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Establishing environmental soil phosphorus thresholds to decrease the risk of losses to water in soils from Rio Grande do Sul, Brazil

Luciano Colpo Gatiboni(1), **Rodrigo da Silveira Nicoloso**(2), **Gilmar Luiz Mumbach**(3)*, **Abelino Anacleto de Souza Junior**(3), **Daniel João Dall'Orsoletta**(4), **Djalma Eugênio Schmitt**(5) **and Thomas Jot Smyth**(1)

(1) North Carolina State University, Department of Crop and Soil Sciences, Raleigh, North Carolina, United States of America.
(2) Empresa Brasileira de Pesquisa Agropecuária, Embrapa Suínos e Aves, Concórdia, Santa Catarina, Brasil.
(3) Universidade do Estado de Santa Catarina, Departamento de Solos e Recursos Naturais, Programa de Pós-Graduação em Ciência do Solo, Lages, Santa Catarina, Brasil.
(4) Bolsista do Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Lages, Santa Catarina, Brasil.
(5) Universidade Federal de Santa Catarina, Departamento de Agricultura, Biodiversidade e Floresta, Curitibanos, Santa Catarina, Brasil.

ABSTRACT: The overloading of soil with manure or mineral fertilizers enhances phosphorus (P) availability, promoting its loss to water bodies and increasing the risk of eutrophication. In this sense, the establishment of an environmental P threshold is a simple and useful tool to classify soils regards its risk of P losses. Here we propose a P-threshold for soils from the state of Rio Grande do Sul (RS) in Brazil, with the soil clay content as the principal variable of the model. Samples from 20 representative soils of Rio Grande do Sul State were collected in the 0.00-0.10 and 0.10-0.20 m layers. Samples were physically and chemically characterized and incubated with P rates varying from 0 to 100 % of its maximum adsorption capacity. After 20 days of incubation, the P availability was determined in water and Mehlich-1 extractant. We assessed trough segmented linear functions the value of P-Mehlich in which the levels of P water enhance abruptly (i.e., breaking point) to determine the P limit for each soil. Subsequently, the P limit values were linked to the clay content in the sample, adopting the linear equation arising from it as the P-threshold. Adding a safety margin of 20 % to the P-threshold equation, we propose a simplified one "P-threshold = 20 + clay". Based on the current critical level of P adopted by the regional recommendation in RG, the equation proposed does not limit the production of the most crop species.

Keywords: P- threshold, phosphate fertilization, phosphate adsorption, clay, mineralogy.

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

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INTRODUCTION

The soils in the Southern region of Brazil are naturally acid and have low natural fertility (Ernani and Almeira, 1986; Bortoluzzi et al., 2015), being necessary to add correctives and fertilizers to obtain an adequate response of plants. The addition of organic waste, such as pig slurry, is an option as a fertilization source. However, it may cause environmental problems when the amount applied does not follow technical criteria (Alleoni et al., 2014; Benjannet et al., 2018). Phosphorus (P) is an important constituent of animal wastes and, at the same time, is a limiting element to the biological activity of the water resources (Zhang et al., 2017). To reduce the risk of environmental contamination, laws seek to establish limits to the application of animal waste (Fatma, 2014), however, in many cases do not take into account the inherent soil properties, such as the chemical constitution and adsorption capacity, which may affect its contamination potential (Heathwaite et al., 2005; Bai et al., 2013; Bortoluzzi et al., 2015).

The state of Rio Grande do Sul (RS) is the third-largest hog producer and second-biggest exporter in Brazil (ABPA, 2018), this being predominantly produced in Center-Northern regions of the state (Figure 1). In RS, the system of swine production is defined as intensive confined, in which many animals are stocked in a reduced space (Guerini Filho et al., 2015). In such a system, the generation of a high quantity of pig slurry is a problem that must be taken into account. Currently, the legislation of Rio Grande do Sul defines that the amount of pig slurry to be applied must be based on the nutrients content and the crop needs, taking into account the resistance of the soil type regarding the environmental impact (Fepam, 2014). The RS soils are classified according to the resistance to the environmental impact (very low, low, medium, and high) and the application of animal wastes in the liquid form are only subject to soils with 0.5 m depth minimum, located in fields with a maximum slope limit of 30 %. Nevertheless, there are no current numeric parameters that set the superior limit of P in soil, that once crossed, would represent a high potential for environmental contamination.

Many studies seek to develop parameters to set the amount of phosphorus that may be added to the soil without water contamination risk (Vadas et al., 2009; Gatiboni et al., 2015; Bortolon et al., 2016; Abboud et al., 2018; Fischer et al., 2018). One of the main and more complex models is the “P-Index”, used in the United States, which takes into

