

Role of Organic Acids in Phosphate Mobilization from Iron Oxide

Sarah E. Johnson* and Richard H. Loeppert

ABSTRACT

Phosphate deficiency often limits crop production in acid tropical soils because of the strong bonding of phosphate by Fe and Al oxides. Organic-acid exudation from roots is one reported plant adaptation to P deficiency. The objective of this study was to predict the efficacy of this P-deficiency stress response in different soil types by investigating the mechanism of organic-acid-induced P mobilization from different oxide minerals. Greater proportions of Fe and initially adsorbed P were released from ferrihydrite when compared with goethite. More P was released and Fe dissolved at pH 4.0 than pH 5.5 or 7.0 from both oxides. For ferrihydrite, the order of effectiveness of the organic ligands for P release at pH 4 was citrate (19% of the total initially adsorbed P) > malate (14%) > tartrate (5%) >> oxalate = malonate = succinate (0.3–1.2%). For Fe release at pH 4, the order was oxalate (18% of total oxide suspension Fe dissolved) ≈ citrate (17%) > malonate (13%) > malate (8%) > tartrate (5%) >> succinate (0.02%). Faster phosphate readsorption in the case of oxalate than citrate probably accounted for the low apparent release of P by oxalate in spite of its greater Fe dissolution. At the smaller adsorbed-P concentration (1/4 of the adsorption maximum), the predominant mechanism of organic-acid induced P release was ligand-enhanced dissolution of the Fe oxide rather than ligand exchange. At 3/4 of the adsorption maximum, ligand exchange contributed to a greater extent to P release. Under low P-fertility conditions, organic-acid exudation would be more effective at increasing P availability in soils dominated by poorly crystalline than well-crystalline Fe oxides.

PHOSPHATE DEFICIENCY often limits crop production in acid tropical soils such as Oxisols, Ultisols, and Andisols. Oxisols and Ultisols contain predominantly well crystalline Fe oxides, such as goethite or gibbsite, and Andisols tend to be dominated by poorly crystalline oxides, such as allophane and ferrihydrite. Native P contents of these soils are often low, and P added as soluble fertilizer is strongly adsorbed to oxide surfaces, making it largely unavailable for plant use (Willett et al., 1988; Parfitt, 1989; Guzman et al., 1994). Inorganic phosphate is bound to Fe-oxide surfaces by an inner-sphere ligand-bonding mechanism (Mott, 1981; Tejedor-Tejedor and Anderson, 1990).

Some plants exhibit P-deficiency stress adaptations that enable them to mobilize poorly available P. These adaptations include exudation of organic acids such as citric, malic, malonic, oxalic, succinic, tartaric, and piscidic from the roots, for example, of pigeon pea (*Cajanus cajan* L.), radish (*Raphanus sativus* L.), rape (*Brassica nigra* L.),

barley (*Hordeum vulgare* L.), rice (*Oryza sativa*), and red clover (*trifolium pratense* L. cv. Hamidori) (Gerke and Meyer, 1995; Otani et al., 1996; Zhang et al., 1997; Kirk et al., 1999; Gahoonia et al., 2000); increased phosphatase activity on or near the root surface, for example, of lupin (*Lupinus albus* L. cv. Kievskij Mutant), tomato (*Lycopersicon esculentum* Mill. cv. Fukuju 2), and rape (Duff et al., 1991; Li et al., 1997); root structure modification (Dinkelaker et al., 1989; Johnson et al., 1996; Gilbert et al., 1997); increased activity of root plasma membrane high affinity phosphate transporters; and increased mycorrhizal association, for example, in tree legumes, potato (*Solanum tuberosum* L. cv. Russett Burbank), and red pine (*Pinus resinosa*) (Ralston and McBride, 1976; McArthur and Knowles, 1993; Surange and Kumar, 1993). Other plant species probably exhibit similar P-deficiency stress responses. The effectiveness and relative importance of each of the individual P-deficiency stress adaptations are influenced by both plant and soil characteristics. The organic acid exudation studies are the most relevant to the current study. Reported exudation rates include citrate exudation by rice roots into soil at 2 to 3% of the dry weight of the rice plant over a 14-d growth period (Kirk et al., 1999) and by barley into nutrient solution at 0.5% root dry weight per day (Gahoonia et al., 2000). In one attempt at using root exudation data from several experiments to develop a model of exudate concentration in soil solution as a function of distance from the root surface, it was concluded that at the root surface, organic acid concentration in soil solution would range from 70 to 200 $\mu\text{mol L}^{-1}$ under P-deficiency or Al-toxicity stress conditions (Jones et al., 1996).

There are two primary mechanisms by which inorganic phosphate might be released from Fe-oxide surfaces in the presence of organic Fe-complexing agents (ligands): (i) ligand exchange (Eq. [1]) and (ii) ligand-enhanced dissolution of the Fe oxide (Eq. [2]). Reductive dissolution of oxides can also occur in the presence of a reducing agent such as ascorbate, dithionite, or an oxidizable metal, or by photoreduction in the presence of oxalate (Ryan and Gschwend, 1991; Suter et al., 1991; Rueda et al., 1992; Stumm and Sulzberger, 1992; Sulzberger and Laubscher, 1995a, 1995b; Reyes and Torrent, 1997). Because there are few ready reductants in the dark root exudation environment of well-drained soils dominated by Fe oxides, except oxalate, which does not act as a reductant in the absence of light (Siffert and Sulzberger, 1991; Deng and Stumm, 1994), reductive dissolution is not considered to be a likely mechanism for release of inorganic P from oxide surfaces by organic acids exuded from roots as a P-deficiency stress response. Ligand exchange (Eq. [1]) is the process by which the organic ligand exchanges for inorganic P at a mineral surface site, thus releasing P into the soil solution (Nagarajah et al., 1968; Parfitt, 1979; Lopez-

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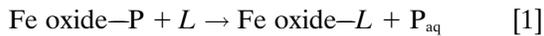
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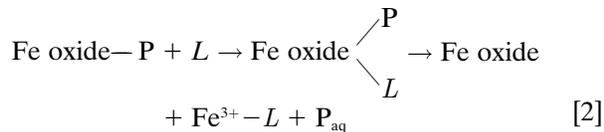
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Hernandez et al., 1986; Hue, 1991; He et al., 1994; Geelhoed et al., 1999):



where L = organic Fe-complexing agent (ligand) and P_{aq} = inorganic phosphate. In the process of ligand-enhanced dissolution (Eq. [2]), the organic ligand is adsorbed at a surface structural-Fe site, resulting in the slow dissolution of the Fe-oxide surface and release of adsorbed P to the soil solution (Earl et al., 1979; Ae et al., 1993; Jones et al., 1996; Kirk et al., 1999):



Both mechanisms involve the formation of surface Fe-ligand complexes. The relative effectiveness of specific organic acids in releasing P by either mechanism is related to the structural stability of the Fe-oxide surface site and the stabilities of the surface Fe^{3+} -ligand and dissolved Fe^{3+} -ligand complexes (Stumm and Furrer, 1987).

The objective of the current study was to investigate the comparative effectiveness of organic acids in P release from well crystalline versus poorly crystalline Fe oxides, and hence to evaluate the hypothetical effectiveness of organic acid release as a P-deficiency stress response in soils dominated by these two categories of Fe oxide. The goals were to elucidate the mechanism of organic acid induced P release, to determine the factors affecting this mechanism, and to assess the relevance of this mechanism to plant P nutrition. The effects of Fe-oxide crystallinity, pH, organic acid, and initial P-adsorption level on the release of P from Fe-oxide surfaces were evaluated. The two Fe oxides utilized in the current study were goethite (a well crystalline Fe oxide with the formula of $\gamma\text{-FeOOH}$) and ferrihydrite (a poorly crystalline Fe oxide with the structural formula $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$; Towe and Bradley, 1967), which are representative of the extremes of Fe-oxide crystallinity found in soils under oxidizing conditions. The three pH levels tested were 4.0, 5.5, and 7.0, which are representative of the pH range found in most tropical acid soils. Six organic acids (citric, malic, malonic, oxalic, succinic, and tartaric) were chosen, based on previous reports that these acids are exuded from the roots of some plants under P-deficiency stress conditions (Gerke and Meyer, 1995; Otani et al., 1996; Zhang et al., 1997; Gahoonia et al., 2000). Both oxides were compared at a low initial P-adsorption level (1/4 of maximum adsorption capacity), representing P-deficient soils. A comparison between P-deficient and P-fertilized soils was represented by using two different initial P-adsorption levels with goethite, 1/4 and 3/4 of maximum P adsorption.

