

Phosphorus release from phosphate rock and iron phosphate by low-molecular-weight organic acids

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Abstract: Low-molecular-weight (LMW) organic acids widely exist in soils, particularly in the rhizosphere. A series of batch experiments were carried out to investigate the phosphorus release from rock phosphate and iron phosphate by low-molecular-weight organic acids. Results showed that citric acid had the highest capacity to solubilize P from both rock and iron phosphate. P solubilization from rock phosphate and iron phosphate resulted in net proton consumption. P release from rock phosphate was positively correlated with the pK_a values. P release from iron phosphate was positively correlated with Fe-organic acid stability constants except for aromatic acids, but was not correlated with pK_a . Increase in the concentrations of organic acids enhanced P solubilization from both rock and iron phosphate almost linearly. Addition of phenolic compounds further increased the P release from iron phosphate. Initial solution pH had much more substantial effect on P release from rock phosphate than from iron phosphate.

Keywords: organic acid; phosphate release; rhizosphere; rock phosphate; iron phosphate

Introduction

A range of low-molecular-weight (LMW) organic acids exist widely in soils, and have fundamental impacts on soil fertility, soil structure and bioavailability of nutrients/contaminants in soils. LMW organic acids are produced in soils from root activities, the decomposition of soil organic matter and microbial metabolism (Fox, 1990a). It is well documented that water-soluble LMW organic acids can facilitate the weathering of minerals and rocks through organometallic complex formation or metal chelation processes (Huang, 1972; Song, 1988; Hinsinger, 2001). Release of phosphorus (P) from sparingly soluble forms of P compounds, such as calcium (Ca)-, iron (Fe)- and aluminium (Al)-bound P by organic anions is of particular importance in plant P nutrition, especially in P deficient soils. Addition of LMW organic acids, such as citric and oxalic acids could significantly increase plant P uptake (Onthong, 1999). Root exudation of wide range of organic anions is a major response of plant roots to P deficiency (Neumann, 1999), a typical example being the exudation of citrate by roots of white lupin in response to P deficiency (Dinkelaker, 1989). Root colonisation by arbuscular mycorrhizal fungi (AMF) is known to improve plant P nutrition (Smith, 1997), and there is increasing evidence showing that the enhancement may involve P mobilisation by external hyphae of AMF (Strullu, 1981; Ness, 2000; Yao, 2001).

The ability of organic acids to release P from sparingly soluble compounds is related to their complexing capacities with various metal ions, such as Ca, iron and aluminium. For Al-P and phosphate rock, it has been suggested that P release may increase with Al stability constant ($\log K$) of the organic acid (Fox, 1990b; Kpombekou-A, 1994). However, it is unclear if P release from Fe-P is also related to Fe stability constants of organic acids, and if reductants (such as phenolic compounds) can further enhance the P release. Concentrations of organic acids and soil pH vary greatly in field soils depending on soil types and vegetation types, it is therefore necessary to examine the effects of pH

and concentrations of organic acids on P release from different P compounds. Furthermore, phenolic compounds exuded from plant roots, or produced by the decomposition of crop residues may facilitate the reduction of iron from Fe^{3+} to Fe^{2+} (Vempati, 1995), which may enhance the P release from Fe-P. Nevertheless, there is little information available on the effect of phenolics on P release from Fe-P.

The present study was to investigate the P solubilization by a range of organic acids with different complexing and chelating abilities from phosphate rock (PR) and ferric phosphate (Fe-P), and to examine the effects of concentrations of organic acids and solution pH on P release from these two compounds.

1 Materials and methods

The rock phosphate used in this study was from North Carolina (P content about 15.7%), it was ground to pass a 0.25 mm sieve. Iron phosphate (analytical grade) was purchased from BDH Chemicals Ltd. (Poole, England). Before the dissolution experiments, phosphate rock and iron phosphate were washed 10 times by distilled water to remove free phosphate. Washed phosphate rock and iron phosphate were dried at 100°C for 24 h, and were ground to pass a 0.25 mm sieve.

