

# LOSS OF EXTRACTION CAPACITY OF MEHLICH-1 AND MONOCALCIUM PHOSPHATE AS A VARIABLE OF REMAINING P AND ITS RELATIONSHIP TO CRITICAL LEVELS OF SOIL PHOSPHORUS AND SULFUR

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## ABSTRACT

The Mehlich-1 (M-1) extractant and Monocalcium Phosphate in acetic acid (MCPa) have mechanisms for extraction of available P and S in acidity and in ligand exchange, whether of the sulfate of the extractant by the phosphate of the soil, or of the phosphate of the extractant by the sulfate of the soil. In clayey soils, with greater P adsorption capacity, or lower remaining P (Rem-P) value, which corresponds to soils with greater Phosphate Buffer Capacity (PBC), more buffered for acidity, the initially low pH of the extractants increases over their time of contact with the soil in the direction of the pH of the soil; and the sulfate of the M-1 or the phosphate of the MCPa is adsorbed by adsorption sites occupied by these anions or not. This situation makes the extractant lose its extraction capacity, a phenomenon known as loss of extraction capacity or consumption of the extractant, the object of this study. Twenty soil samples were chosen so as to cover the range of Rem-P (0 to 60 mg L<sup>-1</sup>). Rem-P was used as a measure of the PBC. The P and S contents available from the soil samples through M-1 and MCPa, and the contents of other nutrients and of organic matter were determined. For determination of loss of extraction capacity, after the rest period, the pH and the P and S contents were measured in both the extracts-soils. Although significant, the loss of extraction capacity of the acidity of the M-1 and MCPa extractants with reduction in the Rem-P value

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did not have a very expressive effect. A “linear plateau” model was observed for the M-1 for discontinuous loss of extraction capacity of the P content in accordance with reduction in the concentration of the Rem-P or increase in the PBC, suggesting that a discontinuous model should also be adopted for interpretation of available P of soils with different Rem-P values. In contrast, a continuous linear response was observed between the P variables in the extract-soil and Rem-P for the MCPa extractor, which shows increasing loss of extraction capacity of this extractor with an increase in the PBC of the soil, indicating the validity of the linear relationship between the available S of the soil and the PBC, estimated by Rem-P, as currently adopted.

**Keywords:** P adsorption, S adsorption, available nutrient, phosphate buffer capacity, extractant.

**RESUMO:** *DESGASTE DOS EXTRATORES MEHLICH-1 E FOSFATO MONOCÁLCICO COMO VARIÁVEL DO P-REMANESCENTE E SUA RELAÇÃO COM OS NÍVEIS CRÍTICOS DE FÓSFORO E DE ENXOFRE NOS SOLOS*

*O extrator Mehlich-1 (M-1), assim como o Fosfato Monocálcico em ácido acético (FMCa), tem na acidez e na troca de ligantes - seja do sulfato do extrator pelo fosfato do solo ou do fosfato do extrator pelo sulfato do solo - os mecanismos de extração do P e do S disponíveis. Em solos argilosos, com maior poder de adsorção de P, ou menor valor de P-remanescente (P-rem), o que corresponde a solos com maior Poder-Tampão de Fosfato (PTF), mais tamponados para a acidez, o pH inicialmente baixo dos extratores é, durante o seu contato com o solo, aumentado em direção àquele do solo, e o sulfato do M-1 ou o fosfato do FMCa é adsorvido por sítios de adsorção ocupados ou não por esses ânions. Tal fato faz com que o extrator perca seu poder de extração, fenômeno conhecido como desgaste de extrator, objetivo de estudo deste trabalho. Escolheram-se 20 amostras de solos, de modo a cobrir a faixa do P-rem (0 a 60 mg L<sup>-1</sup>). Como medida do PTF, foi utilizado o P-rem. Os teores de P e de S disponíveis das amostras dos solos pelo M-1 e FMCa, de demais nutrientes e de matéria orgânica (MO) foram determinados. Para a determinação do desgaste dos extratores, após o período de repouso, foram medidos o pH e os teores de P e de S em ambos os extratos-solos. Houve efeito pouco expressivo, embora significativo, do desgaste da acidez dos extratores M-1 e FMCa com a diminuição do valor de P-rem. Observou-se para o M-1 um modelo linear plateau para desgaste descontínuo do teor do P, com a diminuição da concentração do P-rem ou aumento do PTF, sugerindo que se deve adotar um modelo também descontínuo para a interpretação do P-disponível de solos com diferentes valores de P-rem. Entretanto, observou-se resposta linear-contínua entre as variáveis P no extrato-solo e P-rem para o extrator FMCa, o que evidenciou desgaste crescente desse extrator com o aumento do PTF do solo, indicando a validade da relação linear entre o S disponível do solo e o PTF, estimado pelo P-rem, como atualmente adotada.*

*Palavras-chave:* adsorção de P, adsorção de S, nutriente disponível, poder-tampão de fosfato, extrator.

