

Effects of low-molecular-weight organic acids on phosphorus sorption characteristics in some calcareous soils

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Abstract: Understanding the role of organic acids in phosphorus sorption in soils is very important for economic and environmentally friendly management of soil P. Thus, calcareous surface soils (0-30 cm) from West Azerbaijan Province, Iran, were sampled to study the effect of different organic acids on P sorption. Soil samples (2.5 g) were equilibrated with 25 mL of 0.01 M CaCl₂ solution containing 0-20 mg P L⁻¹ and 5 mmol L⁻¹ of different organic acids (citric, oxalic, and malic acid). The sorption data were well fitted to Freundlich and linear equations but not to the Langmuir equation. The standard P requirements (SPRs) were lower in soils treated with organic acids than in untreated soils. The minimum and maximum values of calculated parameters (extent of sorption, energy of sorption, equilibrium buffering capacity, equilibrium P concentration, and SPR) by Freundlich and linear sorption isotherms were observed in soil 5 (sandy) and soil 4 (clayey-calcareous), respectively. Generally, organic acids decreased the amount of sorbed P and other sorption parameters in the studied soils. Oxalic acid was the most effective reagent for reducing the P sorption.

Key words: Low-molecular-weight organic acids, phosphorus, sorption equations

Introduction

Phosphate minerals are limited nonrenewable sources (Franz 2008). Despite the fact that calcareous soils have a large quantity of total P, its availability for plants is rather limited. Thus, plants grown on calcareous soils frequently suffer from P deficiency to differing degrees. Due to the apparent removal of P from the soil solution, plant-available P content is often very low (below 5 μM) compared to the total amount of P bound to soil minerals and charged sites or fixed into organic forms, which is not available to plants (Randall et al. 2001). Therefore, the availability of P to plants is limited, to a large extent, by the rate of the reactions that replenish soluble P pools.

Ca-phosphate is the main inorganic P fraction in calcareous soils because phosphates are either sorbed onto CaCO₃ surfaces or precipitated as discrete Ca-phosphate minerals or surface precipitates. In contrast, phosphates predominantly precipitate as Fe- and Al-phosphate in acid soils. P sorption capacities of soils are dependent on exchangeable Ca and Mg, soil texture, porosity, pH, ionic strength, and hydraulic conductivity (Bubba et al. 2003). It has been reported that the type of land utilization also influences P sorption capacity (Amapu et al. 2000). Numerous studies have shown that aluminosilicate clay minerals play an important role in P sorption in soils. Generally, those clay minerals

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that possess greater anion exchange capacity due to a positive surface charge have a greater affinity for phosphate ions. In order to overcome adsorption- or precipitation-induced P deficiency, P fertilization is commonly practiced. Thus, long-term application of P fertilizers can increase the total P content at the plow layer to levels above the environmentally safe level. This, in fact, accelerates P loss to surface waters and causes eutrophication (Sui et al. 1999; McDowell et al. 2001). Up to 25% of the applied P can be used by either the plant or microorganisms. Long-term P fertilization can increase downward P mobility in coarse- to medium-textured soils (Zhang et al. 1995).

Plants have also evolved different strategies to overcome P nutrient shortages, either by increasing P-use efficiency or extracting more P from the soil (Raghothama 1999). These strategies include changes to cellular metabolism and root development; initiation of mycorrhizal associations; acidification of the rhizosphere, which can promote the release of nutrients from soil minerals; and the exudation of phosphatases and organic anions solubilizing soil P. The benefits derived from having organic anions in the rhizosphere occur through 2 mechanisms: organic anions compete with phosphate groups for binding sites in the soil, and they form stronger complexes with Al^{3+} , Fe^{3+} , and Ca^{2+} than phosphate does. In particular, P can be released from Ca-phosphate minerals as an organic anion complex with Ca (Jones and Darrah 1994) or block the sorption of P to other charged sites (Lunstrom et al. 1995). Ligand exchange can also occur through the P bound to Fe or Al oxyhydroxides by replacement of the organic anions (Lan et al. 1995). Organic anions can also stimulate microbial activity in the rhizosphere, which is likely to influence the availability of other minerals and nutrients, as well (Yang et al. 2000).

