Revista Brasileira de Ciência do Solo
ISSN: 0100-0683
revista@sbcs.org.br
Sociedade Brasileira de Ciência do Solo
Brasil

Rogeri, Douglas Antonio; Gianello, Clesio; Bortolon, Leandro; Batista Amorim, Magno
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Revista Brasileira de Ciência do Solo, vol. 40, 2016, pp. 1-14
Sociedade Brasileira de Ciência do Solo
Viçosa, Brasil

Revista Brasileira de Ciência do Solo

Division - Soil Processes and Properties | Commission - Soil Mineralogy

Substitution of Clay Content for P-Remaining as an Index of the Phosphorus Buffering Capacity for Soils of Rio Grande do Sul

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ABSTRACT: Mehlich-1 soil extract is currently used in Rio Grande do Sul (RS) and Santa Catarina (SC) States, in Brazil, to evaluate soil phosphorus available to plants and Mehlich-1 is sensitive to soil buffering capacity. This limitation is overcome partly by soil separation into buffering classes based on soil clay content. However, soil clay content has some technical and operational limitations, such as the underestimation of soil clay levels in soils under no-till. The aim of this study was to evaluate the remaining phosphorus (P-rem) compared to soil clay content as an index of the buffering capacity in soils of RS. The relationship between P-rem and soil clay content was assessed using 200 soil samples from a wide range of locations across the state. In 20 representative soil types, P-rem, soil clay content, P maximum adsorption capacity, total and pedogenic Fe contents, amount of P_2O_5 needed to increase soil P in 1 mg kg^{-1} extracted by Mehlich-1 and -3 methods and P capacity factor were determined. Furthermore, a pot experiment was carried out with plants to determine soil P content extracted by Mehlich-1 and -3 at the maximum technical efficiency (MET) and the maximum absorption efficiency (MEA). Correlation analyses were performed between P-rem and soil clay content and, with the attributes of soils involving the P buffering capacity. The relationship between P-rem and soil clay content was described as a decreasing exponential function; however, the adjustment was not adequate to propose critical levels for P-rem. The P-rem index was superior to soil clay index in practically all relationships with the attributes related to the soil buffering capacity of the soils. In some cases, the indexes were similar; however, P-rem was not lower than the soil clay content in any case. The P-rem is a more reliable index to represent soil buffering capacity than the soil clay content in soils from RS, and P-rem might be used to implement soil classes for Mehlich-1 and Mehlich-3 determinations of soil P.

Keywords: Mehlich-1, Mehlich-3, phosphate fertilization, phosphorus adsorption.

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Received: August 21, 2014
Approved: September 14, 2015

How to cite: Rogeri DA, Gianello C, Bortolon L, Amorim MB. Substitution of Clay Content for P-Remaining as an Index of the Phosphorus Buffering Capacity for Soils of Rio Grande do Sul. Rev Bras Cienc Solo. 2016;40:e0140535.

DOI:10.1590/18069657rbcs20140535

INTRODUCTION

Phosphorus (P) is a very reactive element in the soil and can form stable compounds of high bonding energy with colloids (Goldberg and Sposito, 1985); its availability to plants is inversely related to the bond energy involved (Novais and Smyth, 1999; Gatiboni et al., 2007). In the states of Rio Grande do Sul (RS) and Santa Catarina (SC), the estimate of the "available P" for plants is made using the Mehlich-1 method (CQFSRS/SC, 2004). Recently, the Mehlich-3 method has been proposed as a substitute for Mehlich-1 because it is a multi-element extractor and does not overestimate the P availability in soils fertilized with natural phosphate (Schlindwein and Gianello, 2008; Bortolon et al., 2009). However, both extractors are sensitive to soil buffering capacity, so that P extraction decreases with increased buffering (Anghinoni and Bohnen, 1974; Alcântara et al., 2008; Bortolon et al., 2010; Oliveira, 2010). Therefore, to compensate for the deficiency of the method and interpret the extracted concentration, it is necessary to separate the soils into buffering classes, for which the criterion in the states of RS and SC is the clay content.

However, routine textural analysis in laboratories has some limitations because it is time-consuming, onerous and subject to many variations. Furthermore, because it is a measure of particle diameter (in this case smaller than 2 µm), routine textural analysis does not provide any information about the quality of the clay fraction (Bonfim et al., 2004; Novais et al., 2007). In RS and SC, the combination of geological diversity, climate, topography and other processes and formation factors has led to a wide variety of soil types with contrasting mineralogy (Brasil, 1973; Streck et al., 2008). Thus, it is likely that there are inconsistencies in the classification of soils due to the use of only one quantitative criterion, such as clay content, which is not sensitive to attributes related to the P sorption capacity of the soil. Moreover, with the consolidation and development of the no-tillage system, in which there is an increase of the organic matter content, recurrent problems are observed in routine laboratory assays related to the dispersion of clay in soils under this system (Sousa Neto et al., 2009; Miyazawa and Barbosa, 2011).

Within this scenario, it is relevant to assess other indices of soil buffering capacity to establish buffering classes and improve the estimation of the P content in soils by the Mehlich-1 and Mehlich-3 methods. The P-remaining method (P-rem), also known as the single point adsorption isotherm, is a technique that was proposed by Bache and Williams (1971) and is now used by some Brazilian states, together with the clay content, to determine values such as the P buffering capacity index for the classification of soils (Alvarez V et al., 1999; Sousa and Lobato, 2002; Wadt and Silva, 2011). The P-rem is negatively related to clay content (Freire, 2001; Alcântara et al., 2008; Broggi et al., 2010) and has the advantages of being faster and simpler than textural determination, as well as the potential for greater accuracy, because it is sensitive to the quality of the clay fraction and directly evaluates the P immobilization potential; in contrast, the clay content indirectly assesses this information (Alvarez V et al., 2000; Bonfim et al., 2004). In the states of RS and SC, P-rem has never been tested as an alternative to clay content, thus suggesting the potential for investigating the efficiency of this technique in the soil of these states to improve the estimates of P doses to be applied.

Selection of one index instead of another may be performed by means of the correlation coefficient determined between attributes of the soil and plants related to the soil-buffering capacity and the test indices, opting for that which presents the greatest degree of association (Corey, 1987). Moreover, assumptions such as cost per analysis and ease of execution should be taken into account in the selection.

The hypothesis of this study rely on the higher sensibility to access soil clay quality fraction of remaining P compared to soil clay, thus remaining P would be a more suitable index of soil-buffering capacity than soil clay content for interpretation of P concentrations. The objective of this study was to evaluate the method for determining the P-rem content as a substitute for the clay content as an index of the buffering capacity for interpretation of P concentrations extracted by the Mehlich-1 and Mehlich-3 solutions in soils of Rio Grande do Sul.