## INTRODUCTION

The Mehlich-1 extractant (M-1) has the mechanisms of extraction of available P in its acidity (pH 1.2) and in the ligand exchange of its sulfate by soil phosphate. In clayey soils and in those with greater organic matter (OM) contents, more buffered for acidity, the initially low pH of the M-1 increases in direction of that of the soil when shaken together with the soil sample. The sulfate is likewise adsorbed to the adsorption sites occupied by this anion or not. This makes the extractant lose its extraction capacity, an occurrence known as loss of extraction capacity or consumption of the extractant (Novais and Smyth, 1999; Freitas et al., 2013).

In a similar manner, the Monocalcium Phosphate in acetic acid (MCPa), pH 2.2, extracts the available S from the soil by the exchange of the sulfate adsorbed with the phosphate of this extractant. Thus, with the increase in the capacity of P adsorption of the soil in greater clay content or lower remaining P (Rem-P) value, which corresponds to soils with greater PBC, the phosphate of the extractant is also consumed by adsorption sites, including those not yet occupied by S, reducing the extraction capacity of this nutrient as a consequence of the consumption of the extractant.

The practical importance of this consumption is understood in evaluation of results of routine analyses of soil fertility that use Rem-P (Bedin et al., 2003; Bonfim et al., 2004; Corrêa et al., 2008; Fernández R. et al., 2008) or the clay content

(Donagemma et al., 2008) as a measure of PBC, essential for interpretation of the P and S contents obtained. However, in general, the decrease in the Critical Level (CL) of these nutrients with the decrease in Rem-P has not been appropriately understood or described in the literature.

Some disadvantages, such as laboratory difficulties in textural analyses, the frequently incomplete dispersion of clay in tropical soils in general (Donagemma et al., 2003; Vitorino et al., 2003), and the lack of determination of the quality of clay in routine laboratory testing impede and limit the use of clay content as a measure of PBC, making analysis of Rem-P, which is easily and quickly performed, a suitable and more exact measurement of the PBC for this objective (Alvarez V et al., 2000; Corrêa et al., 2011).

Like the essential nature of a measure of buffer capacity of soil acidity for determination of the need for liming, the behavior of P in the soil is dependent on a measurement of the PBC of this soil for interpretation of results of its availability and the consequent recommendation of the optimum application rate of a phosphate fertilizer for growing a plant.

In a functional or practical approach of interpretation of results of available P and S in routine analyses of soil fertility, in regard to applicability and lower cost, with the necessary exactness of a measurement of PBC, the Rem-P method was developed. For this purpose, Bache and Williams (1971) developed a first approximation ("phosphate adsorption index" or "single concentration adsorption") of what is now called Rem-P. These authors established the rate of P added to the soil in order to have a defined concentration of P in the equilibrium solution. This "index", therefore, has a positive correlation with PBC, whereas Rem-P, which measures the "remaining amount" in the equilibrium solution of a constant concentration of P added to the soil, has a negative correlation with PBC.

Novais (1977) used only one of the concentrations of P ( $30 \text{ mg L}^{-1}$ ) among those used for obtaining Langmuir and Freundlich adsorption isotherms in equilibrium after 6 h of shaking with soil samples, which was called Rem-P concentration ("Remaining P in solution"), as a measure of PBC. Negative and highly significant correlations were found between this characteristic and measurements such as the Maximum P Adsorption Capacity (MPAC) of Langmuir, as well as other soil variables closely related to the PBC. After that, Delazari (1979) individually compared the equilibrium concentrations of 5, 10, 20, 30, 40, 50, and  $60 \text{ mg L}^{-1}$  with 1 h of shaking and these same concentrations with the addition of 80 and  $100 \text{ mg L}^{-1}$  with 24 h of shaking used in fitting the Langmuir adsorption isotherm. The correlations with MPAC had an