The most common low-molecular-weight organic acids (LMWOAs) identified in soils are oxalic, succinic, tartaric, fumaric, malic, citric, sinapic, and ferulic acid. Concentrations of LMWOAs in soils are low under favorable environmental conditions; however, these acids may accumulate up to levels that are toxic to plant growth. Soil organic acids are derived from the decomposition of plant and animal residues, microbial metabolism, canopy detritus, and rhizosphere activity (Stevenson 1994). The release

of organic acids by plant roots is now regarded as one of the common mechanisms involved in solubilizing relatively insoluble soil nutrients (Jones et al. 1994). Acidification of the rhizosphere is one of the nutrition-related responses of plants that organic acids have in root exudates. Root exudation with a high concentration of organic acid anions as a result of nutrient deficiency (P deficiency) may lower rhizosphere pH and, consequently, make P more available in calcareous soils (Jones and Darrah 1994). Therefore, organic acid exudation from roots is considered to be one of the mechanisms that plants use to adapt to a P-deficient environment (Chen et al. 2008; McDowell et al. 2008). In the rhizosphere, P should be strongly influenced by the presence of organic ligands. However, there is limited information on the fate of P in the presence of organic acids in natural soil (Masayuki et al. 2010), and the exact mechanism among soil inorganic colloids, organic acids, and P has not been well established. For this reason, an investigation was conducted to study the effect of various organic acids on P sorption characteristics in calcareous soils in order to improve the understanding of the P sorption mechanism in calcareous soils in the presence of organic acids.

Materials and methods

Soil sampling

Surface layers (0-30 cm) of 5 calcareous soil samples belonging to 3 different soil types, Vertic Endoaquepts (soil 1), Typic Calcixerepts (soils 2, 3, and 5), and Vertic Calcixerepts (soil 4), located in different agricultural areas in the northwest of Iran were sampled in July 2009. The soil samples were air dried and ground to pass through a 2-mm sieve before use. Some of the chemical and physical properties of the soils are given in Table 1.

Analytical methods

Soil pH was determined using a 1:5 soil and 0.01 M $CaCl_2$ suspension by a glass electrode, and particle size was determined by the hydrometer method (Gee and Bauder 1986). The $CaCO_3$ equivalent of soils (CCE) was determined by the rapid titration method (Rayment and Higginson 1992). Cation exchange capacity (CEC) was measured by 1 M NaOAc buffered at pH 8.2 (Page et al. 1982). Organic matter

Table 1. Some physical and chemical properties of the studied soils.

Soil no.	Site	pH (CaCl ₂)	CEC ^a (cmol kg ⁻¹)	CCE ^b	OM ^c	Clay Silt Sand			Texture class
						(g kg ⁻¹)			
1	Khalifan	7.4	30	47	27	500	400	100	Clay
2	Sofichi	7.6	29	93	27	470	410	120	Silty clay
3	Rozeh Chai	8.0	27	220	21	330	440	230	Clay loam
4	Pasveh	7.5	38	280	29	560	340	100	Clay
5	Rahdaneh	7.5	21	42	6	100	200	700	Sandy loam

^aCEC = cation exchange capacity;

^bCCE = CaCO₃ equivalent;

^cOM = organic matter.

was determined by dichromate oxidation (Walkley and Black 1934). The organic acids selected for this study were citric, malic, and oxalic acid because of their widespread natural occurrence in soils (Hue et al. 1986).

P sorption in the presence of organic acids

P sorption isotherms were measured to evaluate the effects of organic acids on P sorption. For the sorption experiments, triplicate soil samples (2.5 g) were placed in 50-mL centrifuge tubes, and then 25 mL of 0.01 M KCl solution containing 0-20 mg P kg⁻¹ soil as KH₂PO₄ and 0.005 mol L⁻¹ organic acid ligands (citric, oxalic, and malic) was added to each tube. Two drops of toluene were added to inhibit microbial activity. The suspensions were shaken on an end-over-end shaker at 25 ± 1 °C for 24 h. At the end of the incubation period, the tubes were centrifuged at 3000 rpm for 10 min and filtered through Whatman filter paper (No. 42). P concentration in the supernatant was determined by the molybdenum blue method (Murphy and Riley 1962). Sorbed P was calculated from the difference between the concentration of soluble P added in the initial solution and P in the solution at equilibrium. Sorption parameters were calculated using Langmuir, Freundlich, and linear equations, as described below.

Langmuir equation

The Langmuir sorption equation used to describe reversible sorption for monolayer formation (Holford 1982) is:

$$X = Xm kC / (1 + kC),$$

where X is the amount of sorption fixed by the unit mass of the sorbent (mg P kg⁻¹ soil) at any initial concentration, C is the equilibrium solution concentration of the sorbate (mg L⁻¹), Xm is the maximum monolayer sorption, and k is a constant related to the bonding energy (L mg⁻¹). It is possible to calculate k and Xm from the linear form of the Langmuir equation:

$$X = 1/kXm + C/Xm.$$

Freundlich equation

The Freundlich equation has the form:

$$X = K_f C^{1/n},$$

where X is the quantity of P adsorbed (mg kg⁻¹), c is the equilibrium concentration of P (mg L⁻¹), and K_f and n are constants related to the sorption capacity and the linearity of the sorption isotherm, respectively. The linear regression of $\log c$ against $\log x$ gives a regression coefficient, a slope of n , and an intercept of $\log K_f$ (Barrow, 1978). Linear forms of the Freundlich equation can be written as:

$$\log X = \log K_f + 1/n \log C.$$

Linear equation

The linear equation has the form:

$$X = a + bC,$$

where X is the amount of sorption taken up per unit mass of sorbent (mg P kg⁻¹ soil) and C is the equilibrium solution concentration of the sorbate (mg L⁻¹). The equilibrium buffering capacity (EBC) of the equation is represented by b (Bertrand et al. 2003).