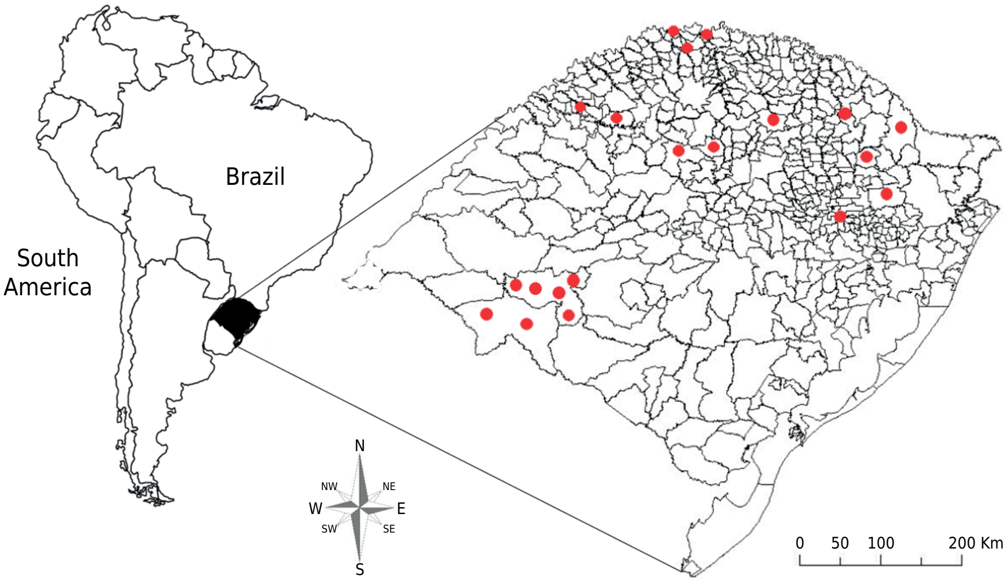

Figure 1. The State of Rio Grande do Sul, Brazil. Red circles represent the sites where the soil samples used in this study were collected.

account variables involved in the P transference, both linked to the soil as a source and to the transfer potential to risk zones (Heathwaite et al., 2005), classifying the risk of P loss, from low to very high (Sharpley et al., 2017). However, other less complex methodologies may be used to determine the capacity of holding P in soil, such as the degree of P saturation (DPS) and the environmental soil P threshold (P-threshold). The DPS is based on the determination of the percentage of P available in soil compared to the sum of the concentration of Fe and Al (Alleoni et al., 2014; Benjannet et al., 2018; Campos et al., 2018), elements which act on the P adsorption (Bortoluzzi et al., 2015; Fink et al., 2016), or even compared to the value of maximum capacity of P adsorption (Pmax) (Bortolon et al., 2016).

The P-threshold determines the maximum amount of P that a certain soil may support before enhancing the risk of losses to the environment. Gatiboni et al. (2015), using an Oxisol from the state of Santa Catarina, proposed the equation "P-threshold = 40 +clay", in which P- threshold is the quantity of P available by the Mehlich-1 extractor, in mg dm^{-3}, and the clay is determined by the densimeter method. Based on that, clayey soils may receive a higher amount of P, once the higher is the clay content, higher is the P adsorption capacity. Nowadays, the P-threshold method is the official parameter used in the state of Santa Catarina, which shares the boundary with Rio Grande do Sul, to determine the maximum quantity of P the soil should have without environmental concerns.

Despite the importance of the clay factor as a parameter to evaluate the capacity of a soil to retain P, we know that this does not explain the whole phenomena of adsorption. Other factors interfere in the capacity of a soil to adsorb P, especially the mineralogy (Bortoluzzi et al., 2015). In this sense, soils with the same grain size composition may present high variation in retention capacity of P in soil (Fink et al., 2016; Rogeri et al., 2016; Benjannet et al., 2018) and, thus, soils with varied mineral composition must be considered for the creation of a more realistic model of P-threshold. Therefore, the goal of this study was to determine the P-threshold for soils with different levels of clay and mineral composition from the state of Rio Grande do Sul.

MATERIALS AND METHODS

Soil sampling and characterization

We collected soil samples from the layers 0.00-0.10 and 0.10-0.20 m in 20 localities from the state of Rio Grande do Sul (Table 1), totaling 40 samples. The two sampled layers are normally used for characterization and recommendation of liming and fertilization (CQFS-RS/SC, 2016). The samples were collected in areas of forest and native grasses, without agricultural use. After collected, they were stoven-dried at 60 °C, milled, and sieved in 2 mm. The soils that presented $pH(H_2O)$ values lower than 6.0 were corrected to such value through the incubation with lime.

Subsequently, the soils were characterized physically and chemically, with the evaluations presented in table 2: grain size, $pH(H_2O)$, H+Al, total organic carbon (TOC), P available, remaining P (P-rem), maximum capacity of P adsorption (Pmax), and Fe and Al in total fractions with low and high crystallinity. In addition, the minimum and maximum values for other soil properties were: 1.3 to 5.0 $cmol_c$ dm^{-3} of H+Al, 0.6 to 7.1 $cmol_c$ dm^{-3} of Ca^{2+}, 0.8 to 5.9 $cmol_c$ dm^{-3} of Mg^{2+}, 0.04 to 1.0 $cmol_c$ dm^{-3} of K^+, 2.8 to 15.8 $cmol_c$ dm^{-3} of CEC pH 7, and 49.7 to 81.2% of BS.

The determination of the content of sand, silt, and clay was held by the simplified hydrometer method and by the pipette method (Teixeira et al., 2017). The $pH(H_2O)$ was determined in a 1:1 soil:water ratio and the values of H+Al determined based on the equation proposed by CQFS-RS/SC (2016). The interchangeable concentration of Ca, Mg, and Al were extracted with the KCl 1 mol L^{-1} solution and determined by atomic absorption

Table 1. Classification and localization of the soils collected in the state of Rio Grande do Sul (RS), Brazil

