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Refining phosphorus fertilizer recommendations based on buffering capacity of soils from southern Brazil

Gilmar Luiz Mumbach(1)*, **Luciano Colpo Gatiboni**(2), **Daniel João Dall'Orsoletta**(3), **Djalma Eugenio Schmitt**(4), **Douglas Luiz Grando**(1), **Abelino Anacleto de Souza Junior**(1), **Fernando Marcos Brignoli**(1) **and Daniel Alexandre Iochims**(1)

(1) Universidade do Estado de Santa Catarina, Departamento de Solos e Recursos Naturais, Programa de Pós-Graduação em Ciência do Solo, Lages, Santa Catarina, Brasil.
(2) North Carolina State University, Department of Crop and Soil Sciences, Raleigh, North Carolina, United States.
(3) Bolsista de Pós-Doutorado do Conselho Nacional de Desenvolvimento Científico e Tecnológico (155424/2018-1), Lages, Santa Catarina, Brasil.
(4) Universidade Federal de Santa Catarina, Departamento de Agricultura, Biodiversidade e Florestas, Curitibanos, Santa Catarina, Brasil.

*** Corresponding author:**
E-mail: gilmarmumbach@hotmail.com

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ABSTRACT: The phosphorus (P) rates recommended for corrective fertilization-P of soils from southern Brazil may be insufficient to reach the critical level for optimal plant growth. This study aimed to quantify the fertilizer-P rates for total correction fertilization with varying soil buffering capacity in the states of Rio Grande do Sul (RS) and Santa Catarina (SC). Soil samples from 0.00-0.10 and 0.10-0.20 m layers were collected from 41 locations distributed in both states. Twelve P rates were applied to each soil, varying between 0 and 100 % of the maximum adsorption capacity (P-max), and incubated for 20 days. After incubation, the extractable P was determined by Mehlich-1. Based on the relationship between applied rates and extracted P, the P buffer capacity (*tr*P_M1) of the soils was quantified, relating it to soil properties. The *tr*P_M1 values, that is, amounts of P_2O_5 required to increase 1 mg dm^{-3} of P extracted by Mehlich-1, varied between 2.4 and 34.5 kg ha^{-1} of P_2O_5. A multiple explanatory equation for the variable P was generated, in which only P-max, clay content, and initial P availability have a significant effect. The P buffer capacity was significantly higher in the soils with the highest clay content, and there was a reduction in *tr*P_M1 for soils with higher initial P availability. Considering 270 soil samples with low P, the P rate to reach the sufficient levels may be 2-folds higher than the values currently indicated for the RS and SC states, especially for soils with more than 40 % of clay. Phosphorus rates for corrective fertilization must be based on the soil clay content and in P initial availability. The fertilizer-P in clayey soils must be increased.

Keywords: phosphate fertilization, corrective fertilization, phosphorus buffering, maximum adsorption capacity.

INTRODUCTION

Soils in southern Brazil are naturally phosphorus (P) deficient and have high adsorption capacity (Almeida et al., 2003; Bortoluzzi et al., 2015). Phosphorus has a high affinity for soil particles, causing low availability to plants and low recovery fertilizer efficiency (Barrow and Debnath, 2018; Zhang et al., 2018). The clay content and mineralogical soil composition have a decisive influence on the retention of P and its availability (Eberhardt et al., 2008; Fink et al., 2016; Rogeri et al., 2016; Reis et al., 2020). Besides, parameters such as pH and organic matter can also affect the P dynamics in the soil (Almeida et al., 2003; Fink et al., 2016), as well as changes in the environment (Bortoluzzi et al., 2015).

In this scenario, the supply of P in quantities enough to suppress the high adsorption capacity of the soil and, at the same time, satisfy the crops demand is the main strategy for achieving desirable yield (Roy et al., 2016). In soils with insufficient P availability, that is, below the critical level (CL), it is recommended to carry out corrective fertilization to raise the soil P content to appropriate level (Sousa and Lobato, 2002; CQFS-RS/SC, 2016). The CL represents the content considered adequate for the maximum economic return of agricultural crops, around 90 and 95 % of maximum relative yield for the states of RS and SC, the CL values vary according to the clay content of the soil and the cultivated plant. Corrective fertilization can be carried out at once, in which the fertilizer is incorporated in the 0.00-0.20 m layer, or splitted, in which the correction is applied concurrently with sowing and basic fertilization in two or more crop years, to gradually raise the soil-test P level (Sousa and Lobato, 2002; CQFS-RS/SC, 2016). Despite the higher initial costs, the supply of P at greater depths, as well as the practice of corrective fertilization, can benefit the response of crops (Hansel et al., 2017; Mumbach and Gatiboni, 2020).

In soils with insufficient P availability, the addition of phosphate fertilizers improves the nutrient use efficiency (Cubilla et al., 2007; Rubio et al., 2008; Reis et al., 2020). The saturation of the adsorption sites with the highest binding energy (Rheinheimer et al., 2003; Oliveira et al., 2014), and the increase in the number of negative electrical charges (Barrow, 2015), reduce the P adsorption, allowing a greater percentual of P available to plants (Barrow and Debnath, 2018; Boitt et al., 2018; Zhang et al., 2018; Mumbach et al., 2020; Thuy et al., 2020). Thus, in corrected soils, the phosphate fertilization has higher efficiency of use by plants, and less amount is needed to meet plant’s demand (Barrow and Debnath, 2018; Withers et al., 2018).

The corrective fertilization rates currently recommended in Brazil’s southern region consider the initial P availability and the clay content of the soil (CQFS-RS/SC, 2016). Despite the consideration of soil buffering variation, the currently recommended rates may be insufficient to reach the CL, especially when corrective fertilization is carried out in new areas without previous phosphate fertilization. Rogeri et al. (2016) evaluated representative soils of the RS state and observed P buffering capacity, between 8.3 and 71.4 kg ha^{-1} of P_2O_5, about 2-folds of those currently recommended by CQFS-RS/SC (2016).

Thus, it is believed that values of P corrective fertilization in force for RS and SC state (CQFS-RS/SC, 2016) are insufficient, especially for soils with higher clay content. This study aimed to quantify the P rates for the total corrective fertilization of contrasting soils in terms of buffering capacity from RS and SC states.

MATERIALS AND METHODS

Soil collection and characterization

Soil samples were collected from 0.00-0.10 and 0.10-0.20 m layers, in 20 and 21 sites of Rio Grande do Sul and Santa Catarina States, respectively, totaling 82 samples (Figure 1). The samples were collected in the main agricultural regions of the states,

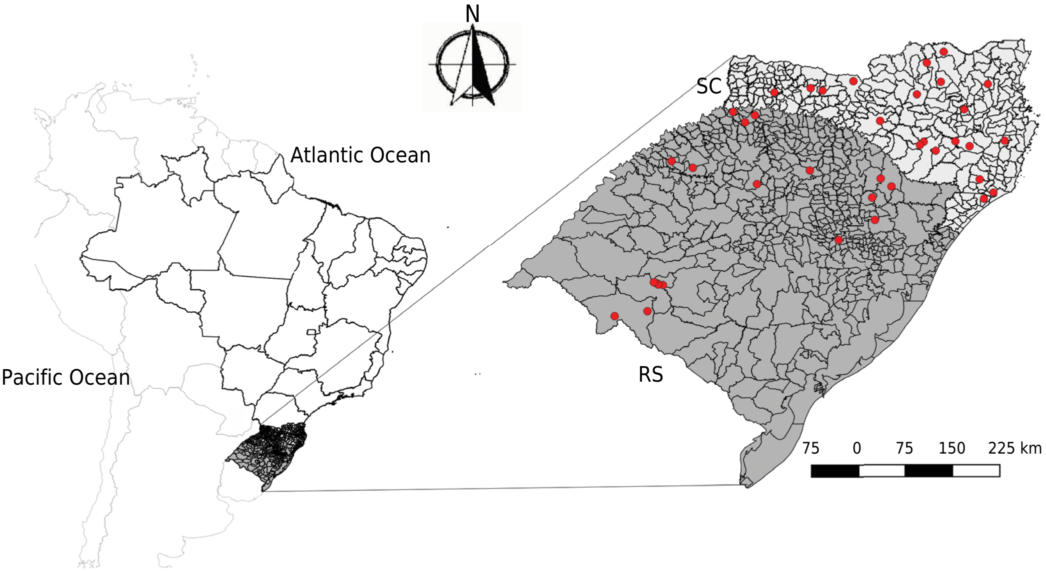

Figure 1. Spatial distribution of the 20 soil collection points in the state of Rio Grande do Sul (RS) and the 21 points sampled in the state of Santa Catarina (SC), Brazil.