The standard P requirement (SPR) of calcareous soils, defined as the amount of P to be added to attain an equilibrium solution concentration of 0.4 mg P L⁻¹ (Samadi 2006), was calculated from the fitted linear equation.

Statistical data analysis

This experiment was conducted in a completely randomized design with 3 replications. All data were subjected to analysis of variance after normality and homogeneity tests (MSTATC software and MINITAB 14.0). Duncan's multiple range test was conducted only when the analysis of variance was significant at $P \leq 0.05$.

Results

Soil properties

Selected chemical and physical properties of the studied soils are shown in Table 1. The soils can be classified as neutral to alkaline with low organic matter. The calcium carbonate equivalent varied from 42 to 280 g kg⁻¹. CEC ranged from 21 to 38 cmol kg⁻¹. Clay content in all soils averaged 392 g kg⁻¹ and ranged from 100 to 560 g kg⁻¹.

Effects of LMWOAs on P sorption

The adsorption isotherms of untreated soils and soils treated with the organic acids are shown in the Figure. P sorption rose with increasing initial P

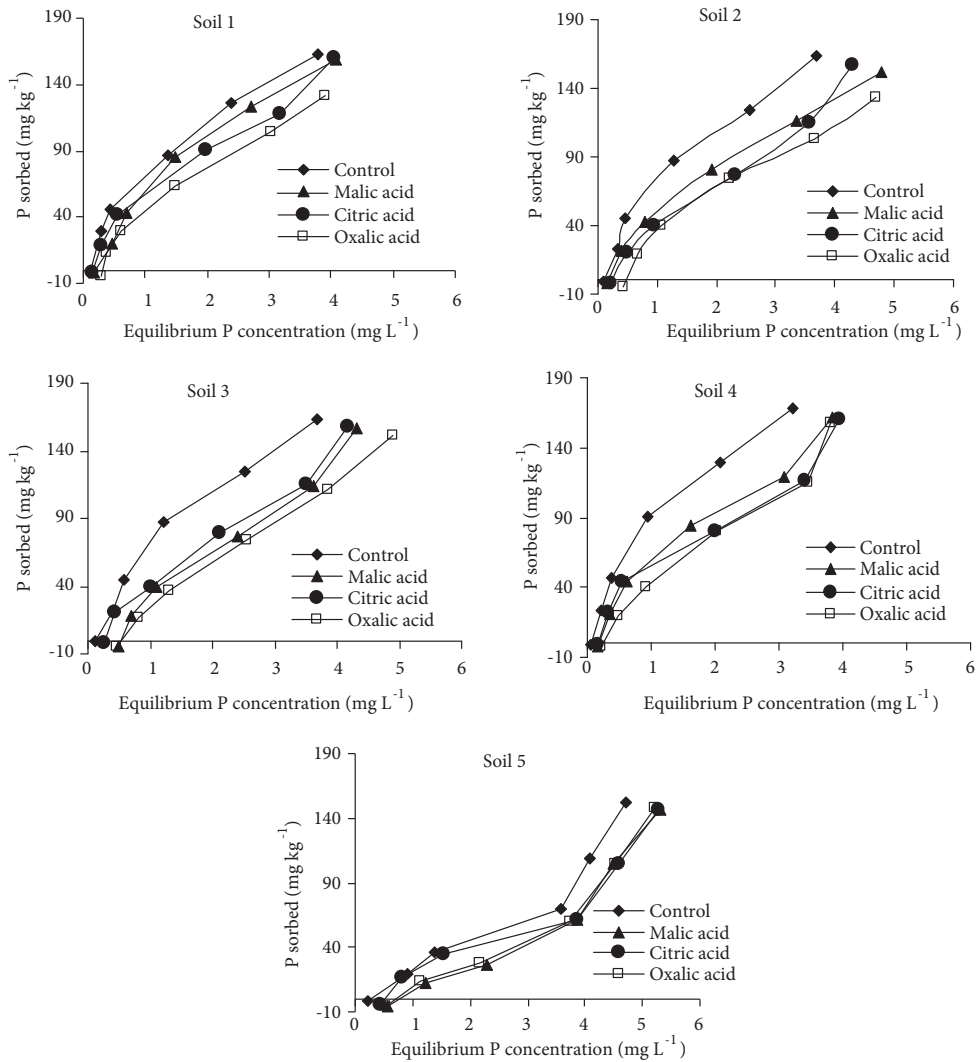


Figure. Phosphorus sorption isotherms for untreated soils (control) and soils treated with malic, citric, and oxalic acid.

concentration in all soils. The x:c ratio was higher for a small initial addition of P. In general, the organic acids were efficient releasing agents for soil P into solutions. Overall, oxalic acid was slightly more effective than the other 2 organic acids in reducing the P sorption.

