

Division - Soil Use and Management | Commission - Lime and Fertilizer

Lime and phosphogypsum application management: changes in soil acidity, sulfur availability and crop yield

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ABSTRACT: Oxisols (*Latossolos*) are widely distributed in tropical zones and generally characterized by high levels of surface and subsurface acidity. In Brazil, most Oxisols are managed under no-till conditions with surface application of acidity amendments. This study aimed to evaluate lime application strategies (incorporated and surface) for achieving the desired soil base saturation (BS%) levels (44, 60, 70, and 90 %) and the effect of phosphogypsum + lime application on soil chemical properties as well as wheat and corn yield in southern Brazil. Lime incorporation was more effective in reducing the soil acidity and increasing Ca²⁺ and Mg²⁺ despite a decrease in organic matter at the soil surface. Phosphogypsum application increased S-SO₄²⁻ and Ca²⁺ availability throughout the deeper soil layers and reduced the Mg²⁺ content in the surface layer. Wheat yield under incorporated lime conditions increased with BS% up to 75, but there was no response to surface application. When phosphogypsum was applied, the wheat yield increased by 8.4 %. For corn, incorporated lime increased the yield up to 445 kg ha⁻¹, which was equivalent to the yield after phosphogypsum application. An increase in the S-SO₄²⁻ level was the main factor related to the increase in crop yields. In the short term, our results suggest that phosphogypsum applied along with lime is more appropriate than incorporating lime under no-till management conditions.

Keywords: base saturation, soil pH, organic matter, Oxisol.



INTRODUCTION

Adoption of no-tillage (NT) management occurred quickly in South America. Countries such as Argentina, Brazil, Paraguay, and Uruguay adopted this management approach over approximately 70 % of the total area (Derpsch et al., 2010) planted with cash crops. Specifically in Brazil, the adoption of the NT approach was encouraged due to the absence of soil disturbance and the positive effects of crop residues on controlling soil erosion and increasing soil organic carbon (SOC), which have contributed to improving soil chemical, physical, and biological properties (Sá and Ferreira, 2018). Currently, Brazil leads the adoption of NT soil management, and in southern Brazil, more than 90 % of cash crop areas are under this management, which promotes higher crop yields (Caires and Guimarães, 2018).

Studies have shown that NT promotes soil chemical property stratification, with high pH and nutrient levels being found in the upper few centimeters of the soil profile (Pauletti and Motta, 2019). However, in the subsurface, the presence of Al^{3+} , determined by the degree of soil weathering (Rabel et al., 2018), causes acidity and restricts root growth and crop access to water and nutrients (Pauletti and Motta, 2019).

Concerns related to soil acidity are well known, and mitigation of its deleterious effects is commonly accomplished by liming. However, with the establishment of the NT approach, surface liming has become widespread. Lime has low solubility, and the products of its reactions have limited mobility in the soil. The action of lime applied at the soil surface without incorporation is slow, making it difficult to reduce the acidity of the subsurface layers of tropical and subtropical soils (Caires et al., 2011; Rheinheimer et al., 2018a).

Currently, there is a lack of understanding about the use of liming application methods for mitigating soil acidity in clayey soils under long-term NT management. The conventional liming application demands complete soil disturbance by tillage at a depth of 0.20-0.25 m, which aims to achieve a better and fast liming reaction in the soil. This method is expensive and does not allow soil quality maintenance because tillage breaks and reduces aggregate soil stability (Amaral and Anghinoni, 2001), decreasing soil water retention (Auler et al., 2017), and other benefits related to the chemical, biological, and hydrological properties enhanced by NT (Derpsch et al., 2010).

Phosphogypsum ($CaSO_4 \cdot nH_2O$) (GY) is a byproduct of the phosphoric acid industry and consists primarily of calcium sulfate; it is widely used for improving soil chemical fertility in many areas worldwide. Phosphogypsum is a neutral salt with higher solubility than lime and has no direct effect on soil pH. However, GY appears to be an alternative for subsurface chemical improvements (deeper than 0.20 m) (Caires et al., 2016). According to Crusciol et al. (2017), GY application promotes decreases in Al saturation and increases in Mg^{2+} , Ca^{2+} , K^+ , $S-SO_4^{2-}$, and BS% in subsurface layers. Additionally, Dalla Nora and Amado (2013) reported improvements in soil chemical quality and in the stability of grain yield due to surface GY application under NT conditions.

There is no scientifically adequate method to determine the appropriate application rates of GY that take into account the different soil environments and cropping systems (Zoca and Penn, 2017). In a systematic review, Tiecher et al. (2018) reported that the critical soil levels (Al saturation >20 % and/or exchangeable Ca <0.5 $cmol_c dm^{-3}$ in the 0.20-0.40 m soil layer) used for GY recommendation in tropical soils are not the same as those observed for subtropical soils under NT in Brazil. They suggest that for grasses on subtropical Oxisols the recommendation criteria based on 10 % saturation of Al [$m\% = Al^{3+} / (Al^{3+} + Ca^{2+} + Mg^{2+} + K^+) \times 100$] and/or 3.0 $cmol_c dm^{-3}$ of Ca^{2+} in the subsurface layer (0.20-0.40 m) are better than the current recommendation based on Al saturation of 20 % and/or 0.5 $cmol_c dm^{-3}$ Ca^{2+} . However, Caires and Guimarães (2018) indicated that the GY recommendation for grain production under continuous NT should be based on the Ca^{2+} saturation in the effective cation exchange capacity

(CEC_e) at 0.20-0.40 m layer. Their method is based on the GY rate required to increase Ca²⁺ saturation up to 60 % in the CEC_e. Nonetheless, GY provides S input in the form of sulfate (S-SO₄²⁻), which is readily taken up by plants. In Brazil, the main factor that governs a crop's response to S fertilization in NT soils is the S-SO₄²⁻ content (Pias et al., 2019), and this nutrient has been neglected in fertilization programs.

Most studies involving lime and GY application have emphasized the initial and residual effects, but there is a scarcity of information on the impact of lime reapplication (Amaral and Anghinoni, 2001) and the combined use of lime and GY (Churka Blum et al., 2013) on soil chemical properties and crop yield. Our hypotheses are as follows: i) in soils with a history of liming, incorporation of lime is more effective for subsurface improvements than NT, but this does not reflect increases in crop yield; ii) in soils under NT management, crops may not respond to the increase in soil BS%; and iii) the yield of corn and wheat increases as sulfur is supplied through GY. This study aimed to evaluate the changes in chemical soil properties as well as wheat and corn yields after reapplication of surface (continuous NT) or incorporated (plow every 4 years) lime doses and surface lime combined with GY in an Oxisol.

MATERIALS AND METHODS

The experiment was set up in 2012 at the Cooperativa Agroindustrial Mourãoense-COAMO experimental farm, located in Campo Mourão County, Paraná State, southern Brazil (24° 05' 28" S, 52° 21' 31" W; altitude, 605 m a.s.l.). According to the Köppen classification system, the climate is Cfa (humid subtropical climate), with an average annual temperature between 20 and 21 °C and annual rainfall ranging from 1600 to 1800 mm. The soil was classified as Oxisol (Soil Survey Staff, 2014) with a very clayey texture (74 % clay), which corresponds to *Latossolo Vermelho distroférico* according to the Brazilian Soil Classification System (Santos et al., 2013). The chemical analyses are presented in table 1.

Prior to the experiment, the area had been managed with NT since 2008 with the following crops: oats (2008), corn (2008/2009), oats (2009), soybean (2009/2010), wheat (2010), soybean (2010/2011), and corn (2011/2012). In May 2012, the experiment was installed with different lime doses, modes of application, and GY doses, as shown in table 2. From 2012 to 2016, soybeans were grown in the summer and wheat was grown in the winter. In June 2016, treatments were reapplied (Table 2), and this study addresses wheat and corn grown immediately after reapplication. The soil properties before lime and GY doses reapplication are shown in table 2. For the reapplication treatment, which aimed to raise BS%, samples were collected in 2016.

