de Lima Camêlo, Danilo; Ker, João Carlos; Ferreira Novais, Roberto; Metri Corrêa,
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SEQUENTIAL EXTRACTION OF PHOSPHORUS BY MEHLICH-1 AND ION EXCHANGE RESIN FROM B HORIZONS OF FERRIC AND PERFERRIC LATOSOLS (OXISOLS)

Danilo de Lima Camêlo[1]*, João Carlos Ker[2], Roberto Ferreira Novais[3], Marcelo Metri Corrêa[4] and Vinício Coelho de Lima[5]

[1] Universidade de São Paulo, Escola Superior de Agricultura "Luiz de Queiroz", Departamento de Ciência do Solo, Programa de Pós-graduação em Ciência do Solo, Piracicaba, São Paulo, Brasil.
[2] Universidade Federal de Viçosa, Departamento de Solos, Viçosa, Minas Gerais, Brasil.
[3] Universidade Federal de Viçosa, Instituto de Ciências Agrárias, *Campus* de Rio Paranaíba, Rio Paranaíba, Minas Gerais, Brasil.
[4] Universidade Federal Rural de Pernambuco, Unidade Acadêmica de Garanhuns, Garanhuns, Pernambuco, Brasil.
[5] Universidade Federal de Viçosa, Curso de Geografia, Viçosa, Minas Gerais, Brasil.
* Corresponding author.
E-mail: danilocamelo@agronomo.eng.br

ABSTRACT

In general, Latosols have low levels of available P, however, the influence of the parent material seems to be decisive in defining the pool and predominant form of P in these soils. This study evaluated P availability by extraction with Mehlich-1 (M-1) and Ion Exchange Resin (IER), from samples of B horizons of Ferric and Perferric Latosols developed from different parent materials. To this end, in addition to the physical and chemical characterization of soils, 10 sequential extractions were performed with M-1 and IER from samples of B horizons (depth between 0.8 and 1.0 m). Total contents of Ca, P, Fe, Al, and Ti were determined after digestion with nitric, hydrofluoric and perchloric acids. The effects of sequential P extractions on Fe oxides were also evaluated from the analyses of dithionite-citrate-bicarbonate and ammonium acid oxalate. The high similarity between contents of P accumulated after sequential extractions with M-1 and IER in soils developed on tuffite indicated a predominance of P-Ca. Higher contents of P after a single IER extraction show greater efficiency in P removal from highly weathered soils, as from the Latosols studied here. The P contents also show the high sensitivity of extractant M-1 in highly buffered soils. Furthermore, a single extraction with extractant M-1 or IER is not sufficient to estimate the amount of labile P in these soils.

Keywords: labile phosphorus, iron oxyhydroxides, tuffite, mafic rocks, total digestion.

RESUMO: *EXTRAÇÕES SEQUENCIAIS DE FÓSFORO POR MEHLICH-1 E RESINA DE TROCA IÔNICA EM HORIZONTES B LATOSSÓLICOS FÉRRICOS E PERFÉRRICOS*

Os Latossolos apresentam, de modo geral, baixos teores de P disponível; no entanto, a influência do material de origem parece ser decisiva na definição do estoque e da forma de P predominante nesses solos. O objetivo deste trabalho foi avaliar a disponibilidade de P, pelos extratores Mehlich-1 (M-1) e Resina de Troca Iônica (RTI), em amostras de horizontes B de Latossolos Férricos e Perférricos desenvolvidos a partir de diferentes materiais de origem. Para tanto, além da caracterização física e química dos solos, foram realizadas 10 extrações sequenciais com os extratores M-1 e RTI em amostras de horizonte B coletadas entre 0,8 e 1,0 m de profundidade. Os teores totais de Ca, P, Fe, Al e Ti foram determinados após digestão com os ácidos nítrico, fluorídrico e perclórico. Os efeitos das extrações sequenciais de P sobre os óxidos de Fe também foram avaliados a partir das análises com ditionito-citrato-bicarbonato e oxalato ácido de amônio. A maior semelhança observada entre os teores de P acumulado após as extrações sequenciais com M-1 e RTI nos solos desenvolvidos de tufito é indicativo da predominância de P-Ca. Os maiores teores de P extraídos pela RTI após uma única extração relevam sua maior eficiência na remoção de P em solos bastante intemperizados como os Latossolos estudados e, ainda, ressalta a elevada sensibilidade do extrator M-1 em solos altamente tamponados. Além disso, uma única extração com o extrator M-1 ou RTI não é suficiente para estimar o fator quantidade de P lábil nesses solos.

Palavras-chave: fósforo lábil, oxihidróxidos de ferro, tufito, rochas máficas, digestão total.

INTRODUCTION

Although P is a macronutrient required by plants in smaller quantities, it is often the main limiting factor of agricultural production in Brazil (Raij, 1991). Tropical soils are typically P-deficient, due to interactions of the element with mineral constituents of the soil. The term P sorption refers to the phenomena of adsorption on mineral surfaces and precipitation in less soluble form, which commonly occurs in tropical acidic soils that are rich in Fe and Al oxyhydroxides, such as Latosols in general (Motta et al., 2002).