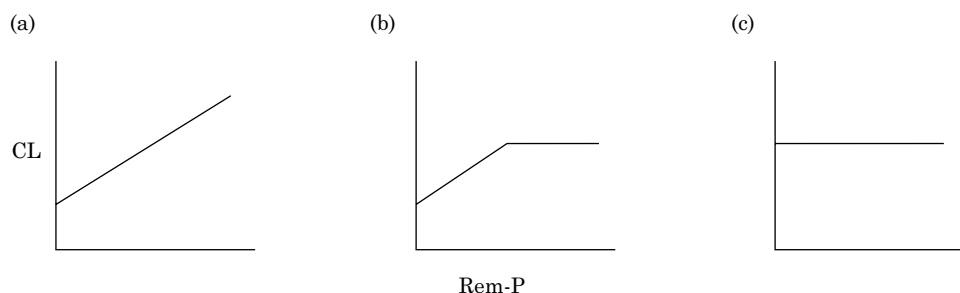
increase in their absolute values, with up to  $30 \text{ mg L}^{-1}$  with 1 h of shaking, and with up to  $60 \text{ mg L}^{-1}$  with 24 h of shaking.

Several studies have shown the suitability (through exactness and simplicity) of the use of the Rem-P 60 ( $60 \text{ mg L}^{-1}$  of P) (Alvarez V et al., 2000; Corrêa et al., 2008), both for interpretations of the results of soil available P (Ribeiro et al., 1999; Bedin et al., 2003; Côrrea et al., 2011) and S (Ribeiro et al., 1999; Souza, 1999; Rampim et al., 2013).

The Rem-P has a probable direct relationship with OM content, since greater OM contents may result in lower P adsorption and greater CLs for this nutrient, given the lower loss of extraction capacity (M-1 sulfate exhaustion) in this condition (Novais and Smyth, 1999; Rheinheimer and Anghinoni, 2001), as opposed to what occurs under the condition of soils with greater clay contents - with greater loss of extraction capacity (Bahia Filho et al., 1983; Neves et al., 1987). In contrast, Eberhardt et al. (2008) found a positive correlation between OM content and clay content in *Latosolo* (Oxisol) samples from the Cerrado (Brazilian tropical savanna).

In a hypothetical example in which, with the increase in years of cropping, there are greater contents of P and S available in the soil, tending to saturate its adsorption sites with these nutrients, the Rem-P should increase (PBC reduced), while the clay content should remain constant (PBC stable). This situation exemplifies the unsuitability of the clay content as a PBC measurement and the suitability of the Rem-P for interpretation of its contents of available P and S.

The change in soil management (from conventional tillage to no-tillage, for example), which may lead to the production of more residues as a consequence of possible greater yields, makes the OM content in the soil increase and, thus, the Rem-P also increases (Andrade et al., 2003; Silva and Mendonça, 2007; Fontana et al., 2008). That suggests that over time (greater OM contents), the interpretation tables of results of soil analyses and fertilizer recommendation should change in the direction of loss of dependence on the CL to the PBC (models "b" and "c" of Figure 1). The same may be noted in regard to the increase in the available P content in the soil over years of cropping or when soils are considered with greater contents of 2:1 clays (CL not very sensitive to or independent of the clay content). Model "c" of figure 1 then becomes more representative of the phenomenon. Thus, over the years of sustainable cropping in Cerrado soils, for example, the interpretation tables of soil analysis for available P and S should become independent of the PBC, unlike what currently occurs with Rem-P or even clay content.



**Figure 1. Relationship between the critical level (CL) of available P by the Mehlich-1 extractant and remaining P (Rem-P) in soils of great loss of extraction capacity (a), of intermediate loss of extraction capacity (b), and without loss of extraction capacity (c). Source: Novais and Smyth (1999).**

The “b” curve of figure 1 was found by Novais and Smyth (1999) upon placing the results of the CL of P by M-1 of nine soil samples as the dependent variable of Rem-P, as a measurement of PBC, obtained by Muniz et al. (1987) under conditions nearer to the beginning of the opening of the Cerrado areas. This observation indicates that the “a” curve of this figure would just not occur at that time of lower P residues and probable lower OM contents in the soils.

The aim of this study was to evaluate the chemical loss of extraction capacity of the extractant M-1 and MCPa from soil-available P and S, respectively, as variables of the increase in buffering capacity of acidity and of the PBC of soils, and suggest the pairing of these losses of extraction capacity with the variation of the CL of these two nutrients in soils with different values of Rem-P.

