Elementos da Natureza e Propriedades do Solo 4

Alan Mario Zuffo
Fábio Steiner
(Organizadores)

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APRESENTAÇÃO

A obra “Elementos da Natureza e Propriedades do Solo” aborda uma série de livros de publicação da Atena Editora, em seu volume IV, apresenta, em seus 21 capítulos, os novos conhecimentos tecnológicos para Ciências do solo nas áreas de biologia do solo, física do solo, química do solo, morfologia e classificação do solo.

O solo é um recurso natural abundante na superfície terrestre, sendo composto por propriedades biológicas, físicas e químicas. Por outro lado, a água também é essencial os organismos vivos e, para a agricultura. Nas plantas, a água é responsável por todo o sistema fisiológico. Ambos os elementos, juntamente com os nutrientes são imprescindíveis para os cultivos agrícolas, portanto, os avanços tecnológicos na área das Ciências do solo são necessários para assegurar a sustentabilidade da agricultura, por meio do manejo, conservação e da gestão do solo, da água e dos nutrientes.

Apesar da agricultura ser uma ciência milenar diversas técnicas de manejo são criadas constantemente. No tocante, ao manejo e conservação da água e do solo, uma das maiores descobertas foi o sistema de plantio direto (SPD), criado na década de 80. Esse sistema é baseado em três princípios fundamentais: o não revolvimento do solo, a rotação de culturas e a formação de palhada por meio do uso de plantas de cobertura. Tais conhecimentos, juntamente com a descoberta da correção do solo (calagem) propiciaram o avanço da agricultura para áreas no Bioma Cerrado, que na sua maior parte é formado por Latossolo, que são solos caracterizados por apresentar o pH ácido, baixa teor de matéria orgânica e de fertilidade natural. Portanto, as tecnologias das Ciências do solo têm gerado melhorias para a agricultura.

Aos autores dos diversos capítulos, pela dedicação e esforços sem limites, que viabilizaram esta obra que retrata os recentes avanços científicos e tecnológicos nas Ciências Agrárias, os agradecimentos dos Organizadores e da Atena Editora.

Por fim, esperamos que este livro possa colaborar e instigar mais pesquisadores na constante busca de novas tecnologias para as áreas de biologia do solo, física do solo, química do solo, morfologia e classificação do solo e, assim, garantir incremento quantitativos e qualitativos na produção de alimentos para as futuras gerações de forma sustentável.

Alan Mario Zuffo

Fábio Steiner

SUMÁRIO

CAPÍTULO 19

RENEWAL OF THE ADSORPTIVE POWER OF PHOSPHORUS IN OXISOL

Gustavo Franco de Castro
Universidade Federal de Viçosa, Campus Viçosa
Viçosa- Minas Gerais

Jader Alves Ferreira
Universidade Federal de Viçosa, Campus Rio Paranaíba
Rio Paranaíba- Minas Gerais

Denise Eulálio
Universidade Federal de Viçosa, Campus Rio Paranaíba
Rio Paranaíba- Minas Gerais

Allan Robledo Fialho e Moraes
Universidade Federal de Viçosa, Campus Rio Paranaíba
Rio Paranaíba- Minas Gerais

Jairo Tronto
Universidade Federal de Viçosa, Campus Rio Paranaíba
Rio Paranaíba- Minas Gerais

Roberto Ferreira Novais
Universidade Federal de Viçosa, Campus Rio Paranaíba
Rio Paranaíba- Minas Gerais

RESUMO: A fixação de fósforo (P) no solo é uma grande preocupação para a comunidade científica, dadas as reservas limitadas deste nutriente. Este trabalho estuda a possibilidade de renovação do poder de fixação de P em solos. As amostras foram coletadas nas profundidades de 0-20 e 20-40 cm em um Latossolo Vermelho. Utilizou-se o delineamento experimental inteiramente casualizado, com esquema fatorial de 2 solos x 4 doses de P x 4 tempos de contato, com três repetições. Subamostras de cada tratamento foram submetidas a análises de P remanescente (P-rem) e P disponível. Para avaliar a possível difusão de P para o interior dos agregados do solo, eles foram selecionados a partir da camada de 0-20 cm dos tratamentos sem P, e com a aplicação de 2250 mg dm^{-3} de P aos 5 e 90 dias de contato . Os agregados foram analisados por microscopia eletrônica de varredura. O P disponível indicou que, para as doses aplicadas, o teor de P diminuiu com o aumento do tempo de contato do fertilizante fosfatado com os solos. A diminuição da P-rem com o aumento do tempo de contato do solo com a fonte P é uma indicação do aumento da capacidade máxima de adsorção de P. A distribuição uniforme de P no interior dos agregados, em menos de cinco dias de tempo de contato, indica que a renovação do poder de adsorção de P no solo, como uma reação lenta, passa por mecanismos adicionais para que este elemento migre para o interior das estruturas do solo.