The intensity of sorption processes depends mainly on the clay content and nature in soils (Bahia Filho et al., 1983; Valladares et al., 2003). Thus, predominantly oxidic soils with higher clay content have higher P adsorption and more Fe and Al-associated P forms than soils with kaolinitic mineralogy (Ker, 1995; Motta et al., 2002). In this sense, oxyhydroxide Fe and Al minerals are the most active components in the clay fraction for P adsorption, and the minerals goethite and gibbsite are mainly responsible for this phenomenon in Latosols (Bahia Filho et al., 1983; Ker, 1995; Fontes and Weed, 1996; Rolim Neto et al., 2004).

Crops also influence P adsorption in different ways. Motta et al. (2002) found increased contents of Ca-associated P forms in cultivated soils with annual phosphate fertilization and occasional liming. A number of effects could be contributing to the reduction of P adsorption and increased P-Ca contents (Motta et al., 2002): liming, affecting the reduction of positive charges and organic matter decomposition, generating lower molecular weight compounds that compete with P for exchange sites, and/or even longstanding phosphate fertilization, promoting the removal of part of the elements in solution (Ca, Fe and Al) by precipitation with P.

When determining the potentially plant-available P content, some authors (Campello et al., 1994; Gatiboni et al., 2002; Rheinheimer et al., 2003) detected significant variations between the contents obtained in a single extraction and in several successive steps with the same extractant. In highly weathered and buffered soils, the values obtained in a single extraction are obviously underestimated, since various energy interaction levels with inorganic colloids, as well as extractant wear, affect the ability of some prediction methods (Gatiboni et al., 2002; Novais et al., 2007; Freitas et al., 2013). Variations in contents of available P can also be a consequence of the predominant form, determining the P contents in weathered soils (Souza Júnior et al., 2012).

Soil laboratories in Brazil use the extractants Mehlich-1 (M-1) and Ion Exchange Resin (IER) as main quantification methods of soil P supply (Silva and Raij, 1999). M-1 is a diluted mixture of hydrochloric and sulfuric acids, and P extraction occurs through exchange of ligands in which the adsorbed phosphate anion is replaced by the SO_4^{2-} anion, conjugate base of sulfuric acid. However, in clayey soils, mainly with higher pH, the P extraction power is compromised, because in addition to a rapid pH increase in the extracting solution in contact with the soil, the SO_4^{2-} anion can be adsorbed at sites so far unoccupied by P, resulting in a phenomenon called extractant wear (Novais et al., 2007).

Ion exchange resin consists of positively and negatively charged organic polymers, whose

desorption process of labile P is induced by a concentration imbalance between the solution and the soil solid phase. Therefore, Silva and Raij (1999) consider its use suitable to estimate the capacity of P supply of the soil because the extraction process resembles the action of plant roots, which would reduce the extractant sensitivity (wear) in soils with high clay content. However, P contents extracted by IER from soils with pronounced P-Ca forms, are similar to those obtained by M-1, given the Ca-drain effect of cationic resin that intensifies P solubilization, which does not occur with anionic resin alone (Freitas et al., 2013). Souza Júnior et al. (2012) reported similarity between the behavior of extractants M-1 and IER in very clayey and buffered soils, treated with Gafsa phosphate, a condition in which the extractant M-1 tends to wear out.

This study assessed P availability by extraction with M-1 and IER, in B horizon samples of Ferric and Perferric Latosols developed from different parent materials.

MATERIAL AND METHODS

The study was conducted in the laboratory of the Soil Department of the Federal University of Viçosa at room temperature. Samples of B horizons of 13 Latossolos Vermelhos ferric and perferric and of one Latossolo Vermelho-Amarelo mesoferric developed from different parent materials were collected between 0.8 and 1.0 m deep, in different regions of the State of Minas Gerais, Brazil. The sampling sites with pronounced influence of parent materials were based on the soil map of the State of Minas Gerais. We sampled soils in the region of the Triângulo Mineiro, developed from basalt (LV_1, LV_2, LV_3, and LV_4), in the Alto Paranaíba region, originated from tuffite or under tuffite influence (LV_5, LV_6, LV_7, LV_8, LV_9, LV_{10}, and LVA_1), in the metropolitan region of Belo Horizonte, derivatives of itabirite (LV_{11}) and amphibolite (LV_{12}), and in the region of Campo das Vertentes, formed from gabbro (LV_{13}).

To show the effect of the parent materials on P contents in the soil, we decided to use subsurface horizons (B Latosols), with no initial P source supply. In this way, we minimized the influence of management (phosphate fertilization and liming), since P has low mobility in oxidic soils, such as Latosols (Novais and Smyth, 1999; Donagemma et al., 2008).

To perform the analyses, samples were used as air-dried fine earth (ADFE), obtained by air-drying, crumbling and sieving (<2 mm).

