular weight organic acids resulted in a mean increase of the  $\text{NaOH-P}_i$  (Fe/Al-bound  $P_i$ ) fraction by 34.7% ( $P < 0.05$ ), and the  $\text{NaHCO}_3\text{-P}_i$  (soil labile  $P_i$ ) fraction by 12.8% ( $P > 0.05$ ). The increase in the  $\text{NaHCO}_3\text{-P}_i$  and  $\text{NaOH-P}_i$  fractions stems from the decrease of the  $\text{HCl-P}_i$  fraction (2.2–26.3%;  $P > 0.05$ ).



**Figure 1:** The kinetics of inorganic P ( $P_i$ ) release by water, oxalic acid, citric acid, and malic acid at  $10 \text{ mmol kg}^{-1}$  soil from the three studied soils (CS: calcareous; NS: neutral, AS: acidic) as a function of time (a) and similar data described by selected kinetic equations: Elovich (b), power function (c), and parabolic diffusion (d).

Following treatment with low molecular weight organic acids, the  $\text{NaHCO}_3\text{-}P_i$  fraction on average increased by 9.6% and 24.1% while the  $\text{NaOH-}P_i$  fraction decreased by 9.2% and 7.7% ( $P < 0.05$ ) for the calcareous and acidic soils, respectively (Fig. 3). In general, oxalic acid was the most effective treatment leading to changes in the concentration of  $P_i$  fractions ( $\text{NaOH-}$  and  $\text{HCl-}P_i$ ) for the calcareous soil. Citric acid was more effective in reducing the  $\text{NaOH-}P_i$  fraction in the acidic soil than the other organic acids or water.

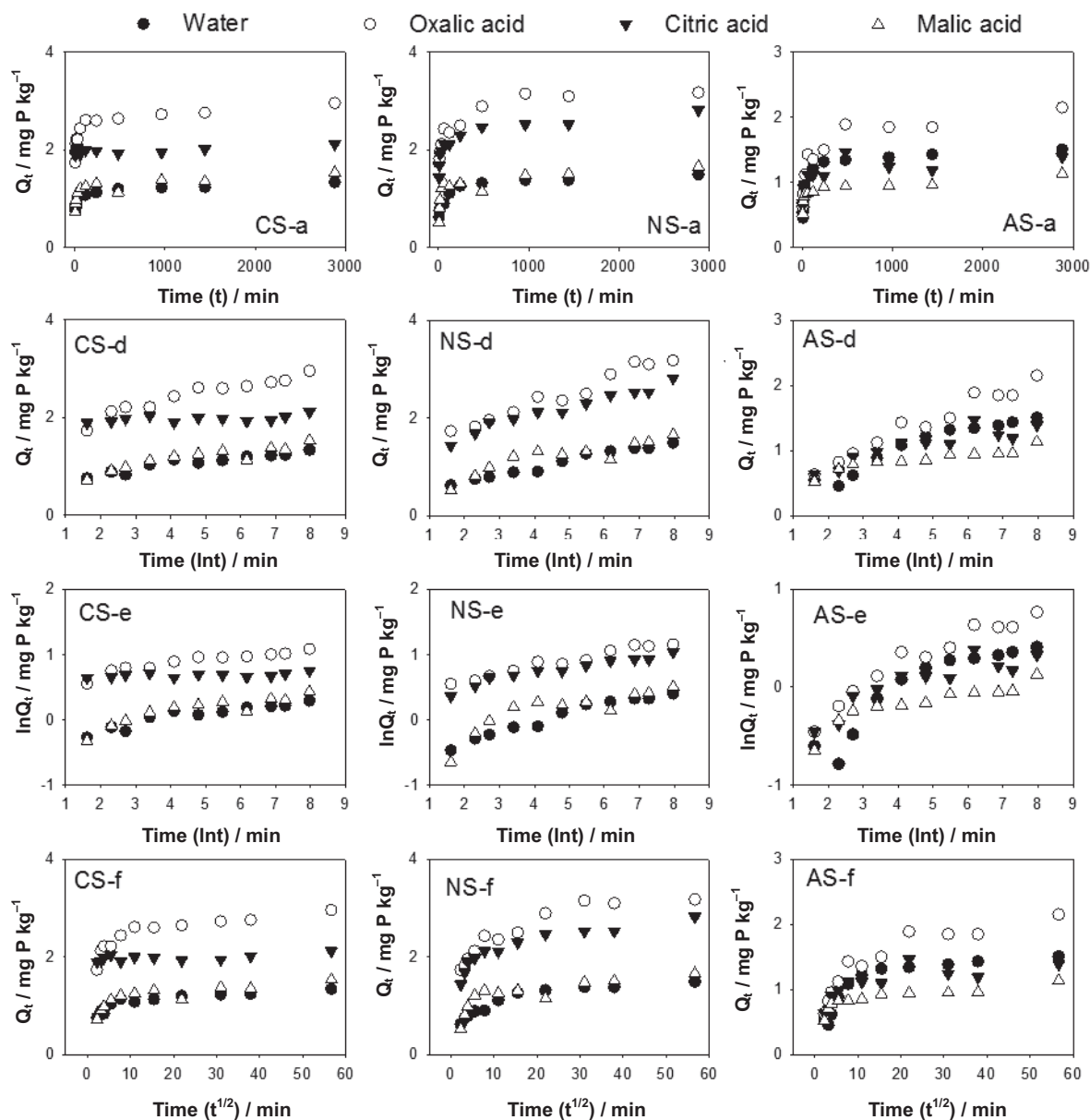
The concentration of labile  $P_o$  ( $\text{NaHCO}_3\text{-}P_o$ ) fractions significantly decreased ( $P < 0.05$ ) after the kinetic experiment, whereas the  $\text{Fe/Al-}P_o$  ( $\text{NaOH-}$  extracted  $P_o$ ) fractions were not significantly affected by treatments (Fig. 4). Low molecular weight organic acids reduced the concentration of the  $\text{NaHCO}_3\text{-}P_o$  fraction, relative to water, by as much as 22.5% ( $P < 0.05$ ) in the calcareous soil, 12.1% in the neutral soil,

and 16.2% ( $P < 0.05$ ) in the acidic soil. The reduction in the concentration of  $\text{NaHCO}_3\text{-}P_o$  fraction was influenced by oxalic acid > citric acid > malic acid for all three soils.