but in areas without anthropic interference, either in areas of the native grassland without grassing or forest, adjacents to crop fields. After collection, the samples were oven-dried at 60 °C for 72 h, ground, and sieved in a 2 mm mesh. Soils with pH(H_2O) below 6.0 were corrected to this value by incubating with dolomitic limestone. For that, doses of 70, 100, and 130 % of the liming requirement according to the current liming recommendations for the soils of the region (CQFS-RS/SC, 2016) were applied to samples of 50 g of soil. After 20 days of incubation, the limestone dose was determined to reach a pH(H_2O) value of 6.0, through the relationship between rates of lime and pH(H_2O) values. Based on the determined dose, the soils were incubated for 20 days. Subsequently, the soils were characterized physically and chemically, and the results are shown in table 1.

The clay content was determined by the pipette method (Teixeira et al., 2017). The pH(H_2O) was determined in a 1:1 soil:water ratio; P and K were extracted with the Mehlich-1 solution (0.0125 mol L^{-1} of H_2SO_4 and 0.050 mol L^{-1} of HCl); the K determination was performed by flame spectrophotometry (DM-62, DIGIMED). The content of total organic carbon (TOC) was determined by spectrophotometry at 645 nm (UV-1800, SHIMADZU) after oxidation by sulfochromic solution. The CEC pH 7.0 was obtained by adding the exchangeable levels of calcium (Ca), magnesium (Mg), potassium (K), and potential acidity (H+Al). The analyses highlighted above were based on methodologies proposed by Tedesco et al. (1995). The altitude measurement was performed at the point of collection of soil samples using GPS.

The remaining P (P-rem) was determined by adding 1 g of soil in falcon tubes containing 10 mL of $CaCl_2$ 0.01 mol L^{-1} and P concentration of 60 mg L^{-1}. After mixing in an “end over end” shaker for one hour, the samples were centrifuged for 15 min at 3000 rotations per minute (rpm) and an aliquot was removed to determine P.

The determination of the maximum P adsorption capacity (P-max) of the soils were carried out by weighing 0.5 g of soil in 15 mL falcon tubes and equilibrated with 10 mL of $CaCl_2$ 0.01 mol L^{-1} containing eight concentrations of P, from 0 to 160 mg L^{-1} of P, which corresponded to doses from 0 to 3200 mg kg^{-1} of P. The samples were stirred for 16 h in an end-over-end shaker 33 rpm and, after separating the soil from the solution by centrifugation at 3000 rpm for 15 min, an aliquot was removed for determination. The P-sorbent was obtained by the difference between the amount added and the amount

Table 1. Identification, classification, location, and characterization of soils collected in the states of Rio Grande do Sul (RS) and Santa Catarina (SC)

Soil(1)	Altitude	Clay(2)		P M-1(3)		TOC(4)		CEC$_{pH7}$(5)		P-max(6)		P-rem(7)	
	m	g kg^{-1}		mg dm^{-3}		g kg^{-1}		cmol$_c$ dm^{-3}		mg kg^{-1}		mg L^{-1}	
		A(8)	B(8)	A	B	A	B	A	B	A	B	A	B
RS1-LB	970	655	678	3.3	1.0	22.6	19.4	15.6	15.4	2313.1	2259.7	9.0	5.3
RS2-LV	900	670	723	5.4	1.9	17.4	13.7	15.8	14.8	1790.2	2023.4	14.0	11.4
RS3-LV	725	359	350	2.7	1.4	9.5	7.4	12.0	10.1	885.1	962.5	19.1	15.7
RS4-LV	475	464	506	13.2	5.3	20.0	10.9	12.5	11.0	912.1	1125.1	20.7	19.3
RS5-LV	218	631	694	5.4	2.2	12.3	9.1	12.2	12.0	1228.1	1235.1	19.8	16.8
RS6-LV	342	614	620	2.0	0.8	12.2	7.8	12.1	8.8	1790.8	1632.5	13.3	11.8
RS7-LV	420	211	232	7.8	3.7	5.6	4.2	7.5	6.7	346.7	351.8	36.0	35.0
RS8-CX	218	203	239	9.9	3.3	24.0	10.8	9.2	10.5	473.7	786.6	30.7	20.4
RS9-LV	563	712	718	7.0	5.7	7.9	4.3	10.9	9.6	1267.2	1606.4	16.9	13.8
RS10-CX	384	410	448	5.4	2.2	10.2	6.2	11.5	11.2	1599.2	1633.6	7.9	11.5
RS11-PBAC	125	122	130	7.1	3.4	4.3	3.7	6.3	5.2	278.1	283.0	42.2	40.1
RS12-TX	124	138	111	13.3	7.2	9.8	8.4	7.9	11.0	696.2	749.9	32.9	28.8
RS13-FT	115	121	120	7.8	3.6	6.4	1.8	4.4	4.0	249.4	217.0	44.8	42.6
RS14-PV	140	98	95	9.6	4.8	6.0	0.5	3.0	2.8	190.8	197.9	46.8	46.6
RS15-PV	165	120	124	9.1	5.0	4.5	2.0	5.2	4.4	302.5	301.8	45.5	44.6
RS16-TX	172	129	134	15.0	8.3	7.1	3.6	8.0	6.9	275.4	410.8	49.1	43.4
RS17-RL	100	245	251	10.4	6.2	20.7	17.1	11.2	10.2	496.4	763.8	34.4	28.3
RS18-LB	873	479	545	6.6	2.3	16.3	11.4	14.7	13.1	2360.4	2580.1	8.6	10.2
RS19-CH	747	332	360	5.0	2.1	15.5	8.1	12.5	11.3	1313.6	1844.1	18.9	12.8
RS20-PV	76	385	397	50.0	20.3	3.7	1.5	5.8	9.6	411.8	702.4	33.7	23.6
SC1-PVA	101	187	190	6.5	3.0	11.1	7.8	7.1	6.8	389.6	362.5	27.4	26.4
SC2-PVA	245	314	320	5.7	2.5	12.5	5.5	10.3	10.7	570.7	671.2	24.7	25.0
SC3-PV	33	263	273	1.4	0.5	13.3	7.6	10.2	10.8	1258.4	1465.7	13.7	7.5
SC4-PA	292	244	248	3.7	2.2	12.8	8.8	9.0	7.3	443.2	366.5	25.1	27.7
SC5-CX	349	272	289	19.8	4.0	16.6	9.3	10.8	12.5	691.1	737.4	18.3	16.4
SC6-CH	930	335	352	2.9	1.3	17.4	14.3	12.5	13.4	1129.8	1471.2	9.5	7.6
SC7-PVA	41	347	383	19.4	3.1	7.8	4.0	9.1	8.0	456.2	578.3	24.8	19.4
SC8-PVA	470	345	346	4.5	2.8	28.3	21.3	10.9	10.7	678.8	663.5	17.7	18.1
SC9-CH	890	330	360	4.7	2.0	27.7	24.3	14.6	13.6	1689.5	2001.9	5.7	3.4
SC10-NV	872	431	444	9.7	3.0	36.9	27.5	14.5	15.5	1915.6	1875.7	5.2	4.5
SC11-NB	898	503	522	1.0	0.7	26.1	18.0	13.2	13.9	2469.4	2638.6	3.8	3.0
SC12-NB	1130	518	559	1.9	0.9	29.6	22.0	13.3	11.1	1877.0	2266.9	9.5	6.0
SC13-NB	1075	585	592	2.3	1.0	21.4	17.0	14.3	11.9	2349.8	2377.8	3.7	3.1
SC14-LB	1063	669	691	3.2	1.5	15.6	13.5	10.6	9.7	1475.8	1561.3	9.8	7.6
SC15-LV	939	670	709	6.7	3.2	22.9	15.4	12.7	13.0	1693.5	1885.5	10.1	6.6
SC16 - LV	686	706	755	24.3	3.0	20.0	9.5	11.0	9.0	1576.9	1892.2	11.5	4.8
SC17-CH	980	440	425	1.6	1.1	23.3	20.0	10.5	10.4	1621.0	1595.2	9.4	8.0
SC18-LB	805	602	632	2.9	1.2	28.4	28.6	12.6	12.9	1810.1	2358.3	6.0	3.7
SC19-CH	885	178	183	8.8	2.8	15.9	10.8	6.6	6.9	895.5	983.6	25.8	24.4
SC20-LV	535	685	727	5.7	2.8	15.4	9.0	11.3	12.3	1575.8	1569.1	11.3	6.7
SC21-CX	659	281	344	11.6	4.4	27.5	11.2	12.6	14.7	1336.0	1323.8	12.9	12.4