In the chemical and physical analyses of soil samples (Table 1), we determined pH in water and solution with KCl (ratio 1:2.5);

exchangeable Ca^{2+}, Mg^{2+} and Al^{3+}, by extraction with KCl 1 mol L^{-1}; potential acidity (H+Al) by titrations after extraction with 0.5 mol L^{-1} calcium acetate at pH 7.0; available P and K after extraction with 0.05 mol L^{-1} HCl solution and 0.025 mol L^{-1} H_2SO_4 (M-1) (Embrapa, 2011); and remaining P (P-rem) by determining the P balance solution after shaking ADFE for 1 h with 0.01 mol L^{-1} $CaCl_2$ solution containing 60 mg L^{-1} of P at a 1:10 soil solution ratio (Alvarez V et al., 2000). The Ca^{2+}, Mg^{2+} and Al^{3+} contents were determined by atomic absorption spectrophotometry, P by colorimetry (Braga and Defelipo, 1974), K by flame photometry, and total organic carbon (TOC) by the Walkley-Black method (Embrapa, 2011). The Ki and Kr indexes were estimated from the analysis of sulphuric digestion (ratio 1:1) in ADFE fraction, and the Si, Al and Fe contents used to calculate the relations were quantified by plasma optical emission spectroscopy (Embrapa, 2011). Particle size analysis was performed according to Embrapa (2011).

The total contents of Ca, P, Fe, Al and Ti were determined by plasma optical emission spectroscopy, after total digestion of ADFE with a ternary mixture of concentrated nitric, hydrofluoric and perchloric acids, according to Embrapa (2011).

Available P contents were determined after 10 successive extractions by IER (50 % resin Amberlite IRA-400 + 50 % resin Amberlite IR-120) saturated with sodium bicarbonate (Raij and Quaggio, 2001) and by the extraction method M-1 (0.05 mol L^{-1} HCl + 0.025 mol L^{-1} H_2SO_4).

For P determination in soil by IER extractions, 2.5 cm^3 soil was placed in a conical plastic recipient of 80 mL, along with 25 mL of deionized water and a medium-sized glass sphere, and shaken in a horizontal device for 15 min at 220 rpm. Then the glass sphere was removed and 2.5 cm^3 of IER, previously treated with 1 mol L^{-1} $NaHCO_3$ at pH 8.5, was added. Next, the mixture containing IER with deionized water was subjected to horizontal shaking for 16 h at 220 rpm. Subsequently, IER was separated from the soil using a polyester sieve (0.4 mm mesh) applying jets of deionized water to wash the retained material. The suspension with soil was transferred again to the plastic containers for subsequent extractions, the pH adjusted to 6.0 with a solution of 0.1 mol L^{-1} HCl to promote flocculation, and the suspension was left to stand for 36 h between one extraction and another. The IER retained in the sieve was transferred individually to 100 mL flasks and 50 mL of a solution with 0.8 mol L^{-1} NH_4Cl and 0.2 mol L^{-1} HCl was added and left to stand for 30 min to eliminate CO_2. Thereafter, the flasks were closed and subjected to horizontal circular shaking for 1 h at 220 rpm. P concentration in the extracted

Table 1. Physical and chemical properties of the B horizons of Latossolos Vermelhos ferric and perferric and Latossolo Vermelho-Amarelo mesoferric

Property	LV_1	LV_2	LV_3	LV_4	LV_5	LV_6	LV_7	LV_8	LV_9	LV_{10}	LV_{11}	LV_{12}	LV_{13}	LVA_1
pH(H_2O)	6.18	5.88	5.68	5.47	5.57	5.02	5.30	5.76	5.89	5.17	5.76	4.96	5.70	4.89
pH(KCl)	4.85	5.90	5.23	5.33	5.53	4.37	4.86	5.39	5.27	4.53	5.29	4.26	6.33	5.40
ΔpH	-1.33	0.02	-0.45	-0.14	-0.04	-0.65	-0.44	-0.37	-0.62	-0.64	-0.47	-0.70	0.63	0.51
OC (g kg^{-1})[1]	8.4	8.4	10.7	11.5	12.2	29.0	9.2	7.7	8.4	23.7	13.0	35.9	10.5	14.2
P (mg dm^{-3})	1.1	0.3	0.2	0.5	0.0	6.5	6.5	2.0	37.5	17.5	0.5	1.1	1.2	0.6
Prem (mg L^{-1})[2]	2.1	0.7	1.8	2.0	1.7	3.9	3.9	0.9	4.0	3.0	2.4	8.4	5.5	4.0
K (mg dm^{-3})	15.0	1.0	3.0	7.0	5.0	1.0	3.0	5.0	2.0	8.0	1.0	16.0	12.0	11.0
Ca^{2+} (cmol$_c$ dm^{-3})	0.36	0.13	0.35	0.15	0.05	0.05	0.20	0.11	0.72	0.09	0.06	0.12	0.07	0.00
Mg^{2+} (cmol$_c$ dm^{-3})	0.30	0.00	0.01	0.01	0.03	0.00	0.00	0.08	0.04	0.01	0.00	0.01	0.20	0.00
Al^{3+} (cmol$_c$ dm^{-3})	0.00	0.00	0.00	0.00	0.00	0.59	0.00	0.00	0.00	0.39	0.00	0.49	0.00	0.00
H+Al (cmol$_c$ dm^{-3})	3.70	2.10	3.20	3.50	3.20	10.90	5.20	3.40	6.10	8.20	4.20	11.10	3.50	8.70
m (%)[3]	0.0	0.0	0.0	0.0	0.0	92.2	0.0	0.0	0.0	76.5	0.0	74.2	0.0	0.0
SB (cmol$_c$ dm^{-3})[4]	0.70	0.13	0.37	0.18	0.09	0.05	0.21	0.20	0.77	0.12	0.06	0.17	0.30	0.03
V (%)[5]	15.9	5.8	10.4	4.9	2.7	0.5	3.9	5.6	11.2	1.4	1.4	1.5	7.9	0.3
CEC$_e$ (cmol$_c$ dm^{-3})	0.70	0.13	0.37	0.18	0.09	0.64	0.21	0.20	0.77	0.51	0.06	0.66	0.30	0.03
CEC$_{7,0}$ (cmol$_c$ dm^{-3})	4.40	2.23	3.57	3.68	3.29	10.95	5.41	3.60	6.87	8.32	4.26	11.27	3.80	8.73
Index Ki[6]	1.54	0.46	0.61	0.36	0.24	0.71	0.24	0.40	0.36	0.65	0.13	0.74	0.70	0.42
Index Kr[7]	0.81	0.27	0.34	0.20	0.16	0.48	0.09	0.21	0.13	0.31	0.03	0.42	0.45	0.33
Coarse sand (g kg^{-1})	20	30	30	40	70	60	60	60	110	80	320	70	110	60
Fine sand (g kg^{-1})	30	50	60	100	80	60	90	60	110	80	40	60	50	50
Silt (g kg^{-1})	270	220	230	230	180	130	360	210	330	200	200	140	150	100
Clay (g kg^{-1})	680	700	680	630	670	750	490	670	450	640	440	730	690	790
Munsel hue	2.5YR	10R	10R	10R	2.5YR	3.5YR	10R	10R	10R	10R	10R	2.5YR	10R	5YR