## 4 Discussion

### 4.1 Kinetics of P release from soils: pattern and processes

Our first hypothesis was that low molecular weight organic acids will increase the rate of the kinetics of both  $P_i$  and  $P_o$  release, which was supported by the higher  $P_i$  and  $P_o$  kinetic parameters with low molecular weight organic acids than water. Release of  $P_i$  and  $P_o$  from soils was rapid during the first 5 to 240 min of the kinetic study and then plateaued as



**Figure 2:** The kinetics of organic P ( $P_o$ ) release by water, oxalic acid, citric acid, and malic acid at 10 mmol kg<sup>-1</sup> soil from the three studied soils (CS: calcareous; NS: neutral, AS: acidic) as a function of time (a) and similar data described by selected kinetic equations: Elovich (b), power function (c), and parabolic diffusion (d).

an apparent equilibrium was reached. This two-phase pattern of initially rapid P release followed by slower release was reported by Smet et al. (1998), Jalali and Zinli (2011) and Jalali and Tabar (2011), and is attributed to a combination of dissolution and desorption process. In the current study, soil NaHCO<sub>3</sub>-P<sub>i</sub> fraction tends to increase after releasing P<sub>i</sub> into soil solution with the addition of low molecular weight organic acids. The kinetics of P<sub>i</sub> release seems to be linked with the moderately labile NaOH-P<sub>i</sub> (Fe/Al-P) or HCl-P<sub>i</sub> (Ca-P) fractions. However, it may be masked due to the re-adsorption of P<sub>i</sub> in NaHCO<sub>3</sub>-P<sub>i</sub> fraction in the process of P<sub>i</sub> release (Freese et al., 1995). In the initial rapid phase, the dissolution of labile surface-adsorbed P is likely to be the dominate process releasing P from soil into solution while the dissolution of the crystalline P compounds will be the rate-limiting step in the

slower P release phase (McDowell and Sharpley, 2003). As we did not monitor soil P fractions throughout the study, it is not possible to confirm the source of P<sub>i</sub> and P<sub>o</sub> during the initial rapid phase, but the significant reduction in HCl-P<sub>i</sub> (Ca-P<sub>i</sub>) or NaOH-P<sub>i</sub> (Fe/Al-P<sub>i</sub>) concentration by the end of the kinetic experiment indicates dissolution of crystalline P compounds occurred, particularly when soil was treated with low molecular weight organic acids. In addition, due to the greater affinities of oxalate for Ca<sup>2+</sup> and citrate for Fe<sup>3+</sup>/Al<sup>3+</sup>, oxalic acid was the most effective in increasing P<sub>i</sub> release rate in calcareous soil while citric acid was the most effective in acidic soil. This confirmed our second hypothesis that oxalic acid is most effective in P<sub>i</sub> release in calcareous soils, while citric acid is the most effective solution for P<sub>i</sub> release in acidic soils.

**Table 2:** Coefficients of determination ( $r^2$ ) and standard errors of estimates (S.E.) for selected kinetic equations used to describe the kinetic release of inorganic P ( $P_i$ ) and organic P ( $P_o$ ) during 2,880 min from calcareous, neutral and acidic soils shaken on an end-over-end shaker with water, oxalic acid, citric acid, and malic acid solutions (1:10 soil: solution ratio with organic acid concentrations of 10 mmol kg<sup>-1</sup> soil).<sup>a</sup>

	Soil type	Treatment	Elovich		Power function		Parabolic diffusion	
			$r^2$	S.E.	$r^2$	S.E.	$r^2$	S.E.
$P_i$ release	Calcareous soil	Water	0.955***	0.11	0.860***	0.20	0.674**	0.29
		Oxalic acid	0.972***	0.37	0.891***	0.19	0.722***	1.17
		Citric acid	0.987***	0.16	0.941***	0.17	0.801***	0.63
		Malic acid	0.969***	0.14	0.941***	0.13	0.788***	0.37
	Neutral soil	Water	0.965***	0.09	0.889***	0.19	0.768**	0.22
		Oxalic acid	0.954***	0.24	0.968***	0.09	0.831***	0.46
		Citric acid	0.991***	0.14	0.977***	0.07	0.821***	0.64
		Malic acid	0.986***	0.08	0.973***	0.08	0.841***	0.26
	Acidic soil	Water	0.869***	0.08	0.853***	0.09	0.816***	0.10
		Oxalic acid	0.946***	0.17	0.939***	0.09	0.735***	0.37
		Citric acid	0.993***	0.15	0.929***	0.14	0.775***	0.89
		Malic acid	0.987***	0.07	0.962***	0.11	0.818***	0.27
$P_o$ release	Calcareous soil	Water	0.908***	0.06	0.878***	0.07	0.694**	0.11
		Oxalic acid	0.913***	0.11	0.873***	0.06	0.686**	0.21
		Citric acid	0.898***	0.06	0.852***	0.03	0.427*	0.05
		Malic acid	0.838***	0.10	0.823***	0.10	0.657**	0.14
	Neutral soil	Water	0.986***	0.08	0.963***	0.06	0.773***	0.15
		Oxalic acid	0.979***	0.05	0.971***	0.04	0.802***	0.25
		Citric acid	0.957***	0.09	0.929***	0.06	0.789***	0.19
		Malic acid	0.802***	0.15	0.721***	0.18	0.615**	0.21
	Acidic soil	Water	0.920***	0.11	0.850***	0.18	0.636**	0.24
		Oxalic acid	0.962***	0.10	0.929***	0.11	0.780***	0.24
		Citric acid	0.801***	0.12	0.791***	0.13	0.543**	0.19
		Malic acid	0.856***	0.06	0.803***	0.09	0.714**	0.09

