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## Elemental sulfur recommendation for pH reduction in soils from Southern Brazil<sup>1</sup>

## Recomendação de enxofre elementar para a redução do pH de solos do sul do Brasil

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#### HIGHLIGHTS:

Elemental sulfur application is an option to decrease the pH of southern Brazilian soils. The soil oxidative potential of elemental sulfur can be estimated by its magnesium concentration, acidity, and base saturation. Decrease the soil pH by one unity required the oxidation of 25 mg of elemental sulfur by kilogram of soil.

**ABSTRACT:** The elemental sulfur (S<sup>0</sup>) application may reduce soil pH, benefiting plants adapted to acid conditions and lessening problems of overliming. Nevertheless, there is no official recommendation for its application. The objective of the study was to quantify the So doses required to reduce the pH of soils from Southern Brazil. The experiment was carried out in the laboratory in a factorial scheme (5  $\times$  5), with a completely randomized design and three replicates. The treatments consisted of five soils, and five doses of So, corresponding to 0, 50, 100, 150, and 200% of the estimated dose need to reach pH 4.0. The applied doses of So resulted in reduction of pH and base saturation (V%) and increase of potential acidity (H + Al). These effects, however, were reduced due to the low rate of oxidation of the S<sup>0</sup> applied (0.76-3.36%). The soil variables correlated with S<sup>0</sup> oxidation were Mg<sup>2+</sup> (0.86\*\*\*), Al<sup>3+</sup> (-0.82\*\*\*), H + Al (-0.89\*\*\*), V% (0.68\*\*\*) and aluminum saturation (m%) (-0.87\*\*\*). In the evaluated soils the oxidation of 50 kg ha<sup>-1</sup> of S<sup>0</sup> was required to reduce one unit of pH in H<sub>2</sub>O.

Key words: sulfur oxidation, sulfate, acidity, overliming

RESUMO: A aplicação de enxofre elementar pode reduzir o pH do solo, beneficiando as plantas adaptadas às condições ácidas e diminuindo os problemas de supercalagem. No entanto, não há recomendação oficial para sua aplicação. O objetivo deste estudo foi quantificar doses de S<sup>0</sup> necessárias para a redução do pH de solos do Sul do Brasil. O experimento foi conduzido em laboratório em um esquema fatorial (5 x 5), com delineamento inteiramente casualizado e três repetições. Os tratamentos foram constituídos por cinco solos e cinco doses de So, correspondente a 0, 50, 100, 150 e 200% da necessidade estimada para atingir pH 4,0. A aplicação de So resultou na redução do pH e da saturação por bases (V%) e no aumento da acidez potencial (H + Al) esses efeitos, contudo, foram reduzidos em função da baixa taxa de oxidação do Sº aplicado (0,76-3,36%). As variáveis de solo correlacionadas com a oxidação  $de S^{0} foram Mg^{2+}(0.86^{***}), Al^{3+}(-0.82^{***}), H+Al(-0.89^{***}), V\%(0.68^{**}) e saturação por alumínio (m\%)(-0.87^{***}).$ Nos solos estudados é necessária a oxidação de 50 kg ha-1 de So para redução de uma unidade de pH em H<sub>2</sub>O.

Palavras-chave: oxidação de enxofre, sulfato, acidez, supercalagem



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#### Introduction

Some plants of agronomic interest are adapted or benefited from high acidic conditions of the soil. Among those are the blueberry (*Vaccinium myrtillus*), yerba mate (*Ilex paraguariensis*), and black-tea (*Camellia sinensis*). Reducing soil pH for the cultivation of these species may be a recommended practice.