PALAVRAS-CHAVE: P ocluso, Difusão de P, Residual de P, Fertilização fosfatada

ABSTRACT: Phosphorus (P) fixation in soil, is of great concern to the scientific community given the limited reserves of this nutrient. This work studies the possibility of renewing the fixation power of P in soils. Samples were collected at the depths of 0-20 and 20-40 cm in a Oxisol. A completely randomized experimental design was used, with a factorial scheme of 2 soils x 4 doses of P x 4 times of contact, with three repetitions. Subsamples of each treatment were subjected to analyses of P remaining (P-rem) and P available. To evaluate the possible diffusion of P to the interior of the soil aggregates, they were selected from the 0-20 cm layer of the treatments without P, and with the application of 2250 mg dm^{-3} of P at 5 and 90 days of contact. The aggregates were analyzed by scanning electron microscopy. The P available indicated that for the applied doses the P contents decreased with the increase in the contact time of the phosphate fertilizer and soils. The decrease in P-rem with the increase in contact time of the soil with the P source is an indication of the increase the maximum adsorption capacity of P. The uniform distribution of P in the interior of the aggregates, at less than five days of contact time, indicates that the renewal of the adsorptive power of P in the soil, as a slow reaction, passes through additional mechanisms for this element to migrate to the interior of the soil structures.

KEYWORDS: P-occluded, Diffusion of P, Residual of P, Phosphating fertilization.

1 | INTRODUCTION

Over a century ago, Heck (1934) said that many soils, particularly those of lateritic formation, presented little response from plants when fertilized with a soluble source of P. The initial thinking that these soils were not deficient in this nutrient was gradually replaced by the finding of their rapid fixation in forms little or not available to plants and that higher P doses were necessary to meet soil demand as a drain competitive with the plant for this nutrient (Menezes-Blackburn et al. 2016; Roy et al. 2016).

When searching the Internet today for “phosphorus dynamic in the soil” or “phosphorus in the plant”, more than 11 million results are found for the first and more than one million were found for the second search. Despite intense research work on this nutrient however there remains even today a question similar to that of the past century: Why Cerrado soils, particularly those more weathered and clayey, which received massive fertilizations with P since century ago, are still unable to dispense the traditional application of large doses of P, as used in previous years of cultivation? Some of these regions, such as PADAP (Alto Paranaíba Directed Settlement Program) created in 1973 in the municipalities of Rio Paranaíba, São Gotardo, Ibiá and Campos Altos (Santos et al. 2013), in Minas Gerais, are cultivated in Oxisols, usually three crops annually, in succession (soy, wheat and corn) and receive annually around a t ha^{-1} of P_2O_5. Why has there not been saturation of the sorptive power of these soils with P?

In these soils, the Fe and Al oxyhydroxides, and with lower expression the kaolinite, are the principal oxyhydroxides responsible for P adsorption (Yoon et al. 2014; Bortoluzzi et al. 2015). In this process, the added P is adsorbed by the solid phase, with the velocity of adsorption and the total quantity adsorbed being dependent of the minerological and chemical characteristics of the adsorbent (Fontes and Weed 1996), the chemical characteristics of the adsorbate (Oliveira et al. 2014) and the degree of saturation of the soil with P (Rheinheimer et al. 2003; Barrow 2008;). Thus, soils may adsorb values around 0.415 mg g^{-1} (Barbieri et al. 2013) 2.930 mg g^{-1} (Mesquita Filho and Torrent 1993) and even 4.0 mg cm^{-3} of P (Ker 1995), with the latter value being equivalent to a phosphating with a soluble source, incorporated in the 0-20 cm layer, corresponding to 18.4 t ha^{-1} of P_2O_5.

When the phosphate soluble fertilizers are applied to the soils, a rapid reaction occurs, characterized by the initial adsorption of P followed by a slow adsorptive reaction, which reduces the efficiency of the fertilizers over time (Barrow 1974; Mendoza 1992). The explanations found in the literature for this slow and continuous reaction include the formation of additional covalent bonds either bidentate or binuclear bonds (Novais and Smyth 1999; Yang et al. 2013; Barrow 2015), diffusive penetration (diffusion) of the P into the aggregates, pores and imperfections in the mineral crystals or between crystalographic domains of the soil minerals (Barrow 1983; Madrid and De Arambarri 1985; Willett et al. 1988; Torrent et al. 1992; Ruan and Gilkes 1996; Barrow 2015; Barrow and Debnath 2014).