## MATERIAL AND METHODS

This study was carried out in the Standard Soil Fertility Laboratory of the Soil Department of the Universidade Federal de Viçosa, Viçosa, Minas Gerais, Brazil. For that purpose, 20 soil samples were taken, air dried, passed through a sieve with a 2 mm screen, and analyzed, chosen so as to cover the Rem-P range - theoretical values from 0 to 60 mg L<sup>-1</sup>, without taking into consideration other chemical or physical properties of the soils, such as origin, texture, color, etc.

For soil analyses (Table 1), the protocols cited in Embrapa (2009) were adopted. Available P and K were extracted by M-1 (0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 0.05 mol L<sup>-1</sup> HCl) in a soil-extractant ratio of 1:10, shaking for 5 min and rest for 16 h. Available S was extracted by a monocalcium phosphate solution, with 500 mg L<sup>-1</sup> of P in 2 mol L<sup>-1</sup> acetic acid (MCPa) in the soil-extractant ratio of 1:2.5, shaking for 5 min and rest for 16 h. For Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup>, a 1 mol L<sup>-1</sup> KCl solution was used, and potential acidity (H+Al) was determined in a 0.5 mol L<sup>-1</sup> calcium acetate solution, pH 7.0. The

Rem-P was obtained after shaking of 60 mg L<sup>-1</sup> of P in a 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution with soil samples in the soil-solution ratio of 1:10 for 1 h. The pH in water was obtained in a soil-water ratio of 1:2.5. The OM content was determined by the Walkley-Black method (Embrapa, 2009).

Phosphorus was determined by colorimetry of the phosphomolybdic complex with reduction with ascorbic acid, K was determined by flame photometry, Ca and Mg were determined by atomic absorption, Al<sup>3+</sup> and H+Al were determined by titration techniques, and S was determined by sulfate turbidimetry (Alvarez V et al., 2001).

For determination of the loss of extraction capacity after the resting period of each extractant (16h), the pH and the S and P contents were measured for both extractants (extract-soil), M-1 and MCPa, respectively.

The values of pH were fitted as dependent variables of the Rem-P of the soils to quantify the decrease (loss of extraction capacity) of the original acidity of each extractant. The same was done for the concentrations of the S in the extract for M-1 and of P for MCPa as variables of the Rem-P, which were plotted and fitted statistically so as to quantify the loss of extraction capacity of the extractants as a variable of the Rem-P values of the soils. These results were also used to verify the probable dependence of that observed in regard to the loss of extraction capacity of the two extractants with the model of decline of the CLs of soil-available P and S, with the increase in the PBC or reduction in the Rem-P.

## RESULTS AND DISCUSSION

### Loss of extraction capacity of the acidity of the extractants

Soil sample 16, with high pH (6.29), 440 g kg<sup>-1</sup> of clay, and OM content of 56.3 g kg<sup>-1</sup> (Table 1) is characterized by high buffering capacity of acidity, just as soil sample 20 (Figure 2), with initial pH of