The experiment was established with a randomized complete block design using a factorial 2 × 4 with three additional treatments and four replicates. The treatments included two methods of lime application, superficial (SL) and incorporated into the soil (IL), and 4 levels of base saturation (BS%): 44 % (typical of the experimental field),

Table 1. Chemical properties of the Oxisol (*Latossolo Vermelho distroférico*) before the experiment implementation

Layer	pH(CaCl ₂)	H+Al	Ca ²⁺	Mg ²⁺	K ⁺	P	SOC	m	BS
m			cmol _c dm ⁻³			mg dm ⁻³	g dm ⁻³	%	
0.00-0.20	5.25	5.28	3.82	0.81	0.51	20.72	25.05	0	50.00
0.20-0.40	4.96	5.61	2.37	0.54	0.37	6.53	21.51	0	37.05

pH:CaCl₂ (0.01 mol L⁻¹) at a soil:solution rate of 1:2.5; H+Al was extracted using the SMP method; Ca²⁺, Mg²⁺, and Al³⁺ contents were extracted using KCl 1 mol L⁻¹; K and P contents were extracted using Mehlich-1; BS: percent base saturation; m% indicates aluminum saturation; SOC (soil organic carbon) was determined using the Walkey and Black method.

Table 2. Chemical characterization was performed in 2016 (4 years after the 1st lime application) to define the doses reapplied in 2016. Doses of lime were applied in 2012 and 2016 and considered the total rate required to reach the desired base saturation (BS%)

Treatment	Layer	pH (CaCl ₂)	m%	Ca ²⁺	Mg ²⁺	K ⁺	CEC	SO ₄ ²⁻	P	Lime rate	
										2012	2016
	m			cmol _c dm ⁻³				mg dm ⁻³		Mg ha ⁻¹	
IL BS% 44	0.00-0.20	4.97	2.05	2.86	0.58	0.39	9.18	4.87	22.81	-	-
	0.20-0.40	4.75	4.91	2.04	0.39	0.28	8.67	4.95	7.91	-	-
IL BS% 60	0.00-0.20	4.79	4.01	2.73	0.63	0.23	9.14	4.96	23.55	1.5	2.3
	0.20-0.40	4.82	4.04	2.14	0.51	0.20	8.00	4.68	7.14	-	-
IL BS% 70	0.00-0.20	5.08	0.00	3.24	0.88	0.29	9.02	4.95	21.37	2.9	2.3
	0.20-0.40	5.23	0.00	2.78	0.70	0.25	8.17	3.97	10.26	-	-
IL BS% 90	0.00-0.20	5.07	0.00	3.03	0.99	0.30	9.87	4.91	20.88	5.5	5.6
	0.20-0.40	4.84	2.95	2.30	0.74	0.25	8.25	5.39	7.80	-	-
SL BS% 44	0.00-0.20	5.00	0.88	3.52	0.74	0.26	9.67	5.10	21.38	-	-
	0.20-0.40	4.74	6.51	2.12	0.41	0.20	7.88	5.13	5.08	-	-
SL BS% 60	0.00-0.20	5.16	0.00	3.47	0.90	0.26	9.59	5.07	30.06	1.5	1.4
	0.20-0.40	4.92	2.69	2.14	0.56	0.19	7.67	4.53	8.02	-	-
SL BS% 70	0.00-0.20	5.24	0.00	3.11	1.00	0.24	8.63	5.05	13.73	2.9	2.1
	0.20-0.40	5.14	0.00	2.55	0.77	0.22	7.98	4.59	6.12	-	-
SL BS% 90	0.00-0.20	5.41	0.00	3.57	1.46	0.21	9.52	4.79	22.44	5.5	4.1
	0.20-0.40	4.80	4.84	2.04	0.73	0.18	8.10	7.29	8.67	-	-
BS60 + GY50 [†]	0.00-0.20	5.29	0.00	4.11	0.86	0.26	9.51	5.39	23.18	1.5	0.6
	0.20-0.40	4.97	0.97	2.40	0.45	0.20	7.66	5.23	5.68	-	-
BS70 + GY50 [†]	0.00-0.20	5.00	0.75	3.09	0.70	0.19	8.59	4.87	26.74	2.9	2.5
	0.20-0.40	4.60	0.12	1.71	0.34	0.15	7.55	6.40	5.39	-	-
BS70 + GY100 [‡]	0.00-0.20	5.06	0.00	3.16	0.65	0.19	8.96	5.98	34.34	2.9	2.8
	0.20-0.40	4.75	8.21	2.01	0.31	0.14	7.81	5.76	7.14	-	-

[†] and [‡] represent the dose of 3.71 and 7.42 Mg ha⁻¹ phosphogypsum (GY) applied in 2012 and 2016, respectively. The GY rate (GYR) of 3.71 Mg ha⁻¹ was calculated as a function of the clay soil content according to the formula $GYR = 50 \times \text{clay} (\%)$ proposed by Souza et al. (2005). The highest GYR dose was determined by evaluating twice the recommended dose [$GYR = 100 \times \text{clay} (\%)$]. IL: incorporated liming; SL: surface liming; GY: phosphogypsum; m%: aluminum saturation; CEC: cation exchange capacity at pH 7.

60, 70, and 90 %. Three additional treatments involving the use of GY were applied as follows: BS% 60 + 3.71 Mg ha⁻¹ GY (60GY50), BS% 70 + 3.71 Mg ha⁻¹ GY (70GY50), and BS% 70 + 7.42 Mg ha⁻¹ GY (70GY100). The GY rate (GYR) of 3.71 Mg ha⁻¹ was calculated according to the formula $GYR = 50 \times \text{clay} (\%)$ as proposed by Souza et al. (2005). The highest GY dose represents the application two times of the recommended dose [$GYR = 100 \times \text{clay} (\%)$]. In 2012, the BS% in the control was 50 %, and in 2016, after reapplication, the BS was 44 %.

Dolomitic limestone was applied with a relative total neutralizing power (RTNP) of 74 and 80 % in 2012 and 2016, respectively. The limestone applied in 2016 contained 28.60 % CaO and 18 % MgO; and GY contained 26 % Ca. Lime rates (LRs) in both years were based on the increase in the BS (Pauletti and Motta, 2019). To determine the necessity for liming using the proposed method, H+Al, the sum of bases ($SB = Ca^{2+} + Mg^{2+} + K^{+}$), CEC at pH 7 ($CEC = SB + H + Al$), and base saturation ($BS\% = (SB \times 100 / CEC)$) were measured. The LR rates were calculated using equation 1:

$$LR \text{ (Mg ha}^{-1}\text{)} = \frac{[(BS2 - BS1) \times CEC]}{RTNP} \quad \text{Eq. 1}$$

in which BS1 represents the initial base saturation (50 % for 2012 and 44 % for 2016), BS2 is the desired base saturation (60, 70, or 90 %), and RTNP is the relative total neutralizing power of the corrective.

Each experimental unit was 12 m long and 7 m wide, totaling an 84 m² area. Lime incorporation was performed using a two-rod moldboard plow, with an effective incorporation depth of 0.20 m. The soil was leveled by heavy harrowing with 20 discs (Ø 0.71 m) and later by light harrowing with 42 disks (Ø 0.51 m).

The wheat crop was sown on June 14, 2016. The cultivar Tbio Toruk[®] was used at a density of 330 plants m⁻², with 0.17 m between rows. Fertilization was performed with 150 kg ha⁻¹ of 16-7-13 (N-P-K). Nitrogen fertilization with 80 kg ha⁻¹ N in the form of urea (45 % N) was added as the top dressing. The harvest was on October 21, 2016; 29 rows were harvested, totaling 54.23 m², and the grain moisture was adjusted to 13 %.

Corn was sown on October 24, 2016 using the hybrid 30F53-VYHR[®]. Fertilization was performed with 300 kg ha⁻¹ of 12-8-10 (N-P-K). Nitrogen (80 kg ha⁻¹) broadcast fertilization was carried out between the V4-V6 stages, and urea (45 % N) was used as the N source. The harvest was on March 20, 2017. Eight central lines (with a spacing of 0.60 m between lines) and 11-m-long plots were harvested, and grain moisture was adjusted to 13 %.