There are references in the literature that prefer the term “P-occluded” to refer to slow adsorption and consequent “disappearing” of P in the soils. According to various authors (Smeck 1985; Yang et al. 2013), P-occluded refers to P physically encapsulated by secondary minerals such as Fe and Al oxyhydroxides. Similarly, Walker and Syers (1976) defined it as a form of P incorporated in layers or coatings formed by the deposition of compounds of Fe and Al. This P-occluded formation follows parallel to the development (weathering) of the soils (Walker and Syers 1976; Smeck 1985; Crews et al. 1995; Izquierdo and Houlton 2013), requiring periods of geologic time (Smeck 1985) of up to 22 thousand years, as suggested by Walker and Syers (1976). According to many of these authors, when the final state of soil development is reached, only two forms of P remain: stable organic-P and the P-occluded, with this being considered unavailable to plants. Smeck (1985) states that even soils with good initial P availability may arrive at a point where the supply of this element may become inadequate, due to P-occluded formation. At this point, the plants would depend only on the mineralization of the organic-P to meet their metabolic requirements. Bolland and Baker (1998) found that the P of one dose applied 20 years ago was essentially no longer available when evaluated after that time period but, on the other hand, increased the effectiveness of a new dose of added P.

Thus, the probable mechanisms involved in the renewal of the adsorptive power of P in the soils, in a more intense way than the more weathered soils, suchas in the Oxisols, are summarized in diffusion of P in solution to the interior of aggregates or pores of minerals of the soil and the occlusion of the P-labile (P non-occluded) previously adsorbed, by the deposition of secondary minerals on this adsorption surface. It may be further speculated that the formation of additional covalent bonds to the former would reduce the initial adsorptive power of the soil, given the consumption of a second bond for the formation of non-labile or P-occluded. According to Barrow and Debaath (2014), although enormous quantities of P are applied to the agricultural soils of the world, little is known about maintaining the supply of this nutrient for the plants.

Thus, the objective of this work was to evaluate the possible renewal of the adsorptive power of P in Oxisol, subjected to different doses of P at different contact times with the soil.

2 | MATERIALS AND METHODS

The experiment was done in the laboratory, at ambient temperature (20-30 ºC), at the Universidade Federal de Viçosa (UFV) - Rio Paranaíba Campus, in Rio Paranaíba, Minas Gerais State, Brazil. The soil used was a Oxisol (USDA 1999), collected in the region of Patos de Minas, in area under a natural forest. The choice of a natural forest an uncultivated area for soil collection is because of soil use and management practices, such as liming, phosphating fertilization, among others, which interfere with chemical and physical characteristics of the soil, with potential to modify results in the present work.

Samples were collected at the depths 0-20 and 20-40 cm, then air dried, ground, and passed through a sieve with a 2 mm mesh, obtaining air-dried fine earth (ADFE). Samples were sent to the Laboratory of Soil Analysis of the Federal University of Viçosa, for chemical and physical characterization of the samples (Table 1).

The mineralogical composition of the soils was determined by X-ray diffraction (XRD). The XRD analyses of the samples, in the form of powder, were done using a graphite crystal with a monochromator to select the radiation of the Cu-$K_{\alpha 1}$ with $\lambda = 1.5406$ Å and a step of 0.02 $^{o} \cdot s^{-1}$ on a Shimadzu XRD-6000, with a scanning angle between 4 and 70 º 2θ.

To evaluate the renewal of the adsorptive power of P of the soils, the treatments were composed of different doses of P and times of contact. Acompletely randomized experimental design was used, in factorial scheme of 2 soils x 4 doses of P x 4 times of contact, with three repetitions, totaling 96 samples.

The total P doses used were 0, 250, 750 and 2250 mg dm^{-3}. The source of P was the MonoAmmonic Phosphate (MAP) with 61 % of P_2O_5 and 12 % of N. The source was solubilized in 90 mL of distilled water and then added to soils (0.5 dm^3) and homogenized. The experimental units were transferred to dry plastic bags (12 x 25 cm), and the water content was increased to Field Capacity (FC). The individual weight of each sample was obtained with the objective of always keeping the humidity close to FC. Finally, the experimental units were incubated in triplicate for 5, 30, 60 and 90 days.

Attribute	$Soil_{layer}$ (0-20 cm)	$Soil_{layer}$ (20-40 cm)
pH_{H2O}	6.04	6.18
P (mg dm^{-3})	32.20	26.80
K (mg dm^{-3})	200	98
Ca^{2+} (cmol$_c$ dm^{-3})	12.74	7.73
Mg^{2+} (cmol$_c$ dm^{-3})	4.16	3.19
Al^{3+} (cmol$_c$ dm^{-3})	0.00	0.00

H+Al ($cmol_c\ dm^{-3}$)	5.40	5.30
SB ($cmol_c\ dm^{-3}$)	17.41	11.17
t ($cmol_c\ dm^{-3}$)	17.41	11.17
T ($cmol_c\ dm^{-3}$)	22.81	16.47
V (%)	76.30	67.80
m (%)	0.00	0.00
MO ($dag\ kg^{-1}$)	6.91	4.22
P-rem ($mg\ L^{-1}$)	11.90	5.70
Course sand ($kg\ kg^{-1}$)	0.118	0.121
Fine sand ($kg\ kg^{-1}$)	0.086	0.100
Silt ($kg\ kg^{-1}$)	0.238	0.210
Clay ($kg\ kg^{-1}$)	0.558	0.569
Texture classification	Clay	Clay

Table 1 – Chemical and physical characterization of the samples of soil

P = Mehlich-1; H + Al = potential acidity; SB = sum of bases; t = effective capacity of cation exchange; T = capacity of exchange of cations at pH = 7; V = saturation by bases; m = saturation by aluminum; OM= organic matter; P-rem = P remaining.