MATERIALS AND METHODS

Iron Oxide Synthesis and Analysis

Goethite and poorly crystalline (2-line) ferrihydrite were synthesized from ferric nitrate by the methods of Schwertmann and

Cornell (1991). Following synthesis, the oxide suspensions were washed either by repeated centrifugation ($1400 \times g$) and resuspension in 0.1 M NaCl ionic strength buffer (for adsorption isotherms) or by dialysis using a 0.0025- μm membrane (for all other experiments). Iron-oxide suspension concentrations were determined by dissolution of 1-mL Fe-oxide suspension aliquots in 2 mL of concentrated HCl, followed by Fe analysis using a PerkinElmer (Norwalk, CT) 3100 flame atomic adsorption spectrophotometer. Iron-oxide identity was confirmed by powder x-ray diffraction (XRD), using a Philips Norelco (Briarcliff Manor, NY) diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. Fe oxide surface areas were measured by N_2 adsorption at liquid- N_2 temperature by means of a flow-through 3-point BET method using a Quantachrome (Syosset, NY) surface-area analyzer.

Phosphate Adsorption Isotherms

Phosphate adsorption isotherms were obtained for ferrihydrite and goethite at pH 4.0 (goethite only), 5.5, and 7.0, with suspensions containing 2.14 g Fe oxide L^{-1} and 0.1 mol NaCl L^{-1} . Phosphate concentration was increased until an apparent plateau was achieved on the adsorption isotherm (not shown), utilizing seven points between 0.027 and 0.213 mol P kg^{-1} Fe oxide for goethite and nine between 0.027 and 2.10 mol P kg^{-1} Fe oxide for ferrihydrite. Each individual phosphate treatment was replicated three times. The pH of each sample was adjusted to pH 4.0, 5.5, or 7.0 by pH-stat titration with 0.1 M HCl or 0.1 M NaOH for 2 min immediately after addition of phosphate and again after 1 h, using a Radiometer (Bronshøj, Denmark) TTT80 automatic titrator. The samples were agitated continuously on a rotary platform shaker for 24 h at 22°C, at which time they were centrifuged at $1400 \times g$ for 15 min followed by filtration of the supernate through a 0.22- μm nominal pore-size membrane filter. The amount of P in the supernate was analyzed by the phosphomolybdate colorimetric method of Murphy and Riley (1962) as described by Kuo (1996), using a Beckman (Fullerton, CA) DU 640B spectrophotometer. Phosphate adsorption was calculated as the difference between the initial P in solution and the P measured in the supernate after the adsorption reaction. The linear form of the Langmuir equation was used to determine the P adsorption maximum for each oxide at each pH.

Influence of Reaction Time on Phosphorus Desorption

Desorption experiments were performed with variable reaction time, with citrate added to ferrihydrite suspensions containing pre-adsorbed phosphate at pH 4.0. Citrate and ferrihydrite at pH 4.0 were chosen as the most likely combination for producing useful results, because pre-experiments had demonstrated easily measurable quantities of Fe dissolution and P release. Phosphate had been adsorbed onto the oxide in quantity sufficient to fill 1/4 of the potential P-binding sites as summarized in Table 1. The reactions were performed in the dark in 120-mL polypropylene bottles, each containing 85 mL ferrihydrite stock solution (8.4 g ferrihydrite L^{-1}) and 5.0 mL of phosphate stock solution (0.0642 M KH_2PO_4). Sample pH was maintained constant by pH-stat titration with 0.5 M HCl during the 24-h adsorption reaction before the initiation of the desorption reaction with the addition of the organic ligand. Fifteen milliliters of the suspension were removed (for a time = 0 measurement of C, Fe, and P) before addition of 10.0 mL of citrate stock solution (0.119 M citrate, pH 4.0). The exact volume of the solution, including titrant additions and periodic sample removal, was recorded for each timed sample throughout the experiment, and this volume was utilized in the calculation of P and Fe dissolution,

Table 1. Sample composition and component ratios at the end of the adsorption and beginning of the desorption reactions.

Iron oxides	P adsorption		Oxide sus- pension conc.	Initial P conc.	Initial organic acid conc.	Organic acid/P adsorption max.†	Organic acid/P adsorbed	Organic acid/total Fe
	P ads. max.‡	level						
	mol P kg ⁻¹		g L ⁻¹	mmol L ⁻¹	mol L ⁻¹	mol mol ⁻¹		
Goethite	0.085	0.021	7.14	0.15	0.0357	58.8	235	0.444
Goethite	0.085	0.064	7.14	0.46	0.0357	58.8	78.3	0.444
Ferrihydrite	1.8	0.45	7.14	3.2	0.0357‡	2.78	11.1	0.480

† P adsorption maxima were determined from the P adsorption isotherms at pH 5.5.

‡ For the kinetics experiment, 0.017 was used instead.

and citrate adsorption. At 1 min and then 1, 2, 6, and 26 h, 15.0-mL samples were removed from the reaction vessel and centrifuged (2900 × *g*). The amounts of Fe and P were measured by ICP as described below. This experiment was replicated three times. The concentration of dissolved citrate was measured by persulfate oxidation using an OI Analytical (College Station, TX) model 1010 wet oxidation total organic-C analyzer. In the presence of Fe, the amount of C measured by this method was accurate at ±10%.

Organic-Acid-Induced Phosphorus-Desorption Experiments

Enough P to fill approximately 1/4 (ferrihydrite and goethite) or 3/4 (goethite only) of the potential P-binding sites of each Fe oxide (as determined from the adsorption maxima at pH 5.5) was adsorbed for 24 h to the oxide. The adsorption reactions were performed in 40-mL polypropylene vials containing 17 mL of Fe-oxide stock suspension (8.4 g Fe oxide L⁻¹) and 1.0 mL phosphate stock solution (0.00304 *M* or 0.00912 *M* KH₂PO₄ for goethite; 0.0642 *M* KH₂PO₄ for ferrihydrite). The pH was adjusted at 15 min, 8 h, and 24 h after P addition to pH 4.0, 5.5, or 7.0 with 0.1 *M* HCl or 0.1 *M* NaOH. The desorption reactions were conducted in the dark with 2.0 mL of organic acid stock solution (0.357 *M* citric, malic, malonic, oxalic, succinic, or tartaric acid, procured in the fully protonated acidic form, and then preadjusted with dilute NaOH to pH 4.0, 5.5, or 7.0) or ionic-strength buffer (0.357 *M* NaCl) added at the beginning of the desorption reaction, after the initial 24-h P adsorption reaction. Desorption experiment sample component ratios are summarized in Table 1, and empirical formulas, molecular weights, and pK_s of the six organic acids are shown in Table 2. Upon addition of the organic acid or ionic-strength buffer solution, the suspensions were titrated continuously in the dark by pH stat for 28 min with 0.5 *M* HCl to maintain constant pH (4.0, 5.5, or 7.0), at which time each sample was immediately centrifuged at 2900 × *g* for 15 min and filtered through a 0.5-μm nominal pore-size membrane filter, stored until eight samples were accumulated (maximum waiting time of 1.5 h), and then centrifuged at 39 000 × *g* for 1 h. The latter centrifugation step

Table 2. Empirical formulas, molecular weights, pK_s, and log K_{Fe} values for the six organic acids.

Organic acid	Formula	M. W.	pK ₁ †	pK ₂ †	pK ₃ †	Log K _{Fe} †‡
		g mol ⁻¹				
Oxalic	(COOH) ₂	90	1.252	4.266	–	8.80
Malonic	CH ₂ (COOH) ₂	104	2.847	5.696	–	9.13
Succinic	(CH ₂) ₂ (COOH) ₂	118	4.207	5.636	–	8.49
Malic	CH ₂ CHOH(COOH) ₂	134	3.459	5.097	–	8.37
Tartaric	(CHOH) ₂ (COOH) ₂	150	3.036	4.366	–	6.95
Citric	C(OH)(COOH) ₂ (CH ₂ COOH) ₂	192	3.128	4.761	6.396	13.12

† NIST (1997).

‡ The complexes represented by these log K_{Fe} values are described by the following equation: M³⁺ + Lⁿ ↔ ML⁽³⁻ⁿ⁾⁺.

was performed to ensure the removal of any trace colloidal material that might affect the accurate determination of dissolved Fe and P. The solutions were analyzed for Fe and P using a Spectro Analytical Instruments (Kleve, Germany) FTP-08 axial inductively coupled plasma optical-emission spectrometer (ICP-OES). The entire experiment was conducted with three replications.