Code	Soil classification$^{(1/2)}$	City	Geographic Coordinates	Altitude
				m
RS1	*Latossolo Bruno*/Ferralsol	Vacaria	28° 30′ 47.2″ S 50° 53′ 36.9″ W	970
RS2	*Latossolo Vermelho*/Ferralsol	Lagoa Vermelha	28° 22′ 33.4” S 51° 4′ 52.9″ W	900
RS3	*Latossolo Vermelho*/Ferralsol	Passo Fundo	28° 14’ 20.1” S 52° 19’ 14.8” W	725
RS4	*Latossolo Vermelho*/Ferralsol	Ibirubá	28° 28’ 25.0” S 53° 14’ 7.2” W	475
RS5	*Latossolo Vermelho*/Ferralsol	Santo Ângelo	28° 04′ 34.7″ S 54°42’53.0” W	218
RS6	*Latossolo Vermelho*/Ferralsol	Cerro Largo	28° 11′ 27.4″ S 54°20’44.4” W	342
RS7	*Latossolo Vermelho*/Ferralsol	Cruz Alta	28° 58′ 44.1″ S 53° 38′ 38.1″ W	420
RS8	*Cambissolo Háplico*/Cambisol	Pinheirinho do Vale	27° 13’ 20.4’’ S 53° 39’ 0.4” W	218
RS9	*Latossolo Vermelho*/Ferralsol	Taquarusu do Sul	27° 24’ 16.3’’ S 53° 26’ 28.8” W	563
RS10	*Cambissolo Háplico*/Cambisol	Iraí	27° 16’ 55.4” S 53° 16’ 10.0” W	384
RS11	*Argissolo Bruno-Acinzentado*/Acrisols	Rosário do Sul	30° 14’ 24.1” S 54° 51’ 44.5” W	125
RS12	*Luvissolo Háplico*/Luvisol	Rosário do Sul	30° 12’ 12.7” S 54° 59’ 09.2” W	124
RS13	*Plintossolo Argilúvico*/Plinthosol	Rosário do Sul	30° 13’ 25.4” S 54° 56’ 58.1” W	115
RS14	*Argissolo Vermelho*/Acrisols	Rosário do Sul	30° 13’ 51.9” S 54° 56’ 45.7” W	140
RS15	*Argissolo Vermelho*/Acrisols	Santana do Livramento	30° 41’ 25.2” S 55° 07’ 50.9” W	165
RS16	*Luvissolo Háplico*/Luvisol	Rosário do Sul	30° 11’ 26.3” S 55° 1’10.2” W	172
RS17	*Neossolo Litólico*/Leptosol	Santana do Livramento	30° 46′ 41.6″ S 55° 41′ 55.6″ W	100
RS18	*Latossolo Bruno*/Ferralsol	Ipê	28° 42’ 26,3’’ S 51° 13’ 38.9 W	873
RS19	*Cambissolo Húmico*/Cambisol	Caxias do Sul	29° 5’ 34.4’’ S 51° 10’ 51.2’’ W	747
RS20	*Argissolo Vermelho*/Acrisols	Teotônia	29° 26’ 32.87’’ S 51°49’ 21.64” W	76

(1) According to the classification proposed by the Brazilian Soil Classification System (Santos et al., 2013). (2) According to the World Reference Base for Soil Resources - WRB (IUSS Working Group WRB, 2014).

spectrophotometry (AAnalyst 200 device, PERKIN-ELMER); the values of available P and K were extracted with the Mehlich-1 solution (H_2SO_4 0.0125 mol L^{-1} and of HCl 0.050 mol L^{-1}), and the determination of K concentration was made through flame photometry. The content of total organic carbon (TOC) was determined by spectrophotometry at 645 nm (UV-1800, SHIMADZU) after oxidation through sulphochromic solution. The values of CEC pH 7.0 and V% were calculated based on the analysis above mentioned. The total content of Fe and Al (Fe-total and Al-total) were extracted through sulfuric extraction, according to the methodology proposed by Teixeira et al. (2017).

The remaining P (P-rem) was determined through the addition of 1 g of soil in falcon tubes containing 10 mL of a solution of $CaCl_2$ 0.01 mol L^{-1} and P concentration of 60 mg L^{-1}. The P solution was prepared using monohydrated potassium phosphate (KH_2PO_4 a.r.). After stirring in an end-over-end stirrer type for one hour, the samples were centrifuged for 15 min to 3,000 rpm and an aliquot was taken to determine P. The determination of the maximum capacity of P adsorption (Pmax) in soils was held through the weighing 0.5 g of soil in 15 mL falcon tubes, with 10 mL solution of $CaCl_2$ 0.01 mol L^{-1} containing eight concentrations of P, from 0 to 160 mg L^{-1}, which corresponded to doses of 0 to 3,200 mg kg^{-1}. The samples were shaken for 16 h in an end-over-end shaker at 30 rpm and after the soil was separated from the solution through the centrifugation at 3,000 rpm for 15 min. The P adsorbed was obtained through the difference between the amount added and the amount recovered in the solution. The data was adjusted by the Langmuir model (Equation 1).

$$P = \frac{\mathrm{k \times Pmax \times C}}{\mathrm{1 + k \times C}} \qquad \text{Eq. 1}$$

in which k is the constant related to the adsorption energy; Pmax is the maximum capacity of P adsorption; and C is the P concentration in the solution.

Incubation of soils containing P and determination of P-threshold

We incubated the soil samples with 12 rates of P, comprehended from 0 to 100 % of the maximum values of Pmax over 20 days. The rates were added through a solution prepared by the dissolution of the triple superphosphate fertilizer milled with deionized water. After the end of the incubation, we dried the soil samples in a stove at 55 °C and, subsequently, sieved them in 2 mm. We determined the values of available P through the Mehlich-1 extractant (P-M1) and the soluble P in water (P-water). The P-water was quantified based on the methodology proposed by Kuo (1996), through the addition of 25 mL of deionized water in 2.5 dm^{-3} of soil; after shaking for one hour in an “end-over-end” shaker, the samples were centrifuged for 15 min at 3,500 rpm and filtered in a qualitative paper of 0.45 μm. At the end of the process, we took an aliquot for determination. All phosphorus determinations were made by the Murphy and Riley (1962) method.