One of the main alternatives for soil acidification is the application of elemental sulfur (S<sup>0</sup>) (Pourbabaee et al., 2020). The oxidation of S<sup>0</sup> reduce the soil pH, in a reaction derived by microbial activity. Several organisms may oxidize S<sup>0</sup> (Lucheta & Lambais, 2012; Zhao et al., 2017), as *Acidithiobacillus* (Malhotra et al., 2002; Mousavi et al., 2006; Tourna et al., 2014; Vitti et al., 2015), *Penicillium* and *Aspergillus* (Li et al., 2010). Their population and activity dynamics are strongly influenced by soil factors, consequently impacting the oxidation of S<sup>0</sup> (Horowitz & Meurer, 2006, 2007; Vitti et al., 2015).

Besides that, in the no-tillage system, in which liming is not incorporated, soil correction is restricted to the surface layers, potentially resulting in the "overliming" effect (Rheinheimer et al., 2018). Therefore, in addition to unnecessary expenses, chemical imbalance detrimental to plant development might occur, as low availability of cationic micronutrients (Saha et al., 2019), ammonia volatilization (Rauber et al., 2017), and formation of calcium phosphate precipitates (Penn & Camberato, 2019).

Although the mechanisms involved in the S<sup>0</sup> oxidation is known, there are no recommendations regarding the amount that needs to be applied to obtain the predetermined pH values. Thus, the objective of the study was to quantify the S<sup>0</sup> doses required to reduce the pH of soils from Southern Brazil.

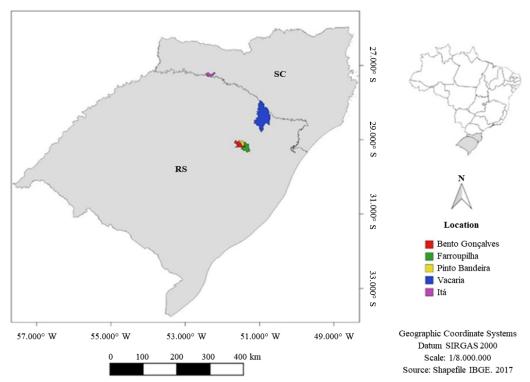
#### MATERIAL AND METHODS

Soil samples were collected from the 0.00-0.20 m layer in five sites, at regions that represent the area of expansion of the blueberry crop over previously limed commercial orchards and crops in southern Brazil (Figure 1). The soil samples collected corresponded to three Ultisols (Bento Gonçalves - RS, Farroupilha - RS and Pinto Bandeira - RS), one Oxisol (Vacaria -RS) and one Inceptisol (Itá - SC), according to Soil Survey Staff (2014).

After being collected, soil samples were dried in an oven with forced circulation of air at 65 °C and then sieved in 2 mm mesh. Subsequently, their chemical attributes were characterized according to the methodologies proposed by Tedesco et al. (1995). The soils of Bento Gonçalves and Vacaria, which presented the lowest pH values, were incubated with doses of limestone to raise the pH to 6.0, as recommended by the CQFS RS/SC (2016). The soils chemical characteristics after pH corrections, if needed, are presented in Table 1.

The experimental design was completely randomized with three repetitions, with the treatments disposed in a  $5 \times 5$  factorial arrangement, being five soils and five doses of  $S^0$ , corresponding to 0, 50, 100, 150, and 200% of the estimated dose need to reach pH 4.0.

The need for  $S^0$  was calculated by estimating the amount of lime to be neutralized in the soil in order to reach the desired pH, and this in turn was estimated by base saturation. In subtropical soils, base saturation of 20% corresponds to pH in  $H_2O$  4.0 (Predebon et al., 2018), a value used as a reference in Eq. 1, which calculates the need for limestone (CQFS RS/SC, 2016).