Theoretical Equilibrium Calculations

Equilibrium constants for the reactions of each of the six organic acids with Fe³⁺ and H⁺ were obtained from the NIST Standard Reference Database (NIST, 1997). These values were converted to activity constants using the Davies equation, and entered into the MINTQA2 speciation program (Allison et al., 1991), as recommended by Serkiz et al. (1996). The equilibrium constants for citrate are summarized in Table 3. The entire list of constants is presented in Johnson (1999). The MINTQA2 speciation program was used to generate ligand and Fe speciation data for equilibrium conditions corresponding to 0.0357 mol organic ligand kg⁻¹ solvent, the presence of infinite solid ferrihydrite or goethite, and a fixed ionic strength of 0.05, to simulate the experimental conditions over a pH range of 3 to 10. Also, experimentally measured values of total dissolved Fe, P, and citrate in solution following desorption reactions were entered into the MINTQA2 speciation program to calculate the saturation state with respect to Fe(III) oxide and Fe(III) phosphate phases.

RESULTS AND DISCUSSION

Phosphate Adsorption Isotherms

The phosphate adsorption isotherms (not shown) indicated greater P adsorption at lower pH due to the greater positive charge of the oxide surface (Goldberg and Sposito, 1984; Cornell and Schwertmann, 1996, p. 242), and greater P adsorption on ferrihydrite than goethite because of the greater surface area of the former (Borggaard, 1983). An adsorption plateau, indicating an approach to maximum adsorption, was observed for each isotherm with standard deviation of the three replicates much smaller than differences between pH treatments (average relative standard deviation of 0.36% for ferrihydrite and 1.8% for goethite). Adsorption maxima at pH 5.5, as determined from the linear form of the Langmuir equation (Table 4) were 1.89 and 0.084 mol P kg⁻¹ oxide for ferrihydrite and goethite, respectively.

The P adsorption maximum for each oxide at pH 5.5 was used to calculate the amount of phosphate added in subsequent desorption experiments to achieve the objective of approximately 1/4 and 3/4 of the maximum, representing low-P soils and P-fertilized soils, respectively. The initial P-adsorption level was kept the same

Table 3. Thermodynamic constants for equilibrium calculations involving citrate.

Species	NIST reaction [†]	NIST log K_{conc} mol L ⁻¹	μ_{\ddagger} for NIST	MINTEQA2 reaction (if different from NIST) [†]	Converted log K_{act} for MINTEQA2
Hcitrate ²⁻	[HL]/[L][H]	6.396	0.0	—	6.396
H ₂ citrate ¹⁻	[H ₂ L]/[HL][H]	4.761	0.0	[H ₂ L]/[L][H] ²	11.157
H ₃ citrate ⁰	[H ₃ L]/[H ₂ L][H]	3.128	0.0	[H ₃ L]/[L][H] ³	14.285
Fecitrate ⁰	[ML]/[M][L]	11.2	0.1	—	13.12
FeHcitrate ¹⁺	[MHL]/[M][HL]	6.7	0.1	[MHL]/[M][L][H]	14.4
Fe(citrateOH) ¹⁻	[MOHL]/[H][ML]	-2.7	0.1	[MOHL]/[H][M][L]	10.21
Fe ₂ (OH) ₂ citrate ₂ ²⁻	[M ₂ (OH) ₂ L ₂]/[H] ² [M] ² [L] ²	21.2	0.1	—	24.4

[†] M = Fe³⁺; H = H⁺; L = fully deprotonated ligand (with 3⁻ charge for citrate). Species in the numerator represent reaction products, and species in the denominator represent reactants.

[‡] M = ionic strength.

across all pH levels, resulting in a small variation between pH levels in the achievement of the 1/4 or 3/4 P adsorption objective (see Table 4). The pH 5.5 maximum P adsorption level was used in the calculations as a compromise between overloading of P in the pH 7 treatments or underloading in the pH 4 treatments. It was necessary to vary the absolute amount of P initially adsorbed on the two different iron oxides to prevent extreme under- or overloading, because of the twenty-fold difference in P sorption capacity between ferrihydrite and goethite (Table 4).

Influence of Reaction Time on Phosphate Release

The influence of time on citrate adsorption and on P and Fe release from ferrihydrite is summarized in Fig. 1. Citrate adsorption was rapid and reached about 35% of total added ligand within the first minute. After the first minute, citrate adsorption slowed appreciably but total adsorption increased to 45% over 26 h. Iron dissolution proceeded rapidly at first and reached its maximum value by about 3 h, after which time the concentration of Fe in solution remained essentially constant. During the time when the Fe oxide was dissolving rapidly (first 10–15 min), P concentration in solution was greatest. When the rate of Fe release decreased (15–180 min), P concentration in solution also decreased steadily. When Fe-oxide dissolution ceased (>3 h), P concentration in solution continued to decrease, until the minimum concentration was attained at approximately 6 h. The decrease in dissolved P indicated readsorption of P onto the Fe-oxide surface. Upon dissolution of the Fe oxide, new surface sites were generated and phosphate and the remaining free citrate competed for adsorption at these sites. Previous studies have shown that phosphate effectively competes with citrate for adsorption at Fe-oxide surfaces (Geelhoed et al., 1998). The correspondence in the current study between the initial Fe dissolution and P release supports the Fe-oxide dissolution mechanism

Table 4. Phosphate adsorption maxima estimated from Langmuir adsorption plots.

Fe oxide	pH	Langmuir adsorption maximum mol P kg ⁻¹ oxide
Ferrihydrite	5.5	1.89
Ferrihydrite	7.0	1.54
Goethite	4.0	0.113
Goethite	5.5	0.084
Goethite	7.0	0.067

(Eq. [2]) as the predominant cause of citrate-induced P release in the case of ferrihydrite at pH 4.

The results of the reaction-time experiment further illustrated the importance of both ligand-enhanced dissolution and P readsorption in the control of phosphate availability. In the soil/plant system, the plant would act as an active phosphate sink, so the possibility of P readsorption would be diminished. For this reason, to compare the relative effectiveness of different organic acid root exudates for increasing P availability to plants, it is necessary to compare them under non-equilibrium conditions, to maximize P mobilization and minimize P readsorption. Because the plant roots would “see” soil solution phosphate at the same time regardless of which ligand is present, it is necessary to compare ligands over the same reaction time. Based on the results summarized in Fig. 1, a reaction time of 30 min was selected.

Non-Equilibrium Comparisons of Oxide, pH, Ligand, and Phosphorus-Adsorption Level Effects on Phosphorus and Iron Release

Oxide

There was considerably greater relative P release (Fig. 2) and relative Fe dissolution (Fig. 3) from ferrihydrite than from goethite in the experiments designed to compare

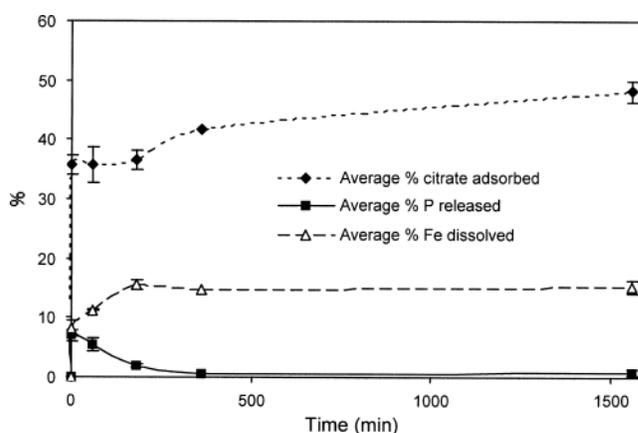


Fig. 1. Relationship between citrate adsorbed, P released, and Fe dissolved over time for citrate-induced P desorption from ferrihydrite at pH 4.0, 0.013 M citrate, and 7.14 g ferrihydrite L⁻¹. The initial P/citrate/P-adsorption maximum ratio was 0.25:1:1. Each data point represents the mean of three replications, with error bars representing standard error.

