Phosphorus adsorption capacity in sandy textured soils with built fertility

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Received in: July 22, 2021 | Accepted in: November 24, 2021

Abstract

The specific adsorption of phosphorus in minerals from the clay fraction of the soil, such as Fe and Al oxyhydroxides, is responsible for the decrease in the availability of this element for plants. In Brazil, this condition is studied substantially in medium to very clayey textured soils, whose adsorption activity is expressive. The aim of this study was to evaluate the maximum phosphorus adsorption capacity (CMAP) in sandy-textured soils with fertility built in the Cerrado biome. Areas with representative soils were selected in the cities Luís Eduardo Magalhães (LEM / BA) and Guaraí (TO), with the following vegetation cover: a) LEM: natural vegetation and cotton; b) Guaraí: natural vegetation and soybean. Soil samples were collected in the 0-20 cm and 60-80 cm layers, in which chemical and physical analyzes were performed periodically, as well as analyzes related to phosphorus adsorption such as Prem and CMAP and PESN. Prem contents are higher in the 0-20 cm layer for the LEM region. The CMAP is not very expressive in the soils of the two studied regions, with the Guaraí soils having higher relative adsorption potential due to the higher values of the CMAP/clay ratio.

Keywords: Phosphate retention. Prem. CMAP. Sandy soils.

Introduction

The expansion of Brazilian agriculture has been taking place preferentially in areas that present a favorable terrain for cultivation operations, low cost per unit of area and in regions with established agriculture. There are soils with the textural classes as sandy, loamy sandy and sandy loam, which are called "light textured soils" (DONAGEMMA *et al.*, 2016) or simply "sandy soils" (HUANG; HARTEMINK, 2020).

With these characteristics, the most expressive soil classes are the *Neossolos Quartzarênicos, Latossolos Vermelhos, Amarelos* and *Vermelho-Amarelos psamíticos e Argissolos Vermelho-Amarelos* and *Amarelos* with a sandy/ medium texture (DONAGEMMA *et al.*, 2016). The greatest occurrence of these soils is verified in the west of Bahia, north and northeast of Tocantins, northwest of Minas Gerais, southwest of Goiás, northeast of Pará, northwest of Paraná, Center-south of Rio Grande do Sul, west of São Paulo and several regions of Mato Grosso and Mato Grosso do Sul. These soils can be listed as main limitations to cultivation the low levels of organic matter, the poor stability of aggregates, and especially the low capacity of water retention, retention and availability of nutrients. On the other hand, the low buffering capacity favors corrections by fertilizers and correctives, mainly phosphorus (P), since it is unavailable for crops in tropical soils.

From this point of view, aiming to evaluate the availability of P as a function of specific adsorption, fixation or precipitation, the studies focus on the evaluation of the remaining phosphorus (Prem), which is used in the evaluation of the buffer capacity of the soil in relation to P, S and Zn. This analysis assesses the availability and affinity of P after a soil sample is subjected to contact with a solution with known P content (ALVAREZ V. *et al.*, 2000). From the Prem, it is possible to determine the maximum phosphorus adsorption capacity (CMAP), which serves as a measure to assess soils regarding the potential for P remobilization.

P sorption is a phenomenon whose intensity and magnitude depend on the soil constituents. As correlated attributes, the clay content, mineralogy, degree of crystallinity of iron oxides, degree of humification and organic matter content stand out (NOVAIS; SMYTH, 1999). However, in addition to the quantitative expression of the soil, a large part of the surface phenomena varies as a function of the zero charge point (PCZ), which controls the dynamics of several elements, especially P. This condition is favored in tropical soils due to the high values of PCZ, conditioning predominantly positive charges and creating favorable conditions for the adsorption of ions, such as phosphate (EBERHARDT *et al.*, 2008).

In terms of mineralogy, it can be evaluated as a source or drain of P. In soils with a low degree of weathering it can function as a source, while in highly weathered soils it can function as a drain (NOVAIS; SMYTH, 1999). In an opposite direction, organic matter indirectly affects phosphate adsorption by inhibiting the crystallization of iron and aluminum oxides (SOURCES; WEED, 1996; BORGGAARD *et al.*, 1990), or even blocking the adsorption sites by means of organic acids of low molecular weight and the coating of the surface of the oxides (FONTES *et al.*, 1992).