The relation between the values of P-Mehlich-1 (independent variable "x") and P water (dependent variable "y") was graphed. Segmented functions (2 segments) were generated to determine the breaking point (P limit), which means, the value of P-Mehlich in which the levels of P-water enhance abruptly. The P limit values and the content of clay in each soil were related, and the linear equation arising from it was considered as P-threshold.

Statistical analysis

The data were submitted to regression analysis among the variables of interest. The models generated were submitted to variance analysis (ANOVA), having the assumptions of normality tested by Shapiro-Wilk. No transformation of the data presented was required. The coefficient of the proposed models was tested by the t-test ($p<0.05$).

RESULTS

General characterization of soils

The soil samples analyzed presented great chemical and texture variability (Table 2) and different behavior when it comes to the potential of P adsorption (Figure 2). The Pmax of the collected soils varied from 190.8 to 2,360.4 mg kg^{-1} in the layer of 0.00-0.10 m and 197.9 to 2,580.1 mg kg^{-1} in the layer of 0.10-0.20 m. In this sense, the amplitude

Table 2. Clay content and chemical characterization of the 20 soils collected in the 0.00-0.10 and 0.10-0.20 m layers in the state of Rio Grande do Sul, Brazil

Code	Clay(1)	Clay(2)	TOC(3)	pH(H_2O)(4)	P-M1(5)	P-rem(6)	Pmax(7)	Fe-Total(8)	Al-Total(8)
	g kg^{-1}				mg dm^{-3}	mg L^{-1}	mg kg^{-1}	g kg^{-1}	
Layer 0.00-0.10 m									
RS1	65.5	70.2	22.6	6.2	3.3	9.0	2313.1	107.5	92.5
RS2	67.0	79.3	17.4	5.8	5.4	14.0	1790.2	128.5	94.5
RS3	35.9	37.4	9.5	6.2	2.7	19.1	885.1	33.4	54.1
RS4	46.4	50.9	20.0	6.2	13.2	20.7	912.1	70.2	62.6
RS5	63.1	70.9	12.3	6.0	5.4	19.8	1228.1	151.0	144.0
RS6	61.4	63.9	12.2	5.9	2.0	13.3	1790.8	151.0	130.1
RS7	21.1	23.2	5.6	6.2	7.8	36.0	346.7	14.1	29.6
RS8	20.3	23.8	24.0	6.6	9.9	30.7	473.7	95.6	79.3
RS9	71.2	75.6	7.9	6.2	7.0	16.9	1267.2	136.5	153.1
RS10	41.0	48.9	10.2	6.2	5.4	7.9	1599.2	149.6	105.8
RS11	12.2	16.2	4.3	6.1	7.1	42.2	278.1	5.0	14.3
RS12	13.8	15.8	9.8	6.2	13.3	32.9	696.2	8.2	21.9
RS13	12.1	15.8	6.4	5.9	7.8	44.8	249.4	5.2	14.1
RS14	9.8	10.5	6.0	6.0	9.6	46.8	190.8	4.7	12.6
RS15	12.0	16.0	4.5	5.9	9.1	45.5	302.5	6.1	16.1
RS16	12.9	14.0	7.1	6.2	15.0	49.1	275.4	7.1	15.6
RS17	24.5	30.6	20.7	5.9	10.4	34.4	496.4	78.4	41.6
RS18	47.9	53.0	16.3	6.2	6.6	8.6	2360.4	96.4	133.8
RS19	33.2	37.7	15.5	6.2	5.0	18.9	1313.6	70.1	89.2
RS20	38.5	35.8	3.7	5.9	50.0	33.7	411.8	24.8	41.0
Layer 0.10-0.20 m									
RS1	67.8	72.4	19.4	6.2	1.0	5.3	2259.7	111.3	89.7
RS2	72.3	73.3	13.7	6.2	1.9	11.4	2023.4	150.6	111.4
RS3	35.0	37.2	7.4	6.2	1.4	15.7	962.5	33.2	52.2
RS4	50.6	55.9	10.9	6.2	5.3	19.3	1125.1	80.0	78.1
RS5	69.4	73.3	9.1	6.2	2.2	16.8	1235.1	158.6	142.4
RS6	62.0	66.0	7.8	5.9	0.8	11.8	1632.5	166.2	131.8
RS7	23.2	23.0	4.2	6.2	3.7	35.0	351.8	15.6	34.7
RS8	23.9	29.7	10.8	6.3	3.3	20.4	786.6	111.8	84.4
RS9	71.8	73.3	4.3	6.2	5.7	13.8	1606.4	142.1	164.0
RS10	44.8	52.2	6.2	6.2	2.2	11.5	1633.6	149.6	105.4
RS11	13.0	17.2	3.7	6.0	3.4	40.1	283.0	4.9	15.2
RS12	11.1	15.8	8.4	6.0	7.2	28.8	749.9	7.8	22.1
RS13	12.0	15.2	1.8	5.9	3.6	42.6	217.0	6.1	15.7
RS14	9.5	10.2	0.5	6.1	4.8	46.6	197.9	4.4	13.1
RS15	12.4	12.2	2.0	6.1	5.0	44.6	301.8	6.2	16.3
RS16	13.4	15.6	3.6	6.2	8.3	43.4	410.8	7.1	15.6
RS17	25.1	32.8	17.1	5.9	6.2	28.3	763.8	77.1	58.1
RS18	54.5	59.7	11.4	6.2	2.3	10.2	2580.1	92.3	142.5
RS19	36.0	39.2	8.1	6.2	2.1	12.8	1844.1	67.8	88.6
RS20	39.7	36.2	1.5	5.8	20.3	23.6	702.4	36.4	80.3

(1) Clay determined by the pipette method. (2) Clay determined by the hydrometer method. (3) Total Organic Carbon by Walkley-Black method. (4) Soil:water at a ratio of 1:1. (5) P extracted through Mehlich-1. (6) Remaining P. (7) Maximum capacity of P adsorption. (8) Total Fe and Al extracted through the sulfuric attack.

