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Phosphorus buffer capacity of soils with medium clay and high organic matter content

Douglas Luiz Grando[(1)*], Marcos de Lima Rodrigues[(1)], Cauan Guerra Martins[(1)], Lucas Peranzoni Deponti[(1)], Djalma Eugenio Schmitt[(2)], Gilmar Luiz Mumbach[(3)], Adriele Tassinari[(1)], Jean Michel Moura-Bueno[(1)], Ana Luiza Lima Marques[(1)] and Gustavo Brunetto[(1)]

[(1)] Universidade Federal de Santa Maria, Departamento de Solos, Programa de Pós-Graduação em Ciência do Solo, Santa Maria, Rio Grande do Sul, Brasil.
[(2)] Universidade Federal de Santa Catarina, Departamento de Agricultura, Biodiversidade e Floresta, Curitibanos, Santa Catarina, Brasil.
[(3)] Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina, Epagri, Escritório Municipal de Maracajá, Santa Catarina, Brasil.

*** Corresponding author:**
E-mail: douglas.agn@hotmail.com

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ABSTRACT: Determining soil phosphorus (P) buffer capacity (PBC) is crucial for establishing optimal P fertilizer rates in corrective fertilization practices. However, in subtropical regions, changes in soil chemical and physical properties, such as soil organic matter (SOM) accumulation and texture modifications, can significantly impact PBC values, altering soil adsorption capacity. Consequently, P rates recommended by generalized guidelines for soil correction in these regions may be insufficient to achieve the critical P level in the soil. This study aimed to define PBC, develop an equation for PBC estimation, and establish P rates for corrective fertilization in soils with high SOM and medium clay content under subtropical climate conditions in Brazil compared with CQFS-RS/SC (2016) recommendation. The study used 29 soils collected from the Serra Gaúcha region, Rio Grande do Sul state, Brazil. Soil samples were collected from native forest areas in the 0.00-0.20 m layer. After drying and sieving, the samples were subjected to incubation with phosphate rates for 30 days. Ten treatments, ranging from 0 to 300 % of the recommended P_2O_5 rate to increase P levels to high sufficiency levels were applied, with three replicates. After the incubation period, Mehlich-1 P (P_M1) levels were determined. The mean PBC value was 26.3 kg ha^{-1} P_2O_5, representing the rate required to increase P_M1 levels by 1.0 mg dm^{-3} in the soil. Terrain altitude was negatively correlated with PBC, while P_M1 showed a positive correlation with SOM content. An equation for estimating PBC was proposed [PBC (kg ha^{-1} P_2O_5) = 49.75 - 0.063A + 0.692Clay - 1.869P_M1]. The current corrective fertilization recommendations for the southern region of Brazil underestimate the P_2O_5 rates for very low and low classes in Serra Gaúcha soils by an average of 1.5 times. Therefore, we recommend adjusting phosphate fertilizer rates, monitoring soil P content, and maintaining SOM levels.

Keywords: correction fertilizer, phosphorus availability, phosphate rates, soil organic carbon, subtropical climate.

INTRODUCTION

Soils in tropical and subtropical regions naturally have low phosphorus (P) availability due to their high adsorption capacity to the functional groups of reactive particles, such as 2:1 and 1:1 clay minerals and iron (Fe), aluminum (Al), and manganese (Mn) oxides (Oliveira et al., 2020; Saentho et al., 2022). Different minerals provide distinct soil adsorption properties, affecting P adsorption energy (Li et al., 2021) and plant availability (Brignoli et al., 2024). Consequently, the natural amounts of available P present in soils do not meet the demand of cultivated species, justifying the P supply via fertilization practices (Ciotta et al., 2021). The soil P content is related to plant total and marketable yield being used to decide on the best fertilization management (Hahn et al., 2024a).

In corrective fertilization, phosphate fertilizers are applied to raise available P levels to the hypothetical critical level (CL) (Ulrich, 1952; Lima Neto et al., 2024). Above this value (optimum P content), the probability of increased yield or improved fruit quality variables is low or nil. Thus, corrective fertilization management is an agricultural practice that aims to maintain the soil nutrient content in the “high” interpretation class (CQFS-RS/SC, 2016; Hahn et al., 2024b), in which the available portions of nutrients in the soil tend to supply more than the plant demand, considering nutrient losses, for example, by erosion (Ferreira et al., 2018).

In most cases, the P rates applied in corrective fertilization in tropical and subtropical soils do not always raise P levels to the CL (Mumbach et al., 2021). This occurs because soils may have large differences in clay, organic matter (SOM), and mineralogy contents, which are the variables that determine the maximum P adsorption capacity (Rogeri et al., 2016). Thus, often, generalized recommendations, which encompass a great variability of soils, may present low efficiency in the assertiveness of phosphate fertilizer rates in corrective fertilization, justifying the estimation of CL and recommendation of phosphate fertilization specific to more homogeneous soil groups (Stefanello et al., 2023).

Phosphorus rates to reach the CL can be obtained by estimating the P buffer capacity (PBC) in soils that must be dried, prepared, and subjected to incubations with different P contents (Reis et al., 2020; Mumbach et al., 2021). With this, it is possible to estimate the most appropriate P rates to be applied in corrective fertilizations. This allows the rationalization of fertilizer use, avoids excess P, and, consequently, the potential for transfer of its forms to surface water (Schmitt et al., 2013a; Gatiboni et al., 2020a; Grando et al., 2021).

In subtropical regions of Brazil, such as the Serra Gaúcha in Rio Grande do Sul (RS), soils generally have medium texture (15 to 35 % clay) and medium (2.6 to 5.0 %) or high (>5.0 %) SOM contents, in addition to iron oxide contents between 5 and 15 % (Flores et al., 2012). This gives these soils physical and especially chemical properties that, together with the particular climatic conditions of this region, differentiate them from other regions of RS and even from other southern Brazil states. Serra Gaúcha is an important fruit-growing region in Brazil, renowned for its production of grapes, peaches, plums, apples, persimmons, and kiwis (Seapdr, 2023). The region’s climatic conditions have a great impact on the growth, productivity, and nutritional status of fruit trees (Andrade et al., 2023; Hahn et al., 2023), which, with the region’s relief, contribute to the variability in soil types (Sarmento et al., 2008; Flores et al., 2012). In addition, currently, the need and rates of nutrients for the region are established based on generalized recommendations proposed by the Commission Chemistry and Soil Fertility for the States of Rio Grande do Sul and Santa Catarina (CQFS-RS/SC, 2016), representing an average of scenarios (soil types, climate, etc.).