Given this observation, even with the expectation of greater availability of P in sandytextured soils, evaluating the potential for adsorption or fixation can ensure, in addition to effectiveness, greater efficiency in the use of phosphate fertilizers. In this sense, two regions of great agricultural importance stand out, one in western Bahia, with at least 35 years of agricultural cultivation - consolidated agriculture, and another in the Middle Valley of Tocantins River, with approximately 10 years of agricultural cultivation - agricultural border. The aim of this study was to evaluate CMAP in sandy textured soils with fertility built in the Cerrado biome.

Material and methods

For the study, areas of intensive agricultural production with differentiated use and management were selected, one in the city Luís Eduardo Magalhães (LEM), in the western region of the state of Bahia, and the other in the city Guaraí, located in the region of Medium Valley of Tocantins in the state of Tocantins.

Luís Eduardo Magalhães is located in Chapadão do Alto Rio Grande, in the Rio Grande hydrographic basin, on the left bank of the São Francisco River. The geomorphology highlights the Western Plateau of the São Francisco in a flat to gently undulating relief and the region's altitude varies from 700 m to 900 m. The geology is related to the Cretaceous period, with sandstones from the Urucuia Group, which are composed of sandstones of different colors, predominantly gray, pink and red, with fine composition, clayey or siliceous cement, sometimes with crossbedding (CPRM, 2008; CASTRO *et al.*, 2010).

The climate is hot and dry, with winter rains, with two well-defined climatic seasons, the dry and cold season from May to September and the hot, rainy season from October to April. The average temperature varies from 18 °C to 34 (INMET, 2010), while the total annual precipitation is between 1,400 mm and 1,600 mm, concentrated between the months of November and March (BATISTELLA *et al.*, 2002).

Guaraí is located on a sedimentary basin of the Tocantins River hydrographic basin. The geomorphology indicates the depression of the Middle Tocantins, and in the longitudinal depression of the Tocantins in a flat to smooth undulating relief and at an altitude between 200 m and 400 m. The geology is related to the sedimentary cover of the Tertiary and/or Tertiary–Quaternary period, with sandstones of varied color and granulometry, as well as claystones and siltstones. The climate is humid/ sub-humid with moderate water deficit and an average annual temperature of 26.5 °C. The total annual precipitation is 1800 mm to 1900 mm, concentrated in the summer and with high intensity (SOUZA *et al.*, 2012).

The soils of both study areas are classified as typical dystrophic *LATOSSOLOS VERMELHO-AMARELOS Distróficos típicos*, medium texture (Luís Eduardo Magalhães) and *NEOSSOLOS QUARTZARÊNICOS Órticos típicos* (Guaraí), according to the Brazilian Soil Classification System (SANTOS *et al.*, 2018).

Areas with the following vegetation cover were selected in each location: a) Luís Eduardo Magalhães: natural vegetation (VN), annual crop in conventional planting (Cotton) and, b) Guaraí: natural vegetation (VN), annual crop in no-tillage (Soybean). Cotton has been cultivated since the 90's, with the soil being prepared with deep harrowing for starting cotton ratoons. Every year there is application of limestone and fertilizing with soluble fertilizers, followed by harrowing. Soybean has been cultivated for approximately 8 years under no-tillage and fertilization with soluble fertilizers in the sowing line.

In each area, soil samples were collected at five points, in the 0-20 cm and 60-80 cm layers. The samples were air-dried, later crushed and passed through a 2.0 mm sieve, obtaining the air-dried fine earth (TFSA). The following routine laboratory analyzes were performed for soils: granulometry (coarse area, fine sand, silt and clay), pH (water), exchangeable cations (Ca, Mg, K, Na, H and Al), available P, organic carbon, organic matter (DONAGEMA *et al.*, 2011).