With the grain yield data from wheat and corn, the relative grain yields were calculated. The yield from each treatment for each crop was divided by the maximum yield obtained. For wheat, the maximum yield was obtained with the 70GY100 treatment, whereas for corn, the maximum yield was obtained with the 60GY50 treatment.

On October 28 and 29, 2016, which corresponded to five months after the lime and GY reapplication, soil sampling was carried out. The sampled profile was stratified into six layers; samples from 0.00-0.05, 0.05-0.10, and 0.10-0.20 m were collected with a shovel, and samples from 0.20-0.30, 0.30-0.40, and 0.40-0.60 m were collected with a Dutch auger. In each experimental unit, two soil samples were taken to obtain a composite sample. The pH was determined in suspensions of CaCl₂ 0.01 mol L⁻¹ (soil/solution 1:2.5 v/v). Exchangeable potassium (K⁺) was extracted with Mehlich-1 solution (H₂SO₄ 0.0125 mol L⁻¹ + HCl 0.05 mol L⁻¹) at a volumetric soil/solution ratio of 1:10 and quantified in a flame photometer. Calcium, Mg²⁺, and Al³⁺ were extracted by using KCl 1 mol L⁻¹ solution (soil/solution 1:10 v/v). Calcium and Mg²⁺ were determined via atomic absorption spectrophotometry (GBC, 932AA) using lanthanum as a suppressor, and Al³⁺ was determined via titration with NaOH 0.0125 mol L⁻¹ solution. The S-SO₄²⁻ extraction was carried out using phosphate ions (P 500 mg L⁻¹) in acetic acid 2.0 mol L⁻¹ (1:2.5 v/v), and subsequent determination was performed using the turbidimetric method (due to the precipitation of S-SO₄²⁻ by barium chloride) and a spectrophotometer (UV-5100 UV/VIS-Metash). The potential acidity (H+Al) was calculated based on SMP. The analysis was performed according to Silva (2009). Aluminum saturation (m%) was calculated as follows: $m(\%) = Al/(ECEC) \times 100$. The soil organic matter (SOM) was determined using a colorimetric method (van Raij et al., 2001), which involves colorimetric determination of the green color of Cr(III) ions reduced by organic carbon (soil:solution 1:10 v/v). The extractive solution was composed of Na₂Cr₂O₇ 0.667 mol L⁻¹ + H₂SO₄ 5 mol L⁻¹.

All variables were tested for the statistical assumptions of data normality (Shapiro-Wilk test) and homogeneity of variance (Bartlett test). The data were subjected to analysis of variance using a Snedecor F test ($p < 0.05$). Regardless of the significance of the F test in the interactions, partitioning was performed. The quantitative factors (levels of base saturation %) were subjected to regression analysis. For lime application methods (surface or incorporated), with only 1 degree of freedom, the F test was conclusive. The comparison between additional treatments (lime + GY) was performed using a Tukey test at 5 % probability. To compare factors 2 × 4 (two lime application methods and four levels of base saturation) with additional treatments, a Dunnett test was used at 5 %

probability. Each soil depth was analyzed individually. Principal component analysis (PCA) was performed with the wheat and corn yields and with the weighted mean of soil property variables for the 0.00-0.20 m and 0.20-0.60 m layers. For this analysis, the data were standardized to mean 0 and variance 1 to eliminate scale effects among variables. The original population ($n = 44$) was reduced to the means ($n = 11$) of replicates of treatments to optimize correlations, therefore increasing the explanation of data variance. Principal components (PCs) that explained a minimum of 80 % of the total variance were selected.

RESULTS

Soil chemical properties

Lime incorporation increased the pH in all layers in the soil profile, while SL application had limited effects down to 0.20 m depth. There were no significant effects of GY on soil pH (Figure 1). When factorial treatments were compared to the additional treatments 60GY50, 70GY50, and 70GY100 showed higher pH values at 0.05 m depth than BS% 44 for SL and BS% 44, 60, and 70 for IL. However, under BS% 90, we detected a higher pH in the SL soil than in the 60GY50 soil (Figure 1a). At the 0.05-0.10, 0.20-0.30, and 0.30-0.40 m layers (Figures 1b, 1d, and 1e), the BS% 90 IL treatment led to significantly higher pH values than the GY treatments. Under the GY treatments, the soil pH was close to the values obtained for BS% 90 SL. The BS% 70 and 90 treatments with IL were more effective for increasing the pH in the 0.10-0.20 m layer than the lime + GY treatments (Figure 1c).

In the surface layer (0.00-0.05 m), Al^{3+} was not detected for any BS% level treatments managed with SL (Figure 2a). On the other hand, IL was more effective for reducing Al^{3+} in the depth from 0.05 to 0.40 m (Figure 2), whereas the SL treatment had limited effect to a depth of 0.10 m (Figure 2b) five months after limestone and GY reapplication. A linear effect of lime dose on Al^{3+} reduction was verified under IL in most layers, except at the 0.00-0.05 and 0.05-0.10 m layers, for which a quadratic model best explained the effect of lime. In addition to pH, there was no effect of GY on Al^{3+} at any depth (Figure 2). Significant differences were observed for the Al^{3+} content only at the 0.05-0.10 and 0.10-0.20 m layers (Figures 2b and 2c). Only the BS% 44 IL was different from GY treatments at 0.05-0.10 m (Figure 2b), and BS% 70 and 90 were more effective for reducing the Al^{3+} content than 60GY50 and 70GY50 (Figure 2c). The highest values of aluminum saturation were observed for the control (BS% 44 SL), reaching 26 and 25 % at the 0.20-0.30 and 0.30-0.40 m layers, respectively, and values were effectively reduced in the IL soil.

Surface liming reduced the potential acidity (H+Al) linearly to a 0.20 m depth, while IL reduced the levels of H+Al in all layers, except at 0.40-0.60 m, with linear models being adjusted (Figure 3). The treatments with GY did not differ in any layer. The comparison between factorial vs. additional treatments showed that at the 0.00-0.05 m layer, the 70GY50 and 70GY100 treatments presented H+Al contents below those in the BS 44, 60, and 70 % in the soil with IL and BS% 44 in the soil with SL (Figure 3a), whereas BS % 90 SL was more effective in reducing potential acidity than 60GY50. At the 0.10-0.20 m layer, BS 70 and 90 % IL were more effective in reducing H+Al than 60GY50 and 70GY50 (Figure 3c). Similarly, in the 0.20-0.30 m soil layer, there was a decrease in potential acidity in BS% 90 soil with IL compared to 60GY50 and 70GY100 soil samples (Figure 3d). No differences were observed at the 0.30 to 0.60 m layers (Figure 3e and 3f).

The Ca^{2+} content increased with soil BS% levels at 0.00-0.05, 0.05-0.10, 0.20-0.30, and 0.30-0.40 m for IL (Figures 4a, 4b, 4d, and 4e) and at 0.00-0.05, 0.05-0.10, and 0.20-0.30 m layers for SL treatments (Figures 4a, 4b, and 4d). At the 0.00-0.05 m layer, the Ca^{2+} levels were higher under SL, whereas for other layers, the levels of Ca^{2+} were higher under IL. There was no difference among GY treatments in Ca^{2+} content (Figure 4). However, changes were observed between the additional vs the main treatments, in which the