(1) According to the classification proposed by the WRB (IUSS, 2015) and by Brazilian Soil Classification System (Santos et al., 2018). LB: Ferralsols/*Latossolo Bruno*; LV: Ferralsols/*Latossolo Vermelho*; CX: Cambisols/*Cambissolo Háplico*; PBAC: Acrisols/*Argissolo Bruno-Acinzentado*; TX: Luvisols/*Luvissolo Háplico*; RL: Leptosols/*Neossolo Litólico*; CH: Cambisols/*Cambissolo Húmico*; PV: Acrisols/*Argissolo Vermelho*; PVA: Acrisols/*Argissolo Vermelho-Amarelo*; PA: Acrisols/*Argissolo Amarelo*; NV: Nitisols/*Nitossolo Vermelho*; NB: Nitisols/*Nitossolo Bruno*. The soils designated between RS1 and RS20 were collected in the Rio Grande do Sul State, in the cities of Vacaria, Lagoa Vermelha, Passo Fundo, Ibirubá, Santo Ângelo, Cerro Largo, Cruz Alta, Pinheirinho do Vale, Taquaruçu do Sul, Iraí, Rosário do Sul, Rosário do Sul, Rosário do Sul, Rosário do Sul, Santana do Livramento, Rosário do Sul, Santana do Livramento, Ipê, Caxias do Sul, and Teotônia, respectively. The soils designated between SC1 and SC21 were collected in the Santa Catarina State, in the cities of Sangão, Lauro Miller, Içara, Pomerode, Rio do Sul, Lages, Blumenau, Rancho Queimado, Bom retiro, Água Doce, Painel, Santa Cecilia, Vargeão, Campos Novos, Faxinal dos Guedes, Lages, Major Vieira, Mafra, Pinhalzinho, and Santa Terezinha, respectively. (2) Clay determined by the pipette method (Teixeira et al., 2017). (3) P extracted by Mehlich-1 (Tedesco et al., 1995). (4) Total organic carbon (Tedesco et al., 1995). (5) CEC$_{pH7.0}$ = Ca^{2+} + Mg^{2+} + K^{+} + (H+Al). (6) Maximum P adsorption capacity, by the Langmuir equation. (7) P remaining, after adding 60 mg L^{-1} of P. (8) A and B refer to soil layers 0.00-0.10 and 0.10-0.20 m, respectively.

recovered in the equilibration solution. The P-sorbed and P-solution data were fitted to the Langmuir equation: P-sorbed = k P-max C / (1 + K C), in which k is the constant related to the adsorption energy, P-max is the maximum P adsorption capacity, and C is the P concentration in the solution.

The P, extracted by Mehlich-1 and in the other evaluations carried out in this study, was determined by the colorimetric method, under a wavelength of 882 nm (Murphy and Riley, 1962).

Incubation and determination of phosphorus buffering capacity (*tr*P_M1)

The soil samples were incubated in the laboratory with an average temperature of 20 °C, with 12 rates of P_2O_5, with three replications, under a completely randomized design. The applied doses were comprised between 0 and 100 % of the maximum value of P-max and were prepared with triple superphosphate fertilizer (43 % of P_2O_5 - water-soluble + CNA). The fertilizer was ground and dissolved in deionized water to facilitate the application and homogenization of the samples. For each experimental unit, 50 g of soil were added to transparent plastic bags, to which the respective amounts of phosphate solution were added. Subsequently, the soil moisture was homogenized to a condition close to 100 % of the field capacity. The amount of water needed for each soil to reach the condition of friable moisture was determined by the touch method.

The incubation was carried out for 20 days. The plastic bags were opened weekly, and the humidity was corrected. After the incubation, the soil samples were dried in a forced ventilation oven at a constant temperature of 60 °C for 48 h and, later, sieved in a 2 mm mesh. The available P was determined by Mehlich-1 extractor. The Mehlich-1 extractor was adopted because it is the official method adopted in the region covered by the study.

The relationships between the P rates and P extracted by Mehlich-1 at the end of the incubation time were performed using linear regressions with one or two linear segments. For the generation of linear regressions of two segments, the “piecewise” option of the SigmaPlot 12.5 software was used. Subsequently, we selected the P rates that resulted in Mehlich-1 extractable P values up to twice the critical levels (CL), established for grain culture (CQFS-RS/SC, 2016). These values represent the upper limit of the P availability class “high”, according to CQFS-RS/SC (2016). Based on this new data set, simple linear equations were generated, and the P buffering capacity (*tr*P_M1) values were determined through the inverse of the angular coefficient of each linear equation (*tr*P_M1 = 1/ angular coefficient). This estimate of soil buffering was called tr_1P_M1. The *tr*P_M1 represents the amounts of P_2O_5 required to increase 1 mg dm^{-3} of P extracted by Mehlich-1.

The tr_1P_M1 values were correlated with the following soil properties: initial P (in the natural condition), clay content, CEC pH 7.0, TOC, P-rem, P-max, and altitude of the collection point. Based on these properties, a multiple linear equation was generated using the option “Backward stepwise regression”, based on the response variable tr_1P_M1.

A new split of the data was carried out, aiming to evaluate the influence of the clay class and the initial P content on the buffering capacity of the soils. For each one of the 41 soils, we created three new linear equations (P rates × P Mehlich-1): i) primary curve that gave rise to the tr_1P_M1; ii) elimination of the lower rates of the “i”, that is, without rates that resulted in P levels classified as “very low”; and iii) elimination of the lower rates of the “ii”, that is, without rates that resulted in P levels classified as “low”. The “i”, “ii”, and “iii” curves aimed to simulate conditions in which the soils were classified as “very low”, “low”, and “medium”, following the established by CQFS-RS/SC (2016). Based on each of the new equations generated, a *tr*P_M1 value was calculated, as previously described, and called tr_2P_M1.

Subsequently, the influence of clay and initial P contents on tr_2P_M1 was evaluated, based on the clay classes and available P described by CQFS-RS/SC (2016). From the statistical separation obtained for these factors, a table of values was generated for recommending total corrective fertilization of P.

Total correction fertilization recommendation based on tr_2P_M1 values

The tr_2P_M1 tabulated values, depending on the clay and the initial P content, were used to simulate a total corrective fertilization recommendation. The estimated values were compared to the recommendation values indicated by CQFS-RS/SC (2016). For tr_2P_M1 values, the amount of corrective fertilization (CF) was obtained based on equation 1, and following the methodology already used in the Cerrado region (Sousa and Lobato, 2002):

$$CF\ (kg\ ha^{-1}\ of\ P_2O_5) = (P\ final - P\ initial) \times tr_2\text{P\_M1} \qquad \text{Eq. 1}$$

In which “CF” represents the amount of phosphate fertilizer to be applied in the 0.00-0.20 m layer for total corrective fertilization; “P final” represents the P-value in the soil to be reached (critical level = CL); “P initial” represents the initial value of P in the soil, and tr_2P_M1 is the P buffer capacity of the soil.