The sorption isotherm parameters of the Freundlich, linear, and Langmuir equations are given in Tables 2 and 3. The results showed that P sorption is described well by the Freundlich and linear equations with a high correlation coefficient; however, the Langmuir equation described the P sorption in the soils poorly (Table 3). Very high regression coefficients ($P < 0.01$) for Freundlich and linear equations in all treatments indicated that these models can be successfully used for describing the sorption process.

Effect of organic acids on the Freundlich constants n and K_f

The Freundlich isotherm constants n and K_f , which represent the intercept and slope of the log-transformed sorption isotherm, may be taken as measures of the extent and the energy of sorption, respectively. The influence of LMWOAs (citric, malic, and oxalic acid) on n parameters of the Freundlich equation are shown in Table 4. The organic acids significantly decreased the Freundlich n parameter. Parameter n ranged from 1.07 to 1.58 in control soils; in soils treated with malic, citric, and oxalic acid, it ranged from 0.7 to 1.28, 1.05 to 1.44, and 0.67 to 1.13, respectively. Results showed that the effects of oxalic acid were significantly greater than the effects of citric and malic acid on the n parameter exponential adsorption equation.

Table 2. Values of correlation coefficient (R^2) of Freundlich and linear equations in control soils and soils treated with organic acids.

Soil no.	Control	Freundlich equation (R^2)			Control	Linear equation (R^2)		
		Malic acid	Citric acid	Oxalic acid		Malic acid	Citric acid	Oxalic acid
1	0.94 **	0.96 **	0.98 **	0.97 **	0.94 **	0.96 **	0.97 **	0.94 **
2	0.96 **	0.99 **	0.99 **	0.98 **	0.95 **	0.97 **	0.98 **	0.98 **
3	0.95 **	0.98 **	0.99 **	0.99 **	0.94 **	0.98 **	0.98 **	0.99 **
4	0.97 **	0.98 **	0.96 **	0.98 **	0.93 **	0.97 **	0.95 **	0.97 **
5	0.93 **	0.97 **	0.94 **	0.97 **	0.91 **	0.93 **	0.92 **	0.94 **

ns, *, and **: not significant, significant at $P < 0.05$, and significant at $P < 0.01$, respectively.

Table 3. Values of the P sorption parameters of Langmuir in control soils and soils treated with organic acids.

Soil no.	Treatment											
	Control			Malic acid			Citric acid			Oxalic acid		
	X_m mg kg ⁻¹	k L mg ⁻¹	R^2	X_m mg kg ⁻¹	k L mg ⁻¹	R^2	X_m mg kg ⁻¹	k L mg ⁻¹	R^2	X_m mg kg ⁻¹	k L mg ⁻¹	R^2
1	246.8	0.44	0.80**	-	-	0.42 ^{ns}	218.6	0.44	0.82**	219.1	0.19	0.57*
2	298.8	0.46	0.88**	205.2	0.42	0.88**	-	-	0.22 ^{ns}	-	-	0.01 ^{ns}
3	309.5	0.30	0.66*	-	-	0.30 ^{ns}	300.7	0.16	0.55*	-	-	0.39 ^{ns}
4	338.4	0.67	0.97**	-	-	0.22 ^{ns}	248.5	0.45	0.75*	249.6	0.31	0.63*
5	-	-	0.41 ^{ns}	-	-	0.10 ^{ns}	-	-	0.42 ^{ns}	-	-	0.25 ^{ns}

ns, *, and **: not significant, significant at $P < 0.05$, and significant at $P < 0.01$, respectively.

Table 4. Values of the exponent term n of the Freundlich equation in untreated soils (control) and soils treated with malic, citric, and oxalic acid.

Soil no.	Treatments			
	Control	Malic acid	Citric acid	Oxalic acid
1	1.50 a	1.26 c	1.40 b	1.13 d
2	1.49 a	1.28 b	1.13 c	0.98 d
3	1.34 a	0.91 c	1.14 b	0.86 c
4	1.58 a	1.29 c	1.44 b	1.10 d
5	1.07 a	0.70 b	1.05 a	0.67 b

Different letters in a row indicate a significant difference between means at $P < 0.05$.

The effect of organic acids was also significant on the Freundlich K_f coefficient ($P < 0.05$) (Table 5). The Freundlich K_f coefficient ranged from 27.83 to 83.93 in control soils. The range of K_f in soils treated with malic, citric, and oxalic acid was 11.87 to 55.06, 24.53 to 60.90, and 12.36 to 51.10, respectively. The presence of these organic acids significantly decreased the Freundlich K_f coefficient.

