COMPETITIVE SORPTION AND DESORPTION OF PHOSPHATE AND CITRATE IN CLAYEY AND SANDY LOAM SOILS[1]

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SUMMARY

The increase of organic acids in soils can reduce phosphorus sorption. The objective of the study was to evaluate the competitive sorption of P and citrate in clayey and sandy loam soils, using a stirred-flow system. Three experiments were performed with soil samples (0-20 cm layer) of clayey (RYL-cl) and sandy loam (RYL-sl) Red Yellow Latosols (Oxisols). In the first study, the treatments were arranged in a 2 × 5 factorial design, with two soil types and five combinations of phosphorus and citrate application (only P; P + citrate; and citrate applied 7, 22, 52 min before P); in the second, the treatments were arranged in a 2 × 2 factorial design, corresponding to two soils and two forms of P and citrate application (only citrate and citrate + P); and in the third study, the treatments in a 2 × 2 × 6 factorial design consisted of two soils, two extractors (citrate and water) and six incubation times. In the RYL-cl and RYL-sl, P sorption was highest (44 and 25 % of P application, respectively), in the absence of citrate application. Under citrate application, P sorption was reduced in all treatments. The combined application of citrate and P reduced P sorption to 25.8 % of the initially applied P in RYL-cl and to 16.7 % in RYL-sl, in comparison to P without citrate. Citrate sorption in RYL-cl and RYL-sl was highest in the absence of P application, corresponding to 32.0 and 30.2 % of the citrate applied, respectively. With P application, citrate sorption was reduced to 26.4 and 19.7 % of the initially applied citrate in RYL-cl and RYL-sl, respectively. Phosphorus desorption was greater when citrate was used. Phosphorus desorption with citrate and water was higher in the beginning (until 24 h of incubation of P) in RYL-cl and RYL-sl, indicating a rapid initial phase, followed by a slow release phase. This suggests that according to the contact time of P with the soil colloids, the previously adsorbed P can be released to the soil solution in the presence of

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competing ligands such as citrate. In conclusion, a soil management with continuous input of organic acids is desirable, in view of their potential to compete for P sorption sites, especially in rather weathered soils.

Index terms: incubation time, Latosol, organic acids, stirred-flow.

RESUMO: *SORÇÃO E DESSORÇÃO COMPETITIVA DE FÓSFORO E CITRATO EM SOLOS DE TEXTURA MUITO ARGILOSA E FRANCO-ARENOSA*

*O aumento de ácidos orgânicos pode induzir à redução da sorção de P em solos. Este trabalho objetivou avaliar a sorção competitiva de P e citrato em solos de textura muito argilosa e franco-arenosa, utilizando o sistema de fluxo contínuo (*stirred-flow*). Foram realizados três experimentos com amostras da camada de 0-20 cm de dois Latossolos Vermelho-Amarelo, texturas muito argilosa (LVA_arg) e franco-arenosa (LVA_fa). No primeiro, os tratamentos foram definidos por fatorial 2 × 5, sendo dois solos e cinco configurações de aplicação de P e citrato no solo (apenas P, P + citrato e citrato 7, 22, 52 min antes do P); no segundo, os tratamentos foram determinados por fatorial 2 × 2, dois solos e duas formas de aplicação de P e citrato no solo (apenas citrato, citrato + P); e, no terceiro, os tratamentos foram definidos segundo um fatorial 2 × 2 × 6, sendo dois solos, dois extratores (citrato e água) e os seis períodos de incubação. O valor máximo da sorção de P no LVA_arg e LVA_fa foi observado na testemunha sem aplicação de citrato, correspondendo a 44 e 25 % do P aplicado, respectivamente. Com a aplicação de citrato, a sorção de P foi inferior em todos os tratamentos. A aplicação de citrato junto com P reduziu a sorção do P aplicado para 25,8 % no LVA_arg e 16,7 % no LVA_fa, em relação à aplicação de P sem citrato. O valor máximo da sorção de citrato no LVA_arg e LVA_fa ocorreu no tratamento sem adição de P, correspondendo a 32,0 e 30,2 % do citrato aplicado, respectivamente. Com aplicação de P, a sorção de citrato reduziu para 26,4 e 19,7 % do citrato aplicado no LVA_arg e LVA_fa, respectivamente. A dessorção de P foi maior com a utilização do citrato. A dessorção com citrato e água foi inicialmente superior (até 24 h de incubação de P) no LVA_arg e LVA_fa, caracterizando uma fase inicialmente rápida, seguida de uma fase lenta, sugerindo que, dependendo do tempo de contato do P com os coloides do solo, o P previamente sorvido pode ser liberado para a solução, se ligantes competitivos como o citrato estiverem presente. Assim, o manejo de solo que adiciona de forma continuada ácidos orgânicos, uma vez que esses apresentam o potencial de competir pelos sítios de sorção de P, seria almejado, principalmente em solos mais intemperizados.*