<sup>a</sup>ns: not significant at  $p < 0.05$ , \*significant at  $p < 0.05$ , \*\*significant at  $p < 0.01$ , \*\*\*significant at  $p < 0.001$ .

Still, we could not confirm that oxalic acid and citric acid were more effective in inducing the  $P_o$  release in calcareous and acidic soils, respectively, since oxalic acid reduced the concentration of the  $\text{NaHCO}_3\text{-}P_o$  fraction more than the other organic acids regardless of soil type. This was taken as circumstantial evidence that  $P_o$  entered the soil solution during the initial rapid P release phase through the rapid desorption and dissolution of the labile  $P_o$  ( $\text{NaHCO}_3\text{-}P_o$ ) fraction. The  $\text{NaHCO}_3\text{-}P_o$  fraction, comprised of  $P_o$  in the soil solution and  $P_o$  that adsorbed on the soil surface, is thought to be rapidly dissolved and easily desorbed from soil surface. (Tiessen and Moir, 1993; Guppy et al., 2000; Vu et al., 2008). However, at the end of the slower  $P_o$  release phase, there was no significant difference in the  $P_o$  concentration within the  $\text{NaOH-P}_o$  fraction, so it is unlikely that chelation by organic acid ligands occurred during the kinetics of  $P_o$  release from the studies

soils. The  $\text{NaOH-P}_o$  ( $\text{Fe/Al-P}_o$ ) fraction was characterized as less labile  $P_o$  that held more strongly by chemisorption to Fe and Al components of soil surface (Hedley et al., 1982). These results were inconsistent with our third hypothesis, indicating that the mechanism for the kinetics of  $P_o$  release involved in low molecular weight organic acids was dissimilar to  $P_i$  release (mainly due to chelating effects of organic acid ligand cations that bind  $P_i$ ).

Time-dependent P-release data were better modeled by Elovich, power function, and parabolic diffusion equations, based on the coefficients of determination ( $r^2$ ) and the standard errors of estimate (S.E.) of the five chosen models fitted to the study data. However, graphical test for the parabolic diffusion model did not present a requisite straight line covering the whole time scale and data led to curved plots for short

**Table 3:** Kinetic parameters of the selected equations describing the kinetic release of inorganic P ( $P_i$ ) and organic P ( $P_o$ ) during 2,880 min from calcareous, neutral, and acidic soils shaken on an end-over-end shaker with water, oxalic acid, citric acid, and malic acid solutions (1:10 soil : solution ration with organic acid concentrations of 10 mmol kg<sup>-1</sup> soil).