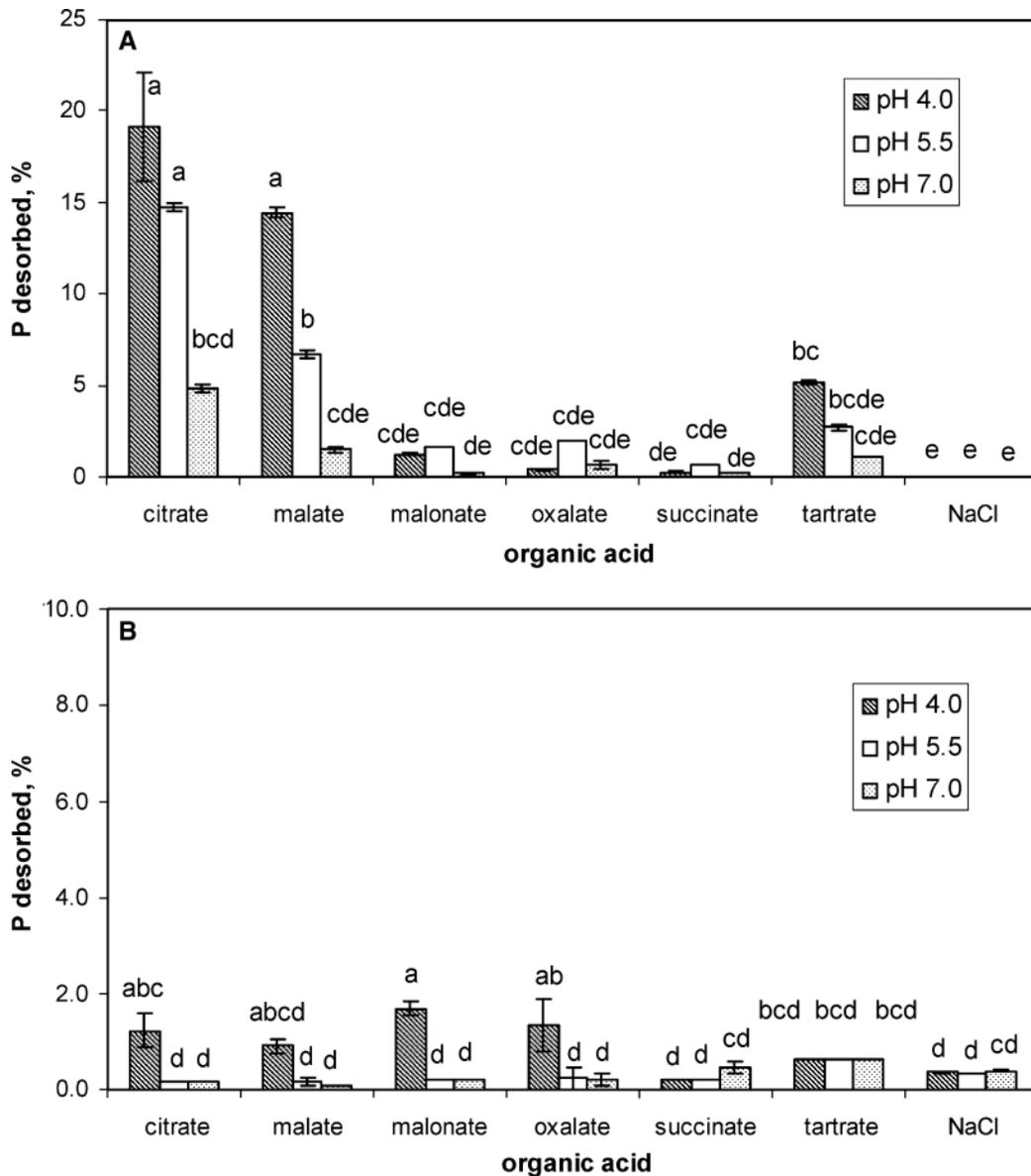


Fig. 2. Influence of pH on organic-acid induced P release from ferrihydrite (A) and goethite (B). Experimental conditions: 7.14-g oxide L⁻¹, 1/4 of P-adsorption maximum, 0.0357 M organic acid, and 28-min reaction at room temperature. Each bar represents the mean of three or more replications, with error bars representing standard error. Different letters represent significant differences by Tukey's at $\alpha = 0.05$.

oxide, ligand, and pH effects on non-equilibrium (28 min) P desorption. For example, at pH 4.0, about 19% of the initially adsorbed P was released (Fig. 2A) and 17% of Fe was dissolved (Fig. 3A) from ferrihydrite by citrate during the 28-min reaction, compared with only 1.2% P released (Fig. 2B) and 0.06% Fe dissolved (Fig. 3B) from goethite. The absolute amount of P released was also much greater (roughly 200 times greater) from ferrihydrite than from goethite. The greater concentration of dissolved Fe in solution in the case of ferrihydrite compared with goethite indicated that ligand-enhanced dissolution (Eq. [2]) was much greater in the case of ferrihydrite.

The property of Fe oxides that principally affects their reactivity is surface area (Borggaard, 1983). Greater surface area results in greater sorption capacity for species such as phosphate and organic anions (Borggaard, 1983), and also results in greater dissolution of Fe from

the surface (Cornell and Schwertmann, 1996, p. 199–200). BET surface areas were 34 and 310 m² g⁻¹ for goethite and 2-line ferrihydrite, respectively, which agreed well with the values reported in the literature for Fe oxides prepared under similar conditions (Cornell and Schwertmann, 1996, p. 95–96, 100; Clausen and Fabricius, 2001; Larsen and Postma, 2001). If the Fe dissolution results of the current study are normalized for surface area, there was still much greater dissolution (mol Fe m⁻² oxide surface area) of ferrihydrite than goethite at pH 4 (which is the only pH at which there was appreciable dissolution of goethite by any of the acids), that is, approximately 32, 12, and 8 times greater with citrate, malonate, and oxalate, respectively. The observation that more Fe was dissolved during the non-equilibrium reactions from surface-normalized ferrihydrite than goethite indicated that the surface dissolution was faster in

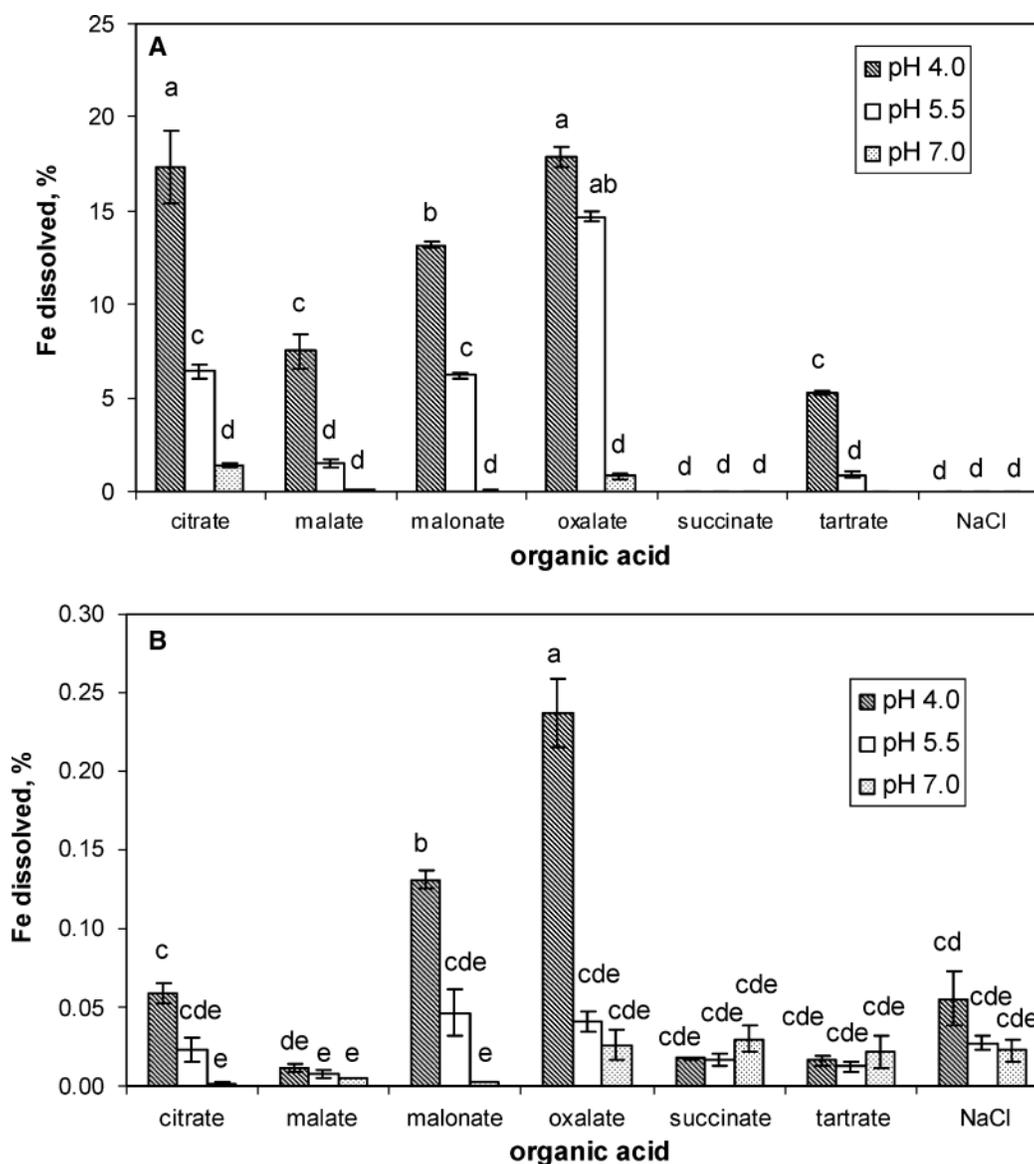


Fig. 3. Influence of pH on organic-acid induced Fe dissolution from ferrihydrite (A) and goethite (B). Experimental conditions: 7.14 g oxide L⁻¹, 1/4 of P-adsorption maximum, 0.0357 M organic acid, and 28-min reaction at room temperature. Each bar represents the mean of three or more replications, with error bars representing standard error. Different letters represent significant differences by Tukey's at $\alpha = 0.05$.

the case of ferrihydrite. If the P adsorption maximum is normalized for surface area (mol P m⁻² oxide surface area), then P adsorption was approximately 2.5 times greater for ferrihydrite than for goethite. By normalizing the initial P adsorption level of goethite and ferrihydrite based on their P adsorption maxima, it was possible to compare the desorption behavior of the respective oxides.