**Table 1. Results of the routine chemical analyses and the clay content of the soils**

Soil	pH(H <sub>2</sub> O)	Rem-P	P	S	K	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	H+Al	SB	t	T	V	m	OM	Clay
		mg L <sup>-1</sup>	mg dm <sup>-3</sup>			cmol <sub>c</sub> dm <sup>-3</sup>					%		g kg <sup>-1</sup>			
1	5.89	3.50	0.70	6.07	2.00	0.05	0.00	0.00	2.70	0.06	0.06	2.76	2.20	0.00	6.30	280
2	5.50	5.00	0.40	11.26	4.00	0.08	0.00	0.00	7.70	0.10	0.10	7.80	1.30	0.00	33.90	530
3	5.56	5.10	0.90	12.46	7.00	0.07	0.01	0.00	6.90	0.10	0.10	7.00	1.40	0.00	25.10	280
4	5.29	8.00	0.60	18.80	14.00	0.08	0.03	0.00	7.70	0.15	0.15	7.85	1.90	0.00	23.90	450
5	4.74	11.00	1.10	30.61	32.00	0.09	0.06	0.39	9.30	0.24	0.63	9.54	2.50	61.90	28.90	260
6	5.12	14.30	0.50	23.62	13.00	0.13	0.02	2.44	3.90	0.19	2.63	4.09	4.60	92.80	7.50	260
7	4.90	17.30	0.80	22.41	11.00	0.47	0.16	0.88	7.40	0.66	1.54	8.06	8.20	57.10	32.60	600
8	4.43	19.00	1.60	29.96	17.00	0.20	0.06	1.66	5.80	0.31	1.97	6.11	5.10	84.30	2.30	740
9	3.72	22.50	1.60	25.69	33.00	0.19	0.11	1.56	8.70	0.39	1.95	9.09	4.30	80.00	41.40	600
10	4.68	24.00	1.50	25.80	53.00	1.65	0.45	0.20	7.60	2.24	2.44	9.84	22.80	8.20	3.84	610
11	5.15	25.70	0.90	19.24	12.00	0.67	0.16	0.49	6.30	0.87	1.36	7.17	12.10	36.00	26.40	480
12	3.89	27.30	23.50	31.16	30.00	0.19	0.10	1.27	5.60	0.37	1.64	5.97	6.20	77.40	24.90	490
13	4.08	31.60	2.00	22.19	39.00	0.59	0.33	0.78	5.20	1.02	1.80	6.22	16.40	43.30	36.40	500
14	4.46	33.40	0.70	26.46	6.00	0.09	0.10	0.78	3.90	0.21	0.99	4.11	5.10	78.80	11.30	150
15	4.87	36.30	1.20	16.51	55.00	0.26	0.27	1.76	8.70	0.68	2.44	9.38	7.20	72.10	41.80	560
16	6.29	38.20	3.80	10.82	91.00	4.08	0.95	0.00	6.00	5.27	5.27	11.27	46.80	0.00	5.63	440
17	4.75	43.30	1.90	17.38	66.00	1.26	0.61	0.59	5.30	2.04	2.63	7.34	27.80	22.40	16.30	150
18	5.63	48.30	4.50	20.01	16.00	0.71	0.14	0.00	2.40	0.90	0.90	3.30	27.30	0.00	0.13	100
19	5.05	53.00	9.10	15.74	165.00	2.09	1.50	0.49	6.90	4.01	4.50	10.91	36.80	10.90	64.60	640
20	7.18	56.10	156.10	5.03	765.00	4.02	2.27	0.10	1.40	8.26	8.36	9.66	85.50	1.20	52.00	390

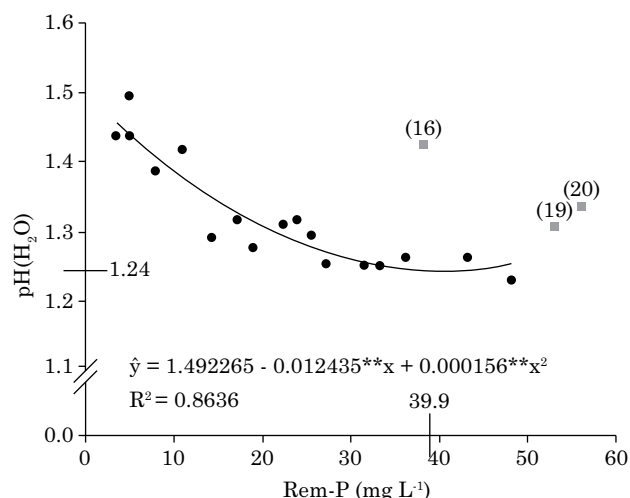
pH in water, in a soil-water ratio of 1:2.5; Rem-P: Remaining phosphorus, obtained after shaking of 30 mg L<sup>-1</sup> of P in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> for 1 h in a soil-solution ratio of 1:10; P and K: extractor M-1 (0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 0.05 mol L<sup>-1</sup> HCl); available S: extracted by 500 mg L<sup>-1</sup> of P in 2 mol L<sup>-1</sup> acetic acid solution; Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>: extractor 1 mol L<sup>-1</sup> KCl; H+Al: determined in a 0.5 mol L<sup>-1</sup> calcium acetate solution, pH 7.0; SB: sum of exchangeable bases; t: effective cation exchange capacity; T: cation exchange capacity at pH 7.0; V: base saturation; m: aluminum saturation; OM: organic matter, determined by the Walkley-Black method.

7.18, OM contents of 52.0 g kg<sup>-1</sup>, and clay contents of 90 g kg<sup>-1</sup>, which caused them greater loss of extraction capacity of acidity of the extract-soil for M-1. A similar situation occurs with soil sample 19 which, although with a lower initial pH of 5.05, has high OM content (64.6 g kg<sup>-1</sup>), and clay content (640 g kg<sup>-1</sup>). Thus, in these conditions of greater buffering of the soil acidity, and in a particular way for the soils with greater initial pH, the loss of extraction capacity of the acidity of the extractant becomes more expressive (Novais and Smyth, 1999; Nolla and Anghinoni, 2006; Viégas et al., 2010). It is noteworthy that these three soils have greater contents of OM and of Rem-P, which suggests a probable negative correlation between OM content and the MPAC or PBC of these soils, as also found by Singh and Gilkes (1991) in samples of 97 highly weathered soils of Australia.