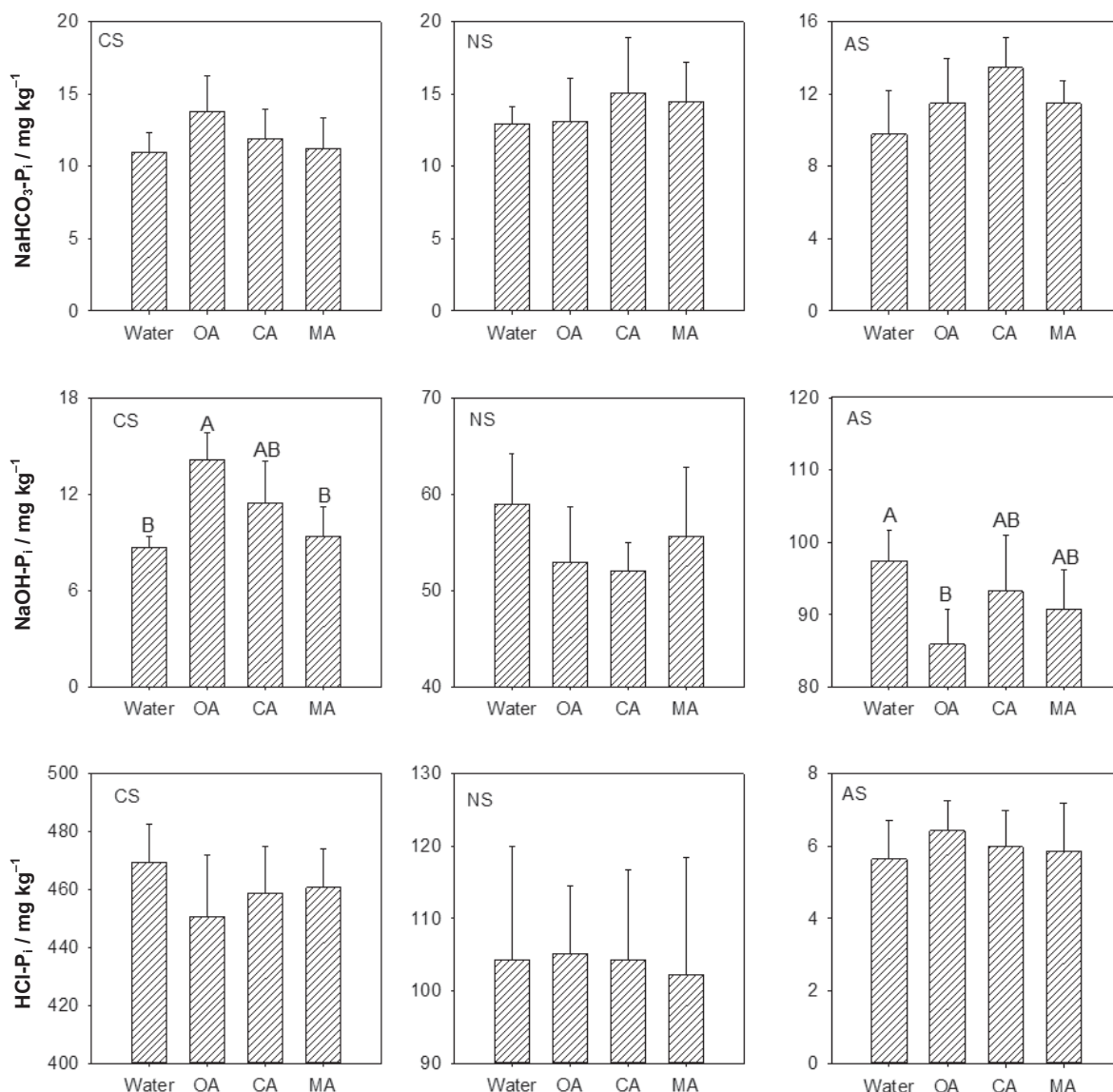
	Soil	Treatment	Elovich		Power function	
			$\alpha$	$1/\beta$	a	b
$P_i$ release	Calcareous soil	Water	0.441	0.221	0.382	0.220
		Oxalic acid	1.112	0.964	1.324	0.242
		Citric acid	0.293	0.623	0.506	0.299
		Malic acid	0.359	0.352	0.493	0.235
	Neutral soil	Water	23.461	0.081	0.734	0.078
		Oxalic acid	133.018	0.157	1.770	0.066
		Citric acid	201.471	0.017	1.899	0.008
		Malic acid	111.039	0.099	0.747	0.090
	Acidic soil	Water	0.272	0.205	0.303	0.235
		Oxalic acid	0.489	0.484	0.719	0.224
		Citric acid	1.037	0.670	1.175	0.210
		Malic acid	0.497	0.292	0.537	0.204
$P_o$ release	Calcareous soil	Water	2.652	0.141	0.544	0.137
		Oxalic acid	43.023	0.249	1.482	0.103
		Citric acid	166.871	0.188	1.391	0.089
		Malic acid	6.836	0.138	0.612	0.132
	Neutral soil	Water	18.551	0.097	0.579	0.104
		Oxalic acid	2.301	0.310	0.945	0.157
		Citric acid	1.282	0.836	1.377	0.221
		Malic acid	0.234	0.286	0.970	0.247
	Acidic soil	Water	0.713	0.173	0.409	0.186
		Oxalic acid	0.975	0.227	0.572	0.176
		Citric acid	16.726	0.109	0.615	0.111
		Malic acid	143.552	0.069	0.561	0.085

**Table 4:** The pH value of treatment solutions and the change in pH of soil suspensions before shaking and after 2,880 min of end-over-end shaking in centrifuge tubes with each treatment (1:10 soil : solution ration with organic acid concentrations of 10 mmol kg<sup>-1</sup> soil).<sup>a</sup>

Treatment	Solution pH	Calcareous soil		Neutral soil		Acidic soil	
		before pH	after pH	before pH	after pH	before pH	after pH
Water	7.13	7.47 A	7.93 B	7.04 A	7.51 B	5.35 A	5.97 B
Citric acid	3.11	6.62 A	7.75 B	4.11 A	5.11 B	3.66 A	4.58 B
Oxalic acid	2.84	6.37 A	7.34 B	3.92 A	5.03 B	3.25 A	4.23 B
Malic acid	3.25	6.89 A	7.92 B	4.26 A	5.22 B	3.58 A	4.45 B

<sup>a</sup>Within each soil, pairwise comparison of the treatment effect on the pH in soil suspension was made before and after 2,880 min of end-over-end shaking, where different capital letters indicate significant differences at  $P < 0.05$ .