The comparison between the rates recommended by the two methods was carried out with a set of 270 soil samples. These samples were obtained in the routine laboratory of CAV/UDESC and comprise soils with extractable P content below the CL for grain crops (CQFS-RS/SC, 2016).

Statistical analysis

The tr_1P_M1 and tr_2P_M1 values were submitted to normality analysis, using the Shapiro-Wilk test and, when necessary, transformed by Box-Cox to meet the normality assumptions. Subsequently, they were subjected to analysis of variance (ANOVA). The correlation between tr_1P_M1 values and soil properties were performed using Pearson’s test ($p<0.05$). The tr_2P_M1 values were compared using the Tukey’s test ($p<0.05$), within the four clay classes and the three availability classes established by CQFS-RS/SC (2016). The statistical analyses were performed, employing SigmaPlot 12.5 and Sisvar 5.6 software (Ferreira, 2014).

RESULTS

P buffering for RS and SC soils

The application of the P_2O_5 rates increased P extracted by Mehlich-1 ($p<0.05$). For many soils, especially the more clayey ones, there were significant changes along with the relationship between the two variables, with significance in the piecewise equations ($p<0.05$). In these soils, the second linear segment’s angular coefficient, which considers the range of doses from the change point (Cp), was higher (Table 2). Considering the whole set of soils, the buffering differences between the first and second segments varied between 1.1 and 4.3 times. However, in some soils, especially the less clayey ones, there was no significant change point, and a single line segment explains the relationship. The behavior of sandy soils showed similarities with the second linear segment obtained in the clayey soils.

Figure 2 shows an illustration of the behavior observed in the set of collected soils. Figures 2a and 2b illustrate soils with high clay content and which present significant segmentation. On the other hand, graphs 2c and 2d show soils with lower clay content, in which only a linear regression explains the relationship between applied doses and levels available in the soil.

Table 2. Phosphorus extracted as a function of the 12 applied phosphorus rates, values of the change point (Cp) of the segmented equations, and values of tr_1P_M1 in soil samples collected in the Rio Grande do Sul (RS) and the Santa Catarina (SC) States

Soil	Soil layer of 0.00-0.10 m				Soil layer of 0.10-0.20 m			
	Region 1	Region 2	Cp	tr_1P_M1	Region 1	Region 2	Cp	tr_1P_M1
			mg dm^{-3}	kg ha^{-1}			mg dm^{-3}	kg ha^{-1}
RS1	0.041**x + 1.3	0.132**x – 54.4	26.4	26.3	0.056**x – 0.3	0.137**x – 71.9	49.3	27.8
RS2	0.064**x + 5.3	0.147**x – 68.6	62.2	22.2	0.056**x – 1.4	0.149**x – 83.9	48.3	27.8
RS3	0.183**x – 0.5	0.239**x – 22.5	71.0	6.1	0.167*x – 1.1	0.243**x – 32.9	72.7	7.1
RS4	0.138**x + 10.0	0.194**x – 10.0	69.3	18.9	0.127**x + 2.6	0.207**x – 35.5	62.6	19.6
RS5	0.080**x + 1.1	0.150**x – 14.6	22.9	19.2	0.080**x + 1.1	0.150**x – 14.6	19.0	17.2
RS6	0.081**x – 2.4	0.175**x – 119.3	98.7	24.4	0.079**x – 2.8	0.182**x – 128.7	93.5	24.4
RS7	0.277**x + 6.4	0.363**x – 17.6	78.0	4.0	0.203**x + 3.0	0.328**x – 12.7	28.4	5.0
RS8	0.071**x + 10.4	0.189**x – 13.4	24.9	12.5	0.071**x + 2.9	0.180**x – 35.0	27.5	14.7
RS9	0.087**x + 2.5	0.194**x – 124.1	105.4	18.5	0.071**x + 2.3	0.198**x – 155.7	90.4	19.2
RS10	0.058**x + 3.1	0.147**x – 100.7	71.1	19.6	0.050**x + 1.1	0.135**x – 96.1	58.1	21.7
RS11	0.408**x + 1.9		-	2.6	0.413**x – 3.4		-	2.8
RS12	0.340**x + 1.2		-	3.9	0.326**x – 2.4		-	4.1
RS13	0.377*x + 1.3		-	3.1	0.259**x + 1.4	0.374**x – 23.5	57.4	3.9
RS14	0.408**x + 1.7		-	3.0	0.294**x + 3.5	0.424**x – 31.3	81.9	3.4
RS15	0.386**x + 4.9		-	2.4	0.353**x + 2.7	0.401**x – 9.4	91.8	2.8
RS16	0.380**x + 13.1		-	2.6	0.384**x + 5.1		-	2.7
RS17	0.118**x + 9.1	0.199**x – 23.0	55.6	8.6	0.114**x + 6.1	0.206**x – 46.9	71.8	9.2
RS18	0.098**x – 2.1	0.132**x – 27.7	75.5	14.3	0.072**x – 0.2	0.139**x – 26.7	28.3	17.5
RS19	0.110**x + 1.5	0.200**x – 96.7	121.4	11.5	0.104**x – 1.5	0.187**x – 68.9	83.1	11.4
RS20	0.534**x + 49.9		-	-	0.341**x + 24.4	0.532**x – 10.7	87.4	3.2
SC1	0.239**x + 8.4		-	3.5	0.234**x + 1.9		-	4.3
SC2	0.165**x + 2.1		-	7.6	0.205**x – 3.6		-	6.5
SC3	0.158**x – 9.9		-	11.5	0.153**x – 13.2		-	14.1
SC4	0.100**x + 4.8	0.129**x – 3.5	33.4	10.6	0.088**x + 2.0	0.141**x – 10.8	23.0	10.3
SC5	0.147**x + 25.7		-	8.7	0.122**x + 2.4	0.166**x – 19.1	62.9	9.3
SC6	0.132**x + 7.2		-	7.5	0.130**x 1 .2		-	8.9
SC7	0.182**x + 16.1		-	5.9	0.111**x + 1.9	0.194**x – 41.0	59.6	11.9
SC8	0.167**x + 3.2		-	6.9	0.156**x + 0.1	0.208**x – 30.9	93.0	8.8
SC9	0.191**x – 12.8		-	10.4	0.134**x – 0.7	0.201**x – 79.6	157.6	9.9
SC10	0.076**x + 9.7	0.279**x – 69.2	39.2	14.9	0.066**x + 1.8	0.281**x – 88.5	29.4	15.2
SC11	0.031**x – 0.3	0.047**x – 12.8	24.2	32.2	0.029**x – 0.3	0.066**x – 38.7	30.0	34.5
SC12	0.048**x + 1.0	0.104**x – 41.8	37.4	27.0	0.044**x – 0.4	0.094**x – 47.3	40.0	32.2
SC13	0.060**x + 2.3	0.173**x – 117.7	66.4	20.4	0.056**x – 0.2	0.163**x – 132.7	68.6	22.7
SC14	0.053**x + 1.0	0.166**x – 105.0	50.8	29.4	0.058**x – 1.0	0.169**x – 91.7	46.4	32.2
SC15	0.060**x + 5.6	0.154**x – 110.8	74.1	21.7	0.049**x + 2.4	0.152**x – 111.0	56.2	25.6
SC16	0.108**x + 26.2	0.187**x – 97.6	233.6	-	0.052**x + 2.1	0.164**x – 110.6	50.3	24.4
SC17	0.085**x – 1.0	0.205**x – 119.4	83.4	16.4	0.072**x – 1.2	0.207**x – 136.4	77.0	16.9
SC18	0.068**x + 2.9	0.226**x – 167.7	76.3	18.5	0.056**x + 0.2	0.204**x – 167.6	63.6	22.2
SC19	0.362**x – 4.1		-	5.0	0.148**x + 1.8	0.305**x – 67.4	67.0	6.7
SC20	0.066**x + 5.6	0.153**x – 58.9	54.4	16.7	0.060**x + 2.1	0.151**x – 78.5	54.8	20.0
SC21	0.128**x + 10.7	0.224**x – 93.0	148.7	9.4	0.157**x + 0.4	0.271**x – 109.7	153.0	9.1

Region 1 and Region 2 represent the linear regressions generated by the relationship between P rates and the content extracted by Mehlich-1 below and above the change point (Cp), respectively. “Cp” represent the change point, that is, P value extracted by Mehlich-1 in which there is an abrupt change in the relationship between the applied rates and the amounts of nutrient available in the soil. “tr_1P_M1” represents the amounts of P_2O_5 necessary to increase the available P by 1 mg dm^{-3} by Mehlich-1. * significant at 5 % error probability. ** significant at 1 % error probability. Note: the determination coefficient (R^2) was greater than 0.94 for all equations.