Termos de indexação: ácidos orgânicos, Latossolo, incubação, stirred-flow.

INTRODUCTION

Most tropical soils have a high P sorption capacity, due to the predominance of Fe and Al oxyhydroxides in the clay fraction. The sorption reduces P availability to plants because the soil sink begins to dominate over the plant sink (Novais & Smyth, 1999). Phosphorus sorption reactions are fast: Gonçalves et al. (1985) observed that about 75 % of the P application was retained in less than half an hour of reaction in Oxisol samples.

The predominant interaction of P with Fe and Al oxyhydroxides determines the P lability and hence plant availability. Phosphorus in solution and weakly sorbed P are considered labile forms of soil P (labile P). Desorption-resistant P with more stable connections characterizes non-labile forms. With increasing soil incubation time, the P availability is reduced, regardless of the soil type or applied P rate (Novais & Smyth, 1999; Broggi et al., 2010; Hamdi et al., 2014).

The kinetics of soil P sorption and desorption are characterized by two phases: a first rapid, followed by a second slower phase (Shariatmadari et al., 2006; Harvey & Rhue, 2008; Fekri et al., 2011; Wang et al., 2013). The sorption and desorption kinetics in soil are mainly controlled by the content of soil organic matter (SOM), clay content, pH and Fe and Al oxyhydroxides (Sharpley, 1983; Nafiu, 2009; Santos et al., 2011). With regard to clay, the number of P sorption sites is greater, when the clay content is higher, reducing P availability (Novais & Smyth, 1999).

Phosphorus sorption in the soil was reduced in the presence of organic acids (Andrade et al., 2003; Souza et al., 2006; Duputel et al., 2013). Organic acids can be retained in the soil with high energy and block P sorption sites (Haynes, 1984). The carboxylic groups, characteristic of these organic acids, can dissociate and release protons in a wide pH range and promote the dissolution of soil minerals (Andrade et al., 2003; Oburger et al., 2011a). A great effectiveness of citrate

was noted in the competition for P sorption sites; this greater competitiveness is due to the higher number of carboxylic groups (tricarboxylic).

The competitive sorption between P and organic acids has been widely tested in closed systems, while in this study, this assessment is proposed with a continuous flow system, by the stirred flow technique. In this system, reactions are relatively fast and the sorption and desorption kinetics can be measured in a single experiment (Sparks et al., 1996; Yin et al., 1997). This technique has been used for many years in several countries to investigate sorption and desorption of metals (Carski & Sparks, 1985; Bar-Tal et al., 1990; Strawn & Sparks, 2000), and also of P, although in fewer studies (Staats et al., 2004; Pérez-Novo et al., 2011).

As the P bindings with the solid phase of very weathered soils are highly stable and the reversibility low, one possibility of soil management would be the continuous addition of organic acids. This would lead to a competitive sorption between P and organic acid, favoring the plant sink and reducing the conversion of labile into non-labile P forms. Thus, the objective of this study was to evaluate the competitive sorption of P and citrate in clayey and sandy-loam textured soils, and to assess the effect of citrate on P desorption during different incubation times of this nutrient in the soil by the stirred flow method.