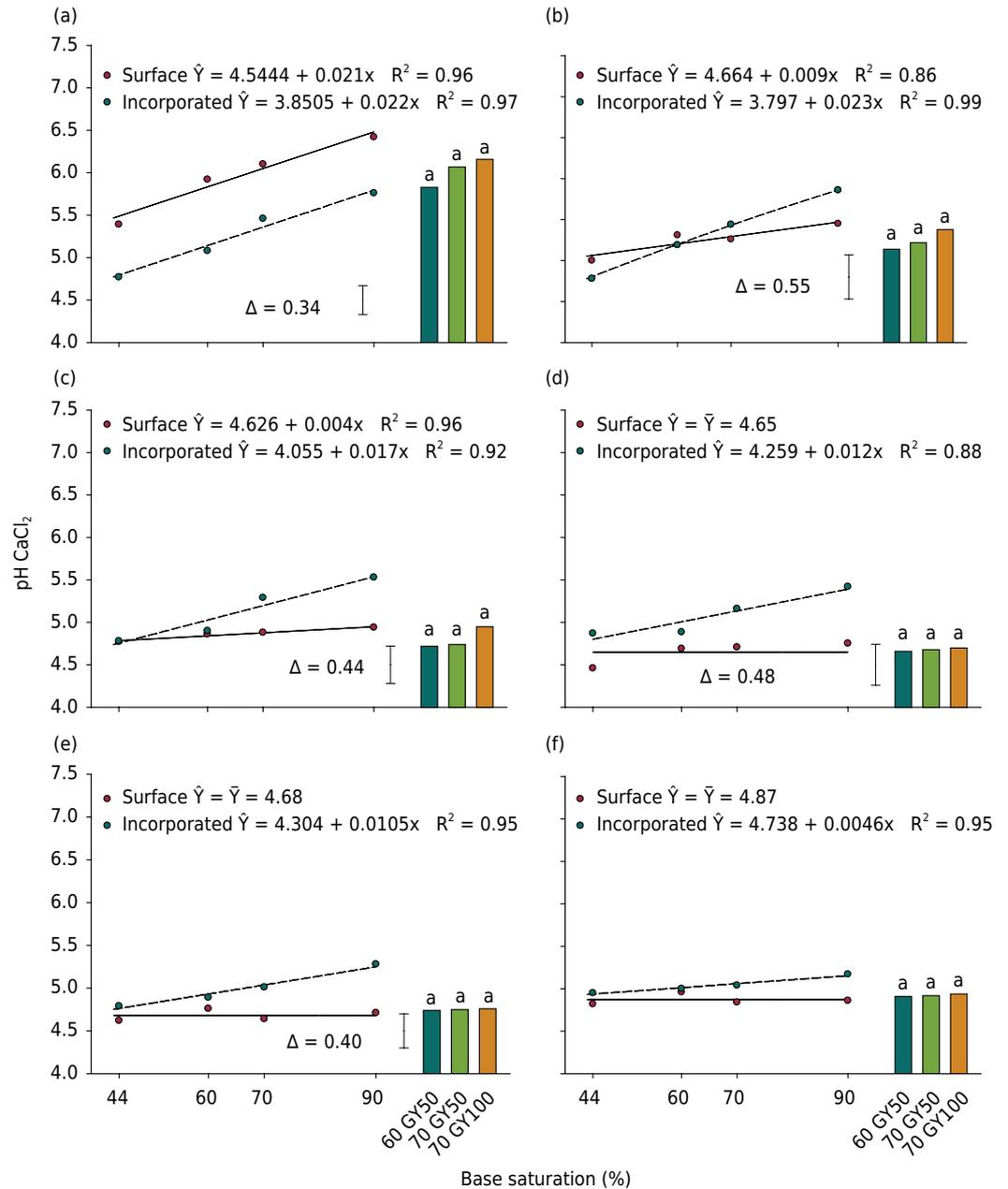


Figure 1. Soil pH after reapplication of lime and phosphogypsum at different layers (m): 0.00-0.05 (a), 0.05-0.10 (b), 0.10-0.20 (c), 0.20-0.30 (d), 0.30-0.40 (e), and 0.40-0.60 (f). Different letters above the bars indicate a significant difference between the treatments with phosphogypsum based on Tukey's test ($p < 0.05$). The vertical bar indicates the DMS between each factorial vs additional treatment based on a Dunnett test ($p < 0.05$). An F test revealed a significant difference between the modes of lime application to the layers presented in figures 1a ($p < 0.00$), 1b ($p < 0.00$), 1c ($p < 0.02$), and 1d ($p < 0.09$).

treatments with GY showed higher Ca^{2+} content than IL treatments at the 0.00-0.05 m layer (Figure 4a). Although IL showed higher levels of Ca^{2+} at the 0.20-0.30 m layer, GY was as effective as IL in increasing the Ca^{2+} content at deeper layers (0.30 to 0.60 m depth) (Figure 4d, 4e, and 4f).

Our results indicate that IL treatment increased the Mg^{2+} content in all layers (Figure 5). The maximum Mg^{2+} values observed were 1.96, 1.86, 1.22, 1.11, 0.89, and 0.59 $\text{cmol}_c \text{dm}^{-3}$ for the 0.00-0.05, 0.05-0.10, 0.10-0.20, 0.20-0.30, 0.30-0.40, and 0.40-0.60 m layers, respectively (Figure 5). Similar to the Ca^{2+} content, the Mg^{2+} content at the 0.05 m depth in soil with SL were higher than those in soil with IL (Figure 5a). Similarly, SL increased the Mg^{2+} linearly down to 0.30 m. The reduction in the Mg^{2+} content at

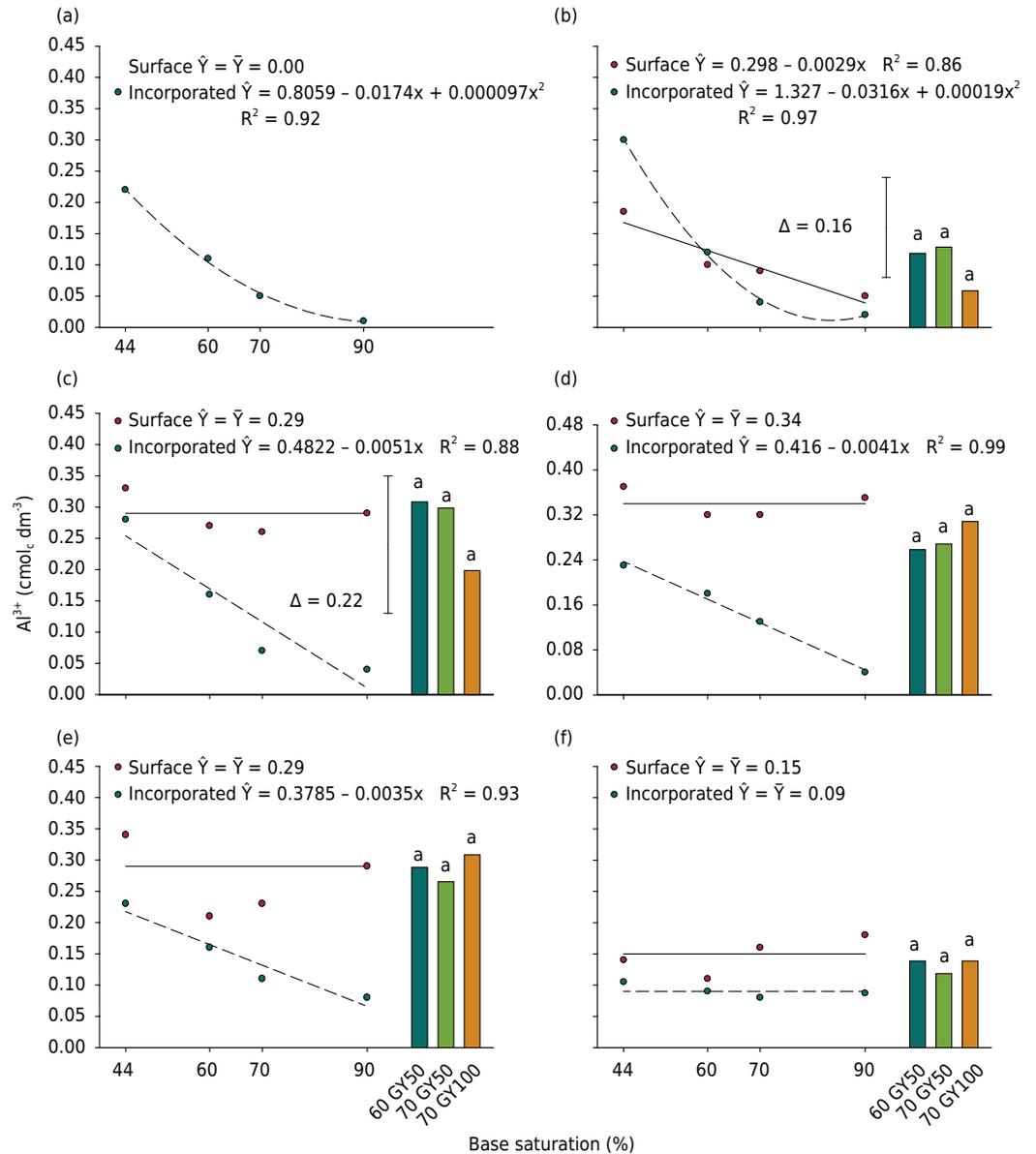


Figure 2. Exchangeable aluminum (Al^{3+}) after reapplication of lime and phosphogypsum at different layers (m): 0.00-0.05 (a), 0.05-0.10 (b), 0.10-0.20 (c), 0.20-0.30 (d), 0.30-0.40 (e), and 0.40-0.60 (f). Different letters above the bars indicate a significant difference between the treatments with phosphogypsum based on Tukey's test ($p < 0.05$). The vertical bar indicates the DMS between each factorial vs additional treatment based on a Dunnett test ($p < 0.05$). An F test revealed a significant difference between the modes of lime application to the layers presented in figures 1a ($p < 0.00$), 1b ($p < 0.00$), 1c ($p < 0.09$), and 1d ($p < 0.10$).