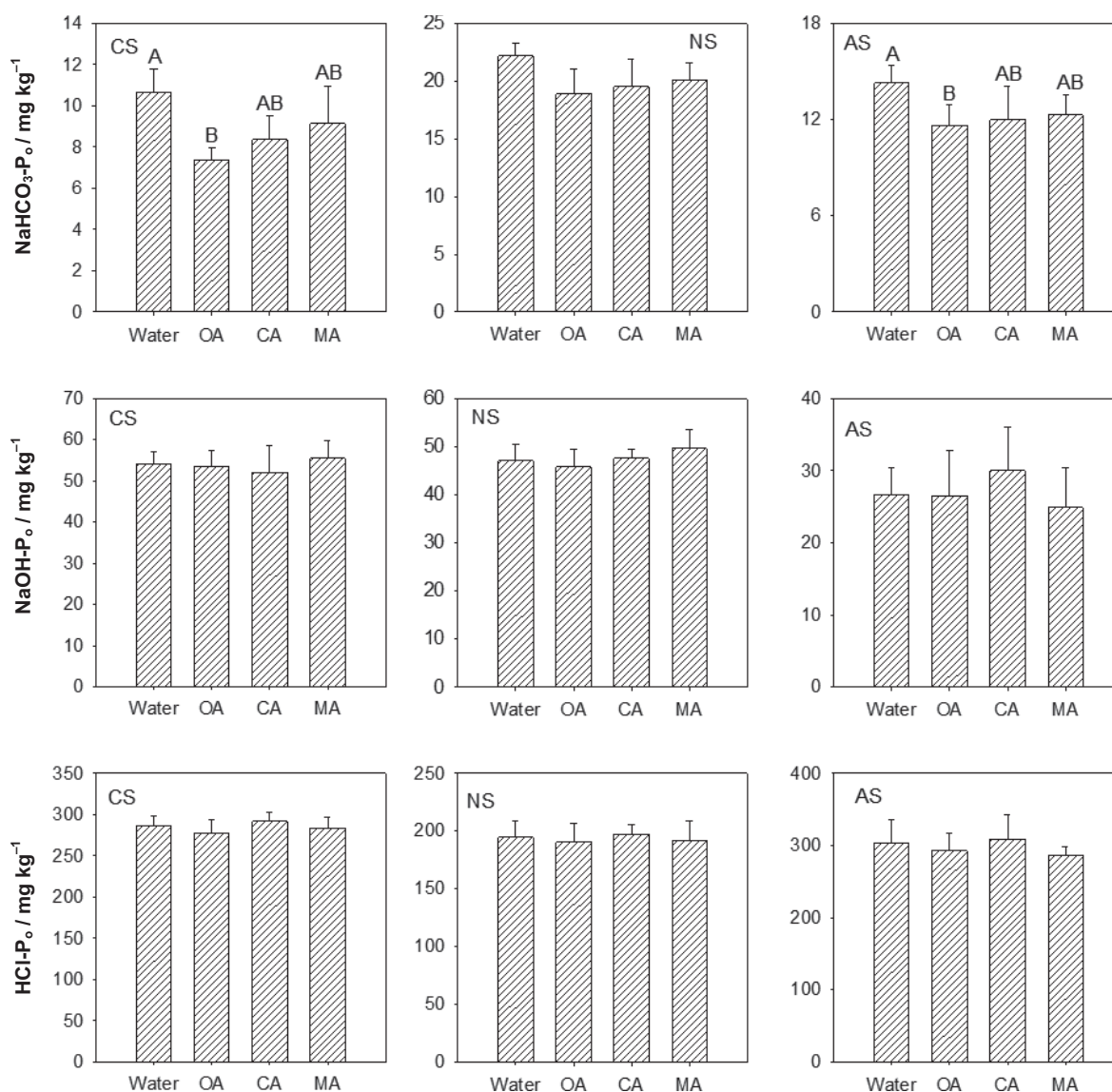
**Figure 3:** Inorganic P ( $P_i$ ) fractions in the three studied soils (CS: calcareous; NS: neutral, AS: acidic) following 2,880 min shaking with water, oxalic acid (OA), citric acid (CA), and malic acid (MA) solutions in a kinetic release study. Columns are the mean and standard deviation bars of three replicates, and those with different letters had significantly different ( $p < 0.05$ ) concentrations of  $P_i$  after the kinetic release study.  $\text{NaHCO}_3\text{-}P_i$ , soil soluble and exchangeable  $P_i$ ;  $\text{NaOH-}P_i$ ,  $P_i$  compounds held more strongly by chemisorption to Fe and Al components of soil surface;  $\text{HCl-}P_i$ , soil Ca bound  $P_i$ .

contact times (Fig. 1: CS-d, NS-d, AS-d; Fig. 2: CS-d, NS-d, AS-d). This suggests that  $P_i$  and  $P_o$  were not released from soils by a diffusion-controlled process similar to the observations by Shariatmadari et al. (2006). The dissolution of the  $\text{Fe}^{3+}/\text{Al}^{3+}$  or  $\text{Ca}^{2+}$  compounds that bind most of P in soils by low molecular weight organic acids may be a possible mechanism for P release according to the well-fitted Elovich model (Hansen and Strawn, 2003), although most of these compounds were the major source of  $P_i$  rather than  $P_o$ . Taghipour and Jalali (2013) also used the power-type equation to describe the kinetics of  $P_i$  release from some calcareous soils by oxalic acid, citric acid, and malic acid at  $10 \text{ mmol L}^{-1}$ . While the power type equation may describe  $P_i$  release by organic acids, involving both dissolution and chelation of mineral-bound  $P_i$  by organic acid ligands (Taghipour and Jalali, 2013), the slope and intercept of the curve suggest that the

Elovich and power type equations provided similar descriptions of the measured phenomena.