During the contact period the samples were monitered weekly by means of weighing, aiming to maintain the humidity initially applied. After the contact period, the samples were dried in a controlled environment at 35 ºC for 5 days. The soils were again passed through a sieve with a 2 mm mesh and then homogenized.

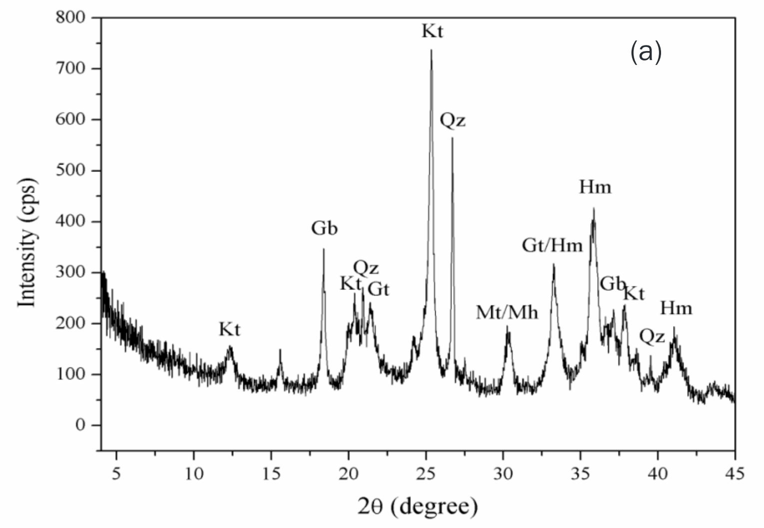
Subsamples of each treatment were subjected to analyses of P remaining (P-rem), and P available by the extractors Mehlich-1 (M-1), Mehlich-3 (M-3) and Anionic resin (AR). P-rem was obtained according to the methodology described by Alvarez V. et al. (2000), shaking for 5 min 10 cm^3 of soil with 100 mL of solution of $CaCl_2$ 10 mmol L^{-1}, containing 60 mg L^{-1} of P. After shaking the solution remained at rest for 16 h, to determine the P-rem. In the extraction by the M-1 (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}) was used a 1:10 soil:solution relation, with shaking for 5 min in a horizontal shaker at 200 rotations per min (rpm) and left at rest for 16 h, according to Braga and Defelipo (1974). The P was extracted by the M-3 (CH_3COOH 0.2 mol L^{-1} + NH_4NO_3 0.25 mol L^{-1} + NH_4F 0.015 mol L^{-1} + HNO_3 0.013 mol L^{-1} + EDTA 0.001 mol L^{-1}) (Mehlich 1984), also in the 1:10 soil:solution relation, with agitation for 5 min in a horizontal shaker at 200 rpm and 16 h of rest. Analyses of P-available by the AR (Amberlite IRA-402) followed the procedures proposed by Raij et al. (2001). The P in the solutions extracted by the different methods were measured by colorimetry, on a molecular absorption spectrophotometer of the phospho-molybdic complex with ascorbic acid reduction.

To evaluate the possible diffusion of P to the interior of the aggregates of the soils, aggregates were selected from the 0-20 cm layer. We chose to evaluate the aggregates of the treatments without the application of P, in comparison to the aggregates with the application of 2250 mg dm^{-3} of P at 5 and 90 days of contact, totaling three samples. Slides were made of the aggregates by means of impregnation with polyesther resin and later ultra-polishing, obtaining final sections for later analysis. The final sections of the aggregates were analyzed and photographed on a scanning electron microscope (SEM) and elemental microanalysis spectrometer (EMS). The areas selected for the three samples of aggregates included their external and internal parts, with the objective of obtaining microchemical maps that indicate the diffusion of P to the interior of the aggregates.

Results were subjected to variance analysis and analysis of regression. In this analysis were evaluated the available P contents as a function of the contact time of the P source with the respective soil doses.