depth was remarkable, as revealed by the angular coefficient of the model fitted to the data (Figure 5). The GY treatments did not differ from each other, but there was a decrease in Mg^{2+} content at the 0.05 m depth when GY was applied (Figure 5). The GY application reduced the Mg^{2+} level at the 0.00-0.5 m layer relative to that in soil subjected to SL treatments and BS% 90 soil with IL, revealing its effects on Mg^{2+} mobility (Figure 5a). At the 0.05-0.10 m layer, the GY treatments led to lower Mg^{2+} levels than BS% 60, 70, and 90 for IL and BS% 90 for SL. Additionally, for BS% 70, the highest dose of GY (70GY100) reduced the Mg^{2+} levels by 0.5 cmol_c dm⁻³ (Figure 5b). In all layers, a notable increase in Mg^{2+} content occurred for BS% 90 IL relative to the treatments with GY (Figure 5).

The levels of $S-SO_4^{2-}$ were not influenced by the BS% treatments with either IL or SL (Figure 6a). Therefore, BS% levels were united to compare only IL and SL treatments.

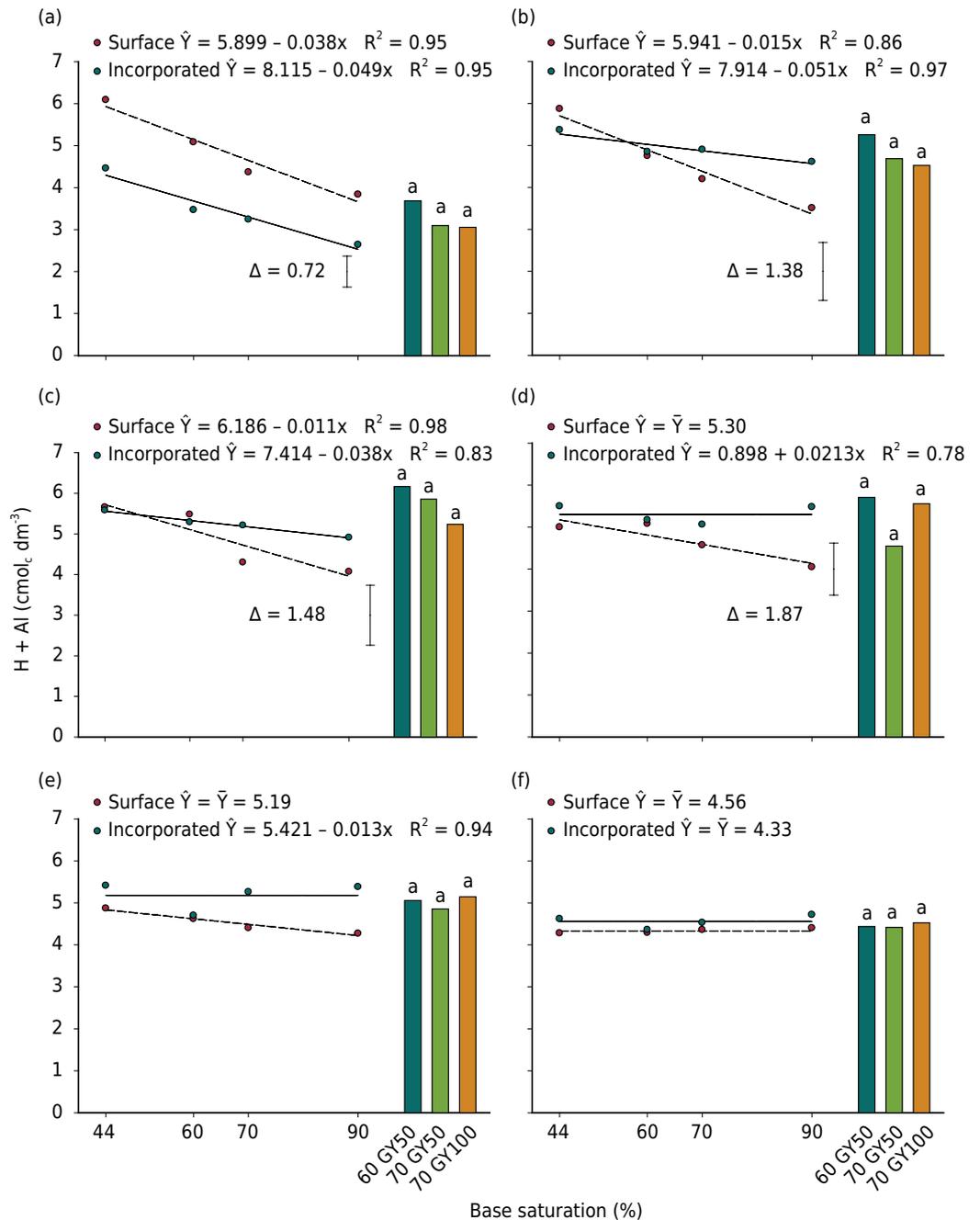


Figure 3. Potential acidity (H+Al) after reapplication of lime and phosphogypsum at different layers (m): 0.00-0.05 (a), 0.05-0.10 (b), 0.10-0.20 (c), 0.20-0.30 (d), 0.30-0.40 (e), and 0.40-0.60 (f). Different letters above the bars indicate a significant difference between the treatments with phosphogypsum based on Tukey's test ($p < 0.05$). The vertical bar indicates the DMS between each factorial vs additional treatment based on a Dunnett test ($p < 0.05$). An F test revealed a significant difference between the modes of lime application to the layers presented in figures 1a ($p < 0.00$), 1b ($p < 0.00$), 1c ($p < 0.04$), 1d ($p < 0.09$), and 1e ($p < 0.08$).

All treatments with GY increased the S-SO_4^{2-} level in all layers. Among the additional treatments, changes in S-SO_4^{2-} were observed in all layers, and a higher S-SO_4^{2-} content was seen under the highest GY rate applied (70GY100), except in the 0.10-0.20 m layer. At the 0.00-0.05 and 0.05-0.10 m layers, the S-SO_4^{2-} content was not different between the 70GY50 and 70GY100 treatments.