#### 4.2 Effectiveness of organic acids to induce $P_o$ and $P_i$ release from soils

Cumulative  $P_o$  release induced by low molecular weight organic acids was greater than that induced by water, and the source of  $P_o$  released was the  $\text{NaHCO}_3\text{-}P_o$  fraction, which was depleted by 12.1–22.5% ( $P < 0.05$ ) during the kinetic experiment with the three soils studied. Although not all were significantly different, there was greater  $P_o$  release in soils treated with oxalic acid than with citric acid or malic acid. This finding might be explained by the lower pH value in solutions with oxalic acid than that with the other organic acids and



**Figure 4:** Organic P ( $P_o$ ) fractions in the three studied soils (CS: calcareous; NS: neutral, AS: acidic) following 2,880 min shaking with water, oxalic acid (OA), citric acid (CA), and malic acid (MA) solutions in a kinetic release study. Columns are the mean and standard deviation bars of three replicates, and those with different letters had significantly different ( $p < 0.05$ ) concentrations of  $P_o$  after the kinetic release study.  $\text{NaHCO}_3\text{-P}_o$  comprises of  $P_o$  in the soil solution and that adsorbed on the soil surface;  $\text{NaOH-P}_o$  covers  $P_o$  compounds held more strongly by chemisorption to Fe and Al components of soil surface; residual P, soil resistant  $P_i$  and  $P_o$ .

water, due to the fact that oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ) is a relatively strong acid with 2 carboxyl groups, and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) and malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ) are weak organic acids, respectively, with three and two carboxyl groups. Although  $P_o$  is mainly associated with organo-mineral complexes (e.g.,  $P_o$  compounds strongly adsorbed to Fe and Al components of soil surface), the release of  $P_o$  by low molecular weight organic acids in this study was not due to chelating effects of organic acid ligand cations (e.g., Fe and Al on clay surfaces) that bind  $P_o$ . This implies that acid strength is more important than chelating ability of low molecular weight organic acids in releasing  $P_o$ . Still, our findings may not be generalizable, as Wei et al. (2010) reported that citric acid release more  $P_o$  than oxalic and malic acids in some neutral and acid forest soils. Although the mechanism was not well explained, there was no significant change in pH of suspensions containing low

molecular weight organic acids in the study of Wei et al. (2010), perhaps due to the buffering capacity of their forest soils. Another difference was that  $P_o$  accounted for 70% of the total P in those forest soils, but no more than 20% of the total P in the agricultural soils of this study. We deduced that  $P_o$  release occurs through different mechanisms than those controlling  $P_i$  release in the presence of low molecular weight organic acids. Still, further studies on  $P_o$  speciation by means of  $^{31}\text{P-NMR}$  would provide insight into the strength of the reactions of low molecular weight organic acids affecting kinetics of  $P_o$  release.

Cumulative  $P_i$  release from soils was greater when treated with low molecular weight organic acids than with water (Fig. 1). Probably the source of  $P_i$  released by low molecular weight organic acids in the present study was the  $\text{HCl-P}_i$

(Ca-P<sub>i</sub>) fraction in the calcareous soil and the NaOH-P<sub>i</sub> (Fe/Al-P<sub>i</sub>) fraction in the neutral and acidic soils, both of which declined significantly ( $P < 0.05$ ) by the end of the kinetic experiment. Although the amount of P<sub>i</sub> mobilized by low molecular weight organic acids was small (0.64–7.25 mg kg<sup>-1</sup>), the dynamic nature of soluble P<sub>i</sub> may make it contribute significantly to plant-available P in agricultural soils. Soil soluble P<sub>i</sub> was thought to be the most available P for immediate biological uptake and keep certain level of equilibrium with other P forms (Schmidt et al., 1997). Oxalic acid was most effective in reducing the Ca-P<sub>i</sub> fraction in the calcareous soil while citric acid was the most effective in reducing the Fe/Al-P<sub>i</sub> fraction, which was also reported by others (Ström et al., 2002; 2005; Andrade et al., 2013). Although we did not investigate the mechanism involved, Ström et al. (2001) found similar results due to the preferential formation and precipitation of Ca-oxalate in calcareous soils and Fe-, Al-citrate in non-calcareous soils.

## 5 Conclusions

In three agricultural soils with contrasting physicochemical properties, the addition of low molecular weight organic acids increased both the concentration and rate of the kinetics of P<sub>i</sub> and P<sub>o</sub> release. The P<sub>o</sub> released upon treatment with low molecular weight organic acids represented 29.7–44.6% of the total P released, and P<sub>o</sub> release from the NaHCO<sub>3</sub>-P<sub>o</sub> fraction was greater when soils were treated with oxalic acid than with the other organic acids, regardless of soil type. While enhanced P<sub>i</sub> release in the presence of low molecular weight organic acids was likely due to accelerated desorption and dissolution process, our findings suggest that the acid strength of solution containing low molecular weight organic acids contributed to the kinetic release of P<sub>o</sub>. In this short-term (2 d) kinetic experiment, chelation by organic acid ligands did not contribute to the kinetic of P<sub>o</sub> release, which promotes the understanding of the mechanisms of P<sub>o</sub> release in the presence of low molecular weight organic acids.

## Acknowledgements

This work is financially supported by *National Natural Science Foundation of China* (Grant No. 41271317, 41101285, and 31470624). Finally we thank the SERG writing group (McGill University) for reviewing earlier versions of the manuscript.

## References

- Andrade, F. V., Mendonça, E. S., Silva, I. R. (2013): Organic acids and diffusive flux of organic and inorganic phosphorus in sandy-loam and clayey Latosols. *Commun. Soil Sci. Plan.* 44, 1211–1223.
- Aulakh, M. S., Kabba, B. S., Baddesha, H. S., Bahl, G. S., Gill, M. P. S. (2003): Crop yields and phosphorus fertilizer transformations after 25 years of applications to a subtropical soil under groundnut-based cropping systems. *Field Crop. Res.* 83, 283–296.
- Bais, H. P., Weir, T. L., Perry, L. G., Gilroy, S., Vivanco, J. M. (2006): The role of root exudates in rhizosphere interactions with plants and other organisms. *Annu. Rev. Plant Biol.* 57, 233–266.