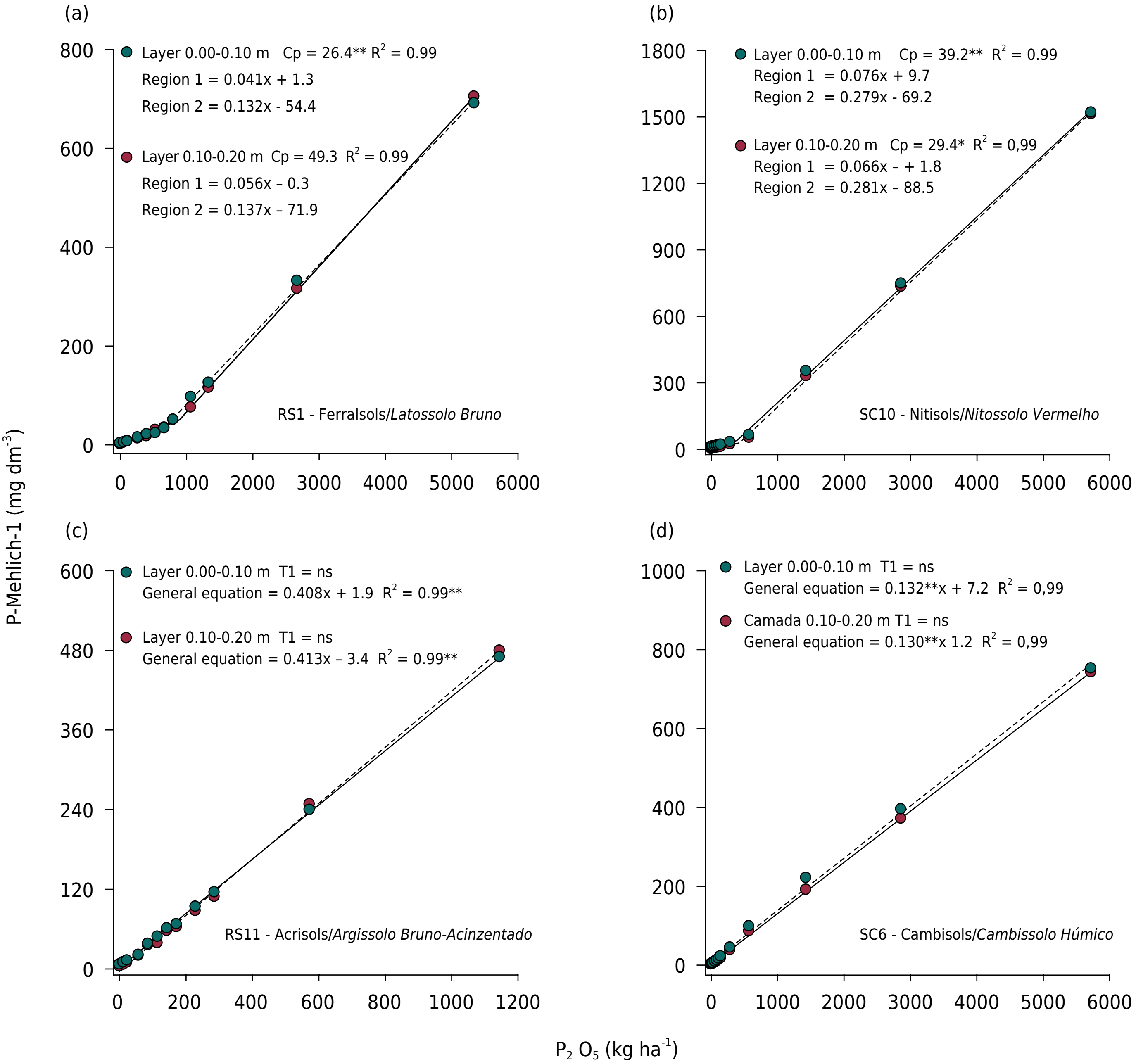

Figure 2. Phosphorus content by Mehlich-1, due to the addition of P rates for RS1 and SC10 and RS11 and SC6 soils, exemplifying soils with and without the significance of segmental equations. Cp: P Mehlich 1, in which the change point occurs between the segmented equations. **: significant at 1 % probability of error. *: significant at 5 % probability of error. NS: not significant. Note: scales are different among plots.

In all soils, the P values at which the change points occurred were observed under conditions of adequate P availability, that is, above the CL values. Based on this and considering that the objective of the present study was to evaluate soil buffering up to the range considered satisfactory to plants, values above the change point were disregarded.

Considering the wide variation in soils' change points, rates that resulting in P levels extracted 2-folds higher than the CL were considered for all soils, that is, maximum amplitude within the appropriate class (CQFS-RS/SC, 2016). The relationships between the selected P rates and P extracted by Mehlich-1 were significant ($p<0.05$). Based on the inverse of the angular coefficient from linear equations, the tr_1P_M1 of the soils was estimated (Table 2). The tr_1P_M1 values, regardless of the collection site, varied between 2.4 and 32.2 kg ha^{-1} of P_2O_5 in the 0.00-0.10 m layer and between 2.7 and 34.5 kg ha^{-1} of P_2O_5 in the 0.10-0.20 m layer.

The tr_1P_M1 values showed a significant correlation with some soil properties (Table 3). The correlations were positive for clay, P-max, CEC, pH(H_2O), TOC, and altitude, for 0.00-0.10 and 0.10-0.20 m layers. There was a negative correlation with the initial P extracted by Mehlich-1 and remaining P, for both layers. Considering this set of variables, it was possible to generate a multiple linear equation through the option “Backward stepwise regression”, aiming to estimate the tr_1P_M1 values, regardless of the soil layer. Only clay content, initial P, and P-max showed a significant adjustment ($p<0.01$). The defined equation was:

$$tr_1\text{P\_M1} = 0.323 + 0.235\mathit{clay} - 0.219\mathit{Pinitial} + 0.004\mathit{P\text{-}max} \qquad \text{Eq. 2}$$

$R^2 = 0.80$; $r = 0.89$; $p<0.001$

The study’s sequence is based on the relationship between the trP_M1 of the soils with the clay content and the initial extractable P levels. Methodologies usually consider these two variables for the phosphate fertilization recommendation in Brazil (Sousa and Lobato, 2002; CQFS-RS/SC, 2016). Since it is not an analysis performed in routine laboratories, P-max was disregarded, thus making its use difficult.

The *tr*P_M1 variations due to clay and initial P availability

The linear equations that gave rise to the tr_2P_M1 values were significant ($p<0.05$). Also, the grouping of tr_2P_M1 values within the clay classes and P availability classes recommended by CQFS-RS/SC (2016) was also significant (Figure 3). There were no differences between the sampled layers.