In light of the above, it is believed that the currently recommended P rates (generalized recommendation) for soil correction in the region of interest may not be sufficient to reach the CL. Therefore, this study aimed to define PBC, an equation to estimate PBC and the P rates (regional recommendation) to be applied in corrective fertilization of soils in the Serra Gaúcha region (RS) comparing with CQFS-RS/SC (2016) recommendation.

MATERIALS AND METHODS

Soil sampling

Soils were collected in six municipalities in the Serra Gaúcha region of Rio Grande do Sul state, southern Brazil (Figure 1). Soil sampling was carried out in the 0.00-0.20 m layer, in 29 native forest areas, without human intervention or history of agricultural cultivation. Soil samples were air-dried, ground, and sieved through a 2 mm mesh and stored for analysis. The region where the soil samples were collected has rocks of acidic (Rhyodacite and Rhyolite) and basic (Basalt) origin, which are the parent materials, respectively, of Cambissolos and Neossolos (Sarmento et al., 2012; Santos et al., 2018), which correspond to Inceptisols and Entisols (Soil Survey Staff, 2014), being the principal soil classes observed in this region.

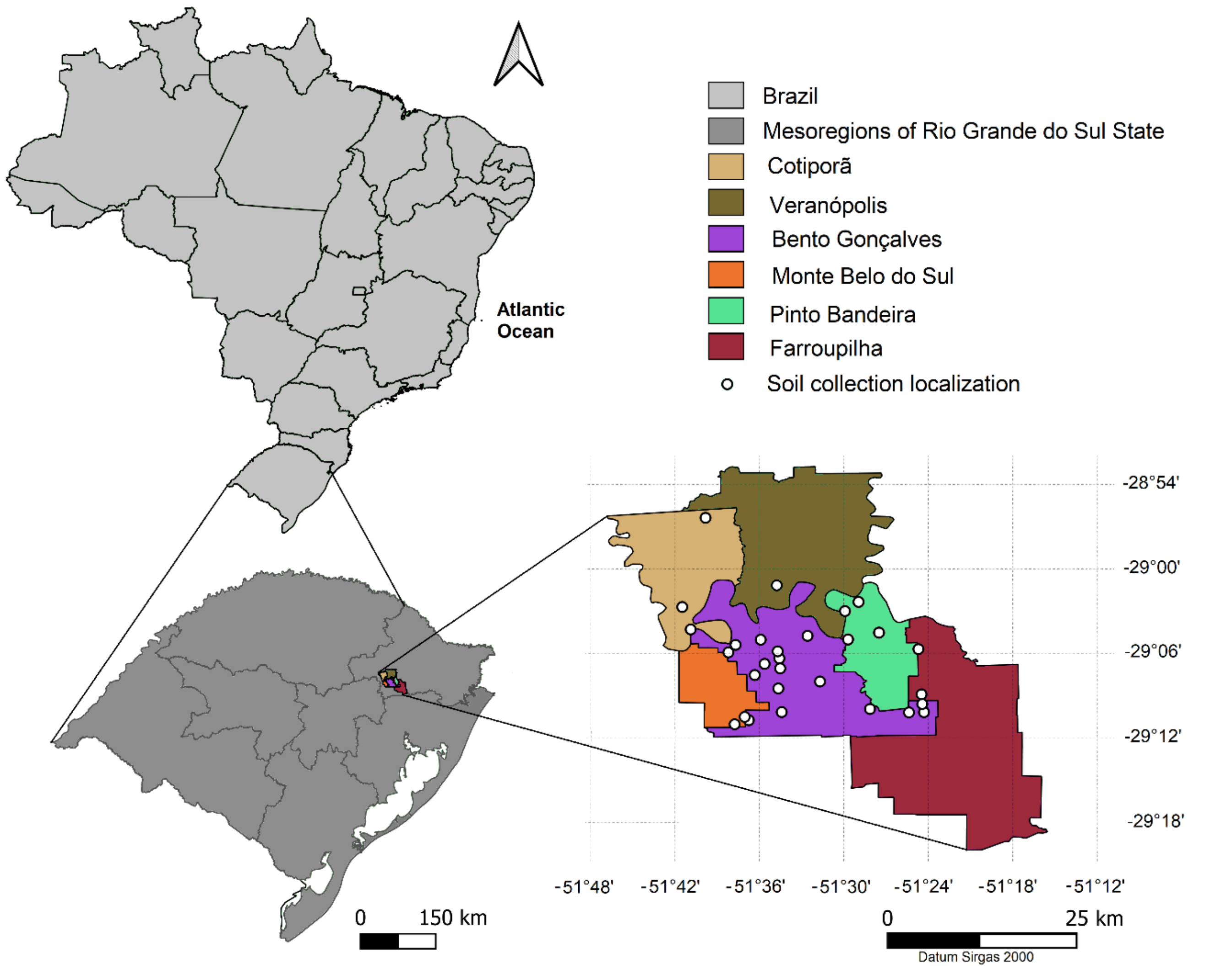

Figure 1. Spatial distribution of the 29 soil collection points in the Serra Gaúcha region, in the Rio Grande do Sul State, Southern Brazil.

Soil chemical and physical analyses

Chemical and physical properties of the soil samples are presented in tables 1 and S1. Clay content was determined by pipette method (Teixeira et al., 2017) after oxidizing the organic matter with hydrogen peroxide (H_2O_2). The pH(H_2O) was determined by the ratio of soil to solution (1:1). The pH-TSM was determined according to the method proposed by Toledo et al. (2012). Available P and K were extracted using the Mehlich-1 solution (0.0125 mol L^{-1} H_2SO_4 and 0.050 mol L^{-1} HCl). The P in the extract was determined by the method described by Murphy and Riley (1962), using a molecular absorption spectrophotometer at 882 nm (UV-Vis V-5000, Metash). Potassium in the extract was determined by flame spectrophotometry (DM-62, Digimed). Total organic carbon (TOC) content was determined by dry combustion method (Yeomans and Bremner, 1988). For that, soil samples were ground in a continuous rolling mill and analyzed in an elemental analyzer (Flash EA1112, Thermo Electron Corporation). Percentage of soil organic matter (SOM) was determined by multiplying the TOC value by 1.724. Exchangeable Ca, Mg, and Al were extracted with KCl 1.0 mol L^{-1}. The $CEC_{pH7.0}$ was obtained by summing the exchangeable elements Ca, Mg, K, and potential acidity (H+Al) (Table S1). Chemical analyses were based on the methodology proposed by Tedesco et al. (1995). Iron content of poorly crystalline oxides ($Fe_{oxalate}$) was extracted with 0.2 mol L^{-1} ammonium oxalate at pH 3.0 in the dark (Schwertmann, 1964). Calcium, Mg, and Fe contents were determined by atomic absorption spectrophotometry (AAnalyst 200, PerkinElmer).