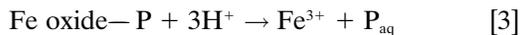
The comparison between ferrihydrite and goethite of Fe and P release supported both the dissolution (Eq. [2]) and ligand-exchange (Eq. [1]) mechanisms of P release. The much greater amounts of Fe dissolved and P released from ferrihydrite than from goethite (both in absolute terms and in percentage of the P adsorption maxima) (Fig. 2 and 3) was consistent with the ligand-enhanced dissolution mechanism of P release (Eq. [2]). Additionally, because phosphate adsorption was only at 1/4 of its maxima, there were surface sites left for

organic ligand adsorption. Because surface site density is greater for ferrihydrite than for goethite (Clausen and Fabricius, 2001), there were a greater number of surface sites available in the case of ferrihydrite for organic ligand adsorption after filling 1/4 with phosphate. The ligands did not compete directly with phosphate for the same sites on either oxide, but there was even less competition on ferrihydrite than goethite. Without such direct competition, ligand exchange was not expected to be significant. If ligand exchange were the primary mechanism of P release, more P release would have been predicted from goethite than ferrihydrite under these experimental conditions due to a greater concentration of organic ligand relative to adsorbed phosphate and available surface sites. Therefore, the observation of greater P release from ferrihydrite suggests that dissolution was the most important mechanism for P release.

There is one argument from kinetics that leaves open the possibility that the P-release trends in the current study might also be consistent with the ligand-exchange mechanism (Eq. [1]). Previous studies, as discussed by Mott (1981), have shown that the rate-limiting step of ligand-exchange reactions involving bound phosphate (Eq. [1]) is the breaking of the bond between phosphate and the oxide surface rather than the initial formation of a bond between the adsorbing exchange ligand and the surface. Therefore, the rate of P exchange from an oxide surface is dependent on the concentration of P on the surface rather than the concentration of the dissolved exchanging ligand. The absolute concentration of adsorbed P was much greater with ferrihydrite than goethite in the current study (Table 1), although the P ratios relative to the adsorption maxima of the different oxides were the same. Hence, the rate of release of P from ferrihydrite should be greater than that from goethite, if the reaction were a ligand-exchange reaction under kinetic control, that is, had not yet reached equilibrium. Over the same reaction time (30 min), more P was indeed released from ferrihydrite (Fig. 2). The experimental observation of greater P release from ferrihydrite than goethite might therefore be partially explained by the greater concentration of adsorbed P and hence greater amount of ligand-exchange (Eq. [1]) per unit weight of oxide.

pH

There was a consistent trend across both oxides and all organic ligands that when there was a significant ($P < 0.05$) pH effect, P release (Fig. 2), and Fe dissolution (Fig. 3) increased with decreasing pH. The effect of pH on ligand-promoted dissolution has been studied extensively (Cornell and Schwertmann, 1996, p. 272–275). In the current study, there was no evidence for proton-promoted dissolution (Eq. [3]) in the absence of an organic ligand, as demonstrated by the negligible Fe dissolution in the NaCl blank (Fig. 3).



The small amount (0.05% of total) of dissolved Fe in the NaCl blank in Fig. 3b most likely represented ultrafine grains of goethite. Ligand-promoted dissolution is caused primarily by ligand adsorption and subsequent detachment of Fe(III)-ligand complexes from the oxide surface. Low pH enhances this process because of protonation of OH groups on the oxide surface, which weakens the structural Fe-O bonds. Protonation also promotes ligand adsorption due to the relative ease of replacement/exchange of H₂O compared with OH⁻ from the positively charged surface in the case of inner-sphere ligand adsorption, or by the greater positive charge at the oxide surface in the case of outer-sphere adsorption (Cornell and Schwertmann, 1996, p. 272–273). A concurrent pH effect is that the ligands become more protonated at low pH, resulting in a less negative charge and a tendency toward less adsorption to the positively charged surface, in the case of outersphere adsorption. Therefore, there is often a pH

at which maximum dissolution occurs and below which dissolution decreases again (Cornell and Schwertmann, 1996, p. 273). The lowest pH (4.0) utilized in the current study, which was designed to represent the pH of some acidic soils, was greater than the lowest pK of most of the acids tested (Table 2), so the ligands were still significantly negatively charged and a decrease in dissolution at low pH was not observed. The exception was succinic acid, which is fully protonated at pH 4, and which did not result in Fe-oxide dissolution at any of the pH values, possibly for other reasons besides its full protonation state, as discussed below.

The effect of pH on P and Fe release was consistent with both the ligand-exchange and dissolution mechanisms (Eq. [1] and [2]), because ligand adsorption onto the surface is important for both mechanisms and is likely promoted by decreasing pH. The results of the current study, that P release increased with decreasing pH (Fig. 2) were consistent with a previous study in which citrate was more effective in reducing phosphate adsorption by goethite at low pH than at high pH, although there was more total P adsorption with or without citrate at low pH (Geelhoed et al., 1998). Table 5 shows the Fe/P molar ratio in solution at the end of the 28-min desorption reactions. In general, high Fe/P ratios (>10) supported the dissolution mechanism of P release, while low ones (<1) supported the ligand-exchange mechanism. At very low levels of dissolved Fe (<0.1 mg L⁻¹), the Fe/P ratio was not very meaningful, so the ratios for the higher pH levels for the smaller P-adsorption level of goethite were omitted from Table 5, as well as most of the ratios from succinate data. The Fe/P ratios were generally greater at lower pH, except in the case of oxalate with goethite at the smaller P-adsorption level, in which case the ratio was significantly higher ($P < 0.05$) at pH 5.5 than at pH 4.0. The observation of high Fe/P ratios (>100) at both pH levels for the oxalate/goethite combination indicated that dissolution was quite important at both pH levels. One possible interpretation of the general trend of higher Fe/P ratios at lower pH is that the dissolution mechanism of P release was more important

Table 5. Fe/P mole ratio in solution after the end of the 28-min desorption reactions. Experimental conditions were as follows: 0.0357 mol organic acid L⁻¹, 7.14 g oxide L⁻¹, low (1/4 potential P-adsorption sites filled) and high (3/4 potential P-adsorption sites filled) levels of P. Each data point represents an average of at least three replicates.

Organic acid	Ferrihydrite low P†			Goethite low P†			Goethite high P†	
	pH 4.0	pH 5.5	pH 7.0	pH 4.0	pH 5.5	pH 7.0	pH 4.0	pH 5.5
	Fe/P mole ratio‡							
citrate	22 cd	9.3 cd	6.5 cd	30 b	74 b	–	0.51 b	–
malate	12 cd	5.3 d	1.5 d	–	–	–	0.87 ab	–
malonate	250 b	86 c	–	41 b	110 b	–	3.5 ab	0.85 ab
oxalate	1000 a	170 b	31 cd	130 b	770 a	–	6.2 ab	2.7 ab
succinate	–	–	–	–	–	–	5.4 ab	–
tartrate	24 cd	7.6 cd	0.78 d	–	–	–	1.2 ab	–

† Different letters within a section (ferrihydrite low P; goethite low P; goethite high P) represent significant differences by Tukey's test at $\alpha = 0.05$.

‡ Where measurable Fe values were too low to calculate meaningful Fe/P ratios, no ratio is provided.

at lower pH and that both dissolution and ligand exchange were operative as pH increased. This interpretation was supported by the observation that dissolution was greater at low pH. However, the ligand adsorption necessary to cause ligand exchange is also expected to be greater at low pH.

Organic Ligand

Citrate and malate released P from ferrihydrite more effectively than the other acids (Fig. 2A). At the smaller initial P-adsorption level (1/4 of the P-adsorption maximum), there was no detectable P release from goethite at pH 5.5 and 7.0, but at pH 4.0, there were small but detectable amounts of P released by malonate, oxalate, citrate, and malate (Fig. 2B).

Citrate and malate were also among the most effective acids in dissolving Fe from ferrihydrite (Fig. 3A). Oxalate dissolved a similar amount of Fe from ferrihydrite, but without releasing nearly as much P as did citrate and malate (Fig. 3A and 2A, respectively). None of the acids dissolved much Fe from goethite, but oxalate and malonate resulted in the greatest dissolution of Fe (Fig. 3B), as they similarly were in the group of acids that released the most phosphate (Fig. 2B).