**Figure 1.** Geographic location of the municipalities in the southern region of Brazil with expansion of the blueberry cultivation area, where soil samples were collected

**Table 1.** Chemical characterization of the 0.00-0.20 m layer of the subtropical soils used in the study

Soil	pН	Al <sup>3+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	H +AI	CEC	<b>T</b> (1)	BS <sup>(2)</sup>	m <sup>(3)</sup>	P	S-SO <sub>4</sub> -	S.O.M. <sup>(4)</sup>	Clay
3011	1	(cmol <sub>c</sub> kg <sup>-1</sup> )					107	(%)		(mg kg <sup>-1</sup> )		(g kg <sup>-1</sup> )		
Farropilha	6.3	0.0	0.4	8.3	3.3	2.1	14.1	42.0	85.0	0.3	47.4	3.1	25	180
Itá	5.9	0.1	0.2	6.9	3.2	3.7	14.1	7.1	73.6	0.7	3.3	9.6	40	510
Pinto Bandeira	6.7	0.1	2.3	9.6	3.4	2.3	17.5	17.6	87.1	0.5	173.1	11.0	36	460
Bento Gonçalves	6.3	0.0	0.3	6.6	6.4	1.9	15.2	18.4	87.3	0.2	9.7	13.6	25	470
Vacaria	6.3	0.1	0.3	7.6	6.3	1.5	15.7	26.2	90.2	0.3	52.2	28.2	42	180

<sup>(1)</sup>T - Clay activity corrected for carbon concentration; (2)BS - Percentual of base saturation; (3)m - Percentual of aluminum saturation; (4)S.O.M. - Soil organic matter

$$LR = \left\lceil \frac{\left(V1 - V2\right)}{100} \right\rceil EC_{pH7.0} \tag{1}$$

where:

LR - limestone requirement in Mg ha<sup>-1</sup>;

V1 and V2 - the desired and initial base saturation values, respectively, in percent; and,

EC pH 7.0 - soil cations exchange capacity estimated at pH 7.0 in cmolc  $kg^{-1}$ .

The negative results obtained by Eq. 1 represent the amount of limestone to be neutralized in the soil in order to reach the desired pH.

Based on the reactions presented in Eqs. 2 and 3, it is possible to observe that there is a need for oxidation of one mol of S<sup>0</sup> to neutralize one mol of CaCO<sub>3</sub>, that is, for the neutralization of 1000 kg of CaCO<sub>3</sub> are theoretically required the oxidation of 321 kg of S<sup>0</sup>.

$$S^{0} + l_{2}^{1}O_{2} + H_{2}O \rightarrow 2H^{+} + SO_{4}^{-}$$
 (2)

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + 2OH^- + CO_2$$
 (3)

Based on the above assumptions, the S<sup>0</sup> doses applied to each treatment were calculated, as detailed in Table 2.

Each experimental unit consisted of 2 L plastic bag containing 250 g of soil. After the application of the treatments, the soil packages were closed, sealing the air inside. The soil was incubated for 90 days at room temperature (25 °C  $\pm$  5) and 80% moisture of the field capacity. The moisture was

**Table 2.** Elemental sulfur doses applied to the five soils from Southern Brazil used in the study, as a function of the percentage empirically estimated to reach pH 4.0

Soil	0	50	100	150	200			
3011	%							
	S applied (g kg <sup>-1</sup> )							
Bento Gonçalves	0.00	1.52	3.04	4.56	6.07			
Vacaria	0.00	1.52	3.04	4.56	6.07			
Itá	0.00	0.94	1.87	2.80	3.74			
Farroupilha	0.00	1.26	2.50	3.77	5.02			
Pinto Bandeira	0.00	1.61	3.22	4.83	6.44			

corrected in periods no longer than three days by weighing, with the packages being opened and the soil homogenized, allowing gas exchange with the external environment. After the incubation period, the soil was again dried in an oven with forced circulation of air at 65 °C, sieved in a 2 mm mesh, and characterized regarding its chemical attributes, according to the methodologies proposed by Tedesco et al. (1995).

The obtained data were checked regarding the assumptions of normality and homoscedasticity by the Shapiro Wilk and Levene tests. Once these assumptions were met, the data were submitted to the analysis of variance and regression for doses, or Tukey test for the soils. Additionally, linear correlations were performed by the Spearman test between the oxidation potential of  $S^0$  and the chemical attributes of the soil. In order to predict the oxidation potential of the soils studied, a multiple linear regression model with the backward stepwise method was used between the significantly correlated variables, treated as independent, and the oxidation potential of  $S^0$ , a dependent variable. In addition, the variation of pH data as a function of  $S^0$  oxidation was submitted to simple linear regression analysis. For all tests  $p \le 0.05$  was assumed using the SigmaPlot12.5 software.