Phosphorus buffer capacity (PBC)

Soils were incubated with $CaCO_3$ when necessary to raise the pH to 6.0, remaining for 30 days at 70 % of field capacity moisture. For that, the previous liming requirement was determined to achieve a soil pH(H_2O) value of 6.0, through the relationship between rates of lime and pH(H_2O) values using the current liming recommendations (CQFS-RS/SC, 2016). To enhance the lime reaction, $CaCO_3$ reagent (99 % purity) was applied, and the soil was mixed twice weekly with distilled water until the estimated weight to maintain a consistent moisture level. After that, plastic bags containing 50 g of soil were incubated with P rates to obtain the P buffer capacity (PBC), in a completely randomized design, with three replications. The applied rates included 0, 25, 50, 75, 100, 125, 150, 200, 250, and 300 % of the rate required to reach the “high” P availability class (CQFS-RS/SC, 2016), following the recommendation proposed by Mumbach et al. (2021), for the 0.00-0.20 m layer (Table S2). The P rates were prepared using the chemical reagent ammonium phosphate ($NH_4H_2PO_4$) dissolved in deionized water. Subsequently, the soil moisture was standardized to a condition close to 70 % of field capacity, and the soil samples were incubated for another 30 days. The plastic bags were kept under a bench with an average temperature of 22 °C, remaining partially open, allowing gas exchange with the moisture weekly corrected.

After the end of incubation, the samples were dried in an oven at 45 °C and again ground and passed through a 2 mm mesh. The P values considered “available” (P_M1) were extracted using the Mehlich-1 solution (0.0125 mol L^{-1} H_2SO_4 and 0.050 mol L^{-1} HCl).

Calculations and statistical analyses

Through graphs containing the P_2O_5 rates (all 10 treatments) and the P_M1 values, linear or two-segment linear regressions were generated. From the inverse of the angular coefficient of each linear regression, the PBC value was obtained [PBC (kg ha^{-1} P_2O_5) = 1/angular coefficient]. The PBC values were subjected to normality analysis, using the Shapiro-Wilk test and, when necessary, were transformed by Box-Cox (Box and Cox, 1964) to meet the normality assumptions. Subsequently, the values were subjected to analysis of variance (ANOVA). The PBC values were compared using the Tukey test ($p<0.05$), within the clay classes (<20 %, 21-40 %, and 41-60 % of clay) and P availability classes (very low, low, and medium) established by CQFS-RS/SC (2016).

Table 1. Soil characterization in the Serra Gaúcha region, Southern Brazil

Soil	Latitude	Longitude	Altitude	Sand	Silt	Clay	SOM	$CEC_{pH7.0}$	$Fe_{oxalate}$
	S	W	m	g kg^{-1}				cmol$_c$ dm^{-3}	g kg^{-1}
1	29° 08’ 30.4”	51° 34’ 39.2”	666	261	447	292	64.6	12.3	3.51
2	29° 07’ 30.0”	51° 36’ 20.0”	174	299	470	230	105.4	40.6	6.16
3	29° 07’ 04.7”	51° 34’ 31.3”	555	429	289	282	65.4	20.0	3.56
4	29° 06’ 22.0”	51° 34’ 35.0”	450	281	391	327	110.2	34.2	3.73
5	29° 05’ 52.0”	51° 34’ 42.0”	212	193	560	247	101.4	33.6	5.80
6	29° 10’ 11.1”	51° 34’ 24.9”	428	299	428	273	45.3	18.2	3.89
7	29° 10’ 45.9”	51° 36’ 45.4”	575	82	575	343	71.6	40.9	4.10
8	29° 11’ 03.1”	51° 37’ 45.8”	550	220	555	225	59.2	18.0	6.86
9	29° 10’ 31.7”	51° 37’ 03.0”	496	314	396	289	40.3	19.0	4.06
10	29° 05’ 56.3”	51° 38’ 12.7”	385	283	415	302	107.9	36.5	4.75
11	29° 05’ 24.4”	51° 37’ 41.7”	113	224	523	253	60.5	33.1	6.63
12	29° 04’ 45.8”	51° 32’ 34.6”	557	180	538	282	84.9	14.7	4.55
13	29° 05’ 02.3”	51° 35’ 54.4”	400	178	514	308	66.3	28.8	4.81
14	29° 08’ 00.7”	51° 31’ 41.5”	619	282	439	279	69.4	16.8	3.65
15	29° 09’ 58.0”	51° 28’ 08.1”	449	236	463	302	99.5	26.0	4.78
16	29° 10’ 12.6”	51° 25’ 21.8”	583	324	424	252	49.6	21.9	4.25
17	29° 10’ 11.6”	51° 24’ 17.8”	578	404	406	190	52.7	15.2	2.30
18	29° 09’ 36.5”	51° 24’ 25.4”	716	199	525	276	47.4	20.8	4.10
19	29° 08’ 55.3”	51° 24’ 28.3”	759	154	426	420	67.4	36.9	3.22
20	29° 05’ 42.5”	51° 24’ 41.4”	495	197	495	308	81.2	23.0	4.25
21	29° 04’ 32.3”	51° 27’ 29.7”	661	241	424	336	71.6	18.1	3.80
22	29° 02’ 21.2”	51° 28’ 57.1”	480	311	410	279	107.8	29.1	1.52
23	29° 03’ 00.4”	51° 29’ 55.2”	254	173	530	297	52.9	15.7	4.37
24	29° 05’ 01.4”	51° 29’ 41.9”	180	200	591	209	62.6	20.3	5.01
25	29° 01’ 10.5”	51° 34’ 46.0”	612	361	356	284	57.5	20.1	3.08
26	29° 56’ 22.7”	51° 39’ 50.0”	639	104	452	444	85.6	33.0	4.02
27	29° 02’ 42.7”	51° 41’ 29.4”	537	327	350	323	82.4	25.4	2.23
28	29° 04’ 18.5”	51° 40’ 53.4”	172	167	574	258	44.2	19.0	4.93
29	29° 06’ 45.5”	51° 35’ 38.0”	505	291	425	284	82.3	24.4	3.54

SOM: Soil organic matter; $CEC_{pH7.0}$: Cation exchange capacity at pH 7.0; $Fe_{oxalate}$: iron oxide content obtained by ammonium oxalate (Fe_2O_3).