The relationship between organic acid structure (Table 2) and Fe dissolution is affected by the stabilities of both the ligand/surface complex and the subsequently dissolved Fe³⁺-ligand complex. Stumm et al. (1985) demonstrated the dissolution rates with ligands that form bidentate mononuclear complexes with surface Al³⁺ in Al oxides decreases from five- to six- to seven-membered rings, and that bidentate ligands adsorb faster than monodentate ligands. In a non-equilibrium system in which the rate-limiting dissolution step is detachment of the ligand-Fe³⁺ complex from the surface, increasing stability of the ring structure of the complex results in an increased rate of Fe release to solution (Stumm et al., 1985). In the current study, oxalate formed a five-membered ring, malonate a six-membered ring, and succinate, malate, and tartrate each formed 7-membered rings, which explained the Fe dissolution trends of the dicarboxylic acids shown in Fig. 3, with the exception of succinate, which resulted in much less desorption than malate and tartrate. A recent infrared spectroscopy study of dicarboxylic acids adsorbed to hematite indicated that while oxalate and malonate formed bidentate mononuclear complexes with Fe³⁺, succinate formed a monodentate surface complex (Duckworth and Martin, 2001). In the current study, there was no measurable dissolution of the oxide in the case of succinate (Fig. 3). Citrate was the only tricarboxylic acid tested in the current study, and it has been previously proposed, based on an infrared study of citrate adsorption on goethite, that each of citrate's three carboxyl groups is bound to a different Fe atom on the surface (Cornell and Schindler, 1980). The relative amounts of Fe dissolved from ferrihydrite and goethite by the different organic ligands at the different pH values agreed well with an oxide dissolution study by Miller et al. (1986).

It would be impossible to dissolve appreciable surface Fe without the concomitant release of adsorbed P from the affected surface sites into solution. Yet oxalate resulted in a relatively large amount of Fe dissolution, nearly 20% of total Fe in the case of ferrihydrite (Fig. 3), without a correspondingly large level of P release (Fig. 2). This anomaly was also demonstrated by its very high Fe/P mole ratios (100–1000) in solution (Table 5). Perhaps for oxalate, the reaction had already proceeded to the point at which a significant amount of P was re-adsorbed, for example, as with citrate in Fig. 1. If the primary mechanism of P release is ligand exchange, it might be expected that some acids that are not as effective at dissolution (e.g., succinate) would still be adsorbed and result in some release of P into solution. Because substantial P release with low Fe dissolution was not observed with any of the acids, the trends relating to organic acid effects on Fe and P release supported oxide dissolution (Eq. [2]) as the primary mechanism of P release. The high Fe/P molar ratios in solution following the 28-min reaction (Table 5) supported the dissolution mechanism of P release. The conclusion that citrate releases P by dissolution of the oxide surface (especially at low pH) is in agreement with the results of Earl et al. (1979), who obtained a linear relationship between P and (Fe + Al) in suspensions of soils treated with citrate. Kirk et al. (1999) also concluded through a combined experimental and modeling approach that the release of P by citrate was predominantly attributable to surface dissolution of oxide rather than ligand exchange. A possible interpretation of the P/Fe relationships is that citrate, malate, and oxalate each resulted in P release by dissolution of the oxide (Eq. [2]), but differed in their competition with P for re-adsorption at newly exposed Fe sites on the oxide surface. For example, oxalate likely resulted in the release of P during rapid dissolution of the oxide, but did not compete as effectively as citrate with P for re-adsorption at the freshly exposed surface sites.

Greater Phosphorus-Adsorption Level on Goethite

Because total P release from goethite at the 1/4 capacity initial P loading level was very low (<2%) (Fig. 2), a new experiment was designed to determine if OA might affect P release at greater initial P levels, representing P-fertilized soils. More P was released from goethite at the greater initial P-adsorption level (3/4 of the P-adsorption maximum) than at the smaller initial P-adsorption level (1/4 of the P-adsorption maximum) (Table 6). A corresponding increase in Fe dissolution at the greater P level was not observed, implying that ligand-enhanced dissolution of the oxide surface (Eq. [2]) was not an adequate explanation for the greater P release at the higher initial P level. On the contrary, for three of the four acids that effected Fe dissolution at pH 4 at the smaller P-adsorption level, Fe dissolution decreased significantly at the greater phosphate level (citrate, malonate, and oxalate, Table 6). Eick et al. (1999) found that pre-adsorbed chromate and arsenate inhibited the oxalate-induced dissolution of goethite, presumably by decreasing the initial

Table 6. Phosphate desorption and Fe dissolution from goethite at low (1/4 potential P-adsorption sites filled) and high (3/4 potential P-adsorption sites filled) levels of P for each organic acid, at pH 4.0 and 5.5, 0.0357 mol organic acid L⁻¹, 7.14 g oxide L⁻¹, and 28 min reaction time. Each data point represents the mean of at least three replicates.

Organic acid	Phosphate desorbed [†]				Fe dissolved [†]			
	Low phosphate		High phosphate		Low phosphate		High phosphate	
	pH 4.0	pH 5.5	pH 4.0	pH 5.5	pH 4.0	pH 5.5	pH 4.0	pH 5.5
	% of initial P				% of total Fe in oxide suspension			
citrate	1.22 fg	0.18 g	5.48 ab	5.30 ab	0.059 cde	0.023 efgh	0.016 gh	0.011 gh
malate	0.91 fg	0.18 g	4.57 abc	4.93 abc	0.012 gh	0.007 h	0.022 efgh	0.006 h
malonate	1.70 efg	0.24 g	3.35 cde	4.50 abc	0.13 b	0.046 cdefg	0.065 cd	0.021 efgh
oxalate	1.34 fg	0.24 g	4.08 bcd	4.75 abc	0.24 a	0.041 cdefgh	0.14 b	0.072 c
succinate	0.18 g	0.18 g	1.58 fg	4.69 abc	0.017 fgh	0.017 gh	0.007 h	0.008 gh
tartrate	0.61 g	0.61 g	3.53 cd	5.97 a	0.016 gh	0.013 gh	0.024 efgh	0.004 h

[†] Different letters within a section (phosphate desorbed vs. Fe dissolved) represent significant differences by Tukey's test at $\alpha = 0.05$.

oxalate adsorption. It is possible that at the greater level of phosphate surface coverage in the current study, there was less oxalate adsorption, resulting in a lower rate of Fe-oxide dissolution. However, if oxalate could not compete with phosphate at the surface to cause dissolution, it is not likely that it could compete with phosphate in a ligand exchange reaction, either. A comparison of the Fe/P molar ratios in solution after the 28-min desorption reactions in the case of goethite (Table 5) indicated that they were much lower (<10) at the high initial P concentration than at the low P concentration (>30). Low Fe/P ratios indicated that ligand-exchange (Eq. [1]) might have been an important P release mechanism. Another possible explanation for the differences in P desorption between high and low initial P-adsorption levels was that at smaller initial P-adsorption levels, the phosphate is bound very tightly to specific P-binding sites, making it difficult to desorb via ligand exchange with the organic ligands. Once these high-affinity sites are filled, additional P might be bound somewhat less strongly to other P-adsorption sites, from which it is possible to competitively desorb P by ligand exchange with the organic ligands (Parfitt, 1989; Katz and Hayes, 1995; Scheidegger and Sparks, 1996). The 3 to 5% P desorption from goethite at the greater initial P level was in agreement with observations of Parfitt (1979), in which 2 to 7% of P was desorbed by citrate and oxalate at high initial P levels (100% of the P-adsorption maximum). While 3 to 5% P desorption from goethite (Table 6) at the greater initial P level was not as large as the 15 to 20% P release from ferrihydrite at the smaller initial P levels (Fig. 2A), it might be enough to significantly enhance plant P uptake from P-fertilized soils that are dominated by well crystalline iron oxides.