- Boschetti, N. G., Quintero, C. E., Giuffrè, L. (2008): Phosphorus fractions of soils under *Lotus corniculatus* as affected by different phosphorus fertilizers. *Biol. Fert. Soils* 45, 379–384.
- Chakraborty, D., Nair, V. D., Chrysostome, M., Harris, W. G. (2011): Soil phosphorus storage capacity in manure-impacted Alaquods: Implications for water table management. *Agr. Ecosyst. Environ.* 142, 167–175.
- Chen, C. R., Condrón, L. M., Xu, Z. H. (2008): Impacts of grassland afforestation with coniferous trees on soil phosphorus dynamics and associated microbial processes: A review. *Forest Ecol. Manag.* 255, 396–409.
- Freese, D., Lookman, R., Merckx, R., Vanriemsdijk, W. H. (1995): New method for assessment of long-term phosphate desorption from soils. *Soil Sci. Soc. Am. J.* 59, 1295–1300.
- Fox, T. R., Comerford, N. B. (1992): Influence of oxalate loading on phosphorus and aluminum solubility in Spodosols. *Soil Sci. Soc. Am. J.* 56, 290–294.
- Fox, T. R., Comerford, N. B., Mcfee, W. W. (1990): Kinetics of phosphorus release from Spodosols: Effect of oxalate and formate. *Soil Sci. Soc. Am. J.* 54, 1441–1447.
- Gerke, J. (1994): Kinetics of soil phosphate desorption as affected by citric acid. *Z. Pflanz. Bodenkunde* 157, 17–22.
- Gerke, J., Beißner, L., Römer, W. (2000): The quantitative effect of chemical phosphate mobilization by carboxylate anions on P uptake by a single root. I. The basic concept and determination of soil parameters. *J. Plant Nutr. Soil Sci.* 163, 207–212.
- Guppy, C. N., Menzies, N. W., Moody, P. W., Compton, B. L., Blamey, F. P. C. (2000): A simplified, sequential, phosphorus fractionation method. *Commun. Soil Sci. Plan.* 31, 1981–1991.
- Hansen, J. C., Strawn, D. G. (2003): Kinetics of phosphorus release from manure-amended alkaline soil. *Soil Sci.* 168, 869–879.
- Harrold, S. A., Tabatabai, M. A. (2006): Release of inorganic phosphorus from soils by low-molecular-weight organic acids. *Commun. Soil Sci. Plan.* 37, 1233–1245.
- Hedley, M. J., Stewart, J. W. B., Chauhan, B. S. (1982): Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46, 970–976.
- Hinsinger, P. (2001): Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant Soil* 237, 173–195.
- Hinsinger, P., Bengouth, A. G., Vetterlein, D., Young, I. M. (2009): Rhizosphere: biophysics, biogeochemistry and ecological relevance. *Plant Soil* 321, 117–152.
- Hocking, P. J. (2001): Organic acids exuded from roots in phosphorus uptake and aluminum tolerance of plants in acid soils. *Adv. Agron.* 74, 63–97.
- Jalali, M., Ranjbar, F. (2010): Aging effects on phosphorus transformation rate and fractionation in some calcareous soils. *Geoderma* 155, 101–106.
- Jalali, M., Zinli, A. M. (2011): Kinetics of phosphorus release from calcareous soils under different land use in Iran. *J. Plant Nutr. Soil Sci.* 174, 38–46.
- Jalali, M., Tabar, S. S. (2011): Chemical fractionation of phosphorus in calcareous soils of Hamedan, western Iran under different land use. *J. Plant Nutr. Soil Sci.* 174, 523–531.
- Jones, D. L. (1998): Organic acids in the rhizosphere—a critical review. *Plant Soil* 205, 25–44.
- Kang, J., Amoozegar, A., Hesterberg, D., Osmond, D. L. (2011): Phosphorus leaching in a sandy soil as affected by organic and inorganic fertilizer sources. *Geoderma* 161, 194–201.