The values of corrective fertilization (CF_1, CF_2) and adopted by CQFS-RS/SC (2016) were also tested for the P availability classes using the Tukey test ($p<0.05$). The CF_1 values were obtained from the individual PBC of each soil, seeking to raise the P levels to the critical level (high class) according to CQFS-RS/SC (2016). The CF_2 values were obtained from the average PBC value for all soils, also seeking to raise the P levels to the critical level (high class). The CF values were compared with each other and in relation to the rate recommended by the regional recommendation system for corrective fertilization in fruit trees (CQFS-RS/SC, 2016). The correlation between PBC values and soil chemical and physical properties was performed using Pearson’s correlation analysis ($p<0.05$). Significant outlier values ($p<0.05$) were removed for the average PBC calculation. Based on the variables analyzed (altitude, SOM, P_M1, $CEC_{pH7.0}$, $Fe_{oxalate}$, clay, sand, and silt), equations were tested to estimate PBC values using multiple linear regression, according to the *lm* function in R software. The variables that did not present significance ($p<0.05$) were removed from the equation (Osborne and Overbay, 2004). The statistical analyses were performed using the R software version 4.2.2 (R Development Core Team, 2022).

RESULTS

General characterization

The PBC values were obtained in the soils subjected to P rates (Figure 2), using linear regression between P_2O_5 rates and the available P content extracted by Mehlich-1 solution (P_M1). Only for soil 5, segmented linear regression was used to represent this effect, obtaining the change point (Cp) value of 12.86 mg dm^{-3} of P_M1 for this soil (Figure 2a). The linear increase in P_M1 content was observed for most soils, but in different magnitudes (Figures 2b, 2c and 2d).

Soils with the lowest PBC were 22, 25, and 27. Meanwhile, soils 5 and 28 showed higher PBC values (Table 2), varying from 12.2 to 120.5 kg ha^{-1} P_2O_5. Soil 5 presented a segmented equation and showed a three-fold reduction between PBC1 and PBC2. Soils 5 and 28 were classified as outliers ($p<0.05$) and removed from the calculation, the mean PBC value was 26.3 kg ha^{-1} P_2O_5.

Relation between PBC and soil properties

The PBC values were negatively correlated with altitude and sand fraction and positively correlated with silt and $Fe_{oxalate}$ (Fe_2O_3) contents, showing no correlation with clay, P_M1, SOM, and $CEC_{pH7.0}$ (Figure 3). Altitude was negatively correlated with Fe_2O_3. The P_M1 content was positively correlated with SOM and $CEC_{pH7.0}$.

Multiple linear regressions were performed and the SOM did not present significance. A regression including altitude values ($p<0.001$), clay ($p<0.018$), P_M1 ($p<0.001$), and $Fe_{oxalate}$ ($p<0.003$) was performed to predict PBC (Equation 1), allowing a better adjustment of the coefficient of determination (R^2 = 0.70).

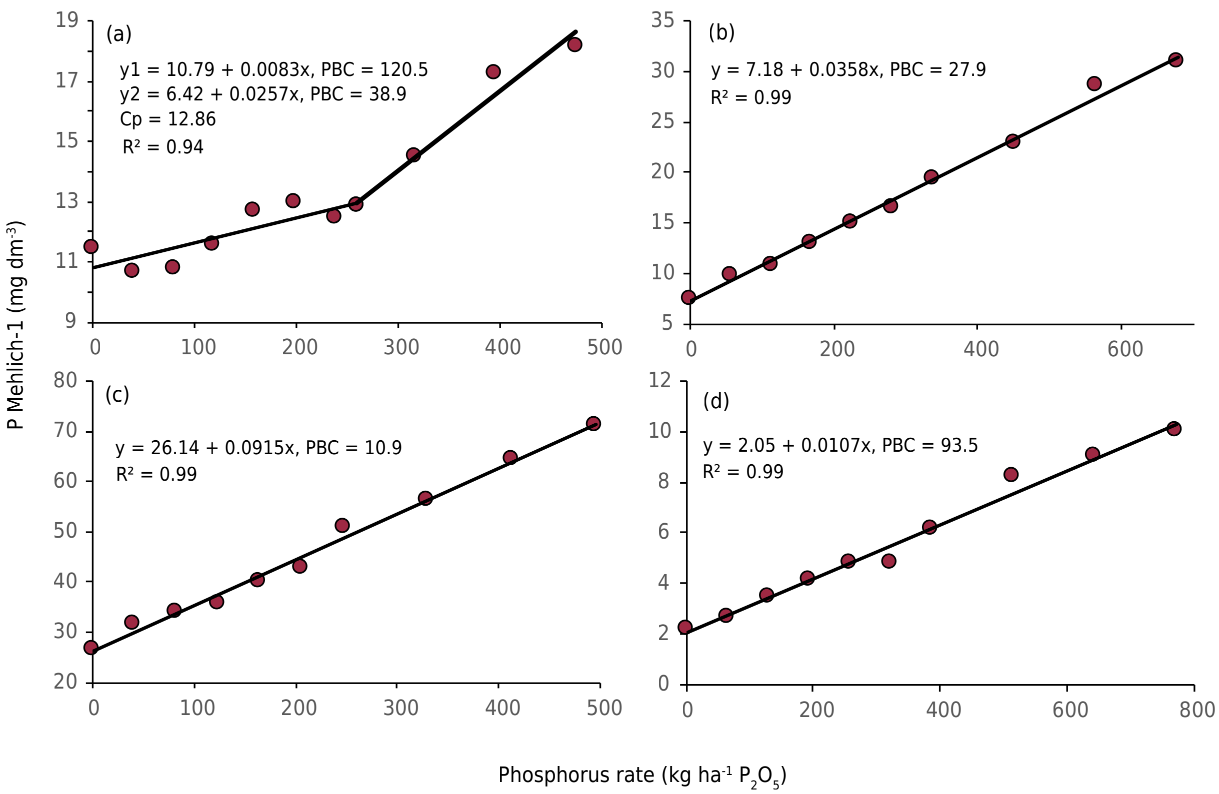

Figure 2. Phosphorus content by Mehlich-1 (P_M1) extractor, following the addition of P_2O_5 rates for Soils 5 (a), 8 (b), 27 (c), and 28 (d). These soils were chosen to exemplify the application of segmental and linear equations. PBC: phosphorus buffer capacity; Cp: P_M1 value at which the change point occurs between the segmented equations. Note: the scales on the x-axis and y-axis differ between plots.