Theoretical Equilibrium Calculations of Iron Solubility

Theoretical equilibrium calculations revealed that the lower solubility of goethite compared with ferrihydrite results in lower equilibrium concentrations of the Fe-organic complexes and total dissolved Fe for goethite compared with ferrihydrite across the entire pH range of 3 to 10 (Fig. 4). Results are shown only for citrate in Fig. 4, but the trends were similar across all acids (Johnson, 1999). The pH ranges of soluble citrate-complexed Fe and of high total-soluble Fe extend sev-

eral pH units higher with ferrihydrite than with goethite (Fig. 4). That is, in the case of ferrihydrite, citrate strongly impacts Fe solubility at pH values up to 9, compared with pH 5.5 in the case of goethite. This result implied that citrate would be considerably more effective in increasing Fe solubility and possibly P release from ferrihydrite than from goethite, especially at pH > 5 . The MINTEQA2 generated theoretical equilibrium levels of total Fe in solution in the presence of each organic ligand indicated that citrate, tartrate, and malate would dissolve the most Fe from ferrihydrite, with slightly more Fe dissolution at pH 4.0 than at pH 7.0

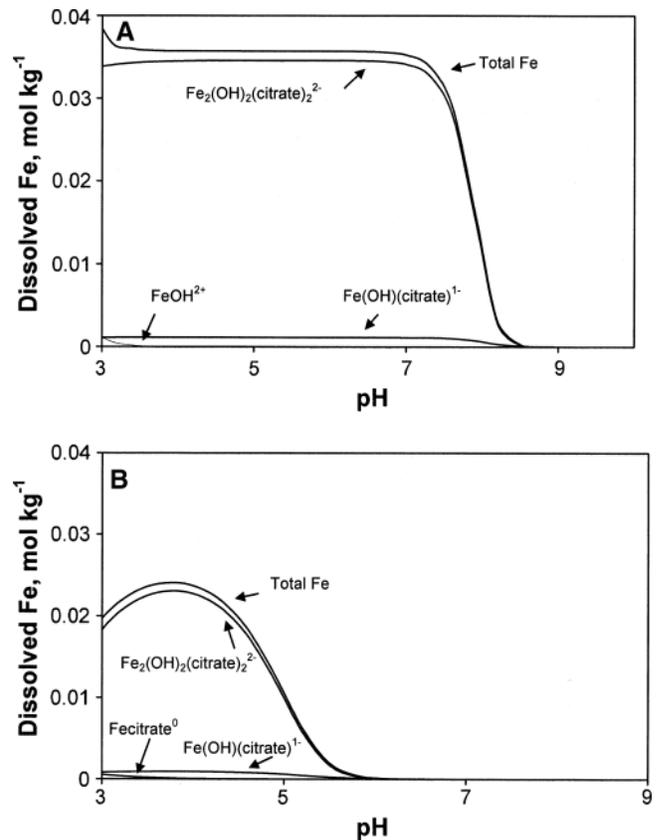


Fig. 4. Influence of pH on concentrations of Fe-containing species and total Fe in equilibrium with ferrihydrite (A) and goethite (B), at 0.0357 M citrate. All calculations were made using MINTEQA2, at 0.05 ionic strength.

(Fig. 5A). Succinate would be expected to dissolve almost no Fe at pH 5.5 and 7.0. In the case of goethite, citrate and oxalate would be expected to dissolve a greater amount of Fe compared with the other ligands, with significantly more Fe dissolution at pH 4.0 than at pH 7.0 (Fig. 5B).

The theoretically calculated equilibrium relationships of the experimental systems represented in Fig. 2 and 3 are summarized in Table 7. This comparison of theoretical equilibrium calculations and the non-equilibrium experimental results provides information about how far each reaction system had proceeded toward equilibrium during the 28-min experiment. In all cases, the experimental systems were undersaturated with respect

to the Fe oxide. The systems were also generally undersaturated with respect to strengite (FePO_4), which means that it is unlikely that ferric phosphate precipitation occurred during the experiment. In almost all cases, the experimental approach to the theoretical equilibrium Fe dissolution (indicated by the percent of total theoretical soluble Fe dissolved during the experiment, Table 7) was closer at pH 4.0 than at the higher pH values and was closer for ferrihydrite than goethite. This result indicated more rapid Fe-oxide dissolution kinetics at pH 4 compared with pH 7. The reactions of oxalate, citrate, and malonate proceeded toward equilibrium faster than the reactions of the other ligands, especially faster than tartrate and succinate (Table 7).

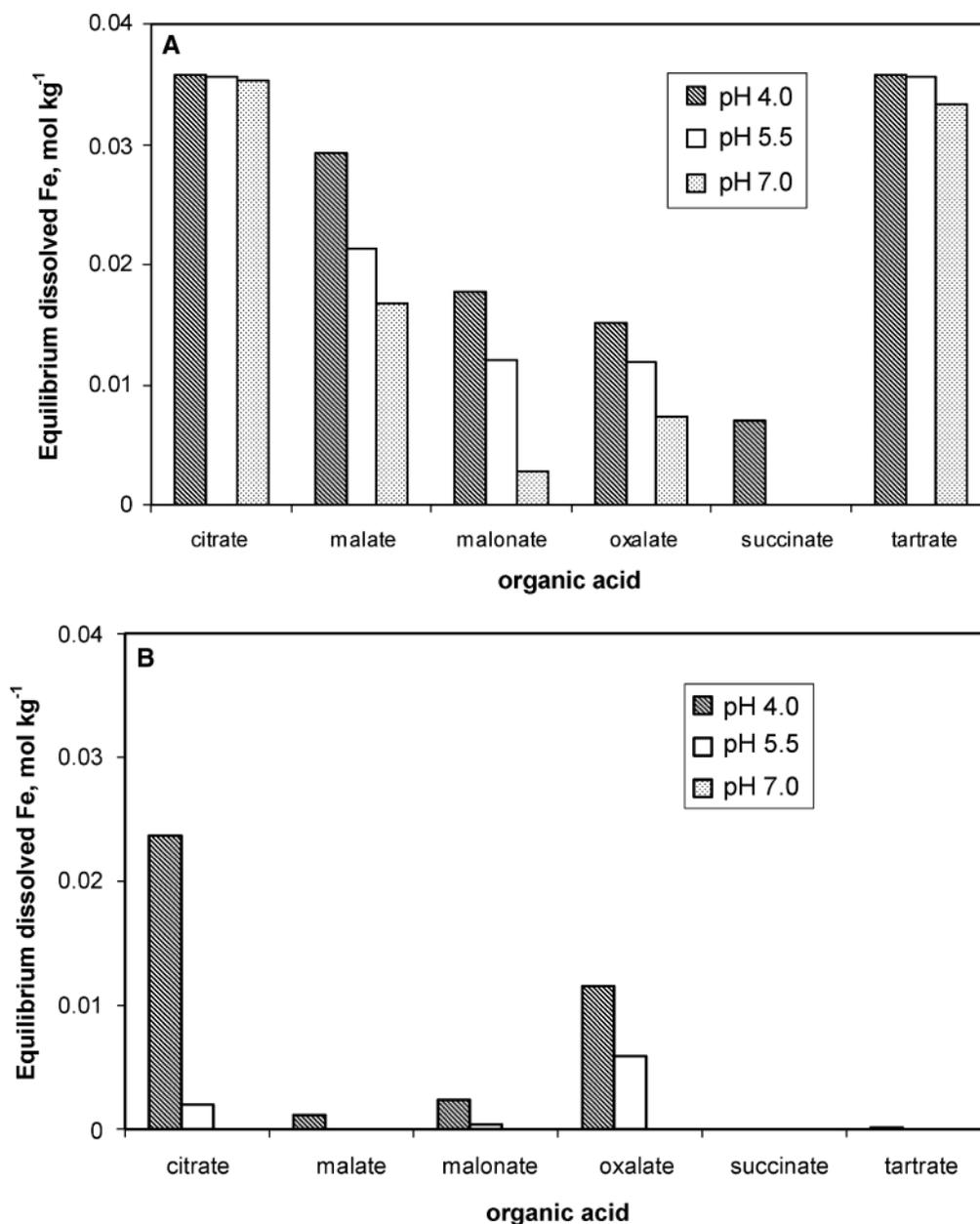


Fig. 5. Influence of pH and organic ligand on concentration of total dissolved Fe in equilibrium with ferrihydrite (A) and goethite (B). These theoretical values were calculated using MINTEQA2, with 0.0357 M ligand and 0.05 ionic strength.

Table 7. Relationships between experimental Fe dissolution and MINTEQA2-calculated theoretical values for Fe dissolution. Theoretical Fe dissolution values were obtained from the total Fe line on the MINTEQA2-generated equilibrium plots similar to that shown in Fig. 3, with 0.0357 mol organic acid L⁻¹ solution and ionic strength of 0.05 mol L⁻¹. Experimental data were measured by ICP following reactions of organic acids with ferrihydrite and goethite at an initial P-loading level of 1/4 of the P-adsorption maximum, 0.0357 mol organic ligand L⁻¹, and 7.14 g oxide L⁻¹.