Nine LMW organic acids (namely acetic, lactic, malonic, malic, tartaric, oxalic, citric, *p*-hydro-benzoic and salicylic acids) and two phenolic compounds (namely catechol and hydroquinone) were purchased from BDH Chemicals Ltd. (Poole, England) and were all at analytical grades. Solutions of organic acids were prepared in either distilled water (for experiments on phosphate rock) or 0.05 mol/L NaCl solution (for experiments on iron phosphate) at various concentrations. The pH of each organic acid solution was measured using pH electrode.

● To compare the solubilizing capacities of the nine organic acids, organic acid concentration of 1 mmol/L was used;

● To study the effect of concentrations of organic acids (lactic, salicylic, malonic, oxalic and citric acids) on P solubilization, concentration levels of 0.1, 0.5, 1.0, 5.0 and 10.0 mmol/L were

used;

● To study the effect of initial solution on P solubilization, three typical organic acids were used, namely lactic, oxalic and citric acids (at concentration of 1 mmol/L). The initial pH was adjusted to 3, 4, 5 and 6 for phosphate rock, and 3.5, 4.5, 5.5 and 6.5 for iron phosphate using either HCl or KOH;

● To study the effect of phenolic compounds on P solubilization from iron phosphate, five organic acids (namely lactic, salicylic, malonic, oxalic and citric acids at concentrations of 0.1 mmol/L) and two phenolic compounds (catechol and hydroquinone at concentrations of 1 mmol/L) were used.

All experiments followed the same procedures, which were described briefly here. Weighed 0.075 g phosphate rock or iron phosphate were put in centrifuge tubes added with 30 ml organic acid solutions. Centrifuge tubes with the suspension were shaken in an end-over-end shaker for 24 h at 20°C. The suspension was centrifuged for 10 min at 6000 r/min and then filtered through No. 42 filter paper (Whatman, USA). The filtrate pH was determined by pH electrode. The phosphorus concentration in filtrate was determined by the ascorbic acid-NH₄-molybdate blue colour method (Murphey, 1962). Fe was determined by colorimetric method, using orthophenanthroline as colour developing reagent (Black, 1965). All experiments were conducted using duplicate.

2 Results and discussion

2.1 Phosphate rock (PR)

There are considerable differences in the capacities of nine organic acids in solubilizing P from PR (Fig. 1). Citric acid had the highest capacity, followed by oxalic and tartaric acids, while acetic and *p*-hydroxybenzoic acids had the lowest capacity. In some organic acids it has been demonstrated that the strength of an acid solution (dissociation constants, pK_a) is an important factor for P solubilization (Manley, 1986; Kpombekou-A, 1994). Results showed that there was a negative relationship between pK_a and P solubilization (Fig. 2, $p < 0.01$), except citric and tartaric acids. Citric acid has always been found to solubilize the highest amount of P from soils or PRs among the organic acids tested (Kpombekou-A, 1994; Bolan, 1994). It seems that the more carboxyl groups in the organic acid the higher amounts of P solubilization, which is in general agreement with the findings of Bolan *et al.* (Bolan, 1994). Solution pH increased significantly after the reaction indicating that P solubilization consumed protons to form HPO_4^{2-}

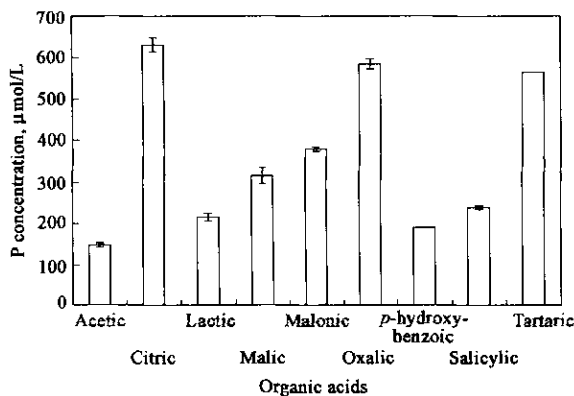


Fig. 1 P release from rock phosphate by nine types of organic acids

or $H_2PO_4^-$ (Table 1). The ΔpH values observed in our experiment were in agreement with those reported by Kpombekou-A and Tabatabai (Kpombekou-A, 1994).