3 | RESULTS AND DISCUSSION

The X-ray diffractograms in the 0-20 and 20-40 cm soil layers presented a profile characteristic of the Oxisols, with the presence of minerals such as hematite, gibbsite, goethite and kaolinite (Figure 1). The predominance, quantity and quality of these clay materials are important factors to be considered in evaluating the phenomena of P adsorption (Neto et al. 2009) and its impact on the availability of this nutrient for the plants (Novais and Smyth 1999). Although there are works in the literature that correlate P adsorption with the soil clay content (Fernández R et al. 2008; Barbieri et al. 2013; Oliveira et al. 2014), in tropical conditions, principally the Fe and Al oxyhydroxides and kaolinite are responsible for P adsorption (Fontes and Weed 1996;Yoon et al. 2014; Bortoluzzi et al. 2015). In these conditions, soils with clayey texture are characterized by presenting a higher adsorption (Motta et al. 2002; Fink et al. 2014; Oliveira et al. 2014) and their intensity and magnitude may influence the source or sink of soil P for the plants (Pinto et al. 2013).



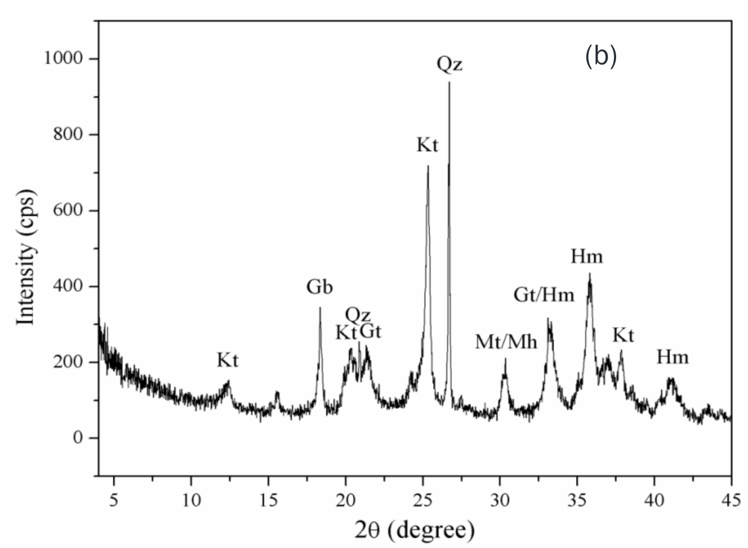


Figure 1 –X-ray diffractograms for: (a) sample from 0-20 cm soil layer and (b) sample from 20-40 cm soil layer. Kt = kaolinite; Gb = gibbsite; Qz = quartz; Gt = goethite; Mt = magnetite; Mh = maghemite; Hm = hematite.

The P contents obtained by M-1, M-3 and AR for the doses 250, 750 and 2250 mg dm^{-3}, decreased, in a general way, with the increase of the contact time of the source of P with the soils (Table 2). By individually analyzing the doses of applied P and the different contact times, it is possible to observe, by means of regression analysis, the influence of the time of the contents of available P obtained by the different extractors used (Table 3). As stated, those values tend to decrease with the increase in contact time for the majority of the cases, but for the treatments where there was no application of the P, time did not significantly influence the contents of P, as expected (Table 3). According to Fernández R. et al. (2008), the minerals of the soil, principally goethite and gibbsite, directly influence the development of non-labeled forms of P. The P associated to these minerals may become occluded, in the interior of the clay minerals (Gustafsson et al. 2012). Barrow (1974) and Mendoza (1992) hypothesized that when fertilizing the soils with phosphate, a rapid reaction occurs, where the initial adsorption of P, followed by a slow adsorptive reaction, may reduce the efficiency of phosphate fertilization over time. According to Parfitt (1979), that slower adsorption step is dependent on time and characterized by P diffusion to the interior of aggregates, from pores and crystallographic imperfections, making the P unavailable to plants. According to Novais and Smyth (1999), that process may be described as the probable aging of P in the clayey soils.

P dose (mg dm^{3-})																
	0				**250**				**750**				**2250**			
	Contact Time (days)															
	5	**30**	**60**	**90**	**5**	**30**	**60**	**90**	**5**	**30**	**60**	**90**	**5**	**30**	**60**	**90**
Extractor	**P-available (mg dm^{-3})**															
M-1 (0-20 cm)	25.10	23.54	24.56	26.47	54.53	49.14	48.69	45.68	141.76	127.89	117.18	110.85	604.22	578.66	561.13	510.01
M-3 (0-20 cm)	12.75	10.79	9.26	9.55	22.26	16.54	16.07	14.99	59.31	43.57	43.37	35.07	318.87	251.39	166.01	160.73
AR (0-20 cm)	76.47	78.50	74.77	75.80	153.57	146.60	137.73	123.29	363.97	325.77	312.63	269.93	1147.57	1078.80	897.40	847.40
M-1 (20-40 cm)	18.35	17.74	18.54	18.45	40.65	39.38	40.93	37.73	112.79	102.56	101.10	96.72	540.68	504.89	499.78	467.65
M-3 (20-40 cm)	6.29	7.42	7.40	8.08	11.44	10.20	11.83	9.64	35.26	33.33	28.69	28.40	186.75	149.14	145.27	131.36
AR (20-40 cm)	74.00	68.23	69.53	68.80	156.07	136.07	132.77	117.23	338.23	322.87	292.90	246.07	1143.67	1046.50	952.47	771.17
	P-rem (mg L^{-1})															
0-20 cm	11.20	10.91	11.01	11.09	12.84	12.04	12.35	11.28	21.28	19.45	15.32	16.79	43.96	37.41	34.23	32.21
20-40 cm	5.68	5.40	5.89	5.22	11.28	9.53	7.24	7.56	16.88	13.75	11.73	10.73	37.35	31.02	28.11	25.97