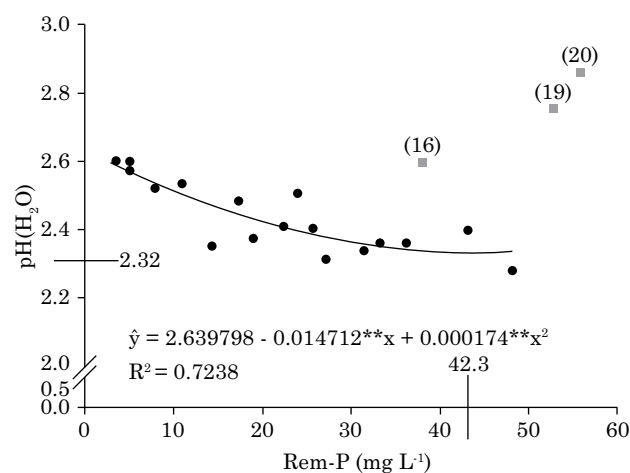
Thus, reduction in P adsorption is expected with the increase in the OM content of soils, as through the addition of organic residues with similar clay contents (Yusran, 2010). A similar situation to that observed for the M-1 extractant in soil samples 16, 19, and 20 (Table 1) occurs for the MCPa extractant in regard to loss of extraction capacity of the acidity, inconsistent with that observed for the other soils.

The pH of the extract-soil estimated for the condition of minimum loss of extraction capacity of the M-1 for Rem-P = 39.9 mg L<sup>-1</sup> is 1.24 (Figure 2). For the MCPa extractant, these values are 42.3 mg L<sup>-1</sup> and pH of 2.32 (Figure 3). These pH values are similar to those originally found in the extractants, i.e. M-1 of 1.2 and MCPa of 2.2. In contrast, under the condition of estimated maximum loss of extraction capacity (Rem-P = 0 mg L<sup>-1</sup> or maximum PBC), the values of pH of the extract-soil for M-1 is 1.49, and for MCPa, it is 2.6. Therefore, it may be seen that, in both extractants, the maximum amplitude of variation of the pH of the extract-soil is small and probably not responsible for the expected decreases of the CLs of P in the soil through M-1 with the increase in the PBC of the soil (reduction in Rem-P) (Ribeiro et al., 1999).

This type of information has practical importance for soils with high contents of the P fraction bonded to Ca (P-Ca), when one might suppose that the M-1 would be less effective in extraction of P-Ca (Silva and Raij, 1999), given the condition more favorable to the loss of extraction capacity of the acidity of the extractant in this condition of soils with greater clay contents.



**Figure 2.** Values of  $\text{pH}(\text{H}_2\text{O})$  of the extract-soil of Mehlich-1, as a variable of remaining P values (Rem-P) of the soils. The three points identified for the soils (■) were excluded from the fit. \*\*: significant at 1 % by the t test. (|) Values of x and y that denote the minimum point.



**Figure 3.** Values of  $\text{pH}(\text{H}_2\text{O})$  of the extract-soil of Monocalcium Phosphate in acetic acid as a variable of remaining P values (Rem-P) of the soils. The three points identified for the soils (■) were excluded from the fit. \*\*: significant at 1 % by the t test. (|) Values of x and y that denote the minimum point.

### Loss of extraction capacity of anions of extractants

In regard to the loss of extraction capacity of M-1 by consumption (sorption) of the sulfate (Figure 4), the three previously excluded soil samples (Figures 2 and 3) exhibit a pattern more

consistent with the other soils considered in figure 4. However, they were removed from the figure due to the anomalous behavior observed for MCPa (Figure 5), as previously observed in the study of the loss of extraction capacity of the acidity in both extractants (Figures 2 and 3).

The same is observed for soil sample 20, with  $156.1 \text{ mg dm}^{-3}$  of available P by M-1 and high OM and clay contents, as already mentioned, as well as for samples 16 and 19 (Table 1); the loss of extraction capacity of this extractant follows the general model presented for the other soils (Figure 4).