MATERIALS AND METHODS

Soil selection

Twenty of the main soil classes that occur in the state of RS were selected (Table 1), prioritizing those which most frequently occur among the 11 physiographic regions, according to their agricultural potential and economic relevance. The samples were collected in the layer 0.00-0.20 m deep, preferably in areas under natural vegetation. Most of the soils had never been cultivated or fertilized. Three soils were selected under crop conditions (Tupanciretã, Ibirubá and São Gabriel) but with P concentrations below the critical level (CQFSRS/SC, 2004). After collection, the soils were air dried, passed through a sieve with a mesh of 2.0 mm (ADSS) and characterized (Table 1).

Table 1. Physical and chemical characterization of the 0.00-0.20 m layer of the soils

Nº	Legend	Soil classification(1)	Collection site	pH(H_2O)	SOM	Al^{3+}	H+Al	CEC	Clay	Silt	Sand	P
					g dm^{-3}		$cmol_c$ dm^{-3}			g kg^{-1}		mg dm^{-3}
1	CHa1	*Cambissolo Húmico Alumínico*	São Francisco de Paula	4.8	100	5.8	27.4	28.0	190	672	138	4.9
2	CHa-2	*Cambissolo Húmico Alumínico*	Vacaria	4.7	56	4.0	14.6	18.4	573	249	178	5.9
3	CX	*Cambissolo Háplico*	Carlos Barbosa	5.2	28	0.2	5.2	10.1	351	376	273	7.6
4	LVaf	*Latossolo Vermelho Aluminoférrico*	Erechim	4.3	46	3.9	23.1	25.2	641	311	48	5.9
5	LVd-1	*Latossolo Vermelho Distrófico*	Passo Fundo	4.7	28	0.9	10.3	13.1	354	132	514	4.9
6	LVd-2	*Latossolo Vermelho Distrófico*	Cruz Alta	4.8	29	0.6	5.2	8.2	458	13	412	4.4
7	LVdf	*Latossolo Vermelho Distroférrico*	Boa Vista das Missões	4.8	31	0.8	4.9	9.8	690	25	60	5.1
8	LVef	*Latossolo Vermelho Eutroférico*	Ibirubá	5.5	33	0	3.9	12.5	412	265	323	10.6
9	MEk	*Chernossolo Ebânico Carbonático*	Aceguá	5.8	41	0	3.7	22.0	510	371	119	9.0
10	MEo	*Chernossolo Ebânico Órtico*	Caçapava do Sul	5.5	48	0	6.2	20.4	289	406	305	7.0
11	MXo	*Chernossolo Háplico Órtico*	Taquara	6.2	27	0	1.8	16.0	130	18.8	682	33.9
12	NVdf	*Nitossolo Vermelho Distroférico*	Rodeio Bonito	5.5	28	0	3.5	10.5	510	379	111	4.3
13	PBAC	*Argissolo Bruno-Acizentado*	Soledade	4.8	46	1.6	14.6	20.6	478	225	297	8.0
14	PVA-1	*Argissolo Vermelho-Amarelo*	Cachoeira do Sul	5.5	35	0.0	3.5	23.1	256	454	290	13.7
15	PVA-2	*Argissolo Vermelho-Amarelo Distrófico*	Tupanciretã	4.8	12	0.8	4.1	5.6	162	44	794	11.2
16	PVA-3	*Argissolo Vermelho-Amarelo*	São Gabriel	5.2	26	0.4	5.5	11.8	248	157	595	9.6
17	PVd	*Argissolo Vermelho Distrófico*	Viamão	5.2	13	0.0	2.0	3.5	90	57	853	3.8
18	RR	*Neossolo Regolítico*	Bagé	5.2	44	0.3	5.5	17.3	271	237	492	8.2
19	SXe	*Planossolo Háplico Eutrófico*	Cachoeira do Sul	5.9	24	0	3.1	12.7	109	239	652	10.0
20	VEo2	*Vertissolo Ebânico Órtico*	Uruguaiana	5.9	58	0	2.9	29.6	460	366	174	8.0
	Mean			5.2	38	0.9	7.6	15.9	359	250	365	8.8
	Median			5.2	32	0.2	5.0	14.5	352	244	301	7.8
	CV (%)(2)			9.0	51	170	93	46	50	69	72	73
	Max.(3)			6.2	100	5.8	27.4	29.6	690	672	853	33.9
	Min.(4)			4.3	12	0	1.8	3.5	90	13	48	3.8

SOM: soil organic matter by wet digestion; Al^{3+}: extracted with 1 mol L^{-1} KCl; H+Al: by the SMP solution; CEC: cation exchange capacity at pH 7.0; P: extracted by the Mehlich-1 method (Tedesco et al., 1995); clay, silt and sand: the pipette method (Claessen, 1997). (1) Classification according to Santos et al. (2013). (2) Coefficient of variation around the mean. (3) Maximum determined value. (4) Minimum determined value.

In addition, 200 soil samples from different locations of the state of RS were selected, which were obtained from samples submitted by producers to the Soil Analysis Laboratory of the Department of Soil Science, Federal University of Rio Grande do Sul (Universidade Federal do Rio Grande do Sul - UFRGS). In these samples, only the clay content and P-rem were determined to establish the degree of association between these measurements in a larger number of samples.

Chemical and physical analyses

Characterization of the soils determined the following (Tedesco et al., 1995): the pH in water, SMP index, cation exchange capacity at pH 7.0 (CEC), organic matter, titratable acidity (H+Al) and concentrations of P, K^+, Ca^{2+}, Mg^{2+} and Al^{3+}. The clay contents were determined by the pipette method (Claessen, 1997). Determination of the P-rem was conducted by adding 5.0 cm^3 of ADSS and 50 mL of a solution containing 60 mg L^{-1} P and 10 mmol L^{-1} $CaCl_2$ to a 100-mL Erlenmeyer flask. After stirring for 5 min, the suspension was left for 16 h according to Alvarez V et al. (2000). The determinations of P, K^+, Ca^{2+}, Mg^{2+} and Al^{3+} were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Sikora et al., 2005).

In the soils, assays were performed related to the buffering capacity of P: (i) Fe and Al contents associated with oxides of low crystallinity and total pedogenic Fe oxides; (ii) maximum adsorption capacity of P (MACP); (iii) P capacity factor (PCF); (iv) P buffering capability - PBC (quantity of P_2O_5 required for a 1 mg kg^{-1} P increase in analysis via the Mehlich-1 and -3 methods).