Effect of organic acids on the equilibrium P concentration and EBC

The equilibrium P concentrations of soils (EPCs) are presented in Table 6. The EPC, which is the intercept value at zero P sorption as determined from sorption isotherms, increased significantly in organic acid-treated soils compared to control soils ($P > 0.05$); however, the effect of oxalic acid was significantly greater than the effects of citric and malic acid. The

EPC of control soils ranged from 0.07 to 0.23 mg L⁻¹; in soils treated with malic, citric, and oxalic acid, it ranged from 0.16 to 0.51 mg L⁻¹, 0.16 to 0.37 mg L⁻¹, and 0.30 to 0.56 mg L⁻¹, respectively.

The P buffer capacity of the control soils varied from 28.81 to 49.50 L kg⁻¹, and it ranged from 29.71 to 39.87 L kg⁻¹, 31.21 to 38.02 L kg⁻¹, and 30.02 to 39.85 L kg⁻¹ in the soils treated with malic, citric, and oxalic acid, respectively (Table 7). The buffering capacity significantly decreased in some soils treated with organic acids ($P < 0.05$). Malic, citric, and oxalic acid had a similar effect on the EBC of soils 2 and 4, whereas the effect of oxalic acid was greater than the effects of citric and malic acid in soil 3.

The SPRs of the soils were calculated from the linear model (Table 8). The value of SPR ranged from 7.76 to 39.59 (average: 28.35) mg P kg⁻¹ for the control

Table 5. Values of the Freundlich coefficient K_f in untreated soils (control) and soils treated with malic, citric, and oxalic acid.

Soil no.	Treatments			
	Control	Malic acid	Citric acid	Oxalic acid
1	67.79 a	55.06 c	60.90 b	51.10 d
2	69.77 a	46.10 b	39.64 c	32.17 d
3	65.93 a	29.79 c	41.09 b	24.28 d
4	83.93 a	54.44 b	55.12 b	41.21 c
5	27.83 a	11.87 c	24.53 b	12.36 c

Different letters in a row indicate a significant difference between means at $P < 0.05$.

Table 6. Equilibrium solution P concentrations (mg L^{-1}) in control soils and soils treated with oxalic, citric, and malic acid.

Soil no.	Treatments			
	Control	Malic acid	Citric acid	Oxalic acid
1	0.10 c	0.20 b	0.16 b	0.30 a
2	0.08 d	0.16 c	0.24 b	0.46 a
3	0.09 c	0.51 a	0.23 b	0.52 a
4	0.07 c	0.17 b	0.17 b	0.23 a
5	0.23 c	0.51 a	0.37 b	0.56 a

Different letters indicate a significant difference between the means at $P < 0.05$.

Table 7. Equilibrium buffering capacity (L kg^{-1}) in control soils and soils treated with oxalic, citric, and malic acid.

Soil no.	Treatments			
	Control	Malic acid	Citric acid	Oxalic acid
1	40.72	39.87	38.02	39.85
2	42.21 a	31.51 b	35.21 b	34.13 b
3	43.36 a	37.59 b	36.74 b	33.07 c
4	49.50 a	39.31 b	35.86 b	39.55 b
5	28.81	29.71	31.21	30.02

Different letters indicate a significant difference between the means at $P < 0.05$.

Table 8. SPR (mg kg^{-1}) in control soils and soils treated with oxalic, citric, and malic acid.

Soil no.	Treatments			
	Control	Malic acid	Citric acid	Oxalic acid
1	31.33 a	23.78 b	24.46 b	23.06 b
2	32.53 a	21.29 b	12.84 c	7.68 d
3	30.54 a	2.49 c	12.43 b	1.31 c
4	39.59 a	13.56 c	22.38 b	13.06 c
5	7.76 a	-12.39 c	2.45 b	-11.78 c

Different letters indicate a significant difference between the means at $P < 0.05$.

soils, and in soils treated with malic, citric, and oxalic acid, it ranged from -12.39 to 23.78 (average: 9.74), 2.45 to 24.46 (average: 14.89), and -11.78 to 23.06 (average: 6.66) mg P kg^{-1} , respectively. However, the effect of oxalic acid on the SPR was greater than the effect produced by citric or malic acid. The P concentration reached sufficient levels for optimum plant growth in soil 5 with oxalic and malic acid treatments.

Discussion

Effects of LMWOAs on P sorption

Phosphate sorption was used here to include all of the processes (mainly adsorption and precipitation) resulting in the removal of phosphate from solutions (Castro and Torrent 1998). In calcareous soils, P sorption is greatly influenced by the sorption and precipitation reactions at calcium carbonate surfaces (Uygur 2009). Other researchers also found that P sorption increased significantly with increasing levels of added P (Akhtar et al. 2003). Our results indicate that LMWOAs (malic, citric, and oxalic acid) have the potential to decrease P sorption in the studied soils.