[1] Organic carbon; [2] Prem: remaining P; [3] Saturation by Al^{3+}; [4] Sum of bases; [5] Bases saturation; [6] Molar ratio ($SiO_2/Al_2O_3 \times 1.7$) obtained by sulphuric digestion; [7] Molar ratio [$SiO_2 \times 1.7/(Al_2O_3 + 0.64 \times Fe_2O_3)$] obtained by sulphuric digestion.

solution with resin was determined by colorimetry, according to Braga and Defelipo (1974).

For P determination in the soil by extractant M-1, 2.5 cm^3 of ADFE were placed in 50 mL centrifuge tubes with 25 mL extractant. The mixtures were shaken vertically (Wagner agitator, 50 rpm/5 min), and after 16 h of sedimentation, aliquots of supernatants were removed to determine P contents (Braga and Defelipo, 1974).

To compose the correlation matrix of mineralogical properties, minerals of the clay fraction were estimated by allocation, according to the method proposed by Resende et al. (1987), using software ALOCA (Moura Filho et al., 1995). Therefore, the chemical elements of the minerals extracted by sulphuric digestion and citrate-bicarbonate-dithionite (CBD) in clay fraction were allocated to the minerals identified by X-ray diffraction (XRD). By calculating the average size of crystal from the half-height width of reflections (104), (110) and (012) of hematite (Hm) and (110) and (111) of goethite (Gt) by the Scherrer equation (Klug and Alexander,

1954), we determined the values of the specific surface area (SSA) for the respective minerals, considering the geometric shape of a sphere for Gt (Schwertmann and Kämpf, 1985) and circular plates (geometric shape of a cylinder) for Hm (Schwertmann et al., 1979; Melo et al., 2001). Isomorphous substitution (IS) of Fe^{3+} by Al^{3+} in the Hm and Gt structure was estimated by the position of reflections of these minerals obtained by XRD, using silicon as an internal standard for offset correction. In Gt, IS was calculated from the equation proposed by Schulze (1984) and, in Hm as in Schwertmann et al. (1979). The relationship Hm/(Hm+Gt) was estimated based on the areas of reflections concerning the plan (012) of Hm and (110) of Gt. The formula used to calculate was proposed by Resende et al. (1987): Hm/(Hm+Gt) = 4 × (Hm012)/4 × A(Hm012) + A(Gt110).

Samples of ADFE were also subjected to five successive extractions with CBD (Mehra and Jackson, 1960) before and after 10 successive P extractions with M-1 and IER and a single extraction with ammonium acid oxalate (AAO) (McKeague

and Day, 1966). The contents of Fe and Al were determined by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

We observed a wide range of contents of total Ca (Ca_T) (29 to 1,554 mg kg^{-1}) and total P (P_T) (810 to 11,211 mg kg^{-1}) in the soils studied (Table 2). Even in the case of highly weathered soils as the Latosols, the Ca total contents found were higher than those observed by Rolim Neto et al. (2009) in Latossolos Vermelhos of two topolito sequences in the Alto Paranaíba region. Higher Ca_T and P_T contents were observed in tuffite-derived soils, particularly in the samples LV_6, LV_7, LV_8, LV_9, and LV_{10}, possibly a result of contributions of P forms linked to Ca (P-Ca) related to the mineralogy of mafic/ultramafic bodies in the Alto Paranaíba region (Barbosa et al., 1970; Rolim Neto et al., 2009). In addition, the positive correlation (r = 0.98**) between Ca_T and P_T contents underscores the influence of P-Ca forms on P contents in the soil (Table 3).