Iron and Al of low crystallinity were extracted by ammonium oxalate (Fe_{OX}) 0.2 mol L^{-1} (Schwertmann, 1964), and Fe attributed to total pedogenic oxides was collected with two successive extractions using dithionite-citrate sodium bicarbonate (Fe_{DCB}) at 80 °C (Mehra and Jackson, 1960). The total concentrations of Fe, Al, P and Mn were determined by sulfuric acid attack according to the procedure described in Claessen (1997). The elements in the extracts were quantified by ICP-OES.

The maximum adsorption capacity of P (MACP) was determined by adding 5.0 cm^3 of soil (the volume of each soil was pre-weighed to express the results in units of mass) to Erlenmeyer flasks with a capacity of 150-mL, to which a solution of 50 mL of 10 mmol $CaCl_2$ L^{-1} was transferred containing different concentrations of P (0, 10, 20, 40, 100, 200, 400 and 500 mg L^{-1}). Next, the sample was shaken for 1 h in a helical motion stirrer and allowed to stand for 16 h. After this period, an aliquot was withdrawn from the supernatant, and the P in solution was determined by ICP-OES. The data obtained were mathematically fitted to the Langmuir equation to acquire the value of MACP and the constant related to the bonding energy (k), as described by Novais and Smyth (1999).

The P capacity factor (PCF) of the soils was determined by means of adsorption and desorption isotherms of P in the soil (Fox and Kamprath, 1970). Sorbed P was determined by adding 30 mL of a $CaCl_2$ solution (10 mmol L^{-1}) with different P concentrations (0, 10, 25, 50 and 100 mg L^{-1}) to 1.0 g of soil. The solutions were maintained in contact with the soil for 72 h, with alternating cycles of agitation ("back and forth" shaker) and rest. Next, the tubes were centrifuged, and the supernatant solution was completely removed; from this, the P was determined by ICP-OES. Desorbed P was determined by adding 30 mL of a $CaCl_2$ solution (10 mmol L^{-1}) to each tube, and the same procedure described for the evaluating sorption was performed. Then, for each soil, a 2nd degree polynomial function was fit between desorbed and sorbed P, where the PCF was considered the coefficient (b1) of the equation.

Experiment with plants

An experiment was conducted with maize plants in pots to obtain the P content in soil extracted by the Mehlich-1 and Mehlich-3 methods in which the maximum production of dry matter (P at the maximum technical efficiency - MTE) and maximum P absorption by the plants (P in maximum absorption efficiency - MAE) occurs. Additionally, the P buffering capacity (PBF) was determined in this study.

The treatments consisted of 20 soils, five P_2O_5 rates (0, 100, 200, 400 and 800 kg ha^{-1}) and three replications in a completely randomized design. The doses were calculated considering a soil mass of 2×10^6 kg ha^{-1}. The rates used were therefore equivalent to 0, 50, 100, 200 and 400 mg kg^{-1} of P_2O_5; however, in this study, they are expressed in the unit kg ha^{-1}. Triple superphosphate (TSP) was used as the P source and was applied to the soil in its powder form. The experimental units consisted of polyethylene pots with 8-L capacity, to which 6 kg of dry soil was added after homogenization with the treatments. The pots were moistened and distributed randomly in an open area, where they were exposed to the weather and, therefore, natural rainfall.

The soils were corrected with a mixture of CaO and MgO at the stoichiometric ratio of 3:1 to reach a $pH(H_2O)$ of approximately 6.0. Furthermore, a solution containing micronutrients was also applied, with concentrations equivalent to 4 mg kg^{-1} of Cu and Zn, 1 mg kg^{-1} of B and 0.1 mg kg^{-1} of Mo. The equivalent of 45 and 42.5 mg kg^{-1} of S and Mg, respectively, were also added to all soils presenting concentrations of these elements below the range “very high” (CQFSRS/SC, 2004). Soils with K contents below 250 mg kg^{-1} were fertilized with KCl to achieve this value. N was applied at planting and during cultivation at a dose equivalent to 125 mg kg^{-1} of N in the form of urea.

Corn (hybrid Pioneer 30F53) was sown ten days after the application of fertilizers, and three plants were cultured per pot for 20 days after emergence. At the end of this period, the plants were cut level with the ground and stored in an oven at 65 °C, until they reached a constant weight, after which the shoot dry mass (SDM) was determined. Subsequently, the plant tissue was ground and digested for quantification of the absorbed P (Tedesco et al., 1995). The P in the extract was determined by ICP-OES.

Soil samples were collected for evaluation of the “available P” before and after cultivation using a Dutch auger to collect three sub-samples from each pot. The samples were dried in an oven at 65 °C and ground in a porcelain mortar. Thus, P was extracted via the Mehlich-1 (Tedesco et al., 1995) and Mehlich-3 methods (Schlindwein, 2003). All determinations were made in duplicate, and data averages are used in the presentation of the results.

The amount of P_2O_5 necessary to increase P by 1 mg kg^{-1} in the analytical result (PBC) was quantified by the inverse (1/b) of the angular coefficient (b) of the 1st degree polynomial equation ($y = a + bx$) adjusted between the P_2O_5 applied doses (independent variable) and P contents extracted by the Mehlich-1 and Mehlich-3 solutions (dependent variable) in soil samples collected after the corn harvest (35 days after fertilizer application). The increase rate in SDM per unit of P_2O_5 applied (DMIR) was obtained from the angular coefficient (b) of the polynomial equation adjusted between P_2O_5 rates and the dry matter production.

Statistical analysis

In the study with plants, the results were submitted to analysis of variance by the F-test ($p<0.05$); when the effects were significant, the data were adjusted by regression analysis. Fitting was performed for the production of shoot dry matter (SDM) and the amount of absorbed P (P-abs) according to the P content in the soil extracted by the Mehlich-1 (M1) and Mehlich-3 methods (M3). In instances of significance, a second-order polynomial function was fit between the variables, and the P content in the MTE was obtained by setting the first derivative of this function equal to zero. For soils for which only linear functions were significant, the highest value of P of the interval was adopted as representative of the maximum production. The P content in the MAE was calculated in a similar manner to the MTE; however, instead of using the shoot dry mass as the dependent variable, the amount of P absorbed by the plants was used. Pearson’s simple linear correlation analysis was conducted between the soil attributes associated with the buffering capacity of P and the measurements of both the P-rem and clay content. The correlation was classified according to the degree of association between the variables as follows: low ($0< |r| <0.50$), moderate ($0.50< |r| <0.75$), strong ($0.75< |r| <0.90$) and extremely strong ($|r| >0.90$). Additionally, soil attributes related to the P buffering capacity were studied using descriptive statistics parameters.