Effect of organic acids on the Freundlich constants n and K_f

The Freundlich equation is often considered to be purely empirical in nature, but it has been used extensively to describe the sorption of phosphate by soils (Arshad et al. 2000; Aslam et al. 2000). Bache and Williams (1971) indicated that sorption energy decreases exponentially with an increase in surface saturation with P. Bertrand et al. (2003) reported that the exponent term n of the Freundlich relationship that describes solid phase P and solution P at equilibrium was more than 1 for most of the studied soils. This indicates that the relationship is curvilinear and suggests that precipitation of P controls solution P concentrations in most soils.

A smaller value of K_f indicates higher amounts of plant-available P in the soil solution. The lowest and highest values of K_f were observed in soil 5 (sandy) and soil 4 (clayey-calcareous), respectively. The K_f value depends on the solution P concentration (Kuo and Lotse 1974) and, because of this, the value of K_f varied from soil to soil.

Effect of organic acids on EPC and EBC

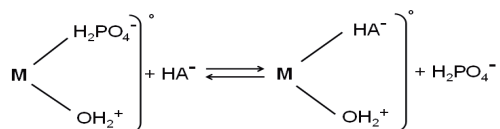
The linear model is an alternative to the Langmuir equation. The quantity/intensity (Q/I) model described by White and Beckett (1964) can be applied to determine P release from soil (Koski-Vähälä and Hartikainen 2001). To determine EPC and P EBC values, Q/I diagrams were plotted by using data in the linear model. The intercept of the line and the slope of the curve represent the EPC and EBC, respectively (curves not shown).

An estimate of EPC values was shown to be more highly related to plant growth than phosphate potential (Wild 1967). In the calcareous soils of northwestern Iran, a concentration of 0.4 mg P L^{-1} in the soil solution can cause maximum growth for most plants (Samadi 2006). The results showed that the EPC was lower than the critical level ($<0.4 \text{ mg L}^{-1}$) in control soils. However, in some soils treated with oxalic and malic acid, P at zero sorption was higher than 0.4 mg L^{-1} , indicating that these soils were able to supply a sufficient amount of P for optimum plant growth (Table 6). The EBC was obtained for each soil from the slope of the linear equation by plotting P sorbed against P concentration at equilibrium for the sorption-dominated part of the isotherm (Bertrand et al. 2003). The EBC of a soil is its ability to moderate changes in the P concentration of the solution phase. P buffer capacities can be related to both plant nutrition and environmental pollution. The greater the EBC of the soil, the higher the P fertilization required to increase the P concentration in the soil. The EBC values can be used to calculate the proportion of added fertilizer P that remains in the soil solution (Rowell 1994). The reciprocal of the EBC is the ratio of the amount of added P that remains in a solution to the amount that becomes sorbed.

Fox (1981) and Afif et al. (1993) indicated that $0.2\text{--}0.4 \text{ mg P L}^{-1}$ is an adequate external P requirement for most crops. The results showed that SPR, which is an estimate of P sorption potential (Wang et al. 2000), decreased significantly ($P > 0.05$) in soils treated with the studied organic acids compared to control soils (Table 8).

In general, organic acids were greatly efficient at decreasing the SPR in soils. Therefore, it seems apparent that in the presence of organic acids, the

amount of P sorption by soils will reduce the effect of the organic ligand depending on the acid strength and the number of carboxyl groups. Among these organic acids, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is a relatively strong acid. 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 with 3 and 2 carboxyl groups, respectively. The mechanism of P sorption in soil and minerals with variable charge was mainly ligand exchange reaction (Haynes and Swift 1989). This was similar to organic acid sorption (Violante and Gianfreda 1995), which can be expressed as:



where M is a metal surface, OH_2^+ and H_2PO_4^- are inorganic ligands, and HA is the organic ligand. The order of addition of the organic anion can influence the reaction, and according to the results, it seems that oxalic, malic, and citric acid are more efficiently and rapidly sorbed onto the soil surface than the phosphate.

In the current study, the effect of oxalic acid on P sorption parameters was greater than the effects produced by citric and malic acid. Khademi et al. (2009) reported that oxalate is slightly more effective than citrate in mobilizing P. Oxalate has a tendency to be precipitated readily in the presence of Ca^{2+}

(Ström et al. 2001) and reduce the content of active carbonates in calcareous soils. It is likely that oxalate was largely precipitated in our studies as Ca-oxalate. In calcareous soils, oxalic acid excretion leads to the dissolution of CaCO_3 and precipitation of Ca-oxalate in the zone of plant roots. In calcareous soils, oxalate may release P that is primarily held in Ca-phosphate minerals through the formation and precipitation of Ca-oxalate (Ström et al. 2001). In contrast, citrate, which has a relatively poor affinity for Ca^{2+} but a greater affinity for Fe^{3+} and Al^{3+} , may release the P predominantly held in Fe-phosphate and Al-phosphate minerals (Ström et al. 2002). This is supported by our experimental results.