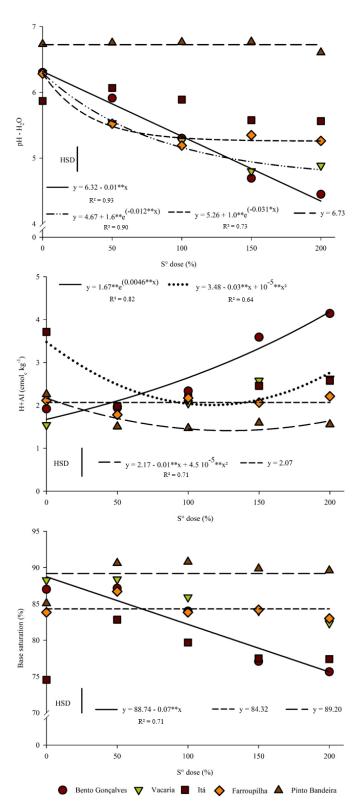
### RESULTS AND DISCUSSION

There was significant effect of the interaction between  $S^0$  doses and soils, for all the variables tested (Table 3). The soil of Bento Gonçalves presented the highest reduction in pH, in the order of 0.01 units per percentage of  $S^0$  applied, which corresponded to 0.03 g kg<sup>-1</sup> of  $S^0$  for this soil (Figure 2A). The soils of Vacaria and Farroupilha presented exponential decay of pH with the increase of the  $S^0$  dose. This reduction was more expressive with the lower dose and later there was a tendency to stabilize at low values. For the Itá soil there was an opposite effect, with small increase in pH caused by the lowest dose and gradual reduction with the others, however, no proper adjustment was possible ( $y = 5.93 + 10^{-4}x - 1.61^{-5**}x^2$ ;  $R^2 = 0.52$ ). The Pinto Bandeira soil has not presented significant pH change according to the  $S^0$  doses.

The application of  $S^0$  proved to be effective in modifying the potential acidity, with different behavior in the soils tested (Figure 2B). Related to the pH result, the Bento Gonçalves soil presented the highest increase of H + Al, varying from 1.67

Table 3. Summary of the analysis of variance and error probability (p-valor) by the F test to the variables evaluated

Source	Degree	Variable evaluated							
of variation	of freedom	pH	V%	H + Al	S-SO <sub>4</sub> -2	S-Oxidized			
Soil	4	p ≤ 0.001	p ≤ 0.001	p ≤ 0.001	p ≤ 0.001	p ≤ 0.001			
Dose of S <sup>0</sup>	4	$p \le 0.001$	$p \le 0.001$	$p \le 0.001$	$p \le 0.001$	$p \le 0.001$			
Soil x Dose of So	16	$p \le 0.001$	$p \le 0.001$	$p \le 0.001$	$p \le 0.001$	$p \le 0.001$			
Error	50	-	-	-	-	-			
CV%		2.7	1.7	12.5	12.7	13.8			



\*\*Significant at  $p \le 0.01$  by t test; HSD: Tukey honestly significant difference at  $p \le 0.05$  **Figure 2.** Water pH (A), H + Al (B), and base saturation (C) in function of  $S^0$  doses in five soils from Southern Brazil