RESULTS AND DISCUSSION

Relationship between the physical and chemical properties of the soils

The selected soils presented clay contents ranging from 90 to 690 g kg^{-1}, with a median of 352 g kg^{-1}, and, for the most part, showed average to high probability (>50 %) of response to phosphatic fertilization, as the P content of almost all soils was below the critical level (CQFSRS/SC, 2004) (Table 1). The distribution of soils in buffering classes using the clay content as an index was two soils in class I (> 600 g kg^{-1}); six soils in class II (400 to 600 g kg^{-1}); seven soils in class III (210 to 400 g kg^{-1}) and five soils in class IV (0 to 200 g kg^{-1}). The original P contents extracted by the Mehlich-1 method were separated in fertility ranges: “Very Low” (three soils), “Low” (eight soils); “Medium” (seven soils) and “High” (two soils).

The soils presented a mean P-rem value of 17.6 mg L^{-1}, median of 15.5 mg L^{-1}, minimum value of 0.5 mg L^{-1} (CHa1-*São Francisco de Pau*la) and maximum of 47.5 mg L^{-1} (PVd-*Viamão*) (Table 2). The P-rem values are usually negatively associated with clay content (Bonfim et al., 2004; Alcântara et al., 2008; Broggi et al., 2010), because P-rem is a measure of non-adsorbed P (Novais et al., 2007). The PVd-*Viamão* soil had the lowest clay content (90 g kg^{-1}) and the highest value of P-rem (47.5 mg L^{-1}). However, the soil with the lowest P-rem value, CHa-1 (0.5 mg L^{-1}), is classified as sandy (190 g kg^{-1} - Class IV) by the current system based on clay (CQFSRS/SC, 2004), suggesting a disagreement in the classification of some soils from RS when using different indices of the P buffering capacity.

The relation between P-rem and clay was described by an exponentially decreasing curve, for both the set of soils selected for the experiments and for a larger number of soils (200 samples), with coefficients of determination of 0.54 and 0.73, respectively (Figure 1). Furthermore, there was also a significant negative linear correlation between P-rem and clay, with $r = -0.70^{**}$ (20 soils) and $r = -0.67^{**}$ (200 soils). When both indices are used in the classification of soils, as is done for soils in the Brazilian state of Minas Gerais (Alvarez V et al., 1999) and for other soils of the *Cerrado* (Sousa and Lobato, 2002), it is interesting to have a significant relationship between them for soils of the region, in order to avoid inconsistencies in classification. For soils of Minas Gerais, Freire (2001) obtained a decreasing quadratic relationship ($R^2 = 0.74$) of clay content with the P-rem.

However, for RS soils, the exponential function fit between the P-rem and clay suggests an ambiguity in interpretation of the P content of soils despite the high coefficient of determination ($R^2 = 0.73$) if both indexes are concomitantly used in separating the soils into buffering classes (Figure 1). This phenomenon is observed because if the arrangement of the points on the graph is examined in more detail, there is a high dispersion of points in the range of 200 to 600 g kg^{-1} clay, with an interval of 400 g kg^{-1} clay and less than 15 mg L^{-1} on P-rem in amplitude. This can be observed by substitution in the adjusted equation between the measurements of the clay ranges currently used by the CQFSRS/SC (2004) in the separation of soils to create corresponding P-rem classes. Based on the equation, the P-rem classes would be Class I (0 to 10 mg L^{-1}), Class II (10.1 to 13 mg L^{-1}), Class III (13.1 to 23 mg L^{-1}) and Class IV (23.1 to 60 mg L^{-1}). From this classification, it can be observed that a small variation of only 3 mg L^{-1} in the P determined in the P-rem extract could classify the soil in Class I (equivalent to > 600 g kg^{-1} clay) or Class III (210 to 400 g kg^{-1} clay). Therefore, statistical reasoning does not apply in this case because if both indices are used in the separation of soils, it could create confusion and give rise to technical questions regarding which soil to use, as the classification and fertilizer recommendations may be different.

The maximum adsorption capacity of P (MACP), a measure that reflects the sorption potential of the soil, presented an amplitude higher than 30 times between the soils (Table 2). The MACP values increased by 63.5 and 1,926.8 mg kg^{-1} for the soils SXe-*Cachoeira do Sul* and CHa1-*São Francisco de Paula*, respectively. The MACP was significantly correlated with the P-rem values ($r = -0.74^{**}$), as expected, because the measurement of P-rem is a point among those used in the adsorption isotherm for determination of the MACP (Vilar et al., 2010; Broggi et al., 2011); however, the correlation was not statistically significant with the clay content ($r = 0.26^{ns}$) (Table 3). Possibly due to the utilization of a large number of mineralogically distinct soils, the results of this work contradicts those of other studies that obtained a significant relationship between the MACP and clay (Corrêa et al., 2011; Pinto, 2012). The lack of significance suggests that the sorption power of P in soil is the result of not only a quantitative measurement of the relative proportion of particle size (<2 µm) but also the mineralogical composition of this fraction and land use history.

Table 2. Chemical attributes and measurements related to the P buffering capacity of the soils studies