The present results showed that added organic acids might cause changes in P sorption characteristics in calcareous soils. The effect of organic acids is likely to be dependent on the soil mineralogy, including soil physical and chemical properties and the type of organic acid. The SPRs in soils treated with organic acids were lower than in untreated soils, and the Freundlich K_f and n constants and the EBC decreased in treated soils. In addition, organic anions cause an increase in the P concentration of soil solution by solubilizing minerals and desorbing P from mineral surfaces. Along with the root exudates, added organic acids can compete with phosphate for binding the sorption sites in the soil, and they form stronger complexes with Al^{3+} , Fe^{3+} , and Ca^{+2} than phosphate does.

References

- Afif E, Matar A, Torrent J (1993) Availability of phosphate applied to calcareous soils of West Asia and North Africa. *Soil Sci Soc Am J* 57: 756-760.
- Akhtar MS, Richards BK, Medrano PA, DeGroot M, Steenhuis TS (2003) Dissolved phosphorus from undisturbed soil cores: related to adsorption strength, flow rate, or soil structure. *Soil Sci Soc Am J* 67: 458-470.
- Amapu IY, Chude VO, Singl U, Jubrin JM, Adam S (2000) Testing a dynamic phosphorus model in the sub-humid Nigeria savannah agro-ecology. In: Proceedings of the 26th Annual Conference of Soil Science Society of Nigeria, Ibadan, Nigeria, pp. 270-278.
- Arshad M, Rahmatullah, Salim M, Yousaf M (2000) Soil properties related to phosphorus sorption as described by modified Freundlich equation in some soils. *Int J Agri Biol* 2: 290-292.
- Aslam M, Sharif M, Rahmatullah, Yasin M (2000) Application of Freundlich adsorption isotherm to determine phosphorus requirement of several rice soils. *Int J Agri Biol* 2: 286-288.
- Bache BW, Williams EG (1971) A phosphate sorption index for soils. *J Soil Sci* 22: 289-301.
- Barrow NJ (1978) The description of phosphate adsorption curves. *J Soil Sci* 29: 447-462.
- Bertrand I, Holloway RE, Armstrong RD, McLaughlin MJ (2003) Chemical characteristics of phosphorus in alkaline soils from southern Australia. *Aust J Soil Res* 41: 61-76.
- Bubba MO, Arias CA, Porix H (2003) Phosphorus adsorption maximum of sands for use as media in subsurface flow cultivated reed beds as measured by the Langmuir adsorption isotherms. *Water Res* 37: 3390-3400.
- Castro B, Torrent J (1998) Phosphate sorption by calcareous Vertisols and Inceptisols as evaluated from extended P-sorption curves. *Eur J Soil Sci* 49: 661-667.