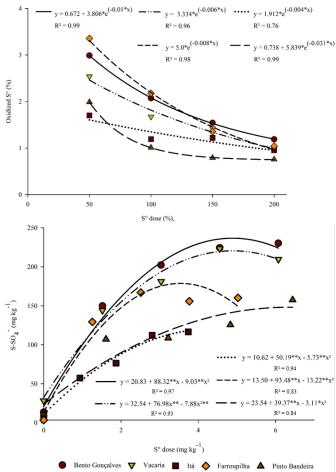
to 4.19 cmolc kg¹ between the lowest and highest S⁰ dose, respectively. For the Vacaria soil, the H + Al increase behaved in a similar way, but in a lower magnitude, however, no proper adjustment was possible (y =  $1.52 + 5.7 \ 10^{-3**}$ x; R²: 0.56). The Itá and Pinto Bandeira soils presented a similar behavior, with reduction of H + Al with the lowest S⁰ dose and gradual increase with the other ones. For the Farroupilha soil there was no effect of the doses upon this variable.

The interaction of processes acting in opposite directions may explain the heterogeneous response of the Itá and Pinto Bandeira soils, regarding the change in pH and H + Al as a function of the S<sup>0</sup> dose. An explanation for the initial increase of soil pH values may be due to the S<sup>0</sup> reaction that produces thiosulfate which, when reacting with H+, forms sulfites, raising the pH (Germida & Jansen, 1993). This reaction, however, is followed by the formation of sulfuric acid and its dissolution in SO<sub>4</sub><sup>2-</sup> and 2H<sup>+</sup>, reducing the soil pH to values below the early ones. Additionally, the specific adsorption of SO<sub>4</sub><sup>2-</sup> to oxides present in the soil culminates with the consumption of H<sup>+</sup> in solution, resulting in an increase in the pH of the medium (Kitadai et al., 2018). This process is favored in clay soils with low activity (Kitadai et al., 2018), as in the case of the Itá soil, the most clayey one and with less clay activity among the evaluated soils, and the Pinto Bandeira soil, which presents the second lowest clay activity (Table 1).

The V% of the Bento Gonçalves soil decreased linearly with the increase of the  $S^0$  dose, at 0.07 percentage points per percentage unit of  $S^0$  (Figure 2C). The V% reduction as a function of  $S^0$  doses was less expressive in the Vacaria soils, and zero for the Pinto Bandeira and Farroupilha soils. Emphasis may be placed on the behavior observed in the Itá soil which, similarly to what is observed for the pH in  $H_2O$  and H+Al, presented a quadratic effect as a function of the  $S^0$  doses: while the lowest dose increases V%, the higher doses decrease its value. The increase in a soil pH, resulting from the addition of limestone, is followed by increase in base saturation (Predebon et al., 2018) and, conversely, the reduction in base saturation is one of the factors related to soil acidification.

In this context, the non-removal of bases, since it is an incubation study in a system without free drainage, might have contributed to a low pH reduction and base saturation of the soils. A secondary effect observed by the application of S<sup>0</sup> is the increase of electrical conductivity (Boaro et al., 2014). This increase is the result of the release of exchangeable cations into the soil solution, due to the increase of H<sup>+</sup> ions in the exchange complex. The non-leaching of these elements may result in their accumulation in the soil, leading to toxic effects to the microorganisms involved in the S<sup>0</sup> oxidation, impairing the maintenance of the process. This effect will be more expressive according to the increase of the S<sup>0</sup> dose (Horowitz & Meurer, 2006).

The application of  $S^0$  is an effective practice for reducing soil pH and modifying other acidity variables, such as H + Al and V% for most soils evaluated and is a potential source of S for plants (Lucheta & Lambais, 2012), by increasing the sulfate concentration ( $SO_4^{2-}$ ) available in the soil (Figure 3B) (Pias et al., 2019; Pourbabaee et al., 2020). The efficiency of  $S^0$  as a soil acidifier and source of S to plants is, however, dependent on its oxidation rate to  $SO_4^{2-}$ . As observed in Figure 3A, the percentage of  $S^0$  oxidized, in comparison to the total applied, varied between 0.75 and 3.35%. Similar to this, the  $SO_4^{2-}$  concentrations presented decreasing increments with increasing doses applied  $S^0$  (Figure 3B). These results indicate the occurrence of limiting factors to the oxidation of  $S^0$ , which will be further discussed.