The contents of total Fe (Fe_T) ranged from 111 to 377 g kg^{-1}, and were highest in LV_{11}, formed from itabirite. Conversely, the Al content extracted by total digestion (Al_T) from the same soil was lowest. The significant correlation (r = -0.78**) between Fe_T and Al_T in the soils studied reflects proportionality of these elements in parent materials (Table 3). Due to the greater sensitivity of iron oxides to oxidation-reduction procedures, they can be solubilized in humid soil environments by the reduction of Fe^{3+} in the structure of pedogenetic Fe oxides, to the easily leachable Fe^{2+} (soluble phase). Therefore, reductions in the Fe_T/Al_T ratio in soils could also be linked to this phenomenon, for example, in LVA_1 samples.

The absence of a significant correlation (r = 0.28$^{n.s}$) between Fe_T and P_T contents (Table 3), suggests that P_T contents in soils are not related to Fe-associated P forms, as the forms linked to Hm and Gt, whose effect on P sorption is well-documented in the literature (Ker, 1995; Fontes and Weed, 1996; Rolim Neto et al., 2004).

The significant correlation between Al_T contents and Ca_T (r = -0.59*) and P_T (r = -0.60*) contents suggests the reduction of Ca and P contents with loss of bases and anions, respectively, throughout the alitization process of soils, as well as the possible occurrence of apatites altered with considerable Al contents replacing Ca or P in their structure, as reported by Rolim Neto (2002) based on micromorphological and microchemistry analyses in Cambiosols in the Alto Paranaíba region. Al can replace Ca^{2+}, in the form of Al^{3+}, and phosphate (PO_4^{3-}) (rarely), in the form of AlO_2, in the structure of apatites. These crystallochemical modifications can cause variations in solubility, reactivity, crystallinity

Table 2. Total contents of calcium (Ca_T), phosphorus (P_T), iron (Fe_T), aluminum (Al_T) and titanium (Ti_T) in air-dried fine earth fraction of the B horizons of Latossolos Vermelhos ferric and perferric and Latossolo Vermelho-Amarelo mesoferric

Profile	Ca_T	P_T	Fe_T	Al_T	Ti_T
	mg kg^{-1}		g kg^{-1}		
LV_1	147.3	1257.7	209.5	121.4	45.3
LV_2	29.6	1516.3	211.7	151.8	41.6
LV_3	112.0	1315.9	216.6	147.2	46.9
LV_4	84.7	1861.5	216.7	143.3	43.2
LV_5	87.0	1700.4	186.8	169.7	54.1
LV_6	231.7	4212.4	133.6	126.3	56.1
LV_7	709.6	6842.5	278.5	97.4	88.4
LV_8	477.5	4669.0	224.7	125.7	71.8
LV_9	1554.4	11211.0	259.1	82.6	87.6
LV_{10}	628.0	6043.3	205.4	98.4	71.4
LV_{11}	161.3	2041.7	377.1	67.1	15.6
LV_{12}	52.7	1141.5	186.7	123.3	20.4
LV_{13}	37.8	810.0	176.3	159.7	10.1
LVA_1	73.8	1431.2	111.0	201.6	49.5

Table 3. Pearson's correlation matrix between the total main elements (calcium - Ca_T, phosphorus - P_T, iron - Fe_T, aluminum - Al_T and titanium - Ti_T) determined in air-dried fine earth fraction of the B horizons of Latossolos Vermelhos ferric and perferric and Latossolo Vermelho-Amarelo mesoferric

	Ca_T	P_T	Fe_T	Al_T	Ti_T
Ca_T	1.00				
P_T	0.98**	1.00			
Fe_T	0.32	0.28	1.00		
Al_T	-0.59*	-0.60*	-0.78**	1.00	
Ti_T	0.75**	0.81**	0.02	-0.25	1.00

* and **: significance of 1 and 5 %, respectively.

and thermal stability (Toledo and Pereira, 2001). Although part of Al_T is associated with the presence of aluminosilicate minerals, low Ki index values (<0.75, except in LV_1) (Table 1), which indicate the predominance of oxide mineralogy in soils, suggest that the negative correlation between Al_T and P_T contents also resulted from the lack of influence of P forms linked to Al, mainly those associated to gibbsite, with a strong effect on the process of P sorption (Ker, 1995; Rolim Neto et al., 2004).

The high content of total Ti (Ti_T) in soils confirms findings of increased contents of this element in soils developed on mafic rocks (Table 2) (Curi and

Franzmeier, 1987; Rolim Neto et al., 2009). The incidence of increased Ti levels in tuffite-derived soils (LV_5, LV_6, LV_7, LV_8, LV_9, and LV_{10}), or under its influence (LVA_1), is related to the higher residual content of anatase and to the significant presence of titanomagnetite and titanomaghemite in these soils (Fabris et al., 1994, 1997a,b). The significant correlations between contents of Ti_T and Ca_T (r = 0.75**), as well as contents of Ti_T and P_T (r = 0.81**), suggest the possibility of using Ti as an indicator of the contents of these elements in soils formed on mafic rocks.