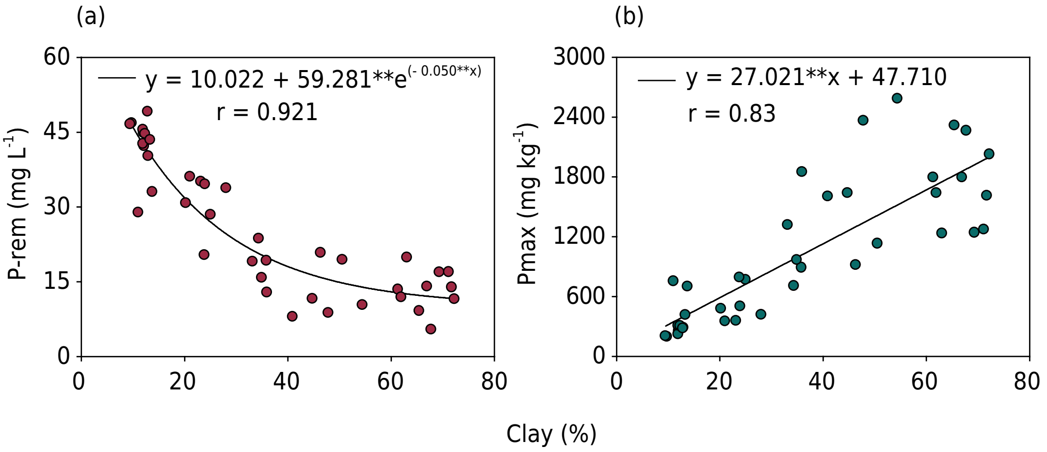

Figure 2. Relations between the content of clay (average between the two methods) to P-rem (a) and Pmax (b), for the 40 samples of soils collected in the state of Rio Grande do Sul, Brazil.

of values in P-rem was high, from 7.9 to 49.1 mg L^{-1} for the layer of 0.00-0.10 m and 5.3 to 46.6 mg L^{-1} for the layer of 0.10-0.20 m.

Environmental critical limit of P

The addition of P rates to the soil increased the values extracted by Mehlich-1 (P-M1) and the quantities of soluble P in water (P-water). We obtained significant relations ($p<0.05$) between the quantities of P-M1 and P-water (Figure 3), for all evaluated soils. The behavior of such a relation is not linear, having values of P-M1 from which the amount of P-water increases abruptly. Based on that, linear equations of two segments were adjusted for each soil and the value of P-M1 in which P-water increases drastically was named “P limit”. Grouping the soils used in the present study in classes of clay content, according to the proposition of CQFS-RS/SC (2016), the P limit varied from 11.6 to 60.5 mg dm^{-3} for soils with up to 20 % of clay, 37.0 to 97.2 mg dm^{-3} for soil with clay from 20 to 40 %, 47.7 to 82.7 mg dm^{-3} for soils with clay between 40-60 %, and 65.4 to 136.7 mg dm^{-3} for soils with over than 60 % of clay. Therefore, the average in values of P limit for the texture classes of 0-20, 20-40, 40-60, and 60-80 % of clay were 37.4, 69.4, 72.0, and 103.7 mg dm^{-3}, respectively.

The relation between the P limit values and the amount of clay in soils is significant ($p<0.05$) (Figure 4a). The P limit equations, based on the analysis of clay through the Pipette method and through the hydrometer method, were “P limit = 26.14 + 1.16 × clay” and “P limit = 24.68 + 1.10 × clay”, respectively, having the P limits values considered in mg dm^{-3} and comparable to the value of P-M1. Based on the linear equation, the values of P limit increase in the 1.16 and 1.10 mg dm^{-3} order for each percentage of clay increase, measured by the pipette and hydrometer methods, respectively. Such equation indicates that P-M1 concentration above P limit may reflect on the substantial loss of the soil capacity to adsorb P and, as a consequence, a significant increase in P loss.

The P limit values presented a positive relationship with the total content of Fe + Al ($p<0.05$) and the latter with the percentage of clay in the soil ($p<0.05$) (Figure 4b). The consideration with a higher number of soils, which presented heterogeneous origin material, mineral composition, and organic composition (Figure 2), may estimate in a wide manner the parameters linked to the prevention of nutrient losses to the environment.

The P limit equations presented above determine the exact point in which there is a higher transference of P from soil to the solution. However, it is debatable, once it does not consider any safety margin. Therefore, as adopted by Gatiboni et al. (2015), it is recommended to reduce the limit by 20 % for safety purposes. Thereby, the equations