Regardless of the P availability class, the lowest tr_2P_M1 values were obtained in soil with <20 % of clay, in which was necessary 3.34 kg ha^{-1} of P_2O_5 to increase one unit of P extracted by Mehlich-1. While soils with a range of 21 to 40, 41 to 60, and >60 % of clay, the tr_2P_M1 was 3, 6, and 7 times higher, respectively (Figure 3a). Based on the three P availability classes described in CQFS-RS/SC (2016), regardless of the clay class,

Table 3. Pearson correlation between the variables analyzed (n = 41), for the layers of 0.00-0.10 and 0.10-0.20 m, considering the set of soils collected in the states of RS and SC

Variable	tr_1P_M1	Clay	P M-1	P-rem	P-max	TOC	CEC	Altitude
tr_1P_M1	-	***	**	***	***	**	***	***
Clay	0.86	-	ns	***	***	*	***	***
P M-1	-0.49	-0.14	-	*	*	ns	*	*
P-rem	-0.73	-0.74	0.35	-	***	***	***	***
P-max	0.82	0.76	-0.38	-0.88	-	***	***	***
TOC	0.48	0.37	-0.29	-0.69	0.62	-	***	***
CEC	0.69	0.69	-0.36	-0.85	0.83	0.69	-	***
Altitude	0.62	0.59	-0.39	-0.75	0.79	0.64	0.69	-
tr_1P_M1	-	***	**	***	***	**	***	
Clay	0.84	-	ns	***	***	**	***	***
P-M1	-0.44	-0.25	-	**	**	**	ns	**
P-rem	-0.74	-0.77	0.42	-	***	***	***	***
P-max	0.82	0.76	-0.42	-0.88	-	***	***	***
TOC	0.42	0.40	-0.41	-0.68	0.65	-	***	***
CEC	0.65	0.59	-0.23	-0.82	0.75	0.68	-	***
Altitude	0.64	0.59	-0.45	-0.72	0.79	0.69	0.59	-

tr_1P_M1 represents the amounts of P_2O_5 necessary to increase the available P by 1 mg dm^{-3} by Mehlich-1. *: significant at 5 % error probability. **: significant at 1 % error probability. ***: significant at 0.1 % error probability.

the values obtained in the “very low” and “low” ranges were equivalent, with an average of 14.6 kg ha^{-1} of P_2O_5, 18.1 % higher than observed for the “medium” class (Figure 3b).

Adjustments in corrective phosphate fertilizer rates for soils in RS and SC

Table 4 presents the association of tr_2P_M1 values in the function of the different classes of clay and P availability classes. It is important to highlight that, although there is no statistical interaction between the factors “classes of clay” and “ranges of P availability”, your consideration may represent a more reliable fertilization recommendation. As no significant differences were depending on the sampled layer, the results show the average values between the 0.00-0.10 and 0.10-0.20 m layers, multiplied by two, since the total correction fertilization is carried out in the 0.00-0.20 m layer.

Based on table 4, the initial P values in the soil and the CL values, it is possible to recommend correction fertilization (CF), according to equation 1 [*CF, in kg ha^{-1} of P_2O_5* = (*P final* - *P initial*) x *tr*P_M1]. A simulation of the use of this equation, based on the tr_2P_M1 values, compared to the current recommendation (CQFS-RS/SC, 2016), is shown in figure 4.

Considering the 270 pre-selected soil samples, there are significant differences in the amounts of P recommended by CQFS-RS/SC (2016) and the results of the present study. There is an underestimation of the rates calculated by the CQFS-RS/SC (2016), mainly for soils with higher clay content. Considering the availability P classes, the two recommendations are similar for the “medium” range for soils with 20 to 40, and <20 %

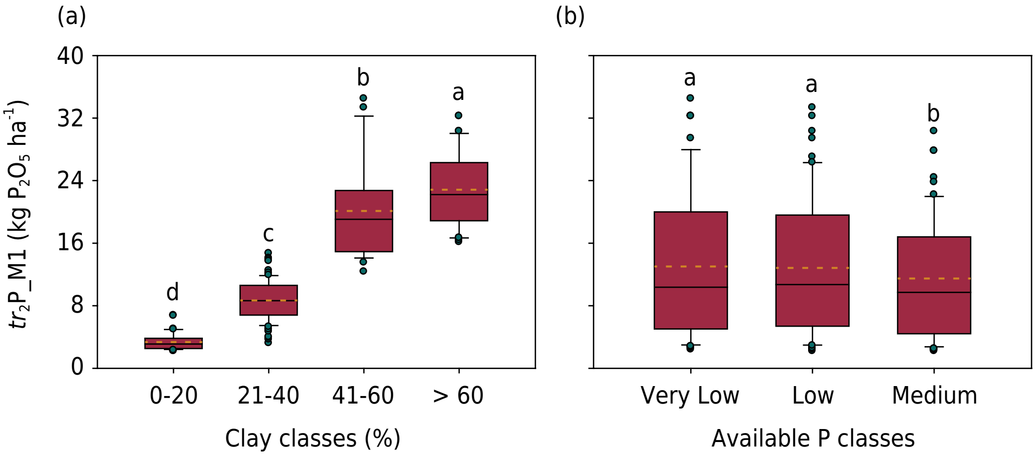

Figure 3. Grouping of phosphorus buffer capacity values (tr_2P_M1) according to clay classes (a) and phosphorus availability classes (b). In both figures, different letters indicate significant statistical differences by the Tukey test ($p<0.05$). Orange dotted lines represent the averages. Green dots represent outliers.

Table 4. The tr_2P_M1 values, according to clay classes and phosphorus availability ranges, for the recommendation of correction phosphate fertilization in the soils of Rio Grande do Sul and Santa Catarina

Clay classes	Phosphorus availability ranges	
	Very Low and Low	Medium
%	kg ha^{-1}	
	tr_2P_M1$^{(1)}$ – 0.00-0.20 m layer	
<20	7.8	6.2
21-40	18.0	16.0
41-60	42.6	31.8
>60	48.4	42.6

(1) tr_2P_M1 represents the amounts of P_2O_5 necessary to increase the available P by 1 mg dm^{-3} by Mehlich-1.