After sequential extractions with M-1 (P_{M-1}) and IER (P_{IER}), P contents ranged from 6 to 439 mg dm^{-3} and from 14 to 441 mg dm^{-3}, respectively (Figure 1). As observed for P_T contents, in soils formed on tuffite, mainly in LV_6, LV_7, LV_8, LV_9, and LV_{10}, the P_{M-1} and P_{IER} values were highest, which reflects the importance of this parent material for P content in these soils. However, the nature of tuffite formation, as well as its mixture with other detrital (recycling) material, allows for great variation in the vertical and horizontal chemical composition of soils, justifying the low P_{M-1} and P_{IER} contents in other samples from tuffite formations (LV_5 and LVA_1). According to Guimarães (1955), tuffite are basic, non-hardened rocks composed of mixtures of pyroclastic debris and volcanic ash, with high contents of Fe, K, Ca and P.

Rolim Neto et al. (2009) found, in a single extraction, low contents of P_{M-1} for Latossolos Vermelhos developed on mafic/ultramafic rocks in the Alto Paranaíba region and suggested the possibility of P translocation to less soluble forms in acidic medium such as those associated with Fe oxides and crystalline Al, with the pedogenetic development of the soil.

The significant correlations between the Ca_T and P_{M-1} contents (r = 0.96**) and P_{IER} (r = 0.97**) deserve greater attention (Table 4). These correlations confirmed the existence of P forms linked to Ca in Latossolos Vermelhos, especially in those developed from tuffite formations in the Alto do Paranaíba region, and highlight the importance of these forms for native P content in the soil. In addition, the similarity found between P contents accumulated after sequential extractions with M-1 and IER, in most tuffite-derived soils also corroborated the predominant occurrence of P-Ca in these soils. Also, the similarity between extractants M-1 and IER represents an additional Ca^{2+} drain, causing more effective solubilization of P-Ca (Figure 1) (Souza Júnior et al., 2012; Freitas et al., 2013). The absence of significant correlations between P extracted by M-1 and IER and crystallographic attributes (IS and SSA) for Gt and Hm, as well as with the ratio Hm/Hm+Gt and some minerals of the clay fraction, aside from confirming the predominance of the P-Ca form in soils, also reflects the importance of the parent material in the soil mineralogical behavior for P (Table 4).
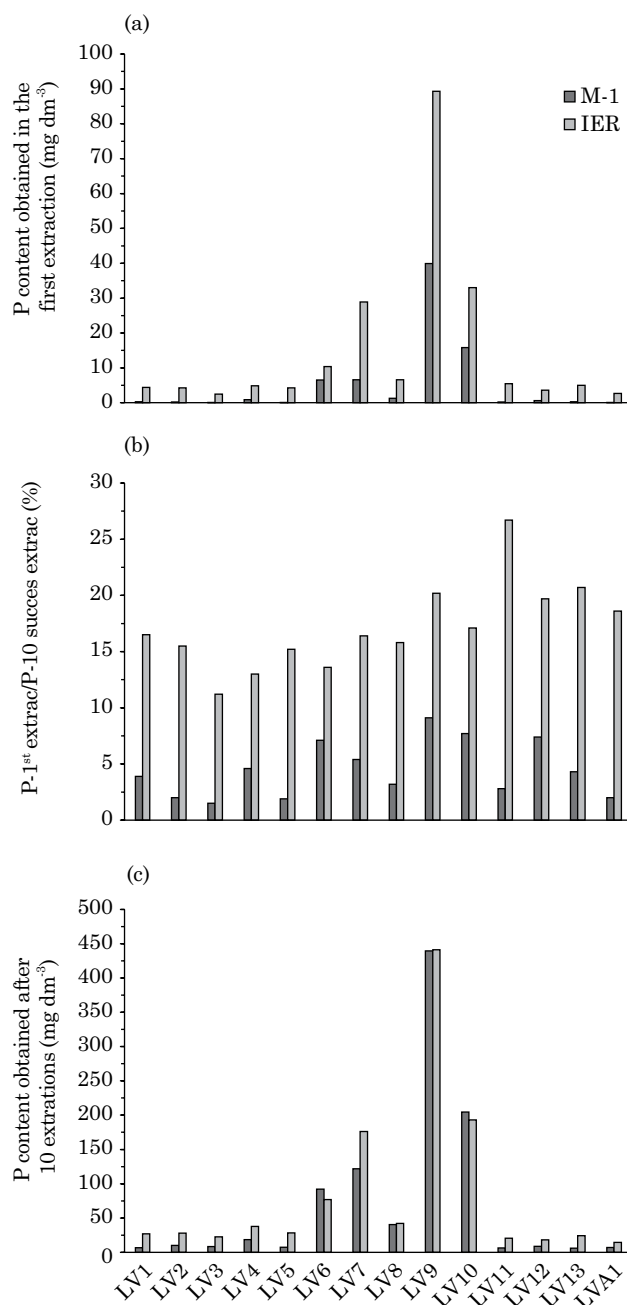

Figure 1. Phosphorus content obtained in the first extraction - P-1st extraction (a), relation between P extracted in the first extraction and the P extracted in 10 successive extractions – P-1st extrac/P-10 succes extrac (b), and P content after 10 successive extractions (c) with extractants Mehlich-1 (M-1) and ion exchange resin (IER) of the B horizons of *Latossolos Vermelhos* ferric and perferric and *Latossolo Vermelho-Amarelo* mesoferric.