The remaining phosphorus (Prem) is obtained in solution after contacting 5 cm³ of TFSA with 50 mL of a 10 mmol L⁻¹ CaCl₂ solution + 60 mg L⁻¹ of phosphorus (ALVAREZ *et al.*, 2000). The Prem content is determined by colorimetry from the filtered solution after one hour of contact and homogenization (TEIXEIRA *et al.*, 2017). From the Prem contents, the Langmuir isotherms were adjusted and the Maximum Phosphorus Adsorption Capacity (CMAP) and the Adsorption Energy (EA) were evaluated.

The Langmuir equation was adjusted to the P-sorbed value, following the determination of CMAP by Eq. 1:

$$x/m = kbC/(1+kC)$$
(Eq. 1)

At which: x/m - P-sorbed [mg (x)/kg (m) of P in the soil], k - constant related to the binding energy P (L mg⁻¹), b - CMAP of the soil (mg kg⁻¹), and C - concentration of P in the equilibrium solution (mg L⁻¹).

To obtain estimates of the constants k and b, the linearized form of the Langmuir equation was used according to Eq. 2:

$$C/(x/m) = 1/kb + C/b$$
 (Eq. 2)

In the samples, the point of null saline effect (PESN) was also determined, which was obtained from the point of zero load (PCZ). The TFSA samples were subjected to contact with three different electrolyte solutions of salt formed by KCI (0.2, 0.02 and 0.004 mol L⁻¹) and under different medium conditions, ranging from acidic to basic. From the solutions, the pH is determined by potentiometric titration and three curves are obtained. Next, the PCZ is obtained by the place where the pH values of the three curves cross (PEREZ *et al.*, 2017). The pH values were obtained using the PESN software for Windows version 1.0 (ALVES *et al.*, 2002).

The Prem and CMAP contents were submitted to Pearson correlation analysis with the attributes obtained in the routine analyses. For the correlation analyses, the Prem contents obtained by volumetric basis were transformed to gravimetric basis following the proposal by Cordeiro *et al.* (2020). The T test was performed between the Prem contents of the 0-20 cm and 60-80 cm layers for the same vegetation cover and location/region.

Results and discussion

Regarding Prem contents, in general there is a decrease with increasing soil depth, being more expressive in Luís Eduardo Magalhães (LEM) (TABLE 1; FIGURE 1). In LEM soils, the contents are between 23 mg dm⁻³ in the 60-80 cm layer, under natural vegetation (VN), and 33 mg dm⁻³ in the 0-20 cm layer, under cotton. In the region of Guaraí they do not differ much in magnitude, with levels between 27 mg dm⁻³ in the 0-20 cm layer, under NV, and 30 mg dm⁻³ in the 0-20 cm layer, under soybean (TABLE 1). Between layers and the same cover, Prem contents are different in LEM soils, with higher contents in the 0-20 cm layer for both covers, while in Guaraí they are equal between the evaluated layers (TABLE 1).

Regarding possible causes for the availability of Prem, the negative correlation with clay at

-0.75** and fine sand at -0.47** stands out, being positive with coarse sand at 0.52**. These correlations are already listed, as in the case of clay, however, the sand fractioning shows a new condition, with the differentiation of the activity of coarse sand and fine sand.

When evaluated in terms of literature data from other regions of the Cerrado biome under VN, the LEM soils have the same Prem contents as Literature 2. of the same textual class (sandy loam), while in Guaraí there is a lower Prem content in comparison with Literature 1. of the same textural class (loamy sandy) (FIGURE 1). This finding reinforces the need for detailed analysis even in soils of the same textural class. In addition, it is motivated that, in addition to Prem, as an option for the evaluation and recommendation of phosphate fertilization, the Prem/clay ratio should be included in a complementary and analogous way, which provides the relative evaluation of Prem as a function of content of clay from each soil sample.