Table 2. Phosphorus extracted as a function of the 10 applied P rates, values of the change point (Cp) of the segmented equations, and values of P buffer capacity (PBC) in soil samples collected in the Serra Gaúcha region

Soil	Equation 1 (y1)	Equation 2 (y2)	Cp	PBC 1	PBC 2	R^2
	Linear equations		$mg\ dm^{-3}$	$kg\ ha^{-1}\ P_2O_5$		
1	y = 18.06 + 0.0555x	-	-	18.02	-	0.99
2	y = 11.23 + 0.0397x	-	-	25.19	-	0.98
3	y = 14.43 + 0.0625x	-	-	16.00	-	0.99
4	y = 29.45 + 0.0627x	-	-	15.95	-	0.99
5	y = 10.79 + 0.0083x	y = 6.42 + 0.0257x	12.86	120.48	38.91	0.94
6	y = 6.33 + 0.0408x	-	-	24.51	-	0.99
7	y = 10.48 + 0.0280x	-	-	35.71	-	0.99
8	y = 7.18 + 0.0358x	-	-	27.93	-	0.99
9	y = 8.17 + 0.03960x	-	-	25.25	-	0.99
10	y = 19.65 + 0.0386x	-	-	25.91	-	0.98
11	y = 11.54 + 0.0177x	-	-	56.50	-	0.99
12	y = 12.54 + 0.0305x	-	-	32.79	-	0.99
13	y = 18.23 + 0.0424x	-	-	23.58	-	0.99
14	y = 14.10 + 0.0494x	-	-	20.24	-	0.98
15	y = 20.13 + 0.0365x	-	-	27.40	-	0.97
16	y = 8.76 + 0.0360x	-	-	27.78	-	0.98
17	y = 12.03 + 0.0576x	-	-	17.36	-	0.99
18	y = 5.31 + 0.03200x	-	-	31.25	-	0.99
19	y = 12.38 + 0.0370x	-	-	27.03	-	0.99
20	y = 17.09 + 0.0443x	-	-	22.57	-	0.99
21	y = 9.80 + 0.0313x	-	-	31.95	-	0.99
22	y = 36.85 + 0.0822x	-	-	12.17	-	0.98
23	y = 4.51 + 0.0169x	-	-	59.17	-	0.99
24	y = 10.81 + 0.0290x	-	-	34.48	-	0.97
25	y = 23.52 + 0.0848x	-	-	11.79	-	0.99
26	y = 7.69 + 0.0296x	-	-	33.78	-	0.99
27	y = 26.14 + 0.0915x	-	-	10.93	-	0.99
28	y = 2.05 + 0.0107x	-	-	93.46	-	0.99
29	y = 28.61 + 0.0701x	-	-	14.27	-	0.99
	Average PBC			26.28*		

Cp: Change point; PBC: Phosphorus buffer capacity; R^2: coefficient of determination. * Outliers values (soils 5 and 28) were not considered to calculate the average PBC (p<0.05).

$$PBC\left(kg\ ha^{-1}\ P_2O_5\right) = 21.14 - 0.045A + 0.712 \times Clay - 1.786 \times P - M1 + 4.488 \times Fe_{ox} \quad \text{Eq. 1}$$

in which: A is the terrain altitude above sea level in meters; clay is the percentage of clay in the soil obtained by the pipette method; P_M1 is the P content obtained by the Mehlich-1 extractor; and Fe_{ox} is the iron oxide (Fe_2O_3) content obtained by ammonium oxalate extractor. The equation parameters were: $R^2 = 0.70$; $R^2(adj) = 0.64$; $p<0.001$; and standard error of estimate = 6.95.

A second multiple linear regression was performed using variables easily obtained in soil analysis reports (Equation 2).

$$PBC\left(kg\ ha^{-1}\ P_2O_5\right) = 49.75 - 0.063 \times A + 0.692 \times \text{Clay} - 1.869 \times P - M1 \qquad \text{Eq. 2}$$

The equation parameters were $R^2 = 0.55$, $R^2(adj) = 0.49$, $p<0.001$, and standard error of estimate = 8.34.

Classification of PBC and corrective fertilization rates

Based on the classification used by the current fertilization manual in the region of interest (CQFS-RS/SC, 2016), the PBC values were grouped according to clay and P availability classes. About clay classes (Figure 4a), it was observed that PBC values were not significantly different. The soils were also classified according to P availability (Figure 4b), showing no difference in PBC between the classes. The mean PBC value of 26.3 kg ha^{-1} P_2O_5 was obtained for the clay and P availability classes of very low, low, and medium.

The corrective fertilization (CF) rates to raise P content to critical levels for fruit species were calculated using equation 3.

$$CF\left(kg\ ha^{-1}\ P_2O_5\right) = \left(P\_M1_{\text{critical level}} - P\_M1_{\text{initial}}\right) \times PBC \qquad \text{Eq. 3}$$

Soils were classified into fertility classes using the PBC values obtained for each soil, and this was called CF_1 (Figure 5). The CF was also calculated using the mean PBC value of 26.3 kg ha^{-1} P_2O_5, which was called CF_2. Both CF rates did not differ from each other. The values proposed by the regional fertilization recommendation (CQFS-RS/SC, 2016) for fruit trees are 250, 170, and 130 kg ha^{-1} P_2O_5 for the very low, low, and medium classes, respectively. The CF_2 values were, on average, 155 and 149 % higher for the very low and low P classes, respectively. Only two soils were classified in the medium P availability class, but the P rates tended to be lower than those proposed by the regional fertilization recommendation (CQFS-RS/SC, 2016). Fertilizer rates to raise P levels to critical levels according to CF_2 were 387, 253, and 46 kg ha^{-1} P_2O_5 for the very low, low, and medium availability classes, respectively.