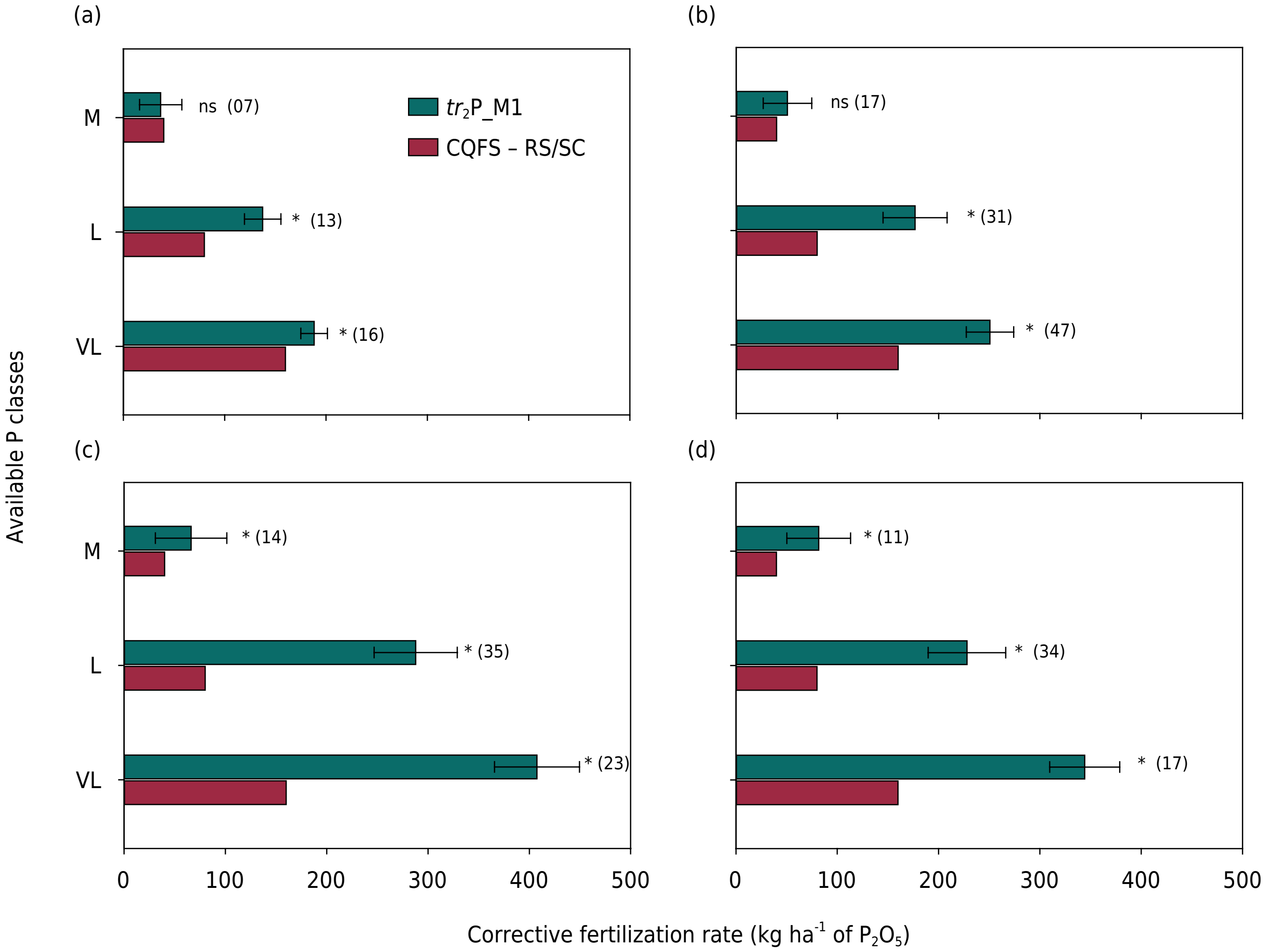

Figure 4. Comparison between corrective fertilization adopted by CQFS-RS/SC (2016) and the recommended by tr_2P_M1 calculation, considering soils with <20 (a), 21 to 40 (b), 41 to 60 (c), and >60 % (d) of clay content, for phosphorus availability class of very low (VL), low (L), and medium (M) to 270 soil samples from Santa Catarina. Horizontal error bars at the top of the bars represent the standard deviation of the mean; ns: not significant; * statistically significant by student t-test ($p<0.05$); The numbers within bracket represent the number of observations for each class

of clay, but in all the other conditions, the values recommended by the CQFS-RS/SC (2016) are lower than those determined based on tr_2P_M1.

In general, regardless of the P availability class, the average correction recommendations considering the results of the present study are 1.3, 1.7, 2.6, and 2.3 times higher than those recommended by CQFS-RS/SC (2016), considering clay content between <20, 21-40, 41-60, and >60 %, respectively. In the same sense, but considering the variations between the classes of P availability, regardless of the clay classes, the average recommendations for correction based on the results of the present study are 1.9, 2.6, and 1.3 times higher than that recommended by CQFS-RS/SC (2016), in the classes as “very low”, “low”, and “medium”, respectively.

DISCUSSION

Phosphorus buffer capacity and related parameters

The differences between the two-line segments generated for the evaluated soils (Table 2) indicate a change in the P buffering capacity with high rates of the nutrient. The reduction in the P needs in soils of greater fertility results from the neutralization of part of the adsorption sites (Oliveira et al., 2014; Barrow and Debnath, 2018) and an increase in the number of negative charges (Barrow, 2015), representing an important change in the dynamics and efficiency of fertilizer P (Rubio et al., 2008; Zhang et al., 2018; Mumbach et al., 2020). In successive fertilization, the P adsorption sites saturation is accompanied by an increase in the participation of more labile P fractions concerning the total accumulated in the soil (Boitt et al., 2018). In clayey soils with reduced P availability, the presence of oxidic minerals, especially those less crystallized (Bortoluzzi et al., 2015), can adsorb P under high binding energy, preventing its desorption. The saturation of these most avid sites can significantly change the buffering capacity, indicated by the second linear segment.

In soil with about 26 % of clay, which received different fertilization systems for 18 years, Zhang et al. (2018) observed abrupt changes in the labile P from an area with a history of phosphate fertilization and cultivated with wheat and corn each year. This change occurred under P surplus above 662 kg ha^{-1} (P added – P exported by plants), with an extractable P of 27 mg kg^{-1}, slightly higher than that considered suitable to produce wheat and corn on the spot. The angular coefficients obtained in Zhang et al. (2018) study, for the relation between P surplus and labile P in soil were 0.04 and 0.29 for condition below and above the change point, respectively, indicating an expressive change in the soil buffering. The reasons for this change cited by those authors were the partial saturation of the main components related to adsorption, such as Ca, Fe, and Al oxides and organic matter. In the same sense, Cubilla et al. (2007), considering soils from Paraguay with great textural contrast and fertilization history, observed that the application of 100 kg ha^{-1} of P_2O_5 represents increases of 5.5 and 3.0 mg dm^{-3} in the extractable P content in soils with a high and low history of phosphate fertilization, respectively.

In our study, the change points occurred above the CL. Despite not having an agronomic reality, the second linear segment can be considered in environmental pollution studies since the loss of P affinity to soil particles increases the risk of losses and environmental contamination. Gatiboni et al. (2008) highlighted high levels of P in the soil, already from the “very high” range, even if not saturating all the adsorption sites, can trigger the transfer of the nutrient to the environment.

The *tr*P_M1 is an indicator of the P adsorption capacity. Its increase due to the higher clay content was expected and is supported in the literature (Rogeri et al., 2016; Reis et al., 2020). Clayey soils tend to have higher Fe and Al contents, elements directly linked to the P adsorption (Bortoluzzi et al., 2015). Thus, clayey soils have a higher P adsorption capacity (Rheinheimer et al., 2003; Oliveira et al., 2014), with both variables being strongly correlated (data not shown). In the same sense, P-rem is an indicative of the soil’s adsorption capacity, in which lower values represent a greater soil sorption potential (Rogeri et al., 2016; Reis et al., 2020). The positive correlation of tr_1P_M1 with potential CEC and TOC can be indirect (Eberhardt et al., 2008). The increase in both has a positive relationship with the clay content (Table 3). It is important to highlight that the organic matter in the soil may have an ambiguous role in the P adsorption capacity of P, that is, increasing the adsorption due to hindrance of oxides crystallization (Abdala et al., 2020) or decreasing due to competition of organic acids and phosphate anion by adsorption sites (Almeida et al., 2003).

The negative correlation of the tr_1P_M1 values with the initial P extractable reiterates the gradual loss of P retention capacity by the soils (Rubio et al., 2008). Schlindwein et al. (2013) observed a small decrease in RS soils buffer capacity with an increase in initial P extractable, assigning this to the partial saturation of adsorption sites. In the study of Cubilla et al. (2007), the need for phosphate fertilizer to increase 1 mg dm^{-3} of P extractable by Mehlich-1 was almost twice as small in the soil with historical fertilization compared to the absence of previous fertilization.

The *tr*P_M1 increase as a function of altitude is due to an increase in adsorption capacity in this condition. There is higher organic matter content and predominance of minerals with low crystallinity under higher altitude (Bortoluzzi et al., 2015). The influence of soil mineralogy on P dynamics is remarkable (Eberhardt et al., 2008; Abdala et al., 2020). Soils with a predominance of oxides have a high P adsorption capacity due to the high points of zero charge (Goldberg et al., 1996). In the South of Brazil predominate iron oxides, like hematite and goethite. Goethite occurs in higher topographies with a higher organic matter content and has a large specific surface area and, consequently, a high capacity to adsorb P (Bortoluzzi et al., 2015; Fink et al., 2016).

Adjustments in the recommendation of total correction fertilization

The increase in soil buffering with the increase in clay content is implicit in the current recommendation for the states of RS and SC (CQFS-RS/SC, 2016), through the recommendation of the same P dosages for values other than CL. However, these *tr*P_M1 values implicit in the recommendation are much lower than those observed in the present study. The CL of P for grain crops, according to CQFS-RS/SC (2016), are 30.0, 18.0, 12.0, and 9.0 mg dm^{-3} for soils with <20, 21-40, 41-60, and >60 % of clay, respectively. Based on these CL and the intermediate of the three availability ranges proposed by CQFS-RS/SC (2016), the *tr*P_M1 values for soils classified according to the P availability in "very low", "low", and "medium" would be 7.2, 5.3, and 8.0 kg ha^{-1} of P_2O_5 for soils with <20 % clay, 12.0, 8.9, and 13.3 kg ha^{-1} of P_2O_5 for soils with 21-40 % clay, 18.0, 13.3, and 20.0 kg ha^{-1} of P_2O_5 for soils with 41-60 % clay and 21.3, 17.8, and 26.7 kg ha^{-1} of P_2O_5 for soils with >60 % clay content, respectively.