Table 2 –P content extracted by Mehlich-1 (M-1), Mehlich-3 (M-3), Anionic resin (AR) and P-remaining (P-rem) as a function of the application of increasing P doses in the 0-20 and 20-40 cm layers of a Oxisol at different contact times

Dose (mg dm^{-3})	Equation	R^2	p
	Soil (0-20 cm)		
	Mehlich-1		
0	M-1 = 24.029 + 0.019^{ns}T	0.333	0.422
250	M-1 = 53.831 - 0.093°T	0.872	0.065
750	M-1 = 141.073 - 0.360*T	0.960	0.020
2250	M-1 = 612.371 - 1.056*T	0.955	0.022
	Mehlich-3		
0	M-3 = 12.362 - 0.038^{ns}T	0.792	0.109
250	M-3 = 20.988 - 0.076^{ns}T	0.740	0.139
750	M-3 = 56.968 - 0.251°T	0.837	0.084
2250	M-3 = 314.323 - 1.947*T	0.901	0.050
	Anionic resin		
0	RA = 77.358 - 0.021^{ns}T	0.242	0.507
250	RA = 156.541 - 0.351**T	0.981	0.009
750	RA = 365.806 - 1.032*T	0.960	0.020
2250	RA = 1168.466 - 3.798*T	0.953	0.023
	Soil (20-40cm)		
	Mehlich-1		
0	M-1 = 18.078 + 0.004^{ns}T	0.179	0.577
250	M-1 = 40.846 - 0.025^{ns}T	0.410	0.360
750	M-1 = 111.221 - 0.171°T	0.862	0.071
2250	M-1 = 539.350 - 0.781*T	0.924	0.039
	Mehlich-3		
0	M-3 = 6.443 + 0.018°T	0.841	0.082
250	M-3 = 11.383 - 0.013^{ns}T	0.220	0.531
750	M-3 = 35.501 - 0.088*T	0.906	0.048
2250	M-3 = 180.212 - 0.586°T	0.829	0.089
	Anionic resin		
0	RA = 72.359 - 0.048^{ns}T	0.452	0.328
250	RA = 154.798 - 0.415*T	0.923	0.039
750	RA = 350.097 - 1.083*T	0.965	0.017
2250	RA = 1175.636 - 4.263*T	0.979	0.011

Table 3- Simple linear regression between the P contents obtained by Mehlich-1 (M-1), Mehlich-3 (M-3) and Anionic resin (AR) as a function of the contact times of the P source with the soil at its respective doses in the 0-20 and 20-40 cm layers of a Oxisol

^{ns} = not significant. °, * and **, significant at 10, 5 and 1 %, by the t test. T = contact time.

In research done by Oliveira (2010), the sensitivity of the extractors M-1, M-3 and AR were also shown in relation to different contact times and P doses. In that study, the author added increasing doses of P (0 to 600 mg Kg^{-1} of soil) in soils with contents from close to zero up to 800 g Kg^{-1} of clay, also testing different contact times (1, 30, 90 and 180 days). In the experimental units with 800 g Kg^{-1} of clay, 30 days of contact and P dose of 600 mg Kg^{-1} of soil, the authors found extractions of 5.36, 1.17 and 4.75 % of total P added for the extractors M-1, M-3 and AR. Thus, as demonstrated by Oliveira (2010), the results found in this work confirmed a lower efficiency of fertilization with the increase in contact time between the soil and the source of P. For these authors, there was a strong tendency to decrease the available P with the increased contact time of the phosphate fertilizer and the soil, which suggests the renewal of the adsorptive power of the clayey soils, and particularly of those richer in Fe and Al oxyhydroxides.