Table 1. Physical and chemical properties of a clayey texture Oxisol (RYL-cl) and sandy-loam texture Oxisol (RYL-sl)

Property	RYL-cl	RYL-sl
Coarse sand (g kg^{-1})	140	225
Fine sand (g kg^{-1})	190	535
Silt (g kg^{-1})	60	50
Clay (g kg^{-1})	610	190
C (g kg^{-1})	10.19	1.60
Total N (g kg^{-1})	0.57	0.00
pH(H_2O)	4.80	4.70
K (mg dm^3)	14.40	2.34
P (mg dm^{-3})	1.31	0.03
P-rem (mg L^{-1})	6.96	22.92
Ca^{2+} ($cmol_c$ dm^{-3})	0.55	0.10
Mg^{2+} ($cmol_c$ dm^{-3})	0.04	0.00
Al^{3+} ($cmol_c$ dm^{-3})	0.78	0.00
Cu (mg dm^{-3})	1.58	0.39
Mn (mg dm^{-3})	5.80	0.88
Fe (mg dm^{-3})	48.83	13.61
MPSC(1) (mg g^{-1})	1.09	0.40
Equivalent moisture (kg kg^{-1})	0.32	0.15

P available and K exchangeable extracted by Mehlich-1 (Braga & Defelipo, 1974); exchangeable Ca, Mg and Al extracted by KCl 1 mol L^{-1}, Al quantified by titration (Defelipo & Ribeiro, 1981). Fe, Cu and Mn extracted by Mehlich-1. (1) MPSC: maximum P sorption capacity.

MATERIAL AND METHODS

Soils samples were collected from the 0-20 cm layer of two Red-Yellow Latosols (RYL), one with a clayey texture (RYL-cl), in Viçosa, Minas Gerais, and the other a sandy loam texture (RYL-sl), in Três Marias, Minas Gerais. Physical and chemical soil properties are listed in table 1. Particle-size analysis was performed with the pipette method adapted by Ruiz (2005) and the C content determined by dichromate oxidation (Yeomans & Bremner, 1988); the total soil N was determined by the Kjehdal method; available P and exchangeable K were extracted by Mehlich-1; Ca, Mg and Al were extracted by 1 mol L^{-1} KCl and the pH measured in water, at a ratio of 1: 2.5. The P content was determined by colorimetry of the phosphomolybdic complex, as described by Braga & Defelipo (1974); K was determined by flame photometry; Ca and Mg by atomic absorption; and Al by titration (Defelipo & Ribeiro, 1981). The elements Fe, Cu and Mn were extracted by Mehlich-1 and determined by atomic absorption spectrophotometry. The remaining P (P-rem) was determined in the reaction solution after shaking the soil for 1 h with $CaCl_2$ containing 60 mg L^{-1} P, at a ratio of 1:10 (Alvarez V. et al., 2000).

The maximum P sorption capacity (MPSC) of the soils was determined as proposed by Olsen & Watanabe (1957) and modified by Alvarez V. & Fonseca (1990). The P concentrations to determine MPSC were calculated based on the P-rem content and each soil was treated with 11 soil P concentrations (0, 10, 20, 30, 50, 70, 90, 110, 140, 170, and 200 mg L^{-1} in RYL-cl, and 0, 5, 10, 15, 25, 35, 45, 55, 70, 85, 100 mg L^{-1} in RYL-sl) (Alvarez V. & Fonseca, 1990). We used 2.5 g air-dried fine soil (ADFS) of each soil and added 25 mL of a 0.01 mol L^{-1} $CaCl_2$ solution containing the P concentrations. The solution was stirred for 24 h and centrifuged for 5 min, to determine the P concentration in the supernatant. The MPSC was estimated by the linearized Langmuir isotherm (Equation 1):

$$\frac{C}{q} = \frac{1}{ab} + \left(\frac{1}{b}\right)C \qquad (1)$$

where C is the P concentration in the reaction solution, in mg L^{-1}; b is the MPSC of the soil, in mg g^{-1}; q is the amount of P sorbed in soil, in mg g^{-1}; and a is a constant related to the binding energy of the element to the soil, in L mg^{-1}.

The sand, silt and clay mineralogy was analyzed. The clay and sand fractions were ground in a mortar and oriented on glass slides for mineral identification by X-ray diffraction. Samples of the sand fraction were mortar-ground and analyzed on glass slides (unoriented). The diffractometer PANalytical,

model X 'PertPRO was used, under CoKα radiation (1.7889 nm) to scan the sample in a range of 4 to 50 $^{o}2\theta$, at intervals of 0.02 $^{o}2\theta$ to 1 step per second, at a voltage of 40 kV and current of 30 mA.