Nº	Soil	P-rem$_{60}$	Fe$_{DCB}$	Fe$_{OX}$	Fe$_{total}$	Al$_{DCB}$	Al$_{total}$	Fe$_{OX}$/ Fe$_{DCB}$	Mn$_{total}$	MACP	k	PBC-M1	PBC-M3	PCF
		mg L^{-1}	g kg^{-1}						mg kg^{-1}		L mg^{-1}	kg ha^{-1} P_2O_5		
1	CHa-1	0.5	14.6	11.0	41.3	1.75	6.9	0.75	20.0	1,926.8	0.1283	66.7	90.9	43.1
2	CHa-2	3.0	15.3	2.4	54.4	1.10	7.8	0.16	40.0	831.5	0.0696	41.7	31.6	39.0
3	CX	14.7	16.9	4.9	67.7	0.43	3.7	0.29	290.0	477.7	0.0290	30.3	25.4	5.2
4	LVaf	1.9	42.4	4.0	133.3	1.45	10.2	0.09	90.0	893.3	0.0754	71.4	61.3	18
5	LVd-1	7.7	11.1	2.3	33.9	0.42	5.1	0.21	30.0	511.9	0.0475	29.4	39.5	7.9
6	LVd-2	7.7	20.7	3.3	61.8	0.45	6.6	0.16	50.0	539.3	0.0517	32.3	41.2	8.8
7	LVdf	7.9	43.0	4.5	128.3	0.74	10.1	0.11	100.0	611.3	0.0474	58.8	57.1	9.9
8	LVef	14.1	34.3	5.8	142.2	0.52	6.1	0.17	230.0	427.1	0.0334	47.6	44.6	7.7
9	MEk	22.6	4.1	3.4	25.3	0.25	4.7	0.84	40.0	285.6	0.0311	16.7	15.4	5.7
10	MEo	18.3	11.7	8.2	42.6	0.24	3.1	0.70	130.0	491.1	0.0146	67.1	67.1	8.4
11	MXo	33.8	9.2	1.9	36.7	0.20	2.3	0.21	90.0	142.1	0.0329	16.9	17.5	3.8
12	NVdf	13.4	48.6	4.7	159.4	0.72	7.3	0.10	260.0	341.1	0.0593	70.4	84.0	10.2
13	PBAC	4.9	11.3	1.9	36.2	0.52	5.8	0.18	20.0	578.6	0.0705	26.3	28.3	10.2
14	PVA-1	16.4	19.9	6.6	55.5	0.41	4.4	0.33	130.0	385.3	0.0341	52.6	61.7	9.9
15	PVA-2	29.8	3.9	0.6	11.9	0.18	2.1	0.15	20.0	132.8	0.0434	8.3	7.4	6.5
16	PVA-3	23.9	6.2	2.9	23.9	0.24	3.5	0.48	60.0	222.4	0.0373	17.9	21.5	4.1
17	PVd	47.5	1.4	0.3	4.5	0.08	0.7	0.20	10.0	64.2	0.0117	10.3	8.5	1.3
18	RR	26.4	5.5	3.9	27.0	0.31	3.7	0.72	50.0	225.3	0.0262	35.7	28.3	3.9
19	SXe	39.3	1.3	1.2	6.6	0.09	1.1	0.98	30.0	63.5	0.0746	13.0	9.7	1.5
20	VEo2	19.2	4.7	4.7	38.7	0.19	3.6	1.00	250.0	306.0	0.0285	55.6	40.7	7.2
	Mean	17.6	16.3	3.9	56.6	0.51	4.9	0.40	97.0	472.8	0.0473	38.5	39.1	10.6
	Median	15.5	11.5	3.6	40.0	0.41	4.5	0.21	55.0	406.2	0.0403	34.0	35.6	7.8
	CV (%)$^{(1)}$	73.1	89.3	66.2	82.4	87.1	54.0	80.5	92.8	87.2	56.8	55.9	62.8	104.2
	Max.$^{(2)}$	47.5	48.6	11	159.4	1.75	10.2	1.0	290	1,926.8	0.1283	71.4	90.9	43.1
	Min.$^{(3)}$	0.5	1.3	0.3	4.5	0.08	0.7	0.09	10	63.5	0.0117	8.3	7.4	1.3

P-rem: P-remaining 60 mg L^{-1}; Fe$_{DCB}$: Fe by dithionite-citrate bicarbonate (Mehra and Jackson, 1960); Fe$_{OX}$: Fe by ammonium oxalate (Schwertmann, 1964); Fe$_{OX}$/Fe$_{DCB}$: Fe oxalate and Fe dithionite ratio; Total Fe, Al and Mn by sulfuric acid attack (Claessen, 1997); MACP: maximum adsorption capacity of phosphorus by the Langmuir isotherm; k: constant related to the binding energy obtained by the Langmuir equation; PBC-M1 and M3: rate of P_2O_5 necessary to increase P by 1 mg kg^{-1} in analysis via the Mehlich-1 and -3 methods; PCF: phosphate capacity factor (dimensionless) obtained by the linear coefficient (b1) of the quadratic equation between P-sorbed and P-desorbed (Fox and Kamprath, 1970). $^{(1)}$ Coefficient of variation for the mean. $^{(2)}$ Maximum encountered value. $^{(3)}$ Minimum encountered value.

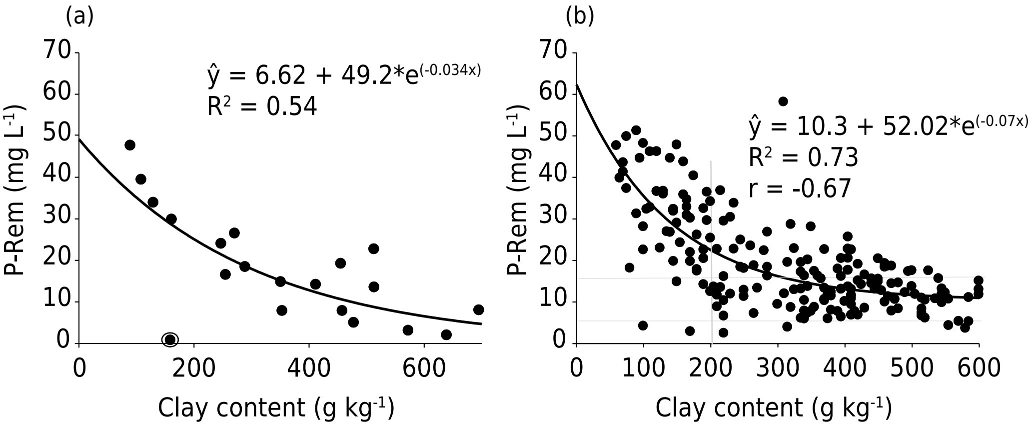

Figure 1. P-remaining (P-Rem) as a function of the clay content in different soil samples. (a) Soils used in the studies with plants; (b) Soils from different regions of the state of RS (200 samples).