\*Significant at  $p \le 0.05$  by t test; \*\*Significant at  $p \le 0.01$  by t test; HSD - Tukey honestly significant difference at  $p \le 0.05$ ; Note that the scales are different

**Figure 3.** Percentage of S<sup>0</sup> oxidized to the sulfate form (A) and concentration of sulfate in the soil (B), in function of S<sup>0</sup> doses in five soils from Southern Brazil

Aerobic soil microorganisms, especially of the genus *Acidithiobacillus*, are responsible for the oxidation of S<sup>0</sup> (Li et al., 2010; Tourna et al., 2014; Pourbabaee et al., 2020; Kulczycki, 2021). These, in turn, are influenced by soil chemical variables, such as initial soil pH, organic matter concentration and adequate nutrient availability (Horowitz & Meurer, 2006; Zhao et al., 2017), associated with physical variables such as particle size, temperature, moisture, and aeration (Germida & Janzen, 1993).

In this study, there was no significant correlation between S<sup>0</sup> oxidation and soil initial pH, probably due to the very close pH values of the soil group studied, ranging from 5.9 to 6.7. According to Horowitz & Meurer (2007), the oxidation rate of elemental S itself is not correlated with pH values, but with the presence or absence of exchangeable Al. The presence of this element may directly impair the oxidation of the elemental S by reducing the microbial activity due to its bacteriostatic effects (Horowitz & Meurer, 2007; Herisson et al., 2014). This factor is corroborated in this study since there was a negative correlation between the potential for S<sup>0</sup> oxidation and the content of exchangeable Al (-0.82\*\*\*).

In general, pH may have an ambiguous effect on the  $S^0$  oxidation, favoring the process in low pH conditions, due to the preference of the major microorganisms involved (Malhotra et al., 2002; Mousavi et al., 2006; Tourna et al., 2014; Zhao et al.,

2017), or disfavoring it, due to the presence of Al (Horowitz & Meurer, 2007; Herisson et al., 2014). Kulczycki (2021) studying the effect of S<sup>0</sup> doses over various types of soils, concluded that lowering soil pH impairs its oxidation rate.

Additionally, the high pH may favor the S<sup>0</sup> oxidation process by consuming the excess of sulfuric acid formed in the reaction, which is detrimental to the continuation of the process (Germida & Janzen, 1993) or by favoring other groups of microorganisms, other than *Acidithiobacillus*, capable of oxidizing S<sup>0</sup> (Zhao et al., 2017). However, the Pinto Bandeira soil, which presented the highest initial pH value among the soils evaluated, 6.7, was also the one with the lowest effect as a function of the S<sup>0</sup> doses, for all the variables assessed.

Besides the initial pH, soil organic matter has been pointed out as an important conditioning factor of the S<sup>0</sup> oxidation (Horowitz & Meurer, 2007; Zhao et al., 2017), due to the dependence of microorganisms on the energy contained in organic compounds (Di Lonardo et al., 2019). In this study, however, there was no correlation between organic matter concentration and S<sup>0</sup> oxidation, possibly due to the organic matter concentration, higher than 25 g kg<sup>-1</sup> not being limited to microbial development. Studies that reveal a relationship between organic matter and S<sup>0</sup> oxidation (Horowitz & Meurer, 2007; Zhao et al., 2017) present lower organic matter values, possibly limiting microbial development.