Quartz was identified in the sand fraction of both soils (RYL-cl and RYL-sl). In the silt fraction of RYL-cl, kaolinite, gibbsite, goethite, and quartz were detected and in that of RYL-sl kaolinite and gibbsite and quartz. In the clay fraction of both soils (RYL-cl and RYL-sl) kaolinite, gibbsite and goethite were found.

Phosphorus sorption and desorption were assessed by the stirred flow technique (Figure 1), similar to the system described by Bar-Tal et al. (1990) and Strawn & Sparks (2000). This technique has been used for many years in several countries in kinetic studies, but is little known in Brazil (Carski & Sparks, 1985; Bar-Tal et al., 1990; Strawn & Sparks, 2000; Staats et al., 2004; Pérez-Novo et al., 2011). The stirred-flow system consists of a tank with N, receptors for stock solutions of P and citrate, a peristaltic pump with a flow rate of 1.58 mL min^{-1}, a 12 mL reaction chamber, magnetic stirrer, two filters (diameter 25 mm, pore size 0.45 μm) to separate the soil from the reaction solution, and tubes for sample collection. In the reaction chamber, a soil:solution ratio of 1:11 was used, as proposed by Bar-Tal et al. (1990), Strawn & Sparks (2000) and Carski & Sparks (1985).

As P source we used KH_2PO_4. The P and citrate solutions were prepared at a molar ratio of 1:1 (P: citrate), and the pH was adjusted to 4.8 with KOH and ionic strength to 10 mmol L^{-1} with KCl.

Effect of P citrate sorption

The treatments were evaluated in a 2 × 5 factorial design with two soils (RYL-cl and RYL-sl), five combinations of P and citrate applications (only P, P and citrate together and citrate applied 7, 22 and 52 min before P). The experiment was arranged in a randomized block design with three replications. Phosphorus and citrate solutions were prepared at a concentration of 0.1290 mmol L^{-1} each.

For the control treatments (P only) and P + citrate together (CiP_j), 1 g of soil was placed in the reaction chamber and the solution (containing a concentration of P or P + citrate) was pumped into the chamber under agitation (Figure 1). The entire volume of the solutions leaving the chamber was collected after the beginning of the flow, after the first 2 min and then every 5 min until 62 min.

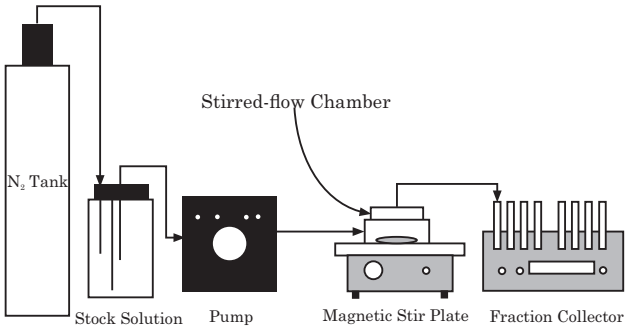

Figure 1. Stirred-flow system (Strawn & Sparks, 2000).

For treatments with citrate application prior to the addition of P (Ci_aP_d), 1 g of soil was placed in the reaction chamber and a citrate solution was pumped into the chamber under stirring (Figure 1). After 7 ($Ci_aP_d7_{min}$), 22 ($Ci_aP_d22_{min}$) and 52 min ($Ci_aP_d52_{min}$) of citrate addition, the flow was stopped and P application initiated. The entire volume of the solutions leaving the chamber was collected initially from 0 to 2 min and then every 5 min, until 62 min. The P concentration was determined by phosphomolybdic complex colorimetry (Braga & Defelipo, 1974).

To estimate P retention by the chamber (control), the above procedure was carried out without the soil sample.

The amount of P in soil sorbed by the different treatments was calculated as the difference between the concentration in the solution leaving the system with and without soil, according to equation 2, proposed by Sparks et al. (1996) and Yin et al. (1997)

$$qa(ti) = \frac{\Sigma\left(\frac{(Cib - Cis)\, j\, \Delta ti}{V}\right)}{W} \qquad (2)$$

where qa(ti): cumulative P sorption at time t, in mg g^{-1}; J: chamber input flow, in L min^{-1}; Δti: time of sampling interval, in min; Cib: P concentration in the effluent during the sampling period, in mg L^{-1}, in the system without soil (control); Cis: P concentration in the effluent during the sampling period, in mg L^{-1}, in the system with soil; V: volume of the reaction chamber in L; and W: soil concentration in the chamber, in g L^{-1}.