Motta et al. (2002) studied P forms in surface horizons of Latosols of cultivated and non-cultivated systems and found higher values for the ratio

Table 4. Pearson's correlation matrix between contents of P accumulated after 10 successive extractions with Mehlich-1 (P_{M-1}) and ion exchange resin (P_{IER}), and minerals of kaolinite clay fraction (Ct), goethite (Gt), hematite (Hm) and gibbsite (Gb), the specific surface area of Gt (SSA_{Gt}) and Hm (SSA_{Hm}), isomorphous substitution of Fe^{3+} for Al^{3+} in Gt (IS_{Gt}) and Hm (IS_{Hm}), the ratio Hm/Hm+Gt and content of Ca (Ca_T) obtained by total digestion of air-dried fine earth[1] of the B horizons of Latossolos Vermelhos ferric and perferric and Latossolo Vermelho-Amarelo mesoferric

	Ct	Gt	Hm	Gb	Hm/Hm+Gt	SSA_{Gt}	SSA_{Hm}	IS_{Gt}	IS_{Hm}	Ca_T
P_{M-1}	-0.33	-0.35	-0.39	-0.28	0.50	-0.32	0.51	-0.33	0.22	0.96**
P_{IER}	-0.37	-0.41	-0.41	-0.028	0.52	-0.19	0.45	0.20	0.20	0.97**

**: significant at 1 %. [1] Minerals of the clay fraction estimated by the allocation method of Resende et al. (1987).

P-Ca/(P-Al+P-Fe) in an acric Latossolo Vermelho under cultivation, developed on fine tertiary sediments that cover the plateaus of Central Brazil, as well as in cultivated and non-cultivated dystroferric Latossolos Vermelhos, developed on tuffite. In the first case, the author attributed the results to liming and heavy phosphate fertilization over the years, because soils with such high contents of available P are rare in Brazil. In the second case, the original P richness of the soil could explain the few variations in contents between cultivated and non-cultivated soils. Corroborating the findings of Motta et al. (2002), in sample LV_6, from an area under native forest, the P contents were attributed to the contribution of the parent material (tuffite). However, in the samples LV_7, LV_9 and LV_{10} from cultivated systems, the contributions of liming and phosphate fertilization during the growing cycle possibly increased P contents in these soils.

Intriguingly, in this study, higher P contents were found in soils with long history of cultivation, leading to questions about P mobility in Latosols, known to be low (Nancy and Smyth, 1999; Donagemma et al., 2008). It is a consensus in the scientific community that Latosols are soils in advanced weathering stages and their formation involves both geochemical and biological processes. Perhaps, analyses of the effects of bioturbation on P mobility in oxidic Latosols, especially of the Fe-rich, could be added, because the consequences for textural and mineralogical homogenization are already known (Ferreira et al., 2011; Resende et al., 2014). According to Lee and Wood (1971), soil accumulation rates due to termite action can vary between 0.05 and 0.4 mm year^{-1}.

Another important aspect was the P rate obtained from the first extraction in relation to total P after all sequential extractions with M-1 and IER (Figure 1). The ratios ranged from 1.5 to 9.1 % and from 11.2 to 26.7 % after extractions with M-1 and IER, respectively. We observed that P_{IER} contents in the first extraction were higher than for P_{M-1} in all soils. This corroborates findings of Gatiboni et al. (2002) in dystrophic Latossolos Vermelhos samples with low contents of available P and with a greater capacity of IER to extract labile P, regardless of soil buffering, because it is not abrasive under these conditions, in contrast to M-1 (Silva and Raij, 1999; Simões Neto et al. 2009). However, in weathered soils, the potentially available P is underestimated because successive extractions with the same extractant remove P from the soil continously (Campello et al., 1994; McKean and Warren, 1996; Rheinheimer et al., 2000; Gatiboni et al., 2002; Rheinheimer et al., 2003).

The sensitivity effect (wear) of extractant M-1 in highly buffered soils could be clearly observed in tuffite-derived soils, especially in samples LV_7, LV_9 and LV_{10}, whose P contents determined by IER were roughly twice those extracted by M-1 after a single extraction. Given the possibility of greater influence of P-Ca in these soils, aside from the effect of P drain of the anionic resin, the strong action of Ca drain of the cationic resin intensifying P solubilization (Souza Júnior et al., 2102; Freitas et al., 2013) led to a greater P removal by IER than by extractant M-1, which had a limited extraction potential, due to the sensitivity effect.

Wide variations were not observed between contents of Fe_2O_3 and Al_2O_3 obtained by CBD and AAO in samples after sequential P extractions with M-1 and IER and samples not subjected to P extractions, indicating an inexpressive effect of P extractants on Fe oxyhydroxide minerals over successive extractions (Figure 2). Therefore, the reaction of acidic ligand anion exchange (PO_4^{3-} for SO_4^{2-}) in inorganic colloidal particles of soil samples under extractions with M-1 (Nancy et al., 2007) and the exchange reaction by difference of electrostatic ionic concentration of the solid phase with the soil solution samples when extracted with IER (Silva and Raij, 1999), do not significantly change the contents of Fe oxyhydroxide minerals in Latosols.