- Chen CR, Condon LM, Xu ZH (2008) Impacts of grassland afforestation with coniferous trees on soil phosphorus dynamics and associated microbial processes: a review. *For Ecol Manage* 255: 396-409.
- Franz M (2008) Phosphate fertilizer from sewage sludge ash (SSA). *Waste Manag* 28: 1809-1818.
- Fox RL (1981) External phosphorous requirements of crops. In: *Soil Testing and Plant Analysis*, 3rd ed. (Ed. RL Westerman). Soil Science Society of America, Madison, Wisconsin, USA, pp. 223-239.
- Gee GH, Bauder JW (1986) Particle size analysis. In: *Methods of Soil Analysis: Physical Properties* (Ed. A. Klute). Soil Science Society of America, Madison, Wisconsin, USA, pp. 383-411.
- Haynes RJ, Swift RS (1989) The effect of pH and drying on adsorption of phosphate by aluminum-organic matter associations. *J Soil Sci* 40: 773-781.
- Holford ICR (1982) The comparative significance and utility of the Freundlich and Langmuir parameters for characterizing sorption and plant availability of phosphate in soils. *Aust J Soil Res* 20: 233-242.
- Hue NV, Craddock GR, Adams F (1986) Effect of organic acids on aluminum toxicity in subsoils. *Soil Sci Soc Am J* 50: 28-34.
- Jones DL, Darrah PR (1994) Role of root derived organic acids in the mobilization of nutrients from the rhizosphere. *Plant Soil* 166: 247-57.
- Jones DL, Edwards AC, Donachie K, Darrah PR (1994) Role of proteinaceous amino acids released in root exudates in nutrient acquisition from the rhizosphere. *Plant Soil* 158: 183-192.
- Khademi Z, Jones DL, Malakouti MJ, Asadi F, Ardebili M (2009) Organic acid mediated nutrient extraction efficiency in three calcareous soils. *Australian J Soil Res* 47: 213-220.
- Koski-Vähälä J, Hartikainen H (2001) Assessment of the risk of phosphorus loading due to resuspended sediment. *J Environ Qual* 30: 960-966.
- Kuo S, Lotse EG (1974) Kinetics of phosphate adsorption and desorption by hematite and gibbsite. *Soil Sci* 116: 400-406.
- Lan M, Comerford NB, Fox TR (1995) Organic anions effect on phosphorus release from spodic horizons. *Soil Sci Soc Am J* 59: 1745-1749.
- Lunstrom US, Van Breemen N, Jongmans AG (1995) Evidence for microbial decomposition of organic acids during podzolization. *Eur J Soil Sci* 46: 489-496.
- Masayuki T, Aya K, Taku K, Masanori K (2010) Effect of organic ligands on phosphate adsorption and availability in Andisols of eastern Hokkaido, Japan. In: *Proceedings of the 19th World Conference of Soil Science, Brisbane, Australia*; published on DVD.
- McDowell RW, Condon LM, Stewart I (2008) An examination of potential extraction methods to assess plant-available organic phosphorus in soil. *Biol Fertil Soils* 44: 707-716.
- McDowell R, Sharpley A, Folmar G (2001) Phosphorus export from an agricultural watershed: linking source and transport mechanisms. *J Environ Qual* 30: 1587-1595.
- Murphy J, Riley JP (1962) A modified single solution method for determination of phosphate in natural waters. *Anal Chim Acta* 27: 31-36.
- Page AL, Miller RH, Keeney DR (1982) *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties (Agronomy)*, 2nd ed. Soil Science Society of America, Madison, Wisconsin, USA.
- Raghothama KG (1999) Phosphate acquisition. *Annu Rev Plant Physiol Plant Mol Biol* 50: 665-93.
- Randall PJ, Hayes JE, Hocking PJ, Richardson AE (2001) Root exudates in phosphorus acquisition by plants. In: *Plant Nutrient Acquisition: New Perspectives* (Eds. N Ae, J Arihara, K Okada, A Srinivasan). Springer-Verlag, Tokyo, pp. 71-100.
- Rayment GE, Higginson FR (1992) Oxalate-extractable iron, aluminum and silicon. In: *Australian Laboratory Handbook of Soil and Water Chemical Methods* (Eds. GE Rayment, FR Higginson). Inkata Press, Melbourne, Australia, pp. 253-256.
- Rowell DL (1994) *Soil Science: Methods and Applications*. Longman, London, UK.
- Samadi A (2006) Phosphorus sorption characteristics in relation to soil properties in calcareous soils of Western Azerbaijan province, Iran. *J Agric Sci Technol* 8: 251-264.
- Stevenson FJ (1994) *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed. John Wiley & Sons, New York.
- Ström L, Owen AG, Godbold DL, Jones DL (2001) Organic acid behavior in calcareous soil: sorption and biodegradation rates. *Soil Biol Biochem* 33: 2125-2133.
- Ström L, Owen AG, Godbold DL, Jones DL (2002) Organic acid mediated P mobilization in the rhizosphere and uptake by maize roots. *Soil Biol Biochem* 34: 703-710.
- Sui Y, Thompson ML, Shang C (1999) Fractionation of phosphorus in a Mollisol amended with biosolids. *Soil Sci Soc Am J* 63: 1174-1180.
- Uygur V (2009) Phosphate sorption in calcareous soils: the role of iron oxide and carbonates. *Asian J Chem* 21: 3001-3009.
- Violante A, Gianfreda L (1995) Adsorption of phosphate on variable charge mineral: competitive effect of organic ligands. In: *Environmental Impact of Soil Component Interactions, Vol. 2* (Eds. PM Huang, J Berthelin, JM Bollag, WB McGill, AL Page). CRC Press, Boca Raton, Florida, USA, pp. 29-38.
- Walkley A, Black IA (1934) An examination of Degtjareff method for determination soil organic matter and a proposed modification of the chromic acid titration method. *Exp Soil Sci* 79: 459-465.
- Wang X, Jackman JM, Yost RS, Linquist BA (2000) Predicting soil phosphorous buffer coefficients using potential sorption site density and soil aggregation. *Soil Sci Soc Am J* 64: 240-246.
- White RE, Beckett PHT (1964) Studies on the phosphate potentials of soils. *Plant Soil* 20: 1-16.
- Wild A (1967) Soluble phosphate in soil and uptake by plants. *Nature* 203: 326-324.
- Yang ZM, Sivaguru M, Horst WJ, Matsumoto H (2000) Aluminum tolerance is achieved by exudation of citric acid from roots of soybean (*Glycine max*). *Physiol Plant* 110: 72-77.
- Zhang TQ, MacKenzie AF, Liang BC (1995) Long-term changes in Mehlich-3 extractable P and K in a sandy clay loam soil under continuous corn (*Zea mays* L.). *Can J Soil Sci* 75: 361- 367.