From the amount sorbed per sampling period, the cumulative sorbed P was computed from the sum of soil P sorption in the sampling period between 0 and 62 min. After the analysis of variance of the cumulative sorbed P content, means were compared by the Tukey test ($p \leq 0.05$), using the statistical program Statistica 7.

Effect of P on citrate sorption

The treatments were arranged in a 2 × 2 factorial design with two soils (RYL-cl and RYL-sl) and two solutions applied to the soil (only citrate or citrate + P). The experiment was conducted in a randomized complete block design with three replications. The citrate and P solutions were both prepared at a concentration of 0.1290 mmol L^{-1}.

In these treatments, 1 g of soil was placed in the reaction chamber and the solution containing a citrate or citrate + P concentration was pumped into the

chamber under stirring (Figure 1). The entire volume of the solutions leaving the chamber was collected after the beginning of the flow, after the first 2 min and then every 5 min until 62 min, as previously described. Citrate concentration was determined by high performance liquid chromatography (HPLC).

To estimate citrate retention in the chamber (control), the above procedure was carried out without addition of the soil sample.

The amount of citrate sorbed per treatment was calculated as described above for P sorption. From the amount sorbed during each interval, cumulative sorbed citrate was calculated as the sum of citrate in the soil sorbed in the period from 0 to 62 min of collection.

After the analysis of variance of the cumulative content of sorbed citrate, means were compared by the Tukey test ($p \leq 0.05$), using the statistical program Statistica 7.

Incubation time and desorption of soil P

The treatments were arranged in a 2 × 2 × 6 factorial design, testing two soils (RYL-cl and RYL-sl), two extractors (citrate 0.1290 mmol L^{-1} and water with ionic strength adjusted to 10 mmol L^{-1} KCl) and six incubation periods of P (0, 6, 24, 240, 480, and 960 h). Time zero (0) corresponded to about 1 min, the time required to close the chamber.

For the experiment, each treatment was incubated with soil with 50 g of P corresponding to 50 % of the MPSC of each soil (RYL-cl = 0.545 mg g^{-1} and RYL-sl = 0.200 mg g^{-1}), 80 % of the field capacity, in a randomized block design.

After the incubation periods, 1 g of soil was placed in the reaction chamber; a solution with the citrate concentration or water was pumped into the chamber under stirring (Figure 1). The entire volume of the solutions leaving the chamber was collected after the beginning of the flow, after the first 2 min and then every 5 min until 62 min, as described above. The P content was determined by phosphomolybdic complex colorimetry (Braga & Defelipo, 1974).

To estimate P desorption in the chamber (control), the procedure described above was applied in the absence of soil.

The amount of P desorbed by the soil in the different treatments was calculated as the difference between the concentration in the solution leaving the system with and without soil, according to the equation proposed by Sparks et al. (1996) and Yin et al. (1997), as described above. From the sum of the desorbed amount at each time, the cumulative desorbed P was obtained, which corresponds to the sum of P in soil desorbed from 0 to 62 min of collection.

For the content of cumulative desorbed P after analysis of variance, regressions of desorbed P according to the incubation period were adjusted using the statistical program Statistica 7.

RESULTS AND DISCUSSION

Effect of citrate on P sorption

Phosphorus sorption in the RYL-cl was 0.173 mg g^{-1}, which was higher than sorption in the RYL-sl (0.099 mg g^{-1}) (Table 2). These values obtained with the stirred flow technique corresponded to 16 and 25 % of MPSC of the RYL-cl (1.09 mg g^{-1}) and RYL-sl (0.40 mg g^{-1}), respectively. The differences between the results obtained with the stirred flow technique and the standard method of MPSC determination are a consequence of the method characteristics. To determine MPSC, the soil was in contact for 24 h with increasing rates P, of up to 200 mg L^{-1} P to RYL-cl and 100 mg L^{-1} P to RYL-sl. This contact time and application rates were higher than those used in the stirred-flow tests.