The SO<sub>4</sub><sup>2-</sup> concentration present in the soil may interfere with the S<sup>0</sup> oxidation. Under high concentration, the SO<sub>4</sub><sup>2</sup>content may limit S<sup>0</sup> oxidation, since it is one of the products of this reaction (Horowitz & Meurer, 2007) and because it has an inhibitory effect on microbial activity (Souza et al., 2015; Garg et al., 2019). This effect might be minimized with the vertical displacement of part of the oxidized S, favoring the maintenance of the oxidation process (Souza et al., 2015), which does not occur in incubation assays, as in the present study. It should be noted that, except for the Farroupilha soil, all soils presented initial S-SO<sub>4</sub>2- values above 7,5 mg kg<sup>-1</sup>, considered adequate by Pias et al. (2019). With the application of S<sup>0</sup> doses, all soils presented values above 100 mg kg<sup>-1</sup> (Figure 3B), ten folds higher than the critical level for sulfur demanding plants as soybeans, (CQFS RS/SC, 2016) and yerba mate (Ilex paraguariensis) (Schmitt et al., 2018). Besides that, S-SO<sub>4</sub><sup>2-</sup> values above 100 mg kg<sup>-1</sup> are considered inhibitory for some microorganisms (Garg et al., 2019).

The granulometric composition of the soil may also influence the amount of oxidized S<sup>0</sup> (Horowitz & Meurer, 2006). However, there was no correlation between S<sup>0</sup> oxidation and the clay concentration of soils in this study. Most likely, one of the effects of granulometry, besides allowing a larger contact area between S<sup>0</sup> and soil, is in the buffering of soil acidity, generally higher in clay soils (Motta & Melo, 2019). Horowitz & Meurer (2006), comparing the effect of S<sup>0</sup> doses in sandy and clay soils, observed that the highest oxidized content occurred in sandy soils, which is attributed to the higher fertility of this soil, especially higher pH and availability of P. However, in the study of these authors, the sandy soil was also the one with the lowest buffering of acidity. This was similar in this study, in which the soils of Bento Gonçalves and Vacaria, with the highest rates of S<sup>0</sup> oxidation and reduction of pH as a function of the doses of S<sup>0</sup>,

are also the soils with the lowest buffering capacity, expressed by their initial H + Al concentration (Table 1).

As already shown, there are many factors that influence the effectiveness of S<sup>0</sup> as a soil conditioner, largely due to its impacts on the microbial activity involved in its oxidation. Understanding these factors in isolation and their interactions is necessary for an adequate estimate of the S<sup>0</sup> dose required with the aim of reducing the pH in H<sub>2</sub>O of the soil.

Regardless of the soil and dose, it was not possible to reduce the pH to the pre-defined value (4.0). Similarly, base saturation was also reduced below the expect 20% (Figure 2C). These results are directly related to the reduced oxidation rate of the applied  $S^0$ , whose variables involved were discussed previously.

As observed in Figure 3B, which shows the amount of S<sup>0</sup> applied in mg kg<sup>-1</sup> of soil, to practically demonstrate its conversion to sulfate, all the soils tend to present a maximum SO<sub>4</sub><sup>2-</sup> concentration. For the Bento Gonçalves and Vacaria soils, the maximum concentration is 237 and 221 mg kg<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup>, respectively; for the Farroupilha and Pinto Bandeira soils, are 178 and 148 mg kg<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup>, respectively; and for the Itá soil is 121 mg kg<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup>. Based on this it is possible to define, for the set of soils studied, the S<sup>0</sup> oxidation potential. This is represented by the amount of S present in the anion SO<sub>4</sub><sup>2-</sup> and its maximum concentration found for these soils. The oxidation potential of S<sup>0</sup> estimated for these soils, according to the equations of Figure 3B, is 79, 73, 40, 60, and 50 mg kg<sup>-1</sup> for the Bento Gonçalves, Vacaria, Itá, Farroupilha, and Pinto Bandeira soils, respectively.

The chemical characteristics that influenced soil oxidation potential of  $S^0$  were  $Mg^{2+}$  (0.86\*\*\*),  $Al^{3+}$  (-0.82\*\*\*), H + Al (-0.89\*\*\*), V% (0.68\*\*\*), and m% (-0.87\*\*\*). Based on some of these variables, the equation below presents the oxidation potential of the studied soils:

$$\Psi_s = 276.44 + 5.70 \text{Mg} - 25.13 (\text{H} + \text{Al}) - 2.17 \text{V}\%$$
 (4)

where:

Ys - S⁰ oxidation potential of the soil in mg kg⁻¹;

Mg and H + Al - values of exchangeable magnesium and potential acidity, both in  $cmol_c kg^{-1}$ ; and,

V% - base saturation in percentage.