Table 1 Increases in solution pH ($\Delta pH \pm$ standard errors) after the reactions between phosphate rock/iron phosphates with nine organics acids at concentration of 1000 $\mu\text{mol/L}$.

Organic acids	Increase in pH (ΔpH)	
	Phosphate rock	Iron phosphate
Acetic	2.91 ± 0.03	0.53 ± 0.02
Citric	2.33 ± 0.10	0.34 ± 0.01
Lactic	3.36 ± 0.03	0.67 ± 0.03
Malonic	3.08 ± 0.12	0.76 ± 0.00
Malic	2.95 ± 0.06	0.56 ± 0.00
Oxalic	3.60 ± 0.06	1.03 ± 0.02
<i>p</i> -hydroxybenzoic	2.98 ± 0.01	0.56 ± 0.01
Salicylic	3.63 ± 0.03	0.75 ± 0.02
Tartaric	3.15 ± 0.03	0.39 ± 0.02

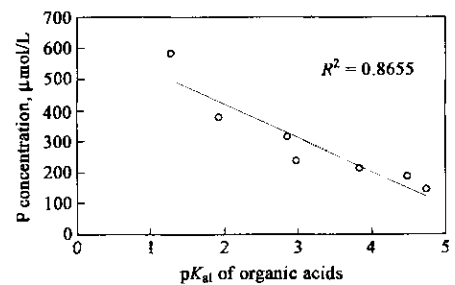


Fig. 2 The relationship between pK_a and P release from rock phosphate by organic acids

Increase in the concentrations of organic acids significantly enhanced P solubilization except oxalic acid (Fig. 3). The relationships between concentrations of organic acids and P solubilization were linear ($p < 0.001$). It is not clear why for oxalic acid at concentrations greater than 1 mmol/L increase did not result in a further enhancement in P solubilization. One possible explanation would be that when concentrations of oxalic acid increased, the precipitation of Ca oxalic on the surface of PR may prevent the further solubilization. In a previous study, Kpombekou-A and Tabatabai (1994) showed that P released from PRs was proportional to Ca released, except that oxalic acid always released more P than Ca indicating the possibility of co-precipitation of Ca and oxalate. However, in soil solutions even very close to the root surface, concentrations of organic acids are unlikely to be greater than

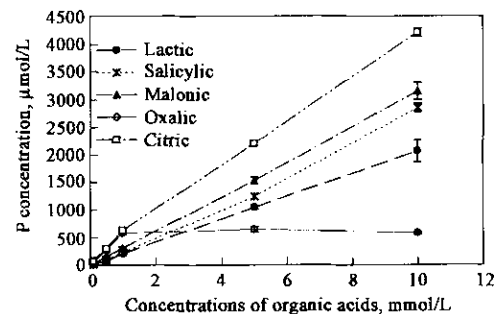


Fig. 3 Effect of the concentrations of organic acids in solution on P release from rock phosphate

1.5 mmol/L (Jones, 1996). Thus it is appropriate to say that within the normal range of concentrations of organic acids in soil solution, P solubilization is linearly related to the concentrations of organic acids.

Solution pH is another factor affecting P solubilization from PR. Increase in solution pH from 3 to 6 significantly reduced P solubilization by monocarboxylic, dicarboxylic and tricarboxylic acids, namely lactic, oxalic and citric acids (Fig. 4), however the effect was more pronounced in monocarboxylic and dicarboxylic acids than tricarboxylic acids. This is not surprising as more carboxylic groups means the organic acid has relatively higher capacity to complex or chelate metal ions, and the contribution from proton is less important.