In both soils, P sorption was reduced when citrate was added, especially when higher amounts of citrate were applied for 22 and 52 min before P application, or when P and citrate were applied together (Table 2). During 62 min of P application at a rate of 1.58 mL min^{-1}, 0.39 mg g^{-1} P was applied to the soils. When no citrate was added, P sorption corresponded to 44.1 and 25.2 % of P applied to the RYL-cl and RYL-sl, respectively (Table 2). With citrate application for 7 min before P application, 34.8 % of P applied was sorbed to RYL-cl. In the RYL-sl, the P sorption with citrate application for 7 min before P was 21.4 % of P applied to the soil. After citrate application for 22 min before P application, P sorption was 0.066 mg g^{-1} lower than that of the control in RYL-cl, reducing sorption to 27.6 % of P applied to the soil. In RYL-sl, citrate application reduced P sorption by 0.049 mg g^{-1}; in this treatment, P sorption was 12.7 % of P applied to the soil. In the longest previous

Table 2. Mean cumulative concentrations, in the sampling period of 0 to 62 min, of P sorbed to soil with clayey texture Oxisol (RYL-cl) and with sandy-loam texture Oxisol (RYL-sl)

Treatment[1]	Sorbed P[2]	
	RYL-cl	RYL-sl
	mg g^{-1} (%)	
Control	0.173 Aa (44.1)	0.099 Ab (25.2)
$Ci_aP_d7_{min}$	0.136 Ba (34.8)	0.084 ABb (21.4)
CiP_j	0.101 Ca (25.8)	0.065 BCb (16.7)
$Ci_aP_d22_{min}$	0.107 Ca (27.6)	0.050 Cb (12.7)
$Ci_aP_d52_{min}$	0.105 Ca (26.7)	0.041 Cb (10.4)

[1] Cumulative P sorption in the soil without citrate application (control), with P and citrate together (CiP_j) and with citrate applied 7, 22 and 52 min before P ($Ci_aP_d7_{min}$, $Ci_aP_d22_{min}$, $Ci_aP_d52_{min}$), after 62 min of reaction. [2] In parentheses, percentage of P applied sorbed to soil. Means followed by the same capital letter in a column and lowercase letter in a row did not differ from each other by the Tukey test at 5 %.

application period of citrate (52 min), P sorption was significantly reduced; RYL-cl sorbed 26.7 % and RYL-sl 10.4 % of P applied to the soil.

The application of P and citrate together reduced P sorption by 0.072 and 0.034 mg g^{-1} in the RYL-sl and RYL-cl soils, respectively (Table 2), corresponding to the sorption of 25.8 % of P applied to RYL-cl and 16.7 % to the RYL-sl. The effectiveness of organic acids in decreasing P sorption in soil has been reported elsewhere (Geelhoed et al., 1999; Johnson & Loeppert, 2006; Moradi et al., 2012).

Effect of P citrate sorption

The evaluation period for citrate sorption was sufficient to record detectable changes. Strom et al. (2001) measured the sorption of organic acid for 60 min and observed that all citrate, malate and oxalate were sorbed to the soil in less than 5 min.

Citrate sorption in the RYL-cl was higher than in RYL-sl (Table 3) and was directly proportional to the MPSC of each soil. Probably, most P sorption sites are similar to those of citrate, which may vary with soil characteristics such as texture, mineralogy and concentration of Fe and Al oxyhydroxides. Phosphorus application together with citrate significantly reduced citrate sorption in both soils (Table 3).

Throughout the 62 min, 2.42 mg g^{-1} citrate was applied to each soil. Citrate sorption was highest (0.778 mg g^{-1}) in RYL-cl without P application, corresponding to 32.0 % of the citrate applied. In the same treatment in RYL-sl, the highest citrate sorption (0.734 mg g^{-1}) was 30.2 % of the citrate applied (Table 3). In the P application to RYL-cl, citrate was significantly reduced by 0.136 mg g^{-1} by citrate sorption; in this treatment, citrate sorption represented 26.4 % of the citrate applied. In RYL-sl, P application also reduced citrate sorption significantly by 0.255 mg g^{-1}, corresponding to 19.7 % of citrate applied to the soil (Table 3). The reduced citrate sorption after P application was probably due to blocking or competition for soil sorption sites, as stated by Oburger et al. (2011b). According to these authors, the higher the content of P, SOM or sulfate, the lower is citrate sorption.