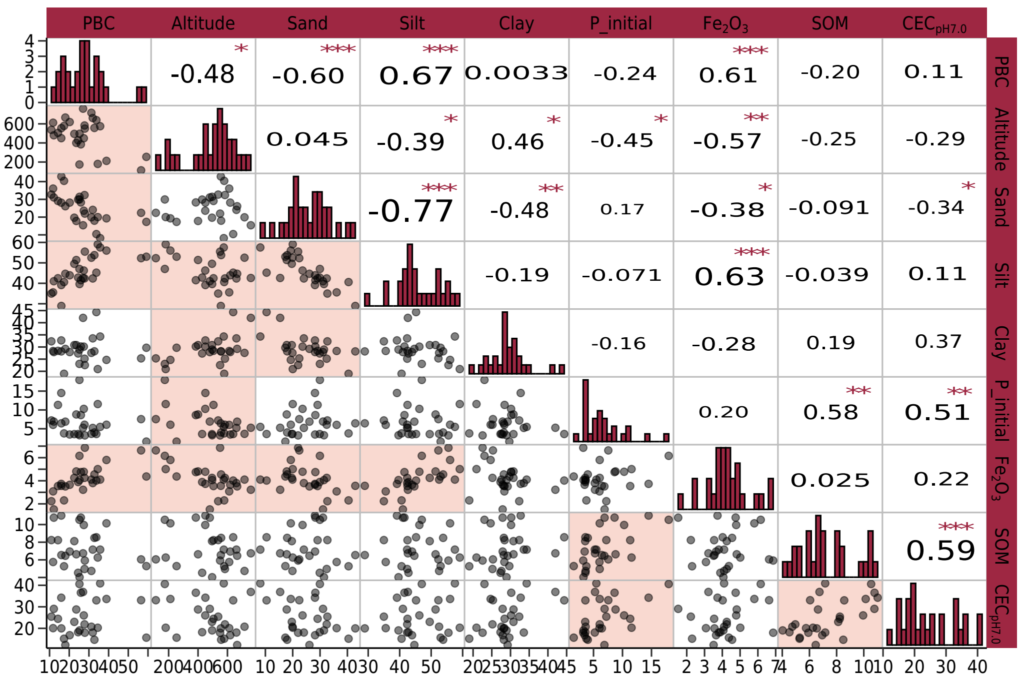

Figure 3. Pearson correlation between phosphorus buffer capacity (PBC) and soil properties in the 0.00-0.20 m layer for native soils (n = 29) from the Serra Gaúcha region, Southern Brazil. P_M1: soil content extracted by Mehlich-1 solution; Fe_2O_3: iron oxide content obtained by ammonium oxalate ($Fe_{oxalate}$); SOM: soil organic matter; Significance level: * p<0.05; ** p<0.01; and *** p<0.001.

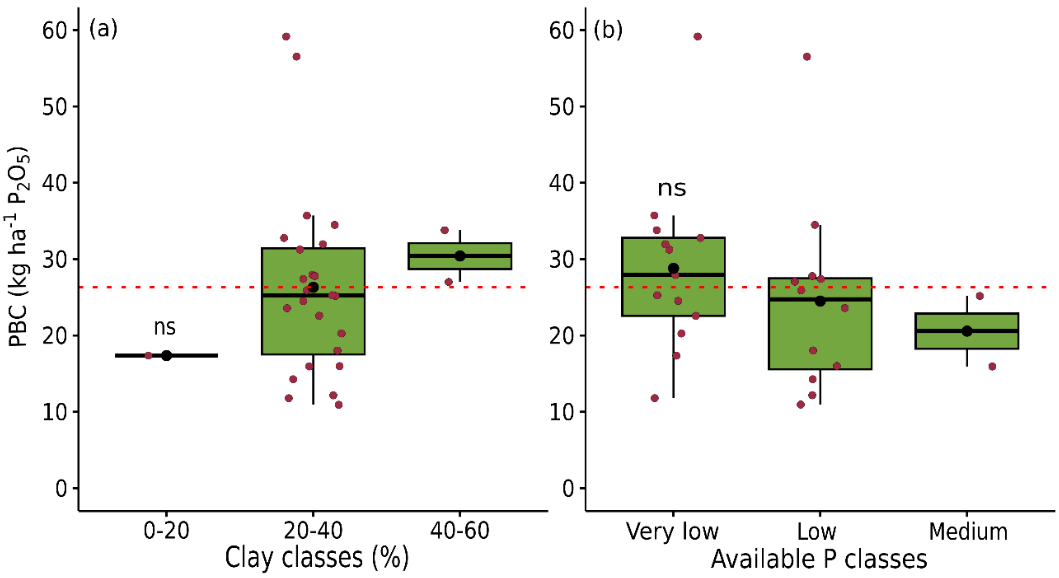

Figure 4. Phosphorus buffer capacity (PBC) values according to clay classes (a) and P availability classes (b) proposed by the regional fertilization recommendation (CQFS-RS/SC, 2016). ns: no statistical significance by the Tukey test ($p<0.05$); dots represent the distribution points; black dots represent the mean; horizontal line inside the box represents the median; red horizontal dotted line represents the general mean PBC, which is equal to 26.3. Outliers values (soils 5 and 28) were removed ($p<0.05$). No soils with clay content >60 % were observed.

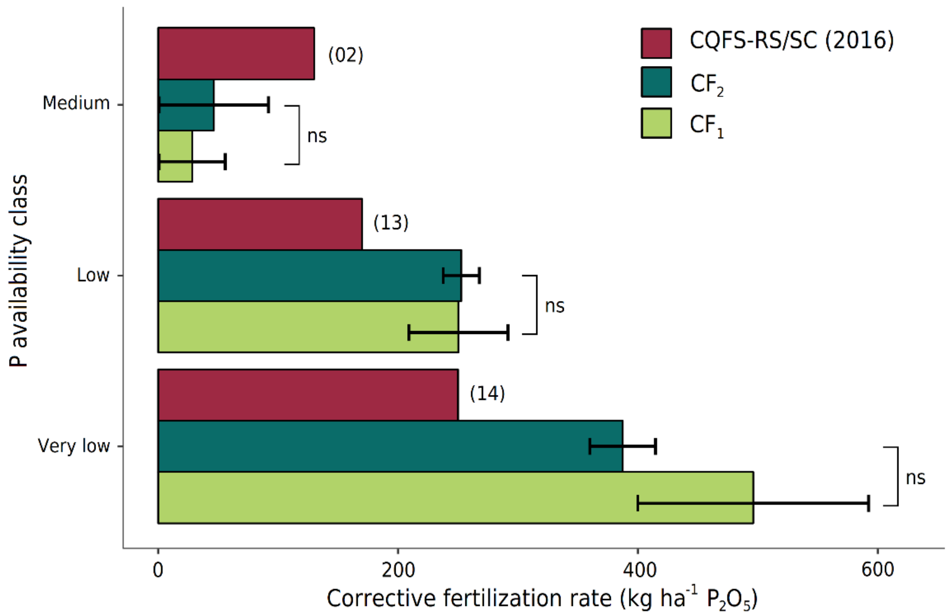

Figure 5. Comparison between corrective fertilization (CF_1, CF_2) and adopted by CQFS-RS/SC (2016), considering soils with P availability class of very low, low, and medium to soil samples from Serra Gaúcha region of Rio Grande do Sul state. CF_1: represents the proposed fertilizer rates according to PBC obtained individually for each soil to improve P levels until the soil critical level. CF_2: represents the adjusted fertilizer rates according to PBC 26.3 to improve P levels until the soil critical level. Horizontal error bars at the top of the bars represent the standard deviation of the mean; ns: not statistically significant by Tukey test ($p<0.05$); The numbers within the bracket represent the number of observations for each class. To convert P_2O_5 (kg ha^{-1}) × 0.436 = P (kg ha^{-1}).