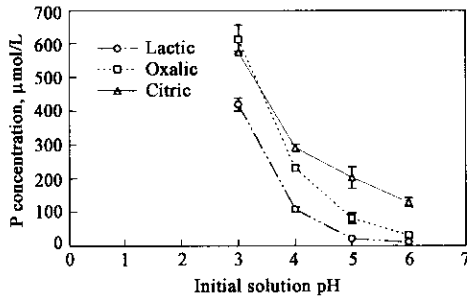


Fig. 4 Effect of solution pH on P release from rock phosphate by three types of organic acids

2.2 Iron phosphate (Fe-P)

P release from Fe-P has rarely been studied in details. Our results showed that capacities of organic acids to solubilize P from Fe-P differed significantly between acid types (Fig. 5). Citric acid again had the highest capacity to solubilize P, the amount of P solubilized by citric acid was almost twice the amount by oxalic acid. Monocarboxylic and aromatic carboxylic acids had the lowest capacity to solubilize P from Fe-P. The ranking of solubilizing capacities of organic acids for PR was not the same as for Fe-P (Figs. 1, 5). There was no significant relationship between pK_{a1} and P solubilization (data not shown) implying that strength of an acid in solution is not an important factor for P (or Fe) solubilization from Fe-P. The amounts of Fe released were generally lower than that of P released indicating that Fe may be reabsorbed on the particle surface or precipitated after being release from Fe-P. Acetic acid only released trace amount of Fe, and *p*-hydroxybenzoic, lactic, salicylic and tartaric acids released much lower amounts of Fe than P. Fe-organic acid stability constants were found to be positively correlated with P solubilization (Fig. 6) except the two aromatic acids. For example, the Fe stability constant for salicylic is 16.3, the highest among the acids tested, but its ability to solubilize P and Fe was among the lowest. Solution pH also increased after the reaction, but to a less extent than phosphate rock, probably due to the hydrolysis of Fe^{3+} , which produced protons (Table 1).

Increase in the concentrations of organic acids enhanced P solubilization by all organic acids tested (Fig. 7). However the magnitudes of increase for acetic, lactic and salicylic acids were much smaller than those for citric and oxalic acids. When the concentration was increased from 0.1 mmol/L to 10 mmol/L, P released by lactic acid only increased by about 100%, while P released by citric acid increased by 28 times. The effect of the initial pH of the solution on P solubilization was tested in four organics acids (Fig. 8), pH did not have much impact on P solubilization by lactic, malonic and oxalic acids, and

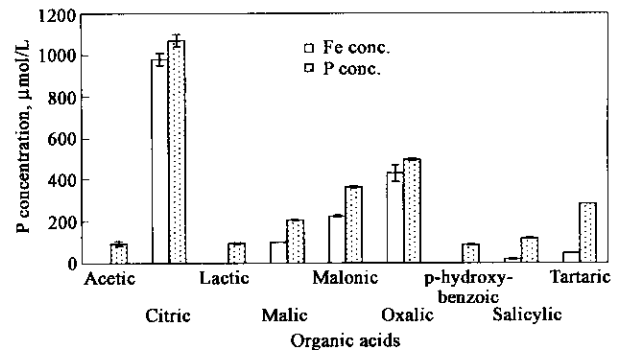


Fig. 5 P and Fe release from iron phosphate by nine types of organic acids

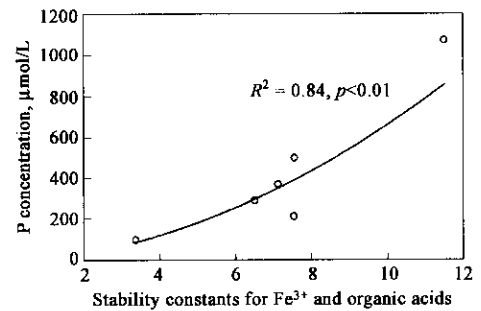


Fig. 6 The relationship between stability constants for Fe^{3+} and organic acids and P solubilization

increase in pH slightly decreased P solubilization by citric acid. In general, pH had much more pronounced effect on P solubilization from PRs than from Fe-P, which indicated that P solubilization from Fe-P is mainly through the complexation and chelation effects, while P solubilization from PRs is through acidification, complexation and chelation effects.