Under natural conditions, sorption of citrate exudated by plants can occur (Silva et al., 2001). The exudated citrate can be sorbed, decomposed or remain in solution for short time periods, competing directly with P for the soil sorption sites (Oburger et al., 2011b).

In general, all citrate application forms were effective in reducing P sorption. The reduction of P sorption by citrate may occur by previous blocking of the sites or by competition between sites. Citrate application can also influence mineral dissolution, mainly by removing Fe and Al from crystalline or poorly crystallized structures, increasing the competitive sorption between P and citrate and reducing the sorption surface of P of the mineral. Anions which remain in the soil can form complexes with cations that also reduce phosphate precipitation (Sposito, 1989). Citrate is sorbed to the soil similar to inorganic anions and its affinity to the surface of minerals is similar to P sorption (Pavinato & Rosolem, 2008). The affinity of the anions for soil sorption sites follows the sequence: phosphate > citrate > malate > acetate (van Hees et al., 2003; Guppy et al., 2005).

Table 3. Cumulative concentrations, in the collection period of 0 to 62 min, of citrate sorbed to soils with clayey texture Oxisol (RYL-cl) and sandy-loam texture Oxisol (RYL-sl) in the absence and presence of P

Treatment	Sorbed citrate[(1)]			
	RYL-cl		RYL-sl	
	mg g^{-1} (%)			
- P	0.778 Aa	(32.0)	0.734 Ab	(30.2)
+ P	0.641 Ba	(26.4)	0.479 Bb	(19.7)

[(1)] In parentheses, percentage of citrate applied sorbed to the soil. Means followed by the same capital letter in a column and lowercase letter in a row did not differ from each other by the Tukey test at 5 %, after 62 min of reaction.

Incubation time and soil P desorption

Citrate application increased the desorption of P applied to soils (Figure 2). For both soils, P desorption in response to citrate application was higher than P desorption with water, in view of the competition of citrate with P for similar soil sorption sites, as already noted by other authors (Geelhoed et al., 1999; Johnson & Loeppert, 2006; Moradi et al., 2012). Oburger et al. (2011a) observed a similar response in P desorption with citrate addition, causing a mean desorption of 13.0 % of the P applied to the soil and only 3.0 % of P was desorbed with water after an application of 24 mg kg^{-1} P.

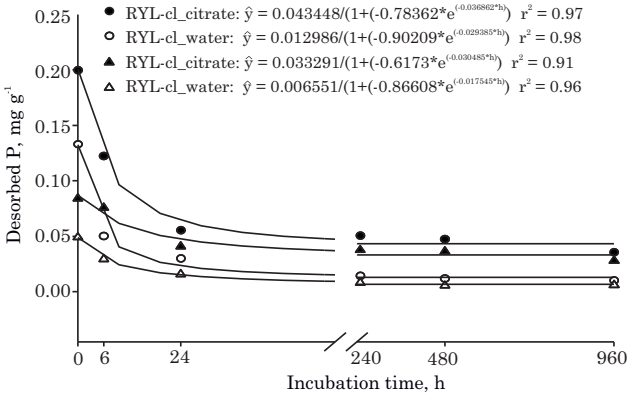

Figure 2. Concentration of desorbed P during 62 min of reaction, in clayey (RYL-cl) and sandy-loam texture Oxisol (RYL-sl), with citrate and water, in incubation periods of 0, 6, 24, 240, 480, and 960 h. * significant at 1 % by the F test.

Phosphorus desorption by citrate can occur under natural conditions by root exudation or organic matter decomposition (Johnson & Loeppert, 2006; Pavinato & Rosolem, 2008). More than 99 % of the organic acid exudates remain within a distance of 1 mm from the root surface, increasing the chances of P desorption in this region (Jones et al. 1996).

During the period of 0-960 h of incubation (Figure 2), two regions of P desorption by citrate and water were observed in the RYL-cl and RYL-sl: one with greater P desorption, from 0 to about 24 h after P incubation and the other with lower P desorption after this incubation period.