DISCUSSION

Soils of the Serra Gaúcha region presented medium texture and high SOM contents (Table 1). Approximately 90 % of the soils analyzed were classified in class 3 (20-40 % clay), and 83 % were classified in the high SOM class (>5 % SOM), according to the

CQFS-RS/SC (2016) classification. The presence of rocks of acid (rhyodacite and rhyolite) and basic (basalt) origin (Modena et al., 2016), combined with the great variability in relief and altitude ranging from 100 to 800 m, contribute to the soils presenting distinct physical and chemical properties (Flores et al., 2012), directly affecting P adsorption. These characteristics explain the wide range observed in PBC in the soils evaluated (Table 2), within a radius of only 20 km where they were collected (Figure 1), which can be affected by modifications in clay, SOM, and pH contents.

Studies by Oliveira et al. (2020) corroborate the results of the present study, since they observed that Cambisols/Inceptisols of high altitude in the RS presented high P adsorption, which was attributed to the high SOM and clay contents. In addition, the great diversity of soils provides a significant difference in the maximum P adsorption capacity (MPAC) (Fink et al., 2014; Gatiboni et al., 2020b). Added to this, Yang et al. (2019) observed that the increase in SOM increased the MPAC and decreased the binding energy and PBC, justifying the range of PBC observed in the present study.

The Serra Gaúcha soils, due to their medium clay and Fe_2O_3 ($Fe_{oxalate}$) contents ranging from 1.5 to 6.9 g kg^{-1}, added to the crystallinity of the clay minerals that make up the soil, the phosphate adsorption capacity may exceed the adsorption capacity of oxides such as goethite and gibbsite (Gérard, 2016), which characterizes soils with the most varied adsorption characteristics. Also, due to the presence of organic compounds in the soil and their negative charges, they increase the adsorption force on the surface of clay minerals and Fe and Al oxides (Ruttenberg and Sulak, 2011; Barrow et al., 2015; Spohn, 2020). Thus, a wide range of chemical species and types of organic P bonds are accumulated in the soil, forming fractions with different labilities (Tiecher et al., 2012; Reusser et al., 2023). All of this contributes to the fact that soils with variation in clay content and SOM accumulation present different degrees of soil adsorption, directly reflecting in the PBC values.

The determination of PBC is carried out with soil samples with deformed structures. However, it is important to note that the use of unstructured soils increases P retention in relation to samples with preserved structure (Gatiboni et al., 2019). This is due to the regulation exerted by the size of soil aggregates on P adsorption (Wang et al., 2024). Thus, it is inferred that management practices that favor soil aggregation contribute in parallel to an increase in the availability of applied P (Wang et al., 2001). This factor can be affected in the soils of the present study by the high SOM contents, ranging from 4 to 11 %, directly affecting soil aggregation. The SOM decreases particle dispersion, reduces the soil specific surface area (Kaiser and Guggenberger, 2003) and, consequently, reduces P adsorption (Fontes and Weed, 1996). Thereby, soils with conservationist management without tillage and with maintenance of cover crops, such as orchards and vineyards, may present lower PBC. Thus, soil fertility monitoring is essential in these cases to maintain adequate nutrient levels for the crops. However, P_M1 values should not exceed levels that can cause P transfers to surface water (Gatiboni et al., 2020b; Grando et al., 2021; Silva et al., 2023).

No simple correlation was observed between clay, P_M1, or $CEC_{pH7.0}$ with PBC (Figure 3). However, when the results were analyzed together to explain PBC, the multiple linear regression (Equations 1 and 2) demonstrated that both clay ($p<0.018$) and P_M1 contents ($p<0.001$) affect the nutrient fixation capacity. This finding was described by other authors who diagnosed a great influence mainly of clay, but in soils with low (<2.5 %) and medium (2.5-5.0 %) SOM contents (Mumbach et al., 2021; Brignoli et al., 2024; Wang et al., 2024). This lack of correlation may occur due to the smaller amplitude of clay classes, with few soils in the classes with <20 % and >40 % of clay (Figure 4a). This can be justified when observing the positive correlation with $Fe_{oxalate}$ (Fe_2O_3), which is a more sensitive analysis (Figure 3 and Equation 1). Also, the studied soils have silt contents between 29 and 59 %, in which part of this silt may be constituted by microaggregates of clay fraction minerals with high stability, cemented by iron oxides (Ker and Resende, 1990), justifying the observed correlation between silt and $Fe_{oxalate}$ with PBC (Figure 3). Additionally, the chemical interactions between soil particles are complex, which justifies the use of analysis by multivariate statistical methods such as multiple linear regression, which showed the effect of clay fraction and P_M1 on PBC (Equations 1 and 2).

Evaluated soils presented an altitude variation of approximately 700 m (Table 1). With that, a negative correlation (-0.57**) between altitude and Fe_2O_3 was observed. In addition to a positive correlation (0.61***) between Fe_2O_3 and PBC (Figure 3). Phosphorus adsorption and desorption reactions are strongly affected by Fe oxide contents and SOM (Fink et al., 2016). Thus, in the region of this study, soils that occur at higher altitudes have lower Fe_2O_3 contents and lower PBC, requiring lower phosphate rates for fertility correction. Also, the Fe oxide contents can interfere with P availability, as they can cause strong adsorption (Oliveira et al., 2020), causing the added P to be retained in the soil and poorly available to plants. Also, soil acidity correction through liming contributes to reducing P adsorption (Wang et al., 2024), increasing the nutrient availability in the soil solution.

The equation proposed by Mumbach et al. (2021) to estimate PBC values for soils in Rio Grande do Sul and Santa Catarina was not efficient in estimating PBC values for the soils in this study (R^2 = 0.03). This is justified because the study used a wide range of soils from two states (98 to 712 g kg^{-1} of clay), which have different characteristics from those observed in the present study. Thus, a new equation (Equation 2) was proposed based on variables easily obtained through a soil analysis. The equation presented a lower coefficient of determination (R^2 = 0.55***) compared to the study by Mumbach et al. (2021), evidencing the intrinsic characteristics of the collection site, which makes these soils different from other regions of southern Brazil, but also reinforces the demand for regionalized studies to estimate soil PBC.