A complementary analysis that helps in evaluating of the adsorptive power of the soils is P-rem. According to Alvarez V. et al. (2000), this measurement may present significant correlation with the soil buffer capacity (SBC) and with the maximum adsorptive capacity of phosphate (MACP). In all experimental units, P-rem was analyzed after the contact time (Table 2). The P-rem values in the 0-20 cm layer were higher than those found in the 20-40 cm layer, consistent with its higher organic matter (OM) content (Table 1). The higher OM content in the soil surface horizons may influence the P adsorptive processes. The organic acids present in the OM may reduce P adsorption by direct competition with P by blocking the adsorption sites and may increase the availability of P for the plants (Andrade et al. 2004; Guppy et al. 2005). In this sense, the highest OM contents on the surface horizons interfere in the P-rem analyses.

The P-rem values of the 0-20 cm soil layer presented significant changes with time only for the 2250 mg dm^{-3} dose (Table 4). In the 20-40 cm layer, there was significance for the doses 250, 750 and 2250 mg dm^{-3}at the different contact times (Table 4). The mean increase of the P-rem values for the soils of the two layers, with the increase of the P dose from 0 to 2250 mg dm^{-3}, indicate the saturation of the adsorption power of the soils (Table 2). On the other hand, for that higher P dose, the decrease of the mean value of P-rem with the increase of the contact time from 5 to 90 days indicates the renewal of the P adsorption power of the soils (Table 2).

The decrease in P-rem with the increased equlibrium time of the soil with the source of P is an indication of the increase of the SBC or MACP values of the soil, as observed in the literature (Fernández R. et al. 2008). The increase of this value implies higher P demand for plant growth and development. In other words, a renewal of the adsorptive power of P by the soil.

The variation in the percentage of P measured by EDS for the three aggregates was 3.61, 5.09 and 5.20 % for aggregates 1, 2 and 3 (Table 5).

The SEM images and the P distribution maps in the soil aggregates are presented in Figure 2. Those maps indicate a uniform distribution of P in the aggregate mass and not only on the aggregate surface, consistent with an apparently unsatisfactory contact time of only five days, for a more intense diffusion.

A study on the effect of the phosphate contact time on the adsorption and migration (diffusion) of phosphate for the interior of ferridrite and goethite particles showed that the adsorption was complete for the goethite at three days of contact, remaining constant up to 260 days, and six days with the ferridrite (Willett et al. 1988). These relatively low contact times indicate the time required for phosphate to migrate to the interior of the particles of the Fe minerals. Large goethite crystals and their few pores caused the phosphate to have rapid access to the surface of this mineral and causes lower migration to the interior of the particles, reaching equilibrium rapidly. This migration of the phosphate throughout the particle in six days of contact with the source of P, although with a small but perceptible presence of phosphate in the center of the particles, occured after a rapid initial adsorption of this anion.

In the present work (Figure 2), a uniform P distribution was observed in the soil aggregates even at the shortest contact time tested (five days) of the P source with the soil and did not visibly differ from the 90 day contact time. This result is consistent with those obtained for ferridrite and goethite by Willett et al. (1988), with rapid and total migration of P in less than five days. The slow P adsorption reactions in soils certainly involve additional mechanisms for P diffusion to the interior of soil structures, restricting availability for plants, since for the sample of the 20-40 cm soil layer, P-rem decreased linearly with contact time up to the longest time tested (90 days) for all applied doses (Table 4).

Dose (mg dm^{-3})	Equation	R^2	p
	Soil (0-20 cm)		
0	P-rem = 11.083 - 0.006^{ns}T	0.040	0.800
250	P-rem = 12.832 - 0.015^{ns}T	0.736	0.142
750	P-rem = 21.036 - 0.061^{ns}T	0.712	0.156
2250	P-rem = 43.107 - 0.133*T	0.910	0.046
	Soil (20-40cm)		
0	P-rem = 5.692 - 0.003^{ns}T	0.150	0.612
250	P-rem = 11.060 - 0.046°T	0.835	0.086
750	P-rem = 16.558 - 0.071*T	0.929	0.035
2250	P-rem = 36.547 - 0.128*T	0.912	0.044

Table 4 –Simple linear regression between the P-remaining (P-rem) content as a function of the contact times of the P source with the soil at its respective doses in the 0-20 and 20-40 cm layers of a Oxisol

^{ns} = not significant. ° and *, significant at 10 and 5 % by the t test. T = contact time.