Phosphorus sorption reactions are fast, and over time the bonds age in the soil (Novais & Smyth, 1999). Phosphorus is initially retained by electrostatic attraction and simple coordinate bonds and, under this condition, the small portion of P in equilibrium with the soil solution is called labile P. This rapid sorption phase is followed by a slower phase consisting of the formation of an additional bond to the first between P and the absorbent surface, transforming labile P in desorption-resistant, non-labile P (Novais & Smyth, 1999; Fernández et al., 2008). Measuring P sorption in Fe and Al oxyhydroxides, Harvey & Rhue (2008) observed that 80 to 90 % of P was sorbed in the first three hours of sorption of these minerals.

Soil P availability after manure (poultry, cattle and goat) application was evaluated after 120 days by Azeez & Averbeke (2010). According to these authors, the P availability initially increases with organic matter mineralization, but 120 days after slurry application, more than 90 % of the mineralized P was no longer available. Similarly, Santos et al. (2011) observed that the longer the soil-P contact time, the lower is the percentage of desorbed P, regardless of the soil type or extractor (Table 4). In RYL-cl, P desorption with citrate was 36.7, 22.4, 10.3, 9.4, 8.6, and 6.6 % of P applied to the soil in incubation periods in soil for 0, 6, 24, 240, 480, and 960 h, respectively.

Table 4. Phosphorus desorbed during 62 min of each incubation period (0, 6, 24, 240, 480, 960 h), in a clayey texture Oxisol (RYL-cl) and a sandy-loam texture Oxisol (RYL-sl)

Incubation period	RYL-cl		RYL-sl	
	Citrate	Water	Citrate	Water
h		%(1)		
0	36.7	24.4	42.0	24.5
6	22.4	9.2	38.0	14.5
24	10.3	5.5	20.5	8.0
240	9.4	2.6	19.0	4.0
480	8.6	2.2	18.0	2.5
960	6.6	1.8	14.0	3.0

(1) Percentage of P in relation to the applied rate, equivalent to 50 % of the MPSC.

The values of water desorption were always below those of citrate, with 24.4, 9.2, 5.5, 2.6; 2.2; and 1.8 % of P applied in the same incubation periods.

In RYL-sl, the percentage of P desorption was higher than in RYL-cl in all incubation periods considering desorption with citrate and water (Table 4). The higher percentage of desorption of P applied to the RYL-sl was mainly due to its lower clay content and lower MPSC. According to Santos et al. (2011), P desorption is related to the properties of a soil, e.g., to clay mineralogy and content. According to Broggi et al. (2010), P sorption is higher in soils with predominantly gibbsite in the clay fraction. These authors reported two extreme values of P desorption in soil incubated for 90 days: 2 % of P applied to an Oxisol and 51 % to a Vertisol. In soils incubated with P up to 60 days, Kaloí et al. (2011) observed that the longer the incubation time, the lower was P recovery, inversely proportional to the content or clay weathering degree.

Duputel et al. (2013) used data modeling to assess the effects of citrate sorption on P availability and observed more effective competition of citrate in weathered soils, in the absence of 2:1 minerals and predominance of goethite. In Oxisols, they observed that the mineral with highest citrate sorption was goethite, leading to increased negative charges, especially at lower pH. In this study, the average pH of the two Oxisols was 4.75.

The P sorption observed in this study reached more than 40 % of the P applied in clayey Oxisol. The problem of P sorption in highly weathered soils is a widely known challenge, calling for strategies to mitigate this phenomenon. The effect of reducing P sorption with citrate application was tested with a stirred-flow system. The resulting data showed that the technique represents an alternative for tests involving P sorption and even includes the possibility of testing sorption followed by desorption, in the same study.

Thus, the results deepen the understanding of sorption and desorption processes and allow conclusions about management possibilities to increase P availability suggesting, for example, the selection of species that produce larger amounts of organic acids with higher amounts of carboxylic groups (ex. citric acid, which is tricarboxylic), or managements that increase organic residues and SOM.

CONCLUSIONS

1. Citrate decreases P sorption in soils, while in turn phosphate is effective in reducing citrate sorption. The lower P sorption in the presence of citrate and the lower citrate sorption in the presence of P is the result of the occupation of sites with similar affinities for P and citrate.

2. Phopshorus desorption with citrate is higher than with water, showing that P availability to plants is probably greater in soils with higher citrate concentrations.

3. In desorption of P to the soil as a function of incubation time, two regions were observed: an initial region of higher P desorption, followed by lower P desorption, resulting in less P available to plants with increasing soil - P contact time.

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