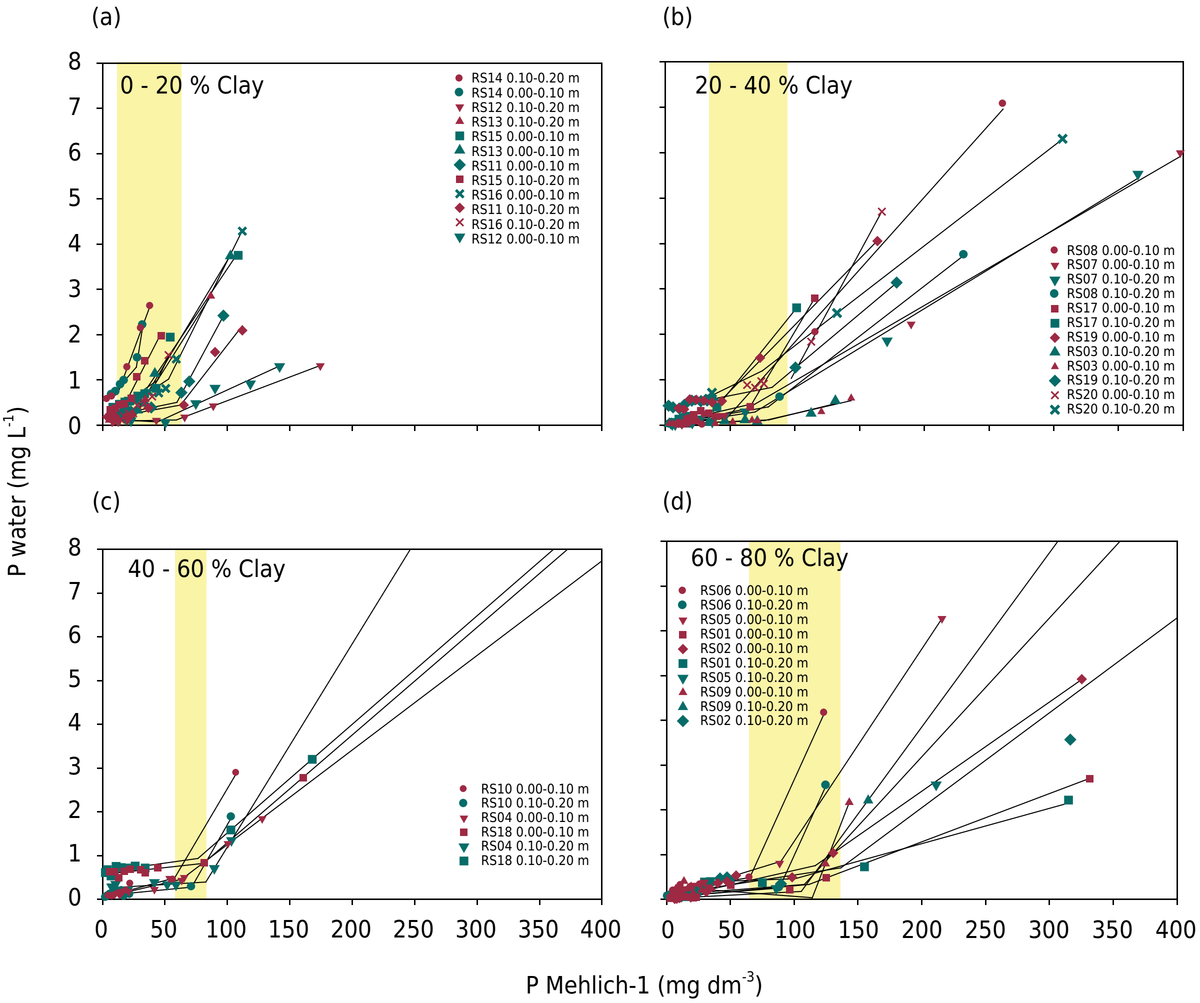

Figure 3. Relation between P-Mehlich-1 and P-water for the 40 samples of soils collected in the state of Rio Grande do Sul, Brazil. The graphics a, b, c, and d represent the range of 0-20 (a), 21-40 (b), 41-60 (c) and 61-80 % (d) of clay, respectively. Red symbols refer to the layer of 0.00-0.10 m, whilst green symbols refer to the layer of 0.10-0.20 m. The yellow stripe represents the amplitude of values of P-thresholds.

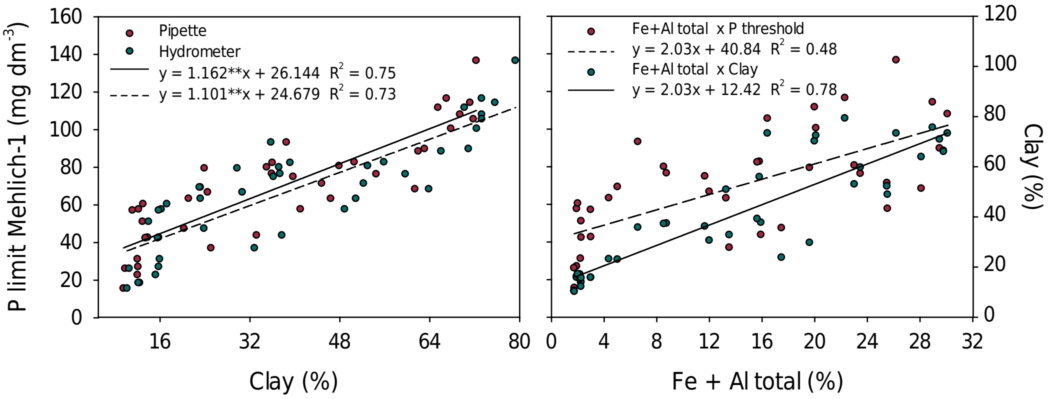

Figure 4. Values of P limit related to the content of clay, using the data of 40 soil samples collected from the state of Rio Grande do Sul, Brazil.

will be “P-threshold = 21.787 + 0.968 × clay” and “P-threshold = 20.371 + 0.918 × clay” to define the clay through the pipette and hydrometer methods, respectively. Based on these equations and aiming at benefitting the usage of the model in agricultural properties, we suggest the adoption of the equation “P-threshold = 20 + clay” for RS soils, which is statistically equivalent to the equations obtained by both methods for the determination of clay (Figure 5a).