The different levels of BS% and GY did not influence the SOM in any layer (Figure 6b). However, IL reduced the SOM content from 56.53 to 39.14 g dm^{-3} at the 0.00-0.05 m

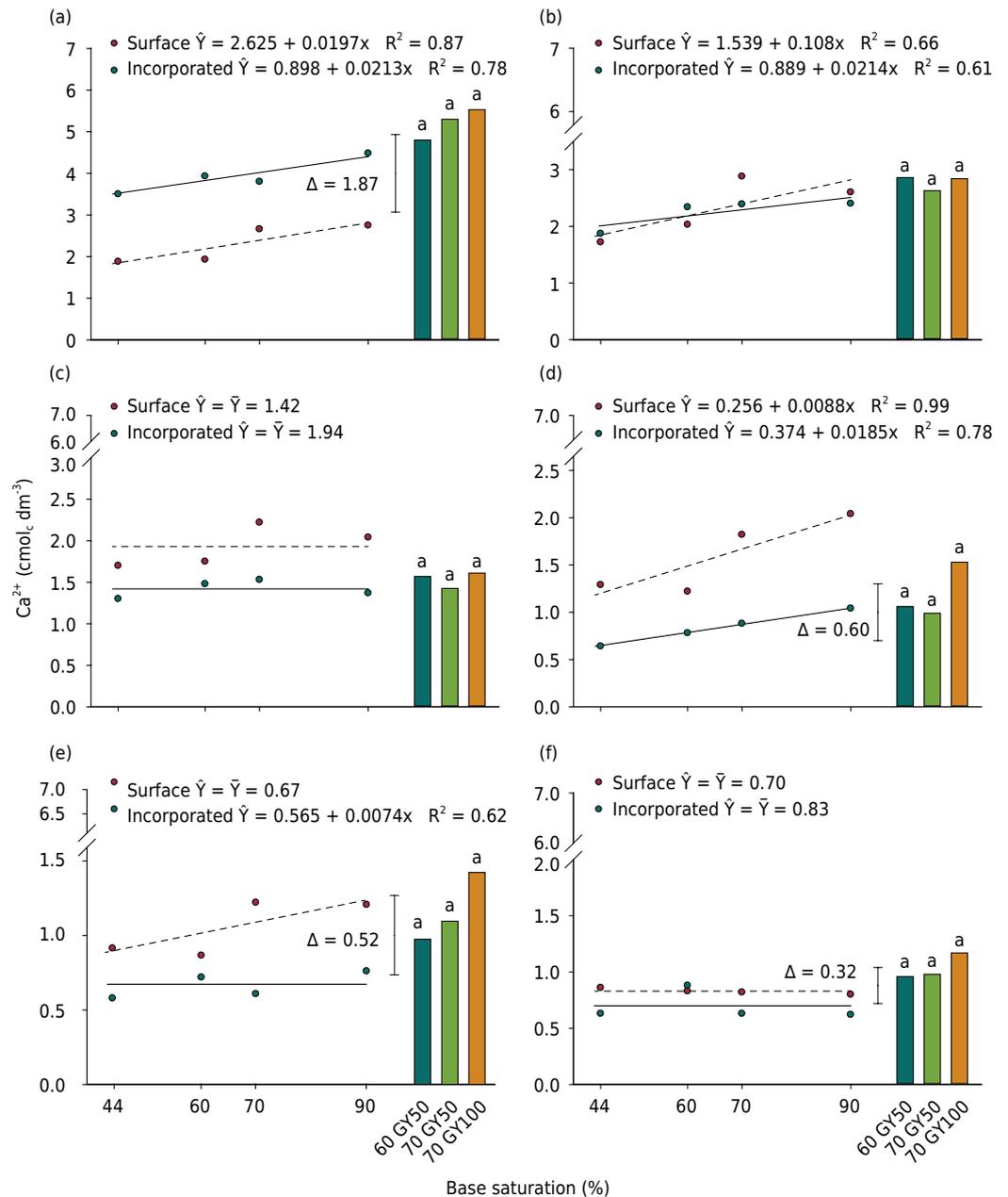


Figure 4. Calcium (Ca^{2+}) content after reapplication of lime and phosphogypsum at different layers (m): 0.00-0.05 (a), 0.05-0.10 (b), 0.10-0.20 (c), 0.20-0.30 (d), 0.30-0.40 (e), and 0.40-0.60 (f). Different letters above the bars indicate a significant difference between the treatments with phosphogypsum based on Tukey's test ($p < 0.05$). The vertical bar indicates the DMS between each factorial vs additional treatment based on a Dunnett test ($p < 0.10$). An F test revealed a significant difference between the modes of lime application to the layers presented in figures 1a ($p < 0.00$), 1c ($p < 0.01$), 1d ($p < 0.00$), 1e ($p < 0.00$), and 1f ($p < 0.03$).

surface layer (Figure 6b) and increased the SOM from 26.13 to 28.78 d dm^{-3} at 0.20 to 0.30 m compared to SL.

Grain yield

Surface lime application did not influence the wheat yield, and the average yield was 5,597 kg ha^{-1} . The maximum wheat yield was obtained with the IL treatment at BS% 75, which was lower than that obtained with SL (Figure 7a). All treatments involving GY increased wheat yield compared to lime application at BS% 44 and 60 under IL. In addition, the yield of the 70GY100 treatment surpassed that of IL BS% 90. Then, GY increased grain yield by 8 % compared to IL treatments.

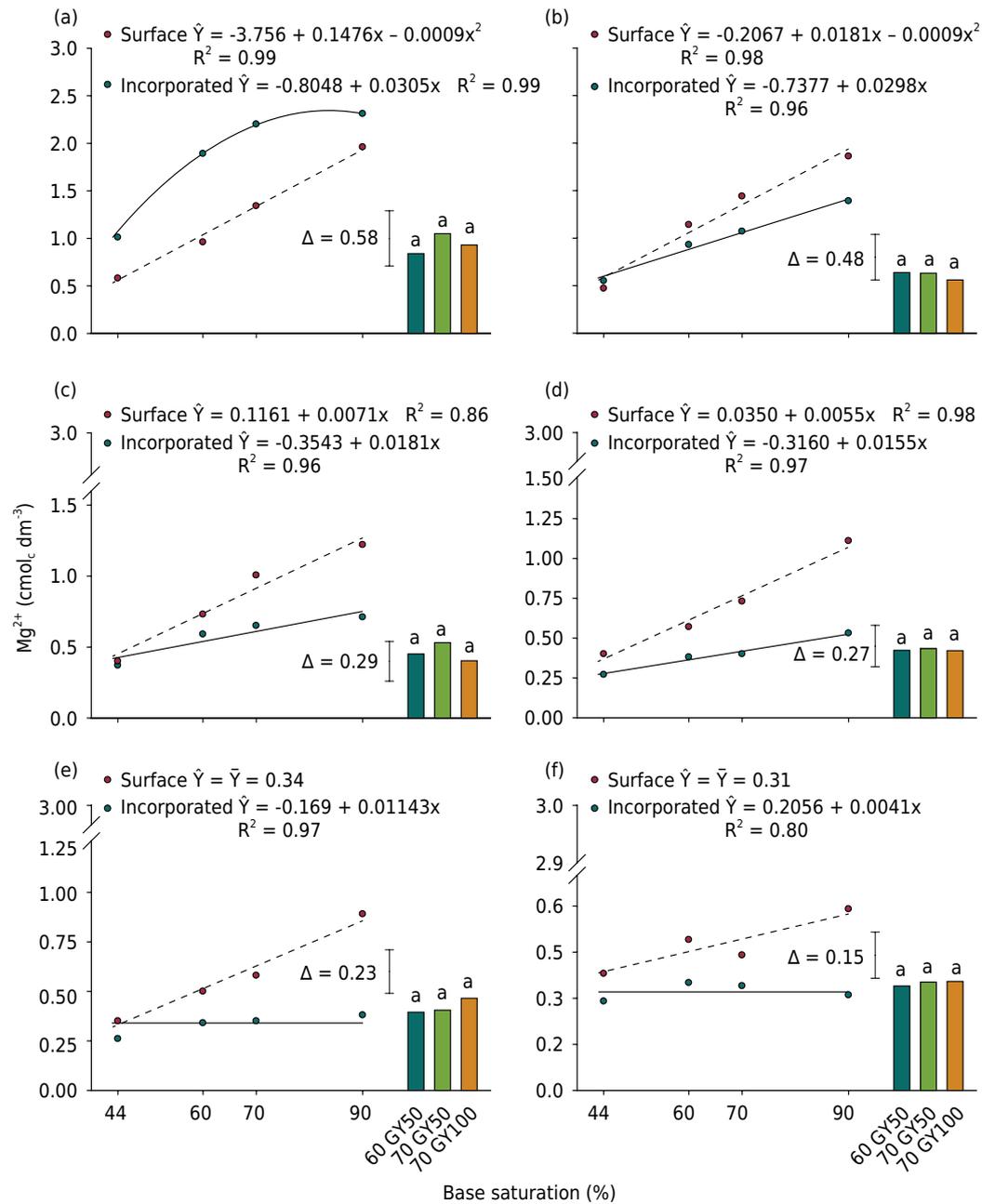


Figure 5. Magnesium (Mg^{2+}) content after reapplication of lime and phosphogypsum at different layers (m): 0.00-0.05 (a), 0.05-0.10 (b), 0.10-0.20 (c), 0.20-0.30 (d), 0.30-0.40 (e), and 0.40-0.60 (f). Different letters above the bars indicate a significant difference between the treatments with phosphogypsum based on Tukey's test ($p < 0.05$). The vertical bar indicates the DMS between each factorial vs additional treatment based on a Dunnett test ($p < 0.05$). An F test revealed a significant difference between the modes of lime application to the layers presented in figures 1a ($p < 0.00$), 1b ($p < 0.03$), 1c ($p < 0.00$), 1d ($p < 0.01$), 1e ($p < 0.00$), and 1f ($p < 0.00$).