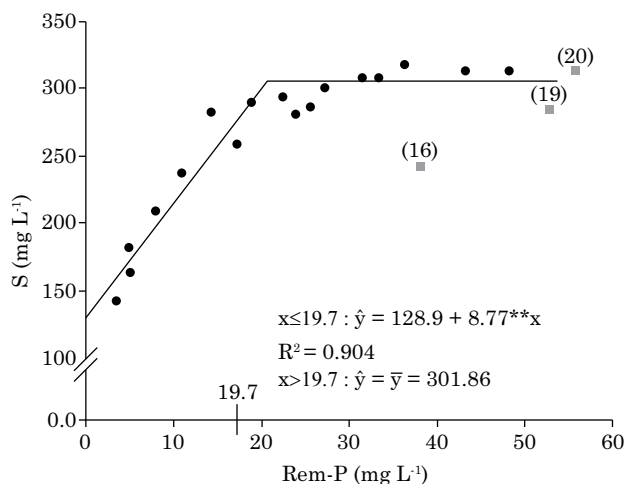
The loss of extraction capacity of the sulfate in M-1 is noteworthy and is shown in the discontinuous model below (Figure 4). This model was theoretically presented by Novais and Smyth (1999), which indicated that for soils with intermediate PBC values (Figure 1b), the loss of extraction capacity of the extractant, sulfate in this case, occurs up to intermediate values of PBC (Rem-P), but not from there on, for the less buffered soils (with greater Rem-P values).

A similar discontinuity for the CL of P by M-1 of different soils obtained by Muniz et al. (1987), when plotted by Novais and Smyth (1999), showed a response curve of the “linear-plateau” type ( $R^2 = 0.90^{**}$ ), similar to that of figure 1b and to the curve of loss of extraction capacity of this extractant as a function of the Rem-P (Figure 4). In this new graphic arrangement of the results of Muniz et al. (1987), Novais and Smyth (1999) observed significant dependence of the CL on PBC in soil with  $\text{Rem-P-30}^{(4)} < 5.33 \text{ mg L}^{-1}$ , which corresponds to an estimated clay content of  $370 \text{ g kg}^{-1}$  [ $\text{M-1P} = 5.31 + 3.51 (\text{Rem-P-30})$ ] and a “linear plateau” for lower clay contents ( $\text{M-1P} = 24.02 \text{ mg dm}^{-3}$ ). It is noteworthy that in the study of Muniz et al. (1987) a linear correlation was found between the CL and Rem-P-30 with the fit  $\text{CL} = 11.2 + 0.9550 (\text{Rem-P-30})$ , with  $r = 0.775^{**}$  and Rem-P, as a measure of the PBC of the soils.

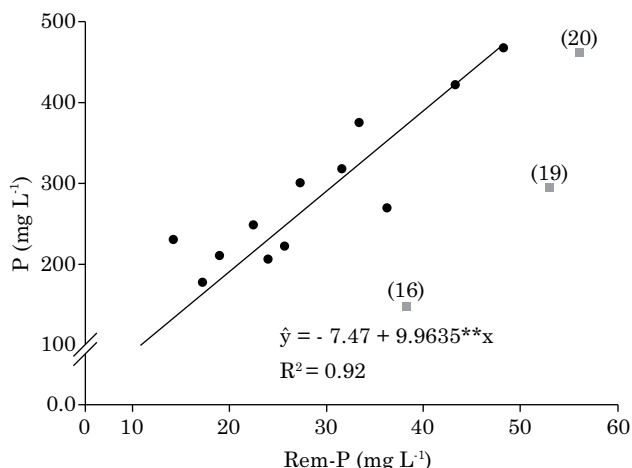
The information obtained in this study reinforces model “b” of figure 1 and, upon comparing it with the loss of extraction capacity of the M-1 observed (Figure 4), indicates an expressive relationship between the PBC of soils and the CLs of available P, as a consequence of the loss of extraction capacity of the extractant, as discussed by Novais and Smyth (1999).

From all this, it may be perceived that the linear relationship between the CL of P in the soil by M-1 and measurements of the PBC such as Rem-P (model “a” in figure 1), although statistically significant, does not in fact portray what happens, i.e., the suitability of model “b” and not of model “a”

<sup>(4)</sup> Remaining-P obtained after shaking of  $30 \text{ mg L}^{-1}$  of P in  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  for 1 h in a soil-solution ratio of 1:10.