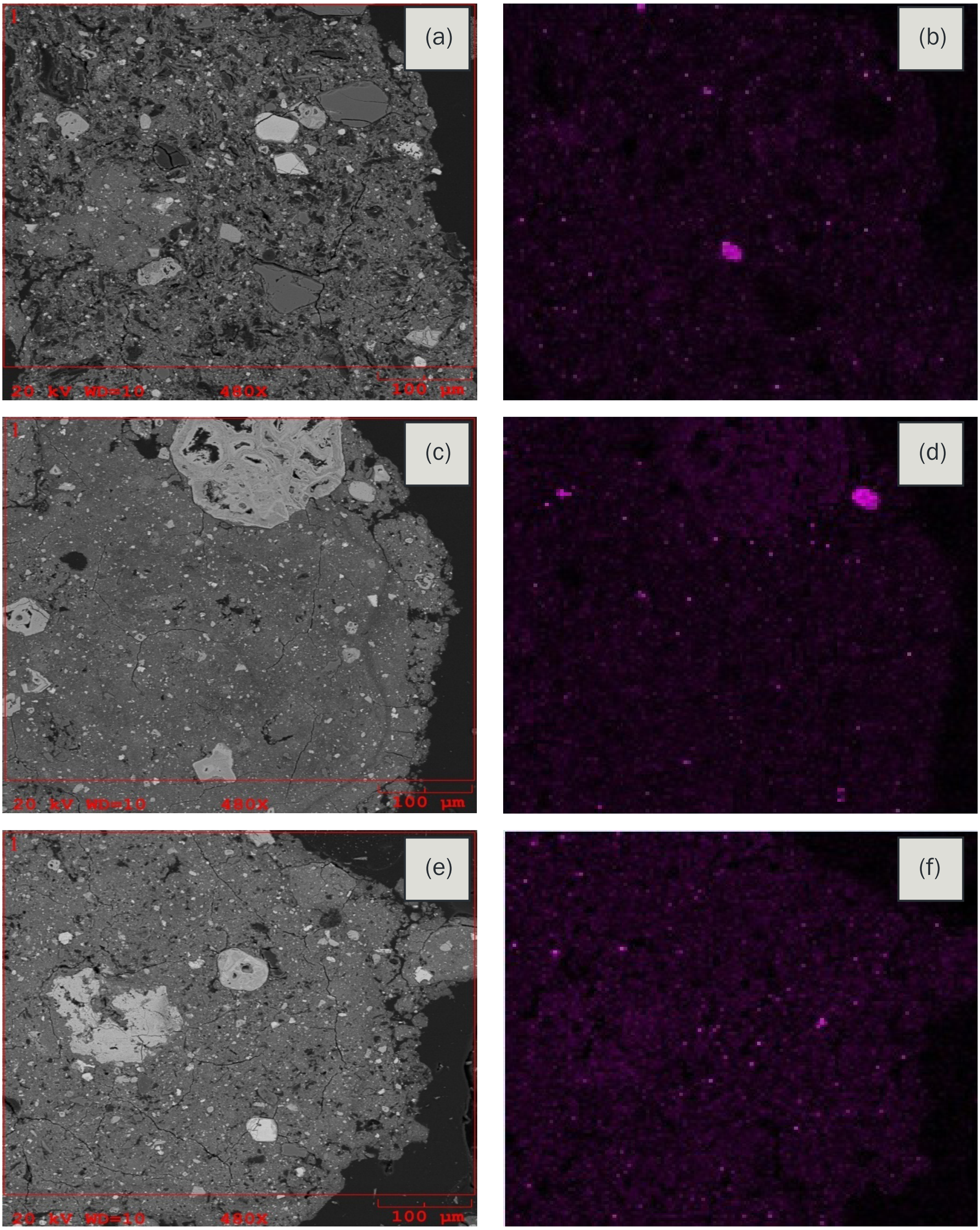


Figure 2 – Images obtained by SEM and microchemical maps of EDS of P for (a) and (b) Aggregate without addition of phosphate fertilizer; (c) and (d) Aggregate after 5 days of contact and 2250 mg dm^{-3} total P dose; (e) and (f) Aggregate after 90 days of contact and 2250 mg dm^{-3} total P dose.

Aggregate	Mg (%)	Al (%)	Si (%)	P (%)	Ca (%)	Fe (%)
1	1.51	29.28	29.87	3.61	3.40	32.34
2	1.35	36.16	24.41	5.09	1.06	31.94
3	1.35	29.22	22.46	5.20	1.51	40.26

Table 5 - EDS data for aggregates analyzed

1 = aggregate without addition of phosphate fertilizer; 2 = aggregate after 5 days of contact and 2250 mg dm^{-3} P dose; 3 = aggregate after 90 days of contact and 2250 mg dm^{-3} P dose.

4 | CONCLUSIONS

The P content obtained by M-1, M-3 and AR showed decreases with the increase of contact time of the phosphate fertilizer and the soils.

The P-rem values in the 0-20 cm soil layer, with higher OM content, presented significant decreases over the contact times only for the 2250 mg dm^{-3} dose. In the 20-40 cm soil layer, with lower OM content, all doses and contact times were significant. The decrease in P-rem with the increased contact time of the soil with the P source is an indicator of the increase of values of the SBC or of the MACP of the soil, implying higher P demand by plants or renewal of the adsorptive power of P in the soil.

The uniform distribution of P in the interior of the aggregates, even at the shortest contact time studied (five days), indicate that the renewal of the adsorptive power of the soil, as a slow reaction, passed through additional mechanisms for this element to migrate to the interior of the soil structures.

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