Table 3. Pearson's simple linear correlation coefficients between P-remaining and clay with soil attributes related to the buffering capacity of P

	P-rem	**Fe_{DCB}**	**Fe_{OX}**	**Fe_{total}**	**Al_{total}**	**Al_{DCB}**	**Fe_{OX}/Fe_{DCB}**	**SOM**	**MCAP**	**Al^{3+}**
Clay	-0.71^{**}	0.66^{**}	0.11^{ns}	0.67^{**}	-0.86^{**}	0.43^{ns}	-0.30^{ns}	0.19^{ns}	0.26^{ns}	0.22^{ns}
P-rem	-	-0.57^{**}	-0.50^{**}	-0.53^{**}	0.85^{**}	-0.75^{**}	0.28^{ns}	-0.57^{**}	-0.74^{**}	-0.61^{**}

	H+Al	K	PCF	PBC-M1	PBC-M3	DMGR	MTE-M1	MTE-M3	MAE-M1	MAE-M3
Clay	0.24^{ns}	-0.14^{ns}	0.26^{ns}	0.50^{*}	0.36^{ns}	-0.69^{**}	-0.57^{**}	-0.55^{*}	-0.64^{*}	-0.57^{*}
P-rem	-0.67^{**}	-0.54^{*}	-0.65^{**}	-0.65^{**}	-0.66^{**}	0.92^{**}	0.65^{**}	0.74^{**}	0.74^{**}	0.78^{**}

^{ns}, **, *: non-significant, significant at 1 and 5 % by the t-test, respectively. P-rem: P-remaining (60 mg L^{-1}); Fe_{DCB} and Al_{DCB}: Fe and Al by dithionite citrate bicarbonate; Fe_{OX}: Fe by ammonium oxalate; Fe and Al total: by sulfuric acid attack; Fe_{OX}/Fe_{DCB}: ratio between Fe oxalate and Fe dithionite; SOM: soil organic matter; MACP: phosphorus maximum adsorption capacity; Al^{3+}: exchangeable Al; H+Al: potential acidity; k: constant related to the bonding energy; PCF: phosphate capacity factor; PBC-M1 and M3: P buffering capacity - rate of P_2O_5 necessary to increase P by 1 mg kg^{-1} in the analysis by the Mehlich-1 and -3 methods; DMGR: dry matter growth rate per unit of applied P_2O_5; MTE-M1 and M3: concentration of P extracted by the Mehlich-1 and -3 methods at the maximum technical efficiency; MAE-M1 and M3: P content of the soil extracted by the Mehlich-1 and -3 methods that resulted in the largest P absorption.

The correlations were moderate between P-rem and the total contents of pedogenic Fe (Fe_{DCB}) and Al_{DCB} (Al resulting from the isomorphic substitutions in Fe oxides and partial dissolution of Al oxides of low crystallinity) ($r = -0.57^{*}$; $r = -0.75^{*}$, respectively) and also between P-rem and Fe of low crystallinity (Fe_{OX}; $r = -0.50^{*}$). Unlike the P-rem, the clay contents moderately correlated only with the Fe_{DCB} ($r = 0.66^{**}$) (Table 3). The lack of correlation between the clay content and Fe_{OX} is an indication that soil clay accumulation is not necessarily associated with the presence of Fe oxides of low crystallinity, which are described as having a high capacity of P adsorption (Hernández and Meurer, 1998; Donagemma et al., 2008). In addition to crystalline Fe oxides and clay minerals 1:1 (such as kaolinite), which have a lower potential to adsorb Fe oxides of low crystallinity, they can also significantly affect the adsorption of P, mainly due to the higher quantity generally found in soils (Torrent et al., 1994; Vilar et al., 2010). In a study with 60 RS soils, Oliveira (2015) found a significant correlation, although weak ($r = -0.31^{*}$), between the P-rem and the area of kaolinite obtained by x ray diffraction. The Fe_{OX}/Fe_{DCB} ratio, which expresses the degree of crystallinity, i.e., the proportion of Fe of low crystallinity in relation to the sum of pedogenic Fe oxides, did not correlate with the P-rem ($r = 0.28^{ns}$) or with clay ($r = 0.30^{ns}$) (Table 3).

The P_2O_5 rates required to increase P by 1 mg kg^{-1} in the analyses (PBC), via the Mehlich-1 and Mehlich-3 methods, after 35 days of phosphatic fertilizer application (Table 2). The rates varied from approximately 7 to 70 kg ha^{-1} and 8 to 90 kg ha^{-1} of P_2O_5 for the Mehlich-1 and

Mehlich-3 methods, respectively. The rate of P_2O_5 to increase P by 1 mg kg^{-1} is also known as the phosphate buffering capacity (PBC) of the soil (Lopes et al., 2004; Sousa et al., 2010) and is directly related to the sensitivity of the Mehlich extractor to the buffering capacity; the more sorptive the soil is, the less P is extracted by the method and the greater the PBC. This information is of great importance in defining doses for corrective fertilization to reach the critical level of P in soils (Schlindwein and Gianello, 2008; Sousa et al., 2010; Schlindwein et al., 2013). The PBC for the Mehlich-1 and Mehlich-3 methods showed a moderately negative correlation with the P-rem. Conversely, correlation with the clay content was weak and was only significant for the Mehlich-1 method ($r = 0.50^{*}$). The absent or weak relationship between the PBC and the clay content suggests that this index may not reflect the real limitations of P extraction by the Mehlich-1 and Mehlich-3 methods, and therefore, soils within the same buffering class by clay content may require very different P rates to achieve a determined level of fertility.

The P capacity factor (PCF) presented a negative association with P-rem ($r = -0.65^{**}$) but did not correlate with the clay content ($r = 0.26^{ns}$) (Figure 2). Although calculated in different ways (Muniz et al., 1985; Shirvani et al., 2005; Pinto, 2012), the PCF is defined by the equilibrium ratio between the quantity factor (Q - adsorbed labile P) and the intensity factor (I - solution P), and represents a measure of interdependence ($\Delta Q/\Delta I$) that exists between the solid phase and solution of the soil, which is also commonly referred to as the P buffering capacity (Novais et al., 2007). The lack of a correlation between clay and the PCF indicates that for some soils, because it is only quantitative, the clay content may be insufficient to explain the complexity of the P adsorption and desorption processes and can thus lead to errors when separating the soils in buffering classes for fertilizer recommendations. For example, although CHa-1 soil has a low clay content (Class IV - 190 g kg^{-1}), it presented the greatest Fe_{OX} content (11 g kg^{-1}), which was approximately three times greater than the mean of the others and may explain its high MACP (> 9,000 kg ha^{-1} P_2O_5) and largest value of PCF (43.1). Furthermore, this soil has high Al^{3+} (5.8 $cmol_c$ kg^{-1}) and SOM (100 g kg^{-1}) contents, which can also contribute to P adsorption by precipitation with Al^{3+} and the formation of ternary complexes with SOM (Mello and Perez, 2009); as in this study, the P-rem also correlated with Al^{3+} ($r = -0.67^{**}$) and SOM ($r = -0.57^{**}$) (Table 3). Bonfim et al. (2004) studied six soils from the state of Pernambuco and found a significant correlation of PCF with clay and P-rem, although the correlation coefficients were higher for P-rem, with values of 0.67^{**} and -0.91^{**}, respectively.