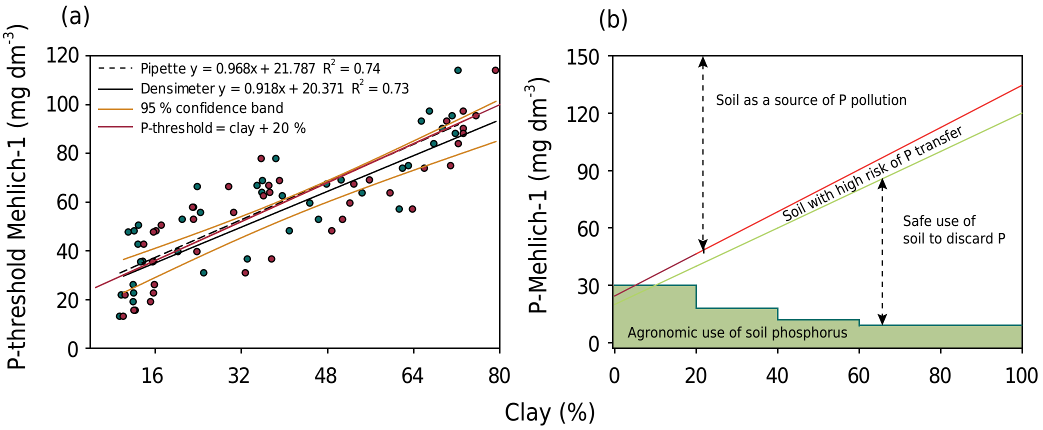

Figure 5. Real and simplified equations for the critical limit of P (P-threshold) indicated for soils of the state of Rio Grande do Sul (a), and critical levels of P for the annual grain crops according to CQFS-RS/SC (2016) and its relation to the P-threshold calculated through the "P-threshold = 20 + clay" equation.

DISCUSSION

Dynamic of P adsorption

The large amplitude of values for the Pmax and the P-rem may be due to various factors, especially to the content of clay in the soil and mineralogical composition (Bortoluzzi et al., 2015; Fink et al., 2016; Rogeri et al., 2016). As for the variation between the layers of 0.00-0.10 and 0.10-0.20 m may be due to the higher content of carbon in the first one (Jiménez et al., 2019). In this study, the increase in the content of clay resulted in an exponential reduction of P-rem, with little variation in soils with more than 40 % of clay and tending to a minimum value of 10 mg dm^{-3} (Figure 2), corroborating the results obtained by Rogeri et al. (2016). As for the Pmax, there was an increase of 27 mg kg^{-1} for each 1 % of additional clay (Figure 2). The content of clay and the parameters that measure the adsorption presented a significant relation, and the dispersion observed may be due to the mineralogical heterogeneity (Bortoluzzi et al., 2015; Fink e al., 2016). In a similar study, using only one soil, with the mixture of it in quantities of sand for the creation of a clay curve, Gatiboni et al. (2015) obtained an almost perfect relation between the Pmax and the content of clay, due to the identical mineralogical composition. In such a study, they observed an increase of 30 mg kg^{-1} of Pmax for each percent rising in clay, which is very similar to those observed here. Also noteworthy is the increase in the dispersion of Pmax values with the increase in clay content (Figure 2b), which may be related to the different ways in which minerals are found under different environmental conditions (Bortoluzzi et al., 2015).

The majority of the negative interference caused by the clay on the P adsorption is due to the presence of Fe and Al (Campos et al., 2018). The forms in which Fe and Al are found in soil may have a distinct influence on the phenomenon of specific adsorption. The fractions that compose less crystalline forms presented a higher capacity of adsorption in comparison to the more crystalline forms (Bortoluzzi et al., 2015; Fink et al., 2016), mainly in soils where such forms are presented in higher contents (Campos et al., 2018). The P limit equation with the percentage of the total Fe+Al in soil (Figure 4b) presented coefficient two times lower than the one generated considerating clay, since the relation between the percentage of total (Fe+Al):clay, for this group of soils, is approximately 2:1.

Soil with lower availability of P presented reduction fractions of it as soluble in water, due to the high affinity of the nutrient to adsorption sites (Gatiboni et al., 2015; Campos et al., 2018). However, the constant addition of P leads to a gradual reduction of the potential for soil retention and, consequently, to the increase in forms of higher lability (Alleoni et al., 2014; Roy et al., 2017; Tiecher et al., 2017; Campos et al., 2018). The increase of P lability is due to the saturation of adsorption sites and to the increase in the negative electrical potential of soil (Oliveira et al., 2014; Barrow, 2015). Nonetheless, it may lead to an environmental problem, once it may enhance the risk of nutrient loss (Vadas et al., 2009). From the moment in which the concentration of P-water gets extremely high, the risk of losing it from the system also enhances. The increase in P-water considerably increases the risk of P loss of the system, through vertical displacement and through superficial outflow (Benjannet et al., 2018; Fischer et al., 2018) which, besides bringing economic harm, may maximize the process of eutrophication of water bodies (Zhang et al., 2017).

P-threshold and agriculture

The Pmax and P-rem estimate the capacity of soils quantitatively to retain P. The use of such parameters to predict the capacity of certain soil to hold P may be considered. Based on the values of Pmax and available P, we get the percentage value of the available fraction of the nutrient comparing to the total quantity possible to be absorbed by the soil. Such an index, known as the degree of P saturation (DPS), may indicate the susceptibility in losing P from the soil to the external environment (Bortolon et al., 2016). As an option, there is the possibility of determining an environmental limit of P (P-threshold), considering one or more parameters related to the P adsorption in soil. The clay, one of the factors that influence the most the retention of P in soil, has been used to determine the P-threshold (Gatiboni et al., 2015), having as main advantages, besides the good relation with the Pmax, being a variable frequently determined in soil analysis.