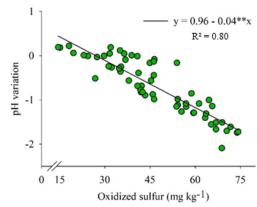
All coefficients of the equation were significant (p  $\leq 0.05)$  and presented  $R^2$  = 0.95.

The relation between the oxidative potential of S<sup>0</sup> and V% and H + Al, as well as to the concentration of exchangeable Al, is known and has been discussed previously. It draws attention, however, to the positive relation between the concentration of exchangeable content of Mg<sup>2+</sup> with the oxidation rate of S<sup>0</sup>. This close relationship may be related to the essentiality of this chemical element in the oxidation process performed by microorganisms. Based on the results of Malhotra et al. (2002) and Mousavi et al. (2006), Mg<sup>2+</sup> is defined as fundamental in the bioxidation of iron sulphate, a process performed by bacteria of the genus *Acidithiobacillus*, which are also involved in the oxidation of S<sup>0</sup> (Germida & Janzen, 1993; Vitti et al., 2015). Studying the factors affecting S<sup>0</sup> oxidation in Brazilian soils, Horowitz & Meurer (2007) found no significant correlation

between the oxidation potential and the exchangeable  $Mg^{2+}$  concentrations. However, the soils grouped as having the highest and lowest oxidation rate by these authors are, respectively, those with the highest and lowest average  $Mg^{2+}$  concentration.

Considering the pH variation observed for the set of evaluated soils, given the difference between the initial and final pH, and the amount of oxidized S<sup>0</sup>, it is possible to establish a linear relationship between these variables (Figure 4). Through this, it is possible to determine that, to reduce the pH in H<sub>2</sub>O in one unit, it is necessary to apply 25 mg kg<sup>-1</sup> of S<sup>0</sup> to the soil. In practical terms and extrapolating the experimental situation tested to field conditions, for the reduction of a pH unit in the arable layer, 0-20 cm deep, it would be necessary to apply 50 kg ha<sup>-1</sup> of S<sup>0</sup>. The success of this practice, however, is conditioned to the oxidation of 100% of the amount of S<sup>0</sup> applied. Corroborating the results of the present study, in a study developed in the United States, on alkaline soils cultivated with blueberry (Vaccinium corymbosum L.), Almutairi et al. (2017) obtained reduction of 0.8 units of pH just one month after the application of 100 kg ha<sup>-1</sup> of S<sup>0</sup>.

Finally, knowing the amount of S<sup>0</sup> required to reduce the pH in one unit and the oxidation potential of the soil, it is possible to estimate in an accurate way the amount of S<sup>0</sup> required to reach the desired pH. Thus, technicians and producers who need to adapt the acidity conditions in areas where overliming has occurred, or even for the conversion of orchards and crops for the cultivation of species benefited by higher soil acidic conditions, gain an important ally with the application of S<sup>0</sup>. However, it is worth to mention the limitations of this work, such as the limited number of soils and the conditions of the incubation environment, such as the absence of drainage. Even so, this preliminary work should be used as a stimulus for future research projects to focus on the understanding of the factors involved in the oxidation of S<sup>0</sup>, and the calibration of this product in more comprehensive conditions, for its use as a soil acidity conditioner.



\*\*Significant at  $p \le 0.01$  by t test

**Figure 4.** Variation of soil pH according to the total amount of oxidized S

#### Conclusions

- 1. The application of elemental S reduces soil pH.
- 2. For the evaluated soils from Southern Brazil, the application of 50 kg of elemental S per hectare is required to reduce one unit of pH in  $\rm H_2O$ , conditioned to the oxidation of all the elemental S applied.

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