Assuming that the measurement of PCF estimates the real buffering capacity of the soil that is perceived by plants, the selection of clay content and/or P-rem as an index of this measurement may result in different classifications, mainly from soils with outlier values (Figure 2). The three soils presenting the highest PCF values were CHa1-*São Francisco de Paula*, CHa2-*Vacaria* and LVaf-*Erechim*, with values of 43.1, 39.0 and 18.0 (dimensionless), respectively. In the current classification adopted by the CQFSRS/SC (2004), which uses the clay content as an index, these soils are classified into three distinct buffering classes, namely, CHa-1 (Class IV - 190 g kg^{-1} clay), CHa-2 (Class II - 570 g kg^{-1} clay) and LVaf (Class I - 641 g kg^{-1} clay). Conversely, the three soils showed the highest MACP values (>3,500 kg ha^{-1} of P_2O_5) and lowest P-rem values (<3.0 mg L^{-1}). Therefore, if using the measurement of P-rem as the buffering capacity index, the three soils would be in the class of highest buffering capacity (Class I), which is consistent with their high PCF (Figure 2).

Relationship of the buffering capacity with the measurements of plant development

The production of shoot dry matter (SDM) increased as a function of P rates applied in all evaluated soils (Table 4). For some soils, the SDM yield was linear even when using high P rates, making it impossible to obtain the maximum point. For these cases, the extracted P content at the highest applied P rate was considered the maximum technical efficiency (MTE), as previously used by researchers in other studies (Muniz et al., 1985; Bonfim et al., 2004; Schlindwein and Gianello, 2008); however, these authors used the critical content (90 % of the MTE) instead of the MTE. In this study, the P content in the MTE was used instead of the critical content, as the latter is generally used

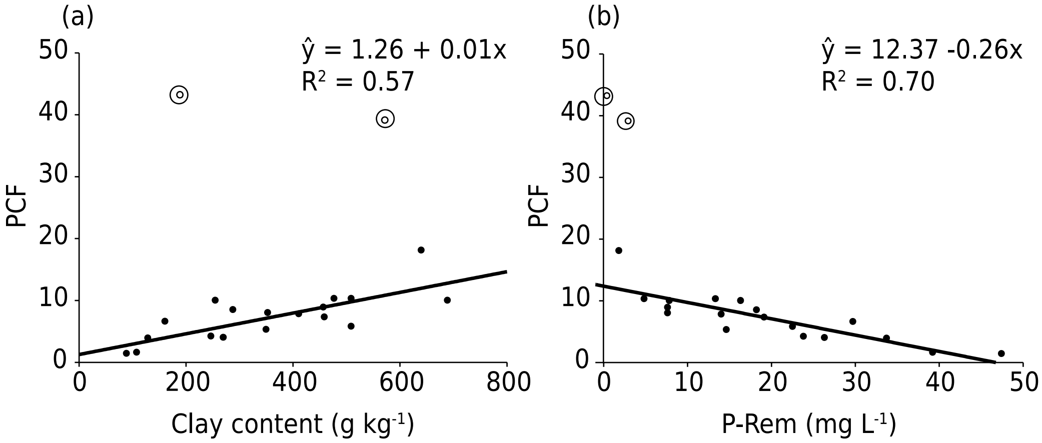

Figure 2. Regression between the P capacity factor (PCF) and the clay content (a) or the P-remaining values (P-Rem) (b). The outliers (circled points) were excluded from the regression calculation, for two soils classified as Cambisoslo Húmico Alumínico (CHa-1 and CHa-2).

Table 4. Polynomial regression equation, coefficient of determination (R^2) and phosphorus content for maximum technical efficiency (MTE) extracted by Mehlich-1 (MTE-M1) and Mehlich-3 methods (MTE-M3)

Soil	Mehlich-1			Mehlich-3		
	Equation[1]	MTE-M1[2]	R^2	Equation [1]	MTE-M3[2]	R^2
		mg kg^{-1}			mg kg^{-1}	
CHa-1	$\hat{y} = 0.38 + 0.1397 x$	17.0	0.82	$\hat{y} = 0.50 + 0.167 x$	12.9	0.85
CHa-2	$\hat{y} = -0.67 + 0.267 x$	24.1	0.92	$\hat{y} = -0.19 + 0.185 x$	27.0	0.75
CX	$\hat{y} = -3.19 + 0.467 x$	36.1	0.94	$\hat{y} = -1.27 + 0.384 x$	39.5	0.94
LVaf	$\hat{y} = 2.79 + 3.886 x$	19.0	0.98	$\hat{y} = -1.26 + 4.63 x$	18.9	0.94
LVd-1	$\hat{y} = -0.45 + 0.283 x$	33.2	0.98	$\hat{y} = -0.29 + 0.386 x$	23.0	0.96
LVd-2	$\hat{y} = -1.64 + 0.61 x - 0.0103 x^2$	29.5	0.96	$\hat{y} = -1.27 + 0.644 x - 0.011 x^2$	23.1	0.94
LVdf	$\hat{y} = -0.19 + 0.257 x$	21.3	0.93	$\hat{y} = 0.35 + 0.261 x$	18.8	0.85
LVef	$\hat{y} = -9.56 + 1.56 x - 0.034 x^2$	22.8	0.90	$\hat{y} = -6.98 + 1.39 x - 0.031 x^2$	21.9	0.91
MEk	$\hat{y} = -14.86 + 2.08 x - 0.028 x^2$	37.1	0.93	$\hat{y} = -4.04 + 1.02 x - 0.0099 x^2$	51.8	0.88
MEo	$\hat{y} = -25.4 + 4.92 x - 0.1679 x^2$	14.6	0.96	$\hat{y} = -10.87 + 2.617 x - 0.078 x^2$	16.5	0.95
MXo	$\hat{y} = -7.89 + 0.303 x$	80.1	0.81	$\hat{y} = -1.03 + 0.454 x - 0.001 x^2$	51.1	0.95
NVdf	$\hat{y} = -5.20 + 1.384 x$	13.2	0.96	$\hat{y} = -2.27 + 1.22 x$	12.2	0.99
PBAC	$\hat{y} = -0.91 + 0.226 x$	37.0	0.98	$\hat{y} = -0.73 + 0.236 x$	34.6	0.97
PVA-1	$\hat{y} = -21.62 +2.82 x - 0.060 x^2$	23	0.63	$\hat{y} = -28.54 + 4.38 x - 0.113 x^2$	19.4	0.74
PVA-2	$\hat{y} = -0.92 + 0.26 x - 0.0016 x^2$	81.2	0.99	$\hat{y} = -0.24 + 0.196 x - 0.001 x^2$	98.3	0.99
PVA-3	$\hat{y} = -2.27 + 0.44x - 0.0048x^2$	46.7	0.94	$\hat{y}= -0.62 + 0.350 x - 0.0034 x^2$	51.5	0.95
PVd	$\hat{y} = -2.21 + 0.57 x - 0.0052 x^2$	50.4	0.96	$\hat{y} = -1.48 + 0.446 x - 0.0034 x^2$	65.6	0.97
RR	$\hat{y} = -20.68 + 2.52 x - 0.044 x^2$	28.7	0.91	$\hat{y} = -10.35 + 1.58 x - 0.024 x^2$	32.7	0.97
SXe	$\hat{y} = -2.13 + 0.52 x - 0.0055 x^2$	47.2	0.95	$\hat{y} = -0.08 + 0.33 x - 0.0026 x^2$	63.9	0.96
VEo2	$\hat{y} = -10.33 + 2.11 x - 0.047 x^2$	22.3	0.92	$\hat{y} = -8.29 + 1.51 x - 0.0268 x^2$	28.2	0.86