Organic acid	Oxide	pH	Theoretical [Fe]		Exp. % of theo [Fe]†	Sat. index, goethite†	Sat. index, ferrihydrite†	Sat. index, strengite‡
			mol Fe L ⁻¹					
							Log Ω	
citrate	ferrihydrite	4.0	3.57 × 10 ⁻²	1.28 × 10 ⁻²	36	-	-5.320	-0.742
citrate	ferrihydrite	5.5	3.57 × 10 ⁻²	4.09 × 10 ⁻³	11	-	-4.658	-1.910
citrate	ferrihydrite	7.0	3.52 × 10 ⁻²	8.18 × 10 ⁻⁴	2	-	-2.461	-1.994
citrate	goethite	4.0	2.37 × 10 ⁻²	4.64 × 10 ⁻⁵	0	-0.464	-	-4.320
citrate	goethite	5.5	1.99 × 10 ⁻³	1.81 × 10 ⁻⁵	1	-1.83	-	-4.904
citrate	goethite	7.0	1.05 × 10 ⁻⁶	-	-	-	-	-
malate	ferrihydrite	4.0	2.92 × 10 ⁻²	5.31 × 10 ⁻³	18	-	-4.477	-0.160
malate	ferrihydrite	5.5	2.13 × 10 ⁻²	1.07 × 10 ⁻³	5	-	-3.816	-1.367
malate	ferrihydrite	7.0	1.68 × 10 ⁻²	6.24 × 10 ⁻⁵	0	-	-1.874	-1.903
malate	goethite	4.0	1.12 × 10 ⁻³	9.10 × 10 ⁻⁶	1	-0.897	-	-3.996
malate	goethite	5.5	1.03 × 10 ⁻⁶	-	-	-	-	-
malate	goethite	7.0	7.93 × 10 ⁻¹³	-	-	-	-	-
malonate	ferrihydrite	4.0	1.77 × 10 ⁻²	9.29 × 10 ⁻³	52	-	-3.315	-0.073
malonate	ferrihydrite	5.5	1.20 × 10 ⁻²	4.40 × 10 ⁻³	37	-	-3.295	-1.445
malonate	ferrihydrite	7.0	2.82 × 10 ⁻³	3.05 × 10 ⁻³	1	-	-2.281	-3.257
malonate	goethite	4.0	2.37 × 10 ⁻³	1.05 × 10 ⁻⁴	4	-1.469	-	-4.294
malonate	goethite	5.5	3.78 × 10 ⁻⁴	3.65 × 10 ⁻⁵	10	-1.049	-	-
malonate	goethite	7.0	7.73 × 10 ⁻⁸	-	-	-	-	-
oxalate	ferrihydrite	4.0	1.50 × 10 ⁻²	1.22 × 10 ⁻²	81	-	-3.066	-0.337
oxalate	ferrihydrite	5.5	1.19 × 10 ⁻²	1.01 × 10 ⁻²	85	-	-3.102	-1.202
oxalate	ferrihydrite	7.0	7.32 × 10 ⁻³	5.85 × 10 ⁻⁴	8	-	-2.240	-2.621
oxalate	goethite	4.0	1.15 × 10 ⁻²	1.90 × 10 ⁻⁴	2	-5.981	-	-8.931
oxalate	goethite	5.5	5.88 × 10 ⁻³	3.24 × 10 ⁻⁵	1	-3.112	-	-8.354
oxalate	goethite	7.0	1.57 × 10 ⁻⁶	2.07 × 10 ⁻⁵	-	-	-	-
succinate	ferrihydrite	4.0	6.94 × 10 ⁻³	1.32 × 10 ⁻⁵	0	-	-2.786	-0.171
succinate	ferrihydrite	5.5	9.08 × 10 ⁻⁶	-	-	-	-	-
succinate	ferrihydrite	7.0	2.64 × 10 ⁻⁸	1.51 × 10 ⁻⁵	-	-	-	1.869
succinate	goethite	4.0	1.05 × 10 ⁻⁷	1.39 × 10 ⁻⁵	-	-	-	-
succinate	goethite	5.5	1.11 × 10 ⁻¹⁰	1.32 × 10 ⁻²	-	-	-	-
succinate	goethite	7.0	3.24 × 10 ⁻¹³	2.39 × 10 ⁻⁵	-	-	-	1.073
tartrate	ferrihydrite	4.0	3.57 × 10 ⁻²	3.71 × 10 ⁻³	10	-	-4.171	-0.325
tartrate	ferrihydrite	5.5	3.56 × 10 ⁻²	6.55 × 10 ⁻⁴	2	-	-3.404	-1.352
tartrate	ferrihydrite	7.0	3.33 × 10 ⁻²	2.67 × 10 ⁻⁴	1	-	-2.693	-
tartrate	goethite	4.0	1.32 × 10 ⁻²	2.67 × 10 ⁻⁴	1	-	-2.693	-
tartrate	goethite	5.5	6.60 × 10 ⁻⁷	1.01 × 10 ⁻⁵	-	-	-	-
tartrate	goethite	7.0	2.82 × 10 ⁻⁹	1.76 × 10 ⁻⁵	-	-	-	-

† In some cases, the % comparison and the saturation index values are not listed due to theoretical [Fe] values that were less than ICP Fe detection limits.

‡ Saturation indices for strengite are missing in some cases because there was no measurable P in solution.

In previous studies, Fox et al. (1990), Bolan et al. (1994), and Lan et al. (1995), found a strong correlation between P release from Al oxide in Spodosols and log K_{A1} (formation constant of the organic ligand with Al). Such graphs provide information relating the experimental oxide dissolution and P release to the stability of the dissolved mononuclear bidentate complex (for dicarboxylate ligands) or the mononuclear tridentate complex (for the tricarboxylate citrate). The mononuclear complex is important as the probable precursor for dissolution of Fe from the oxide surface (Stumm and Furrer, 1987). In the current study, graphs of P release (not shown) and Fe dissolution vs. log K_{Fe} (Fig. 6) did not reveal consistent trends. Several factors that likely contributed to the poor correlation between Fe dissolution and log K_{Fe} in the current study were the variable reaction rates for the different ligands and the especially low equilibrium Fe solubilities in the Fe oxide/succinate systems.

CONCLUSIONS

At low initial P adsorption and low pH levels, there was evidence for oxide dissolution (Eq. [2]) as the primary mechanism of organic-acid induced P release

from Fe-oxide surfaces rather than ligand-exchange (Eq. [1]), especially in the case of the poorly crystalline

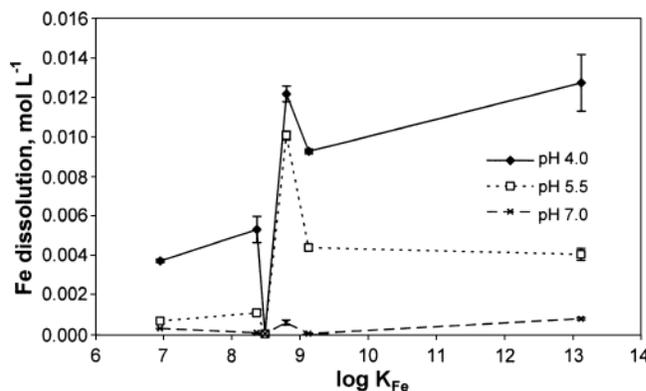


Fig. 6. Experimentally determined Fe dissolution from ferrihydrite versus the formation constants (log K_{Fe}) of the FeL^{3-n} complexes. Formation constants were obtained from the NIST Database 46, and experimental data were obtained from reactions of 7.14-g ferrihydrite L⁻¹ (1/4 maximum P-adsorption sites filled) with 0.0357 M organic ligand for 28 min. Each data point represents the mean of three replications, with error bars representing standard error. Each point represents one of the six organic ligands, according to log K_{Fe} as presented in Table 2.

ferrihydrite. There was strong correspondence between Fe dissolution and P release during the initial stages of the 24-h citrate reaction with ferrihydrite. Because ferrihydrite solubility is much greater than goethite solubility, it is logical that the dissolution mechanism of P release would be more important for ferrihydrite than goethite. There was very little P release from goethite at low initial P levels in spite of the high ratio of organic acid to P-adsorption maximum (60:1). The observation that there was more P release from goethite at the greater initial P level without an increase in Fe dissolution (Table 6) indicated that ligand-exchange might be more important when there is more P present to be desorbed.

The implication of these results for management and crop breeding programs is that organic-acid exudation by plant roots might not be expected to substantially influence P desorption from soils at low initial P adsorption levels, especially those in which the P solubility is controlled by well crystalline Fe oxides, for example, Oxisols and Ultisols. Because more P was released by organic acids from well crystalline Fe oxides when the initial P level was larger, plants with organic-acid exudation P-deficiency stress responses might be able to influence phosphate desorption from fertilized soils. Because di- and tri-carboxylic acids, such as citrate, tartrate, and malate, cause dissolution of poorly crystalline iron oxides, such as ferrihydrite, thereby releasing P into the soil solution, organic-acid exudation might effectively increase plant P acquisition from soils with appreciable concentrations of poorly crystalline Fe oxide.

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