The recommendation based on the PBC of the Serra Gaúcha presented rates higher than those currently recommended by the current recommendation system (CQFS-RS/SC, 2016). The correction fertilizer (CF) rates for fruit species were performed using the individual PBC values for each soil (CF_1) and the average PBC of 26.3 kg ha^{-1} P_2O_5 (CF_2) to raise P levels to the "high" availability class (Figure 5), being these values compared with the P_2O_5 rates indicated by CQFS-RS/SC (2016). Consequently, the CF rates currently recommended by the Commission on Soil Chemistry and Fertility (CQFS-RS/SC) are, on average, underestimated by a factor of 1.5 and are therefore insufficient to elevate soil phosphorus (P) levels to the adequate range (high fertility class) required for the target crops. In the study by Mumbach et al. (2021), the average PBC value for the very low and low availability classes was 18 kg ha^{-1} P_2O_5 for soils in Rio Grande do Sul and Santa Catarina. In a study by Rogeri et al. (2016), the average PBC value was 38.5 kg ha^{-1} P_2O_5 for soils in RS. However, it is important to note that these two studies were carried out on several types of soils (Latossolos/Oxisols, Cambissolos/Inceptisols, Vertissolos/Vertisols, Argissolos/Ultisols, among others) from different regions of the state of RS, which are characterized by the high variation in the SOM, clay and mineralogical composition of the soils (Almeida et al., 2017; Dalmolin et al., 2017; Pedron and Dalmolin, 2019).

A positive correlation (0.58**) was observed between SOM and P_M1 (Figure 3). This is because SOM is an important compartment of labile and moderately labile soil P (Schmitt et al., 2013b). Thus, part of this organic P can be mineralized, made available to plants (Steffens et al., 2010), and contribute to the increase in P_M1. Therefore, it is essential to maintain SOM levels, which contributes to the increase in P (Figure 3). Thus, soils with higher SOM values require lower correction rates to reach the critical P level according to equations 1 and 2. In addition, the amount of P added to reach the optimum level for absorption by crops depends on the specificity of the soil.

We highlight that in the year of fertility correction with phosphate application, the efficiency of P use by plants will be lower (McLaughlin et al., 2011). Soils with a history of phosphate fertilization have a lower need for phosphate application to raise the P_M1 content by one unit (Barrow, 2018; Khan et al., 2018). This occurs due to the greater saturation of the soil functional groups responsible for P adsorption, mainly in the soil layer that receives fertilization.

A peculiarity was observed in the soils of this study (Cambissolos/Inceptisols and Neossolos/Entisols) regarding the proportion of air-dry fine soil (<2 mm) and rock fragments with diameter >2 mm. On average, 38 % of the total volume of soil collected in the diagnostic layer (0.00-0.20 m) was composed of rock fragments (data not shown). Rocks and their fragments can contribute to the accumulation and availability of nutrients to plants (Zheng et al., 2021). Also, decrease the amount of useful soil in the diagnostic layer (0.00-0.20 m), which limits the volume of soil explored by plants. The soil layer to be corrected (0.00-0.10 or 0.00-0.20 m) affects the amount of fertilizer needed to raise P levels to the desired levels (Schlindwein et al., 2013). In addition, the presence of parent material can decrease the amount of useful soil in the layer of interest, so the P rate is higher than recommended to reach the levels considered adequate.

Regions with great variability in soil, climate, and relief, such as the Serra Gaúcha, do not allow for a generalized fertilization recommendation. Therefore, we highlight the importance of soil analysis for monitoring fertility, adjusting fertilizer rates, and reducing P losses by erosion or surface runoff, which is aggravated by soil slope increase (Grando et al., 2021, 2023). Also, this study shows the importance of regionalizing fertilization recommendations, seeking to select soil groups with characteristics that represent the study region, providing greater reliability in nutritional management.

CONCLUSION

Soils of the Serra Gaúcha region exhibit high biogeochemical variability, providing a wide range of P buffer capacity (PBC). An average PBC value of 26.3 kg ha^{-1} P_2O_5 was obtained and represents the amount of fertilizer required to raise the P content extracted by the Mehlich-1 extractor (P_M1) in the soil by 1.0 mg dm^{-3}.

According to multiple linear regression, altitude, clay, and P_M1 were effective predictors of PBC. The equation PBC (kg ha^{-1} P_2O_5) = 49.75 - 0.063A + 0.692Clay - 1.869P_M1, was proposed for the Serra Gaúcha soils, using variables easily obtained from soil analysis reports.

The current P rates used by the Rio Grande do Sul and Santa Catarina recommendation system for correcting P levels in soils cultivated with fruit species are underestimated an average of 1.5 times for soils in the Serra Gaúcha region, which has naturally low P contents, hindering crops from achieving their critical levels. Therefore, we recommend adjusting phosphate fertilizer rates, monitoring soil P content, and maintaining SOM levels, as this is an important P compartment in the system.

SUPPLEMENTARY DATA

Supplementary data to this article can be found online a https://doi.org/10.6084/m9.figshare.28761455

DATA AVAILABILITY

All data was generated or analyzed in this study.

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AUTHOR CONTRIBUTIONS

Conceptualization: Douglas Luiz Grando (equal) and Gustavo Brunetto (equal).

Formal analysis: Cauan Guerra Martins (equal), Douglas Luiz Grando (lead), Lucas Peranzoni Deponti (equal) and Marcos de Lima Rodrigues (equal).

Investigation: Cauan Guerra Martins (equal), Douglas Luiz Grando (lead), Lucas Peranzoni Deponti (equal) and Marcos de Lima Rodrigues (equal).

Project administration: Cauan Guerra Martins (equal), Douglas Luiz Grando (lead), Gustavo Brunetto (lead), Lucas Peranzoni Deponti (equal) and Marcos de Lima Rodrigues (equal).

Writing - original draft: Adriele Tassinari (equal), Ana Luiza Lima Marques (equal), Cauan Guerra Martins (equal), Djalma Eugenio Schmitt (equal), Douglas Luiz Grando (lead), Gilmar Luiz Mumbach (equal), Gustavo Brunetto (equal), Jean Michel Moura-Bueno (equal), Lucas Peranzoni Deponti (equal) and Marcos de Lima Rodrigues (equal).

Writing - review & editing: Adriele Tassinari (equal), Ana Luiza Lima Marques (equal), Cauan Guerra Martins (equal), Djalma Eugenio Schmitt (equal), Douglas Luiz Grando (lead), Gilmar Luiz Mumbach (equal), Gustavo Brunetto (equal), Jean Michel Moura-Bueno (equal), Lucas Peranzoni Deponti (equal) and Marcos de Lima Rodrigues (equal).

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