Cover	Layer	P _{rem}	P _{available}	MO	AG	AF	Clay	. Tortural Class				
	cm	mg dm ⁻³		g kg ⁻¹				Textural Class				
LEM												
Cotton	0-20	37 (6) ⁽¹⁾ a	57 (29)	10.0 (1.9)	458 (96)	315 (72)	201 (35)	Sandy clay loam				
Cotton	60-80	23 (3) b	1	4.6 (0.7)	394 (127)	295 (71)	293 (42)	Sandy clay loam				
VN	0-20	33 (3) A	1	8.7 (1.4)	523 (123)	246 (142)	136 (17)	Sandy loam				
VN	60-80	23 (1) B	1	4.3 (0.8)	434 (88)	337 (79)	196 (17)	Sandy loam				
Guaraí												
Soybean	0-20	30 (2)	35 (31)	9.2 (1.7)	498 (118)	388 (97)	81 (17)	Loamy sandy				
Soybean	60-80	28 (1)	1	1.7 (0.8)	496 (122)	360 (77)	90 (20)	Loamy sandy				
VN	0-20	27 (2)	2 (1)	9.1 (2.4)	421 (32)	414 (143)	87 (11)	Loamy sandy				
VN	60-80	28 (1)	1	2.2 (0.4)	402 (26)	447 (19)	115 (20)	Loamy sandy				

Table 1. Soil attributes in different covers and layers in LEM and Guaraí

VN: Natural Vegetation; Prem: remaining phosphorus; Available P: available phosphorus; MO: Organic matter; AG; Coarse sand; AF: Fine Sand; (1) Standard deviation of samples in parentheses. Different lowercase or uppercase letters differ significantly by the t test p < 0.05.

Source: Authors' elaboration (2021).

Figure 1. Average soil Prem contents in different covers and layers in LEM and Guaraí. Standard deviation from the mean is represented by bars. Literature 1 = Loamy Sandy Texture. Literature 2 = Sandy Loam Texture. Literature 3 = Sandy Clay Loam Texture. Literature = Bedin et al. (2003); Souza et al. (2006); Fernández et al. (2008); Pinto et al. (2013); Sandim et al. (2014).



Source: Authors' elaboration (2021).

As for the contents of maximum phosphorus adsorption capacity (CMAP), there is an increase in values with increasing soil depth (TABLE 2; FIGURE 2). In LEM soils, CMAP contents are between 129 and 221 mg kg⁻¹ in the 0-20 cm and 60-80 cm layers, both under VN (TABLE 2). In Guaraí the contents are between 150 mg kg⁻¹ in the 0-20 cm layer under soybean and 176 mg kg⁻¹ in the 60-80 cm layer under VN.

Regarding CMAP contents, the correlation is positive with clay ($r=0.53^*$), being attributed to the iron and aluminum oxyhydroxides present in the clay fraction, which have high specific adsorption capacity or P fixation (PARFITT, 1978; SPOSITO, 1989). This high specific adsorption capacity of the oxides is due to the electropositivity generated on the surface as a function of the variable charges in the pH condition of the soil solution due to the high values of the zero charge point (PCZ) and zero salt effect point (PESN) (SPOSITO, 1989; EBERHARDT *et al.*, 2008). In this sense, according to the PESN assessment, the values are, in general, higher than the pH values (in water), confirming electropositivity (TABLE 2).

On the other hand, there is a negative correlation with MO ($r = -0.59^{**}$). Thus, the presence of MO minimizes the potential for adsorption of P by minerals from the clay fraction, as it works by blocking the adsorption sites by means of low molecular weight organic acids and by covering the surface of the oxides (SOURCES *et al.*, 1992).

As for the magnitude of the CMAP contents in the present study, it is low and represents approximately half of the contents obtained in other soils with the same textural class in the literature (FIGURE 2). This finding results in the greater availability of P in the soils of this study, since there is less need for phosphate to saturate the positively charged and active sites in specific adsorption. This fact, when associated with other practices that favor the maintenance and/or increase of soil organic matter, configures favorable conditions for a greater supply of P for agricultural crops.

In this work, as a complementary form of evaluation, the CMAP/clay ratio is presented, which is effective to evaluate the relative adsorption capacity of the clay fraction. In LEM soils the values are between 0.7 to 1.1 mg of P per g of clay, while in Guaraí the values are between 1.3 to 2.0 mg of P per g of clay. With these values of the CMAP/clay ratio, the higher relative adsorption capacity of Guaraí soils stands out.