- Kuo, S., Huang, B., Bembenek, R. (2005): Effects of long-term phosphorus fertilization and winter cover cropping on soil phosphorus transformations in less weathered soil. *Biol. Fert. Soils* 41, 116–123.
- Lan, M., Comerford, N. B., Fox, T. R. (1995): Organic-anions effect on phosphorus release from spodic horizons. *Soil Sci. Soc. Am. J.* 59, 1745–1749.
- Li, H. G., Shen, J. B., Zhang, F. S., Lamber, H. (2010): Localized application of soil organic matter shifts distribution of cluster roots of white lupin in the soil profile due to localized release of phosphorus. *Ann. Bot.* 105, 585–593.
- Lotrario, J. B., Stuart, B. J., Lam, T., Arands, R. R., O'Connor, O. A., Kosson, D. S. (1995): Effects of sterilization methods on the physical characteristics of soils: Implications for sorption isotherm analyses. *Bull. Environ. Contam. Toxicol.* 54, 668–675.
- Makhani, M., Isaac, M. E. (2014): Rhizosphere dynamics under nitrogen-induced root modification: The interaction of phosphorus and calcium. *J. Plant Nutr. Soil Sci.* 177, 624–632.
- McDowell, R., Sharpley, A. (2003): Phosphorus solubility and release kinetics as a function of soil test P concentration. *Geoderma* 112, 143–154.
- Moradi, N., Sadaghiani, M. H. R., Sepehr, E., Mandoulakani, B. A. (2012): Effects of low-molecular-weight organic acids on phosphorus sorption characteristics in some calcareous soils. *Turk. J. Agric. For.* 36, 459–468.
- Nafiu, A. (2009): Effects of soil properties on the kinetics of desorption of phosphate from Alfisols by anion-exchange resins. *J. Plant Nutr. Soil Sci.* 172, 101–107.
- Nwoke, O. C., Diels, J., Abaidoo, R., Nziguheba, G., Merckx, R. (2008): Organic acids in the rhizosphere and root characteristics of soybean (*Glycine max*) and cowpea (*Vigna unguiculata*) in relation to phosphorus uptake in poor savanna soils. *Afr. J. Biotechnol.* 7, 3617–3624.
- Ohno, T., Zibilske, L. M. (1991): Determination of low concentrations of phosphorus in soil extracts using malachite green. *Soil Sci. Soc. Am. J.* 55, 892–895.
- Palomo, L., Claassen, N., Jones, D. L. (2006): Differential mobilization of P in the maize rhizosphere by citric acid and potassium citrate. *Soil Biol. Biochem.* 38, 683–692.
- Raghothama, K. G. (1999): Phosphate acquisition. *Annu. Rev. Plant Phys.* 50, 665–693.
- Schmidt, J. P., Buol, S. W., Kamprath, E. J. (1997): Soil phosphorus dynamics during 17 years of continuous cultivation: A method to estimate long-term P availability. *Geoderma* 78, 59–70.
- Shariatmadari, H., Shirvani, M., Jafari, A. (2006): Phosphorus release kinetics and availability in calcareous soils of selected arid and semiarid toposequences. *Geoderma* 132, 261–272.
- Smet, J. D., Vanderdeelen, J., Hofman, G. (1998): Effect of soil properties on the kinetics of phosphate release. *Commun. Soil Sci. Plan.* 29, 2135–2147.
- Sparks, D. L. (1995): Kinetics of metal sorption reactions, in Allen, H. E., Huang, C. P., Bailey, G. W., Bowers, A. R. (eds.): Metal speciation and contamination of soil. CRC Press, Boca Raton, FL, USA, pp. 35–58.
- Strobel, B. W. (2001): Influence of vegetation on low-molecular-weight carboxylic acids in soil solution—a review. *Geoderma* 99, 169–198.
- Ström, L., Owen, A. G., Godbold, D. L., Jones, D. L. (2001): Organic acid behaviour in a calcareous soil: sorption reactions and biodegradation rates. *Soil Biol. Biochem.* 33, 2125–2133.
- Ström, L., Owen, A. G., Godbold, D. L., Jones, D. L. (2002): Organic acid mediated P mobilization in the rhizosphere and uptake by maize roots. *Soil Biol. Biochem.* 34, 703–710.
- Ström, L., Owen, A. G., Godbold, D. L., Jones, D. L. (2005): Organic acid behaviour in a calcareous soil implications for rhizosphere nutrient cycling. *Soil Biol. Biochem.* 37, 2046–2054.
- Taghipour, M., Jalali, M. (2013): Effect of low-molecular-weight organic acids on kinetics release and fractionation of phosphorus in some calcareous soils of western Iran. *Environ. Monit. Assess.* 185, 5471–5482.
- Toor, G., Bahl, G. (1999): Kinetics of phosphate desorption from different soils as influenced by application of poultry manure and fertilizer phosphorus and its uptake by soybean. *Bioresource Technol.* 69, 117–121.
- Tiessen, H., Moir, J. O. (1993): Characterization of Available P by Sequential Extraction, in Cater, M. R., Gregorich, E. O. (eds.): Soil Sampling and Methods of Analysis. Lewis Publishers, Boca Raton, FL, USA, pp. 293–306.
- Turner, B. L. (2008): Resource partitioning for soil phosphorus: a hypothesis. *J. Ecol.* 96, 698–702.
- Verma, S., Subehia, S. K., Sharma, S. P. (2005): Phosphorus fractions in an acid soil continuously fertilized with mineral and organic fertilizers. *Biol. Fert. Soils* 41, 295–300.
- Vu, D. T., Tang, C., Armstrong, R. D. (2008): Changes and availability of P fractions following 65 years of P application to a calcareous soil in a Mediterranean climate. *Plant Soil* 304, 21–33.
- Wang, C., Wang, Z., Lin, L., Tian, B., Pei, Y. (2012): Effect of low molecular weight organic acids on phosphorus sorption by ferric-alum water treatment residuals. *J. Hazard. Mater.* 203–204, 145–150.
- Wei, L. L., Chen, C. R., Xu, Z. H. (2010): Citric acid enhances the mobilization of organic phosphorus in subtropical and tropical forest soils. *Biol. Fert. Soils* 46, 765–769.
- Xavier, F. A. da S., de Oliveira, T. S., Andrade, F. V., de Sá Mendonça, E. (2009): Phosphorus fractionation in a sandy soil under organic agriculture in Northeastern Brazil. *Geoderma* 151, 417–423.
- Xiao, K., Katagi, H., Harrison, M., Wang, Z. Y. (2006): Improved phosphorus acquisition and biomass production in Arabidopsis by transgenic expression of a purple acid phosphatase gene from *M. truncatula*. *Plant Sci.* 170, 191–202.
- Zamuner, E. C., Picone, L. I., Echeverria, H. E. (2008): Organic and inorganic phosphorus in Mollisol soil under different tillage practices. *Soil Till. Res.* 99, 131–138.
- Zhang, T. Q., MacKenzie, A. F., Liang, B. C., Drury, C. F. (2004): Soil test phosphorus and phosphorus fractions with long-term phosphorus addition and depletion. *Soil Sci. Soc. Am. J.* 68, 519–528.