The buffering behavior depending on the P availability ranges, also varies. The CQFS-RS/SC (2016) considered that there are only variations in the P buffering when the P availability goes from "very low" to "low", with a reduction of 33 %, without any change between the classes "low" and "medium". The data from the present study, as already presented, indicate similar buffering between the "very low" and "low" ranges, with a reduction of 18 % when the "medium" range is considered.

Consequently, the correction fertilization recommendation to the 270 soils showed discrepancies in the values based on the present study and those indicated by the CQFS-RS/SC (2016). The differences are greater with the increase in clay content, as also observed by other studies in the region. Rogeri et al. (2016), considering soils from RS, observed quantities of 65 kg ha^{-1} of P_2O_5 to increase the P Mehlich-1 in 1 mg dm^{-3}, on soils with more than 60 % clay. On the other hand, Schlindwein and Gianello (2008), considering experiments conducted under the no-tillage system (NT) in RS, observed buffering closer to those considered by CQFS-RS/SC (2016): for the 0.00-0.20 m layer, the P_2O_5 amount necessary to increase Mehlich-1 in 1 mg dm^{-3} were 7.5, 10.0, 15.0, 20.0, and 30.0 kg ha^{-1} in soils with <10, 10-25, 26-40, 41-55, and >55 % of clay, respectively.

An important point to be considered, justifying the high values obtained in the present study, is soil aggregation level. The greater P needs due to the intense mobilization of the soil results from the contact of the fertilizer with a larger volume of soil and also from the breakdown of soil aggregates and, consequently, exposure of previously protected P adsorption sites, increasing the soil's buffer capacity, compared to the same soil, but under NT (Wang et al., 2001; Gatiboni et al., 2019). In a soil cultivated under NT, for example, soil aggregation reduces the number of binding sites exposed, reducing the "active" buffering of the soil. Wang et al. (2000) studied a group of 10 soils from Hawaii. They highlighted that parameters such as aggregates size, especially for soils with high clay content and heterogeneous mineralogical constitution, can improve the buffer power estimate.

The use of tabulated and separated values according to classes, despite representing an advance compared to single dosages, can still present deviations. In this way, some questions are raised, such as i) the real corrective phosphate dosage for soil with 22 %

clay and another with 35 % clay, both in the same class, will it be the same? ii) and if this 35 % soil were collected in two different plots, both in the "very low" availability range, but one with a value of 1 mg dm^{-3} and the other with a value of 5 mg dm^{-3}, the recommendation would be the same? Both conditions must present deviations, especially in the function of the clay classes.

An alternative to correct the potential errors cited above would be the consideration of variations in clay content and initial P regardless of classes. Based on this, considering the tr_2P_M1 values obtained through the incubation of each soil and its interaction with the clay content and the initial P values, obtained for each relationship "P rates x P extracted by Mehlich-1", the multiple linear equation was generated: "[tr_2P_M1, *kg* ha^{-1} *of* P_2O_5 = 0.44 + (0.80 x clay) - (0.02 x clay x P initial)], (R^2 = 0.78** and r = 0.88**)", were "tr_2P_M1" is the P_2O_5 ha^{-1} amount to increase on 1 mg dm^{-3} the P in the layer of 0.00-0.10 m; "clay" represents the clay content determined by the pipette method, in percentage; "P initial" represent the natural P extracted by Mehlich-1. The generation of *tr*P_M1 values based on this equation and the subsequent recommendation for correction fertilization resulted in values highly correlated to those obtained based on table 4 (r = 0.87 = $p<0.01$). Based on this, the adoption of tabulated values may still be a better alternative for making use easier.

It is worth mentioning that all adjustments to the *tr*P_M1 values were based on CL for grain crops. However, other three culture groups are indicated in the liming and fertilization manual for the RS and SC states (CQFS-RS/SC, 2016). While a single CL is considered to irrigated rice, for high and low demand cultures, the CL values are 1.5 and 0.7 times those recommended for grain crops, respectively. Thereby, the correction fertilization needs also to consider these variations, according to the plant species of interest.

In general, the results presented in this study alert to the possibility of inconsistency in the P recommended for corrective fertilization, especially on more buffered soils. However, the use of the values presented here and the decision-making for corrective fertilization, should consider a more global assessment. For example, in soils with insufficient P associated with other restrictions, as a frequent occurrence of drought periods, acidity and/or compaction, investment in a good soil profile correction can bring benefits in the short and long term. However, in soils with consolidated NT, getting high yields and without physical and chemical soil restriction, corrective fertilization may not be a viable practice. In this condition, the gradual correction at sowing in banding application may represent a more advantageous practice.

There is a need for adjustments in the dosages used for correction fertilization under field conditions. These studies should consider soils with contrasting characteristics, as well as the plant species of interest since nutritional demands vary. In the same sense, seeking to define the correct fertilization rates for both the procedure that involves incorporating the arable layer and the one carried out on banding, concomitantly with sowing, is imperative.

CONCLUSIONS

The dosage of phosphorus corrective fertilization currently recommended in the Rio Grande do Sul and Santa Catarina states is insufficient to reach critical levels, mainly in soils with high clay content.

Clay content and initial P avaliability should be considered for a better estimative of total correction fertilization. Based on the classes already used by "Comissão de Química e Fertilidade do Solo dos Estados do Rio Grande do Sul e Santa Catarina", the P buffering of the soils must be separated into the four clay classes (until 20, between 21-40, between 41-60, and greater than 60 %) and into the P availability classes “very low and low” and “medium”.

The degree of soil mobilization/grinding can directly influence the buffering values. In this sense, to recommend the same correction fertilization rates in soils with different soil management systems can result in large deviations.

AUTHOR CONTRIBUTIONS

Conceptualization: Luciano Colpo Gatiboni (lead) and Gilmar Luiz Mumbach (supporting).

Methodology: Gilmar Luiz Mumbach (equal) and Luciano Colpo Gatiboni (equal).

Formal analysis: Gilmar Luiz Mumbach (lead), Abelino Anacleto de Souza Junior (supporting), Daniel João Dall’Orsoletta (supporting), and Luciano Colpo Gatiboni (supporting).

Investigation: Gilmar Luiz Mumbach (lead) and Abelino Anacleto de Souza Junior (supporting).

Resources: Luciano Colpo Gatiboni (lead) and Gilmar Luiz Mumbach (supporting).

Data curation: Gilmar Luiz Mumbach (lead), Abelino Anacleto de Souza Junior (supporting), Daniel João Dall’Orsoletta (supporting), and Luciano Colpo Gatiboni (supporting).

Writing – original draft: Gilmar Luiz Mumbach (lead), Abelino Anacleto de Souza Junior (supporting), Daniel Alexandre Iochims (supporting), Daniel João Dall’Orsoletta (supporting), Djalma Eugenio Schmitt (supporting), Douglas Luiz Grando (supporting), Fernando Marcos Brignoli (supporting), and Luciano Colpo Gatiboni (supporting).

Writing – review and editing: Gilmar Luiz Mumbach (lead), Abelino Anacleto de Souza Junior (supporting), Daniel Alexandre Iochims (supporting), Daniel João Dall’Orsoletta (supporting), Djalma Eugenio Schmitt (supporting), Douglas Luiz Grando (supporting), Fernando Marcos Brignoli (supporting), and Luciano Colpo Gatiboni (supporting).

Visualization: Gilmar Luiz Mumbach (lead).

Project administration: Luciano Colpo Gatiboni (lead), Daniel João Dall’Orsoletta (supporting), and Gilmar Luiz Mumbach (supporting).

Funding acquisition: Luciano Colpo Gatiboni (lead).

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