Notably, due to the data obtained in this study, the need to recommend phosphate fertilizers based on Prem contents is reinforced. According to Alvarez *et al.* (2017), Prem is more

suitable than clay content as an indirect measure of the buffer capacity of the soil in relation to P, which can be extended to S and Zn, as it is sensitive to the mineralogical nature of the clay fraction of the soil.

Additionally, Prem is sensitive to the variation in the buffering power of the soil in relation to these nutrients caused by changes in the soil organic matter content. With this technicalscientific condition, it is possible, through Prem's interpretation, to elaborate an evaluation and recommendation of optimized fertilization regarding the application of phosphate fertilizers and guarantee the necessary amount of P for agricultural cultures.

In this sense, some manuals include Prem for the assessment and recommendation of nutrients, such as the 5th Approach -Recommendations for the use of correctives and fertilizers in Minas Gerais (RIBEIRO *et al.*, 1999), for the Cerrado - Cerrado: soil correction and fertilization (SOUZA, *et al.*, 2004) and for Acre (WADT; SILVA, 2011).

Cover	Layer	Faultion (1)	R²	CMAP Binding Energy ⁽²⁾		рН								
	cm	Equation		mg kg ⁻¹	L mg ⁻¹	water	PE3N							
LEM														
Cotton	0-20	Y= 11.819x-264.08	0.9783	147	-0.0258	5.9 (0.3) ⁽³⁾	5.1							
Cotton	60-80	Y= 4.7473x-45.957	0.9968	211	-0.1033	5.2 (0.8)	6.5							
VN	0-20	Y= 7.7581x-131.67	0.9918	129	-0.0589	4.7 (0.2)	5.1							
VN	60-80	Y= 4.5199x-41.702	0.9993	221	-0.1084	5.0 (0.05)	6.2							
Guaraí														
Soja	0-20	Y= 6.6626x-99.372	0.9984	150	-0.0670	6.3 (0.4)	5.4							
Soja	60-80	Y=5.8651x-76.631	0.9995	171	-0.0765	5.0 (0.3)	6.8							
VN	0-20	Y=5.8748x-76.116	0.9960	170	-0.0771	4.6 (0.2)	5.2							
VN	60-80	Y=5.6906x-71.717	0.9991	176	-0.0793	5.4 (0.2)	5.0							

Table 2. Linear equation of the Langmuir isotherm, pH water and PESN of soils in different covers and layers in LEM and Guaraí.

 $^{(1)}Y=C/(x/m)$ in g g⁻¹; CMAP = maximum phosphate adsorption capacity; $^{(2)}$ Constant a related to the phosphate adsorption energy to the soil. $^{(3)}$ Standard deviation of samples in parentheses. PESN: No saline effect point. **Source:** Authors' elaboration (2021).

Figure 2. Average CMAP contents of soils in different covers and layers in LEM and Guaraí. Standard deviation from the mean represented by bars. Literature 1 = Loamy Sandy Texture. Literature 2 = Sandy Loam Texture. Literature 3 = Sandy Clay Loamy Texture. Literature = Fernández *et al.* (2008); Souza *et al.* (2006); Pinto *et al.* (2013).



Source: Authors' elaboration (2021).

Conclusions

The remaining phosphorus contents (Prem) are higher in the 0-20 cm layer in the LEM region.

The maximum phosphate adsorption capacity (CMAP) is not very expressive in the soils of the two studied regions.

Among the regions studied, Guaraí soils have the highest relative adsorption potential due to the higher values of the CMAP/clay ratio.

Acknowledgments

To CNPq for the Scientific Initiation Scholarship of the third author. To the financial support of the Embrapa projects: "Novos paradigmas no conhecimento dos solos frágeis para a produção agrícola do Brasil" (New paradigms in the knowledge of fragile soils for agricultural production in Brazil) – FRAGISSOLO (02.11.05.003.00.00) and, "Sustentabilidade da agricultura em solos de textura leve em áreas de intensificação agrícola no bioma Cerrados" (Sustainability of agriculture in light textured soils in areas of agricultural intensification in the Cerrados biome) – ARENOSSOLOS (02.12.01.019.00.00).

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