**Figure 4. Sulfur concentration in the extract-soil of Mehlich-1, as a variable of remaining P values (Rem-P) of the soils. The three points identified for the soils (■) were excluded from the fit. \*\*: significant at 1 % by the t test. (|) Indicates the Rem-P value for the beginning of the plateau.**



**Figure 5. Phosphorus concentration in the extract-soil of Monocalcium Phosphate in acetic acid as a variable of remaining P values (Rem-P) of the soils. The three points identified for the soils (■) were excluded from the fit. \*\*: significant at 1 % by the t test.**

of figure 1, as considered in the studies developed in our conditions over decades (Côrrea et al., 2008, 2011; Simões Neto et al., 2009). With the increase in the OM content in soils, as a consequence of conservationist practices adopted (Rheinheimer and Anghinoni, 2001; Gatiboni et al., 2007) or increase in the remaining P content over various croppings, or both, the probable “current” model should lean toward model “c” (Figure 1).

Thus, it is possible to speculate that in the “5<sup>th</sup> approximation” (Ribeiro et al., 1999), the

interpretation table of the P availability classes in soils that have their values increased in a linear manner with the increase in Rem-P, under the condition for less loss of extraction capacity, is not sufficiently correct, even if the adopted model “a” of figure 1 may be significant, since greater values of  $R^2$ , as well as better theoretical support with the adoption of model “b”, would be obtained. From the results of loss of extraction capacity of M-1 in extraction of soil-available P (Figure 4), the need for changes in the P availability classes may be indicated, such that for Rem-P values greater than 19.7 mg L<sup>-1</sup> (Figure 4), the values of the CL of P remain constant, regardless of Rem-P values. The clay content corresponding to this value of Rem-P was not able to be estimated, given the non-significant correlation between the two variables ( $r = -0.229$ ), under the conditions of this study.

Tables from other states [Ribeiro et al. (1999), CQFS-RS/SC (2004), Oliveira (2003), among others] should receive similar treatment. In the recommendation manual for the states of Rio Grande do Sul and Santa Catarina (CQFS-RS/SC, 2004), classification of available P content through M-1 as a variable of the clay content establishes a negative dependence between these two variables, but positive with Rem-P (model “a” of figure 1). However, in the case of flooded soils, only one class is considered, with 41 to 60 % clay, suggesting, for these conditions, the suitability of model “c”.

In the loss of extraction capacity of the MCPa extractant, through adsorption of its phosphate during extraction of available S, its fit with model “a” of figure 1 is noted. This model indicates that with the occurrence of lower values of PBC, associated with the greater values of Rem-P, there is a linear loss of extraction capacity of phosphate during extraction (Figure 5). As a consequence of this behavior, the interpretation table of soil-available S, like that of the “5<sup>th</sup> approximation” (Ribeiro et al., 1999), establishes greater CLs of this nutrient with the increase of Rem-P of the soil, consistent with the curve of loss of extraction capacity of the extractant (Figure 5). A mean value of the availability class of this nutrient considered as adequate starts from 4.6 mg dm<sup>-3</sup> of S for soils with Rem-P from 0 to 4 mg L<sup>-1</sup> and reaches a maximum value of 22.6 mg dm<sup>-3</sup> in those less buffered soils, with Rem-P from 44 to 60 mg L<sup>-1</sup> (Alvarez V et al., 1999). Thus, the discontinuous model “b” (Figure 1) that portrays the loss of extraction capacity by consumption of the sulfate during extraction of the M-1 with the increase in PBC, i.e., reduction in Rem-P values, does not apply to MCPa. It is thus plausible to indicate the suitability of the current tables of interpretation of available S in regard to their theoretical linear model of dependence to the loss of extraction capacity of the extractant, but not of available P by M-1.

## CONCLUSIONS

The loss of extraction capacity of the acidity of the extractants Mehlich-1 (M-1) and Monocalcium Phosphate in acetic acid (MCPa) is not very expressive, indicating the small practical effect of this loss of extraction capacity on analysis of P and S available in the soil.

The discontinuous loss of extraction capacity of the  $\text{SO}_4^{2-}$  of M-1 occurs in soils with intermediate values of Phosphate Buffering Capacity in a "linear plateau" model. In contrast, the loss of extraction capacity of the  $\text{H}_2\text{PO}_4^-$  of MCPa is linear and continuous throughout the amplitude of variation of remaining P (Rem-P).

The discontinuous model for loss of extraction capacity of M-1 indicates a likewise discontinuous model for interpretation of soil-available P. In contrast, the linear model observed for MCPa indicates a likewise linear relationship between the critical levels of S and the values of Rem-P of the soils, as currently adopted.

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