The corn grain yield was not affected by liming (Figure 7b). However, comparing the methods of application, IL increased the yield by $445 kg ha^{-1}$ compared to SL. With the 60GY50 treatment, corn yield was greater than that with SL treatment and IL BS% 70. There was no difference among the GY treatments in either crop yield (Figures 7a and 7b).

Multivariate correlations

The PCA among the weighted mean of soil properties at the 0.00-0.20 m layer and crop yields explained 78.52 % of the data variance, in which wheat and corn yields were strongly correlated with $S-SO_4^{2-}$ levels (Figure 8a). Higher yields and $S-SO_4^{2-}$ levels were

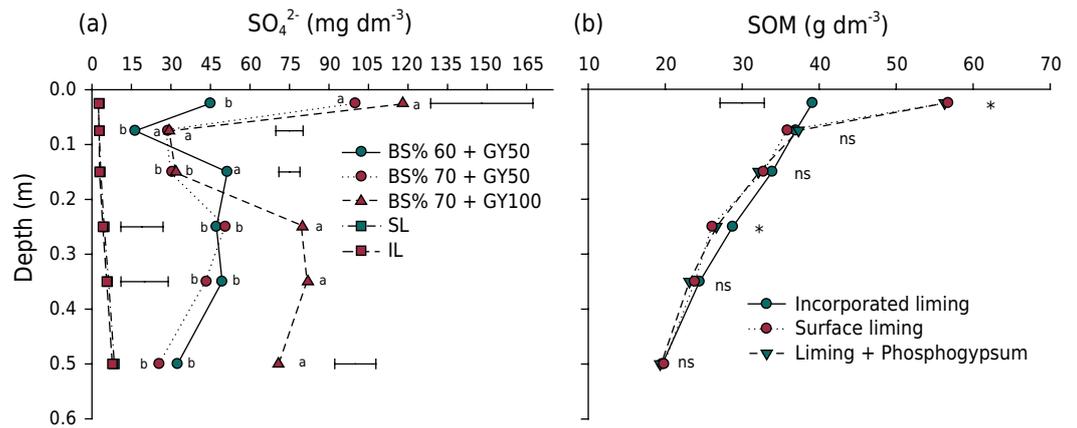


Figure 6. Sulfate content ($S\text{-SO}_4^{2-}$) at different depths (a) after surface and incorporated liming ($n = 16$) and liming + phosphogypsum (4). The horizontal bars indicate the DMS between treatments with phosphogypsum vs lime application determined by a Dunnett test ($p < 0.05$). Different letters at the same depth indicate a significant difference between phosphogypsum treatments based on Tukey's test ($p < 0.05$). Soil organic matter (SOM) content (b) after lime application on the surface, via incorporation, and with phosphogypsum. * and ^{ns} indicate a significant difference and absence of effect at the same depth, respectively, determined by an F test ($p < 0.05$). The horizontal bar indicates the DMS between the mode of limestone application and additional treatments (phosphogypsum + lime) at a depth of 0.00-0.05 m.

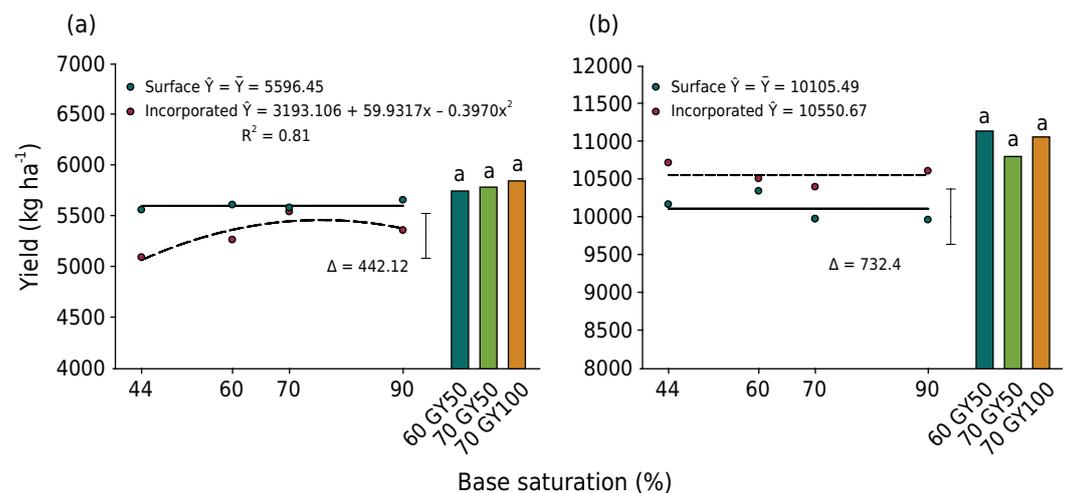


Figure 7. Yield of wheat (a) and corn (b) after reapplication of lime and phosphogypsum. Different letters above the bars indicate a significant difference between the treatments with phosphogypsum based on Tukey's test ($p < 0.05$). The vertical bar indicates the DMS between each factorial vs additional treatment determined by a Dunnett test ($p < 0.05$). An F test revealed a significant difference between the modes of lime application in wheat ($p < 0.00$) and corn yield ($p < 0.00$).

associated with GY treatments, regardless of the BS level. Additionally, the wheat yield was related to Ca levels in soil and a lower extent to SOM (Figure 8a). In this layer, the GY treatments and $S\text{-SO}_4^{2-}$ were negatively related to the Mg levels in the soil. The PCA for the 0.20-0.60 m layer explained 82 % of the data variance and showed a higher correlation of crop yield with $S\text{-SO}_4^{2-}$ levels, which was also related to the GY treatments (Figure 8b). For this layer, corn yield was also related to the Ca level.

Crop yields were not related to soil pH or m% in either layer (Figures 8a and 8b). However, a higher pH was related to BS above 70 % in the 0.00-0.20 m layer, regardless of the method of application (Figure 8a), while in the 0.20-0.60 m layer, a higher pH was related to the IL method (Figure 9b). In both layers, pH and m% were negatively correlated, while pH and Mg were positively correlated.

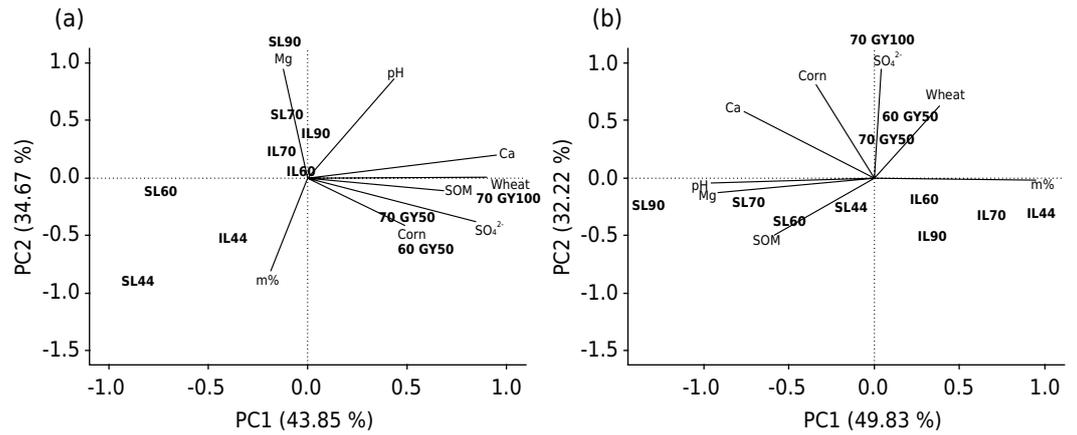


Figure 8. Biplot between PC1 and PC2 ($n = 11$) between wheat and corn yields and soil properties in the 0.00-0.20 m layer (a) and 0.20-0.60 m layer (b), which explain 78.52 and 82.05 % of the variance, respectively. In bold are the treatments, in which SL represents surface liming; IL represents incorporated liming; 44, 60, 70, and 90 represent base saturation (%); GY50 represents the recommended phosphogypsum rate (3.71 Mg ha^{-1}); and GY100 represents twice the recommended phosphogypsum rate (7.42 Mg ha^{-1}).