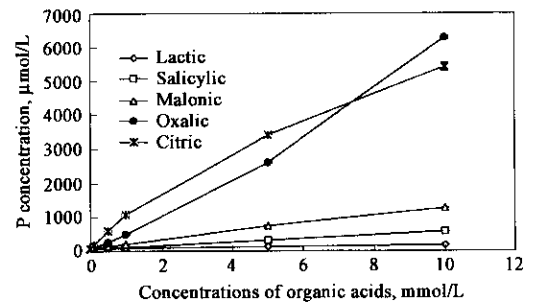


Fig. 7 P release from iron phosphate by organic acids at different concentrations

The effects of phenolic compounds on P release from Fe-P by 5 types of organic acids at concentration of 0.1 mmol/L are shown in Table 2. Addition of the two phenolic compounds, catechol and hydroquinone significantly increased the release of both P and Fe from Fe-P by all the organic acids tested indicating that phenolic compounds may be involved in the reduction of iron from Fe^{3+} to Fe^{2+} thereby increasing the solubility of Fe-P. Hydroquinone and catechol had similar ability in solubilizing P, but it seemed that hydroquinone released more Fe than catechol (Table 1). When concentrations of organic acids were increased to 1 mmol/L, the effect of phenolic compounds on P solubilization was marginal (data not shown). Exudation of phenolics by plant roots can occur in many plant species (Bekkara, 1998; Fletcher, 1995), the

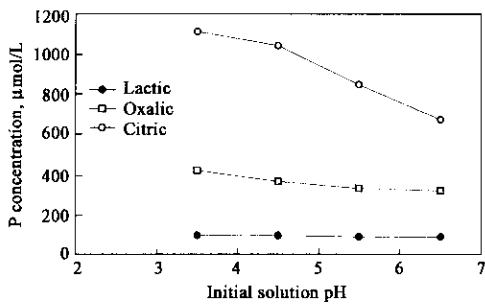


Fig. 8 Effect of solution pH on P solubilization from iron phosphate

results highlighted the potential importance of these phenolic compounds in plant P nutrition, particularly in highly weathered soils. As there is limited information available on the effects of root exudation of phenolic compounds on the solubility of Fe-bearing compounds, there is scope for further research on the potential role of these compounds in plant P nutrition in various plant species.

Table 2 Effect of phenolic compounds (1000 μmol/L) on P and Fe solubilization (μmol/L ± standard errors) from iron phosphate by different organic acids at concentration of 100 μmol/L

Organic acids	Fe	P
Lactic	Nd	85 ± 1
Lactic + catechol	14 ± 5	107 ± 5
Lactic + hydroquinone	21 ± 4	104 ± 2
Salicylic	Nd	90 ± 1
Salicylic + catechol	15 ± 5	108 ± 2
Salicylic + hydroquinone	22 ± 3	109 ± 1
Malonic	Nd	101 ± 2
Malonic + catechol	21 ± 0	118 ± 2
Malonic + hydroquinone	27 ± 2	113 ± 1
Oxalic	29 ± 0	120 ± 0
Oxalic + catechol	46 ± 3	152 ± 3
Oxalic + hydroquinone	34 ± 0	145 ± 1
Citric	53 ± 7	193 ± 0
Citric + catechol	63 ± 5	237 ± 12
Citric + hydroquinone	69 ± 5	230 ± 2

3 Conclusions

In summary, different types of low molecular weight organic acids had different ability to release P from both rock phosphate and iron phosphate. P release from rock phosphate is mainly related to the acid strength (pH) of the organic acid as well as the complexation and chelating effects; while P release from iron phosphate is largely due to the complexation and chelating effects of the organic acid. Increase in solution pH had much more pronounced effect on P solubilization from rock phosphate than from iron phosphate. Addition of phenolic compounds increase P solubilization from iron phosphate.

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