Significant correlations between the content of Fe_2O_3 extracted by AAO in samples without P extraction and the contents of P_{M-1} (r = 0.79**) and P_{IER} (r = 0.81**), along with the slightly lower values of Al_2O_3 in soil samples after sequential P extractions by M-1 and IER (Figure 2), reflect the possible participation of forms of Fe and Al oxyhydroxide minerals of low crystallinity in P content of soils, as observed by Fontes and Weed (1996).
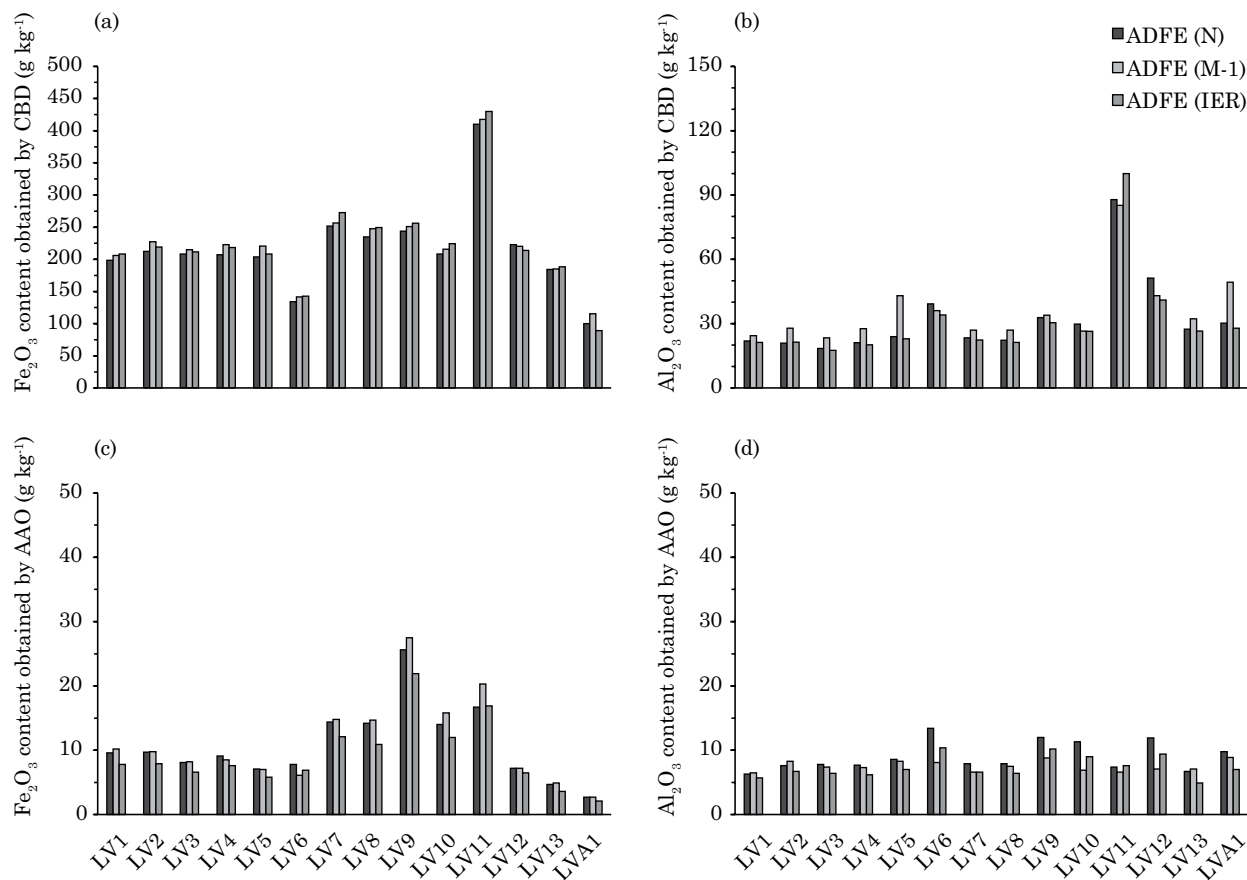
Figure 2. Fe₂O₃ (a) and Al₂O₃ (b) contents obtained by successive extractions with citrate-bicarbonate-dithionite (CBD); Fe₂O₃ (c) and Al₂O₃ (d) contents obtained by single extraction with acid ammonium oxalate (AAO) in air-dried fine earth (ADFE) samples, before (ADFE₍N₎) and after 10 sequential extractions with Mehlich-1 (ADFE₍M-1₎) and ion exchange resin (ADFE₍IER₎) of the B horizons of Latossolos Vermelhos ferric and perferric and Latossolo Vermelho-Amarelo mesoferric.

CONCLUSIONS

The higher contents of total P in tuffite-derived soils show strong contribution of this rock to the P pool in these soils.

The highly significant correlations observed between the contents of total Ca and P extracted by Mehlich-1 (M-1) and by ion-exchange resin (IER) indicate pronounced influence of P-Ca in soils, particularly in Latossolos Vermelhos formed on tuffite in the Alto Paranaíba region.

Ion-exchange resin was more efficient to determine P availability, for removing larger amounts in the first extraction in all soils.

A single extraction with M-1 or IER is not sufficient to estimate the amount factor of P in highly weathered soils, such as Latosols, because successive extractions with the same extractant continously remove P from the soil, as reported in the literature.

ACKNOWLEDGEMENTS

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