With the increase of the clay content, the breakpoint is higher (Figure 3), that is, the amount of P-M1 that the soils can support is greater (Gatiboni et al., 2015). In the study carried out by Gatiboni et al. (2015), the breaking values for soils with 20, 40, 60, and 80 % was 59, 86, 101, and 118 mg dm^{-3}, respectively. In a general view, the larger variation in P limit was observed for soils with greater clay content, soils that presented a higher number of adsorption sites and, consequently, higher capacity to adsorb P (Oliveira et al., 2014; Rogeri et al., 2016). In addition to it, we must emphasize that the soils presented a great variation of mineralogy and TOC, factors that also influence the P adsorption (Bai et al., 2013; Bortoluzzi et al., 2015; Fink et al., 2016; Jiménez et al., 2019).

Based on the values of “P limit” and clay content, the equation “P-threshold = 20 + clay” is proposed for the delimitation of P contents in soils of RS. The equation is much more restrictive than indicated by Gatiboni et al. (2015) for the soils of Santa Catarina State (P-threshold = 40 + clay). It is believed that this major restriction comes from the diversity of soils present in RS, especially by the presence of soils with low clay content, whereas for Santa Catarina only one original soil was used, which presented high Pmax (Oliveira et al., 2014).

It is important to highlight that this model concerns the topsoil (0.00-0.10 m) in no-tillage system, as well as the one used in Santa Catarina (Gatiboni et al., 2015). The displacement of P below this layer can find less saturated regions, in which the nutrient can be retained, not reaching groundwater. However, saturation in the first layers of soil is a strong indication of the risk of losses, such as by runoff (Bertol et al., 2017). On the other hand, in soils conducted under a conventional tillage system, diagnosis can be performed in the 0.10-0.20 m layer.

The management of phosphate fertilization to provide adequate conditions for plant growth is based on the determination of values at critical levels (CL). The values of CL proposed by CQFS-RS/SC (2016) varied according to the content of clay and the crop groups. Relating the CL values to the equation proposed for the P-threshold in soils of Rio Grande do Sul (P-threshold = 20 + clay) (Figure 5b), we can perceive that the restriction caused by the model in P-threshold, through the application of P, does not limit the agricultural production.

The values of P-threshold are superior to the CL for grain crops, pastures, and forest species, belonging to the group of normal demand and low P, respectively, regardless of the types of clay. This way, the rates of P considered satisfactory for obtaining the higher technical performance were below the concentration considered as with high pollutant potential. This highlight is important for the crops growing in soils with low clay content (<20 %), in which the values that may cause losses are slightly below the CL. Furthermore, considering the high demanding species, the P-threshold may limit the acquisition of the maximum economic performance for soils with less than 20 % of clay, especially those that present lower adsorption capacity (Guardini et al., 2012; Campos et al., 2018). In this condition, seeking to meet both the needs for obtaining adequate agricultural performance and environmental protection, the farmers must seek to enhance the rates of P to the proper level. At the same time, use other protective management, such as the split of fertilizer rates, reducing the chance of transferring P to water resources.

We based the P-threshold herein proposed "P-threshold = 20 + clay" on soils with different parent materials and collected in different regions from RS. It takes into account just the content of clay in the soil and, indirectly, the mineralogical composition, disregarding other important properties, such as the ones related to transportation. The addition of other properties that help to better describe the dynamics of P applied to the different types of soil is necessary. Besides, include more soil samples into the model might increase its predictive capacity. However, such a simplified model represents a starting point for the management in the application of P to the soil, serving as a tool for environmental agencies and other sectors, public or private, which act on the environmental control and inspection.

CONCLUSIONS

The environmental phosphorus threshold established here for soils of Rio Grande do Sul State is equal to: "P-threshold = 20 + clay"; in which P-threshold is the maximum P level of the soil extracted by Mehlich-1 in mg dm^{-3}, and "clay" is the clay content determined through the pipette or densimeter method, in %.

The levels of phosphorus considered adequate to obtain the maximum economic return in agricultural systems such as grains, pastures, and forest crops productions are below the P-threshold, regardless of the type of soil.

The high demands for phosphorus in fast cycle cultivation systems, such as vegetables, can lead to a risk of loss to the environment. In these cases, the P-threshold could be equal to the critical levels of the crops, associated with soil conservation practices.

A phosphorus environmental threshold based on the clay content of the soil proves worthwhile. However, the evaluation of more soil types and other variables controlling phosphorus transfer to the environment is a step forward to improve the model.

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AUTHOR CONTRIBUTIONS

Conceptualization: Luciano Colpo Gatiboni (lead), Thomas Jot Smyth (lead), and Djalma Eugenio Schmitt (supporting).

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

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

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

Resources: Luciano Colpo Gatiboni (equal) and Rodrigo da Silveira Nicoloso (equal).

Data curation: Luciano Colpo Gatiboni (equal), Gilmar Luiz Mumbach (equal), and Abelino Anacleto de Souza Junior (supporting).

Writing - original draft: Gilmar Luiz Mumbach (lead), Luciano Colpo Gatiboni (supporting), Rodrigo da Silveira Nicoloso (supporting), Abelino Anacleto de Souza Junior (supporting), Daniel João Dall'Orsoletta (supporting), and Djalma Eugenio Schmitt (supporting).

Writing - review and editing: Gilmar Luiz Mumbach (equal), Luciano Colpo Gatiboni (equal), Rodrigo da Silveira Nicoloso (equal), Abelino Anacleto de Souza Junior (equal), Daniel João Dall'Orsoletta (equal), and Djalma Eugenio Schmitt (equal).

Visualization: Gilmar Luiz Mumbach (lead).

Supervision: Thomas Jot Smyth (supporting).

Project administration: Luciano Colpo Gatiboni (lead) and Rodrigo da Silveira Nicoloso (supporting).

Funding acquisition: Luciano Colpo Gatiboni (equal) and Rodrigo da Silveira Nicoloso (equal).

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