(1) Regression equation adjusted between phosphorus contents (x = mg kg^{-1}) extracted by the methods and the shoot dry mass (y = g per pot) of the culture. (2) MTE: for the quadratic equations was calculated by making the first derivative of the equation equal to zero; for linear equations, the P concentration extracted at the greatest applied dose was considered.

in reference to soil content at the maximum economic efficiency, which is obtained in field calibration experiments, is influenced by the price of fertilizers and products (Cate and Nelson, 1973) and usually fluctuates around 90 % of the MTE (CQFSRS/SC, 2004). However, due to the difficulty of conducting a field calibration experiment, the P contents were used in the MTE as analogues of the critical content to perform correlation analysis for the selection of indices.

Phosphorus levels for the MTE obtained by the Mehlich-1 and Mehlich-3 methods varied as a function of the different soil buffering capacities (Table 4). The soils presenting the extreme values were NVdf-*Rodeio Bonito* and PVA2-*Tupanciretã*, with levels of 13.2 and 81.2 mg kg^{-1} with Mehlich-1 and 12.2 and 98.3 with Mehlich-3, respectively. The contents of "available P" for the MTE of both extractors presented moderately negative correlations ($0.5< |r| <0.75$) with the main measurements associated with the soil buffering capacity (MACP, PCF, PBC). This indicates that the increase in soil buffering capacity reduces the amount of P extracted by the methods for MTE, corroborating with the CQFSRS/SC (2004), which is attributed to lower critical contents to compensate for the sensitivity of the Mehlich-1 extractor as the buffering capacity of the soils increases, in this case, using the clay content as the index.

The content of "available P" for the MTE was significantly correlated with both the clay content and the P-rem values. The correlation was negative with coefficients of -0.57** and -0.55* for clay and positive with coefficients of 0.65** and 0.74** for the P-rem for the Mehlich-1 and Mehlich-3 models, respectively (Table 3). Although the coefficients were moderate, the correlations indicate that compared to clay, the P-rem showed a greater capacity for the identification of sensitivity of the extractors considering the soil buffering capacity. Similarly to that which occurred in the MTE, the P contents for which the maximum absorption efficiency (MAE) were also better related to the P-rem (Table 3). This information corroborates with that of Bonfim et al. (2004), who found better relations of the critical content of P in the soil for *Brachiaria brizantha* with the P-rem than with clay, with coefficients of -0.31* and -0.38** for clay and 0.54** and 0.68** for P-rem for the Mehlich-1 and Mehlich-3 models, respectively. Similarly, in a study of soils from the state of Pernambuco, Broggi et al. (2010) found higher correlation coefficients between the critical content and P-rem compared to that with clay.

The shoot dry mass growth rate (DMGR) per unit of P_2O_5 applied to the soil was best related to the values of P-rem compared to clay (Table 3). The DMGR showed an extremely strong, positive correlation with P-rem ($r = -0.92^{**}$) and a moderate correlation with clay ($r = -0.69^{**}$). The DMGR is dependent on the sorption capacity and the original P content of the soils. Thus, low growth rates can occur in soils where "available P" levels are high or in very sorptive soils, which require high P rates to compensate for the low availability to plants as a function of the strong adsorption to the solid phase. Because the majority of selected soils presented low concentrations of "available P", the DMGR may be associated with the soil buffering capacity, which can be determined by the correlation ($r >0.60$) with other measurements related to the soil buffering capacity (MACP, PCF and PBC). However, due to the higher correlation coefficients, the P-rem index was more sensitive to variations of the response potential of plants to the applied P.

In general, the P-rem index was superior to the textural measurement in almost all relationships made with the attributes related to the soil buffering capacity. In some scenarios, there was equality between the indices; however, there were no situations where the P-rem was lower than clay. Thus, compared to the clay content, the measurement of P-rem showed to be more suitable for the separation of soil into classes for the interpretation of P extracted by the Mehlich-1 and -3 methods. However, the P-rem values in soil can be dynamic over time (Fontana et al., 2008), unlike the clay content, which does not vary over the average time period. Thus, agricultural practices that affect the P adsorption process can alter the P-rem values in soil over the years and, therefore, modify the class; this practice would alter the critical P content in the interpretation, whereas in practice, it may not necessarily be altered. For example, Guareschi et al. (2012) found an increase of P-rem in the soil of 6.9 to 16.7 mg L^{-1} in an area with pasture (*Brachiaria decumbens*) and in a no-tillage planting system (20 years of implantation), respectively. Therefore, Sousa and Lobato (2003) suggested that the P-rem is determined in soils that have not been subject to phosphatic fertilizers or with high response potential to P. The authors also suggested not to repeat the process in subsequent years because it is expected that its value increases in old areas, those well fertilized with P and those with consolidation and evolution of the no-tillage planting system.

CONCLUSIONS

P-rem is a more reliable index of the soil buffering capacity than clay content and may be used to classify soils of the state of RS into buffering classes if there is the intention to continue using both Mehlich-1 and Mehlich-3 to estimate P availability to plants.

A significant relationship was observed between P-rem and clay, but the adjusted equation was inadequate to propose critical levels for P-rem.

Concomitant use of clay content and P-rem for the separation of soils from RS into classes for interpretation of P extracted by the Mehlich-1 and Mehlich-3 methods may lead to different classifications of some soils.

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