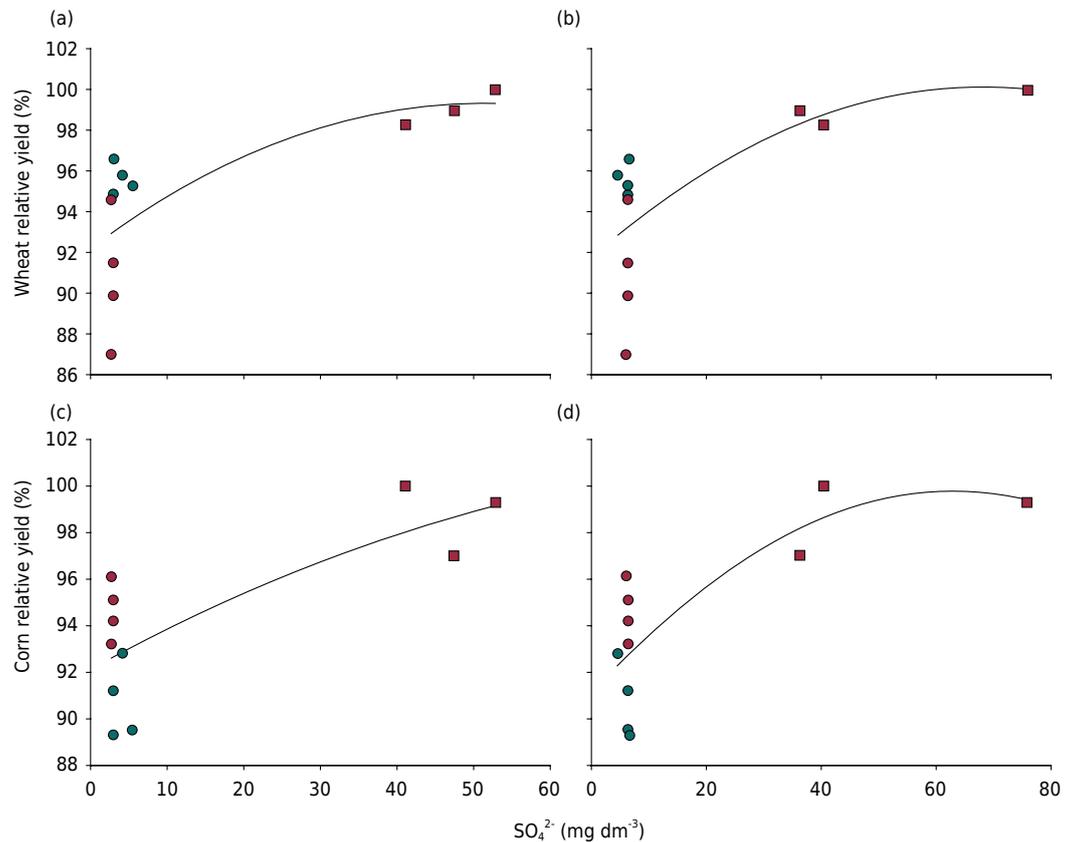


Figure 9. Relationship between sulfate content (S-SO_4^{2-}) in 0.00-0.20 (a, c) and 0.20-0.60 m (b, d) soil layers and relative yield of wheat and corn in response to incorporated (●) or surface lime (●) or to surface lime combined with phosphogypsum application (■). The relative grain yields were calculated by dividing the yields by the maximum yield in each crop.

Thus, the highest relative wheat and corn yields were obtained at an S-SO_4^{2-} content above 40 mg dm^{-3} (Figure 9). Only the treatments with GY application resulted in such SO_4^{2-} content levels. With only lime application, the S-SO_4^{2-} content was below 10 mg dm^{-3} in both layers and both crops. In the case of wheat, the relative yield ranged from 87-94 % with IL and from 95-97 % with SL (Figures 9a and 9b). For corn, SL resulted in relative yields from 89-93 %, whereas IL resulted in a yield range of 93-96 % (Figures 9c and 9d).

DISCUSSION

Soil chemical properties

Lime incorporation was more effective than surface liming for increasing the pH and reducing or maintaining the Al^{3+} content below $0.3 \text{ cmol}_c \text{ dm}^{-3}$ throughout the soil profile (Figures 1 and 2). These effects occur due to reactions between Al^{3+} and HCO_3^- and OH^- released from lime dissociation, because lime incorporation provides better contact between lime and soil particles. Although differences existed among the treatments with GY and BS%, the predominant factor in the reduction of Al^{3+} was the presence of lime and the subsequent increase in soil pH (Figure 8). The lack of GY effects may be related to the low Al^{3+} content in the soil, as observed by Fontoura et al. (2019). However, several studies report a decrease in Al^{3+} at depth after GY application (Crusciol et al., 2017; Michalovicz et al., 2018). Van Raij (2008) suggested some hypotheses to explain the mechanisms involved. One is the release of OH^- by S-SO_4^{2-} through ligand exchange, with the formation of hydroxylated aluminum, a mechanism called the “self-liming” effect. Another mechanism is the precipitation of aluminum associated with the formation of minerals [e.g., jurbanite, alunite and/or basaluminite, as cited by Pavan (1986)]. Another possibility is the leaching of aluminum along with GY byproducts, which may in part be favored by the formation of ion pairs or complexes, such as AlSO_4^+ or aluminum fluoride (van Raij, 2008).

The higher efficiency of IL was similar to the results reported by Rheinheimer et al. (2018a), who stated that lime incorporation was faster and more efficient for reducing the acidity at deeper layers. Vargas et al. (2019) verified that a similar effect was observed for acidity mitigation 12 years after surface or incorporated lime application. Our results could be explained by the high crop residue addition, high precipitation, and high doses of lime used.

Crop residues on the soil surface after NT management have positive effects on the reduction of soil acidity and Al^{3+} content (Miyazawa et al., 1993) due to the formation of chemical complexes (chelates) with organic components. The increase in SOM and dissolved organic compounds contributes to Al^{3+} complexation, thus reducing its activity and toxicity, which explains the absence of Al^{3+} at the 0.00-0.05 m layer and the low values observed at the deeper layers.

The results show that IL was more effective than SL at increasing Ca^{2+} at depth. However, when SL was combined with GY, an increase in the Ca^{2+} level was also observed at deeper layers. Thus, the use of GY was more effective in improving soil fertility in the profile with the advantage of avoiding soil disturbance, which promotes soil organic carbon losses and soil structure damage. Under subtropical conditions, Churka Blum et al. (2013) observed an increase in the Ca^{2+} content at depths up to 2 m when lime and GY were combined.

Under NT conditions, liming effects at deeper layers depend on the physical condition of the soil. Under compacted soils, low lime particle movement may restrict the effects of lime to a few centimeters on the soil surface. The results obtained by Tiritan et al. (2016) suggest that lime surface application effects did not differ from lime incorporation due to the absence of surface compaction, allowing surface liming to be performed on NT soils without compaction.

Our results indicate that GY application decreased the Mg^{2+} content in the superficial layers (Figures 5 and 8). Similar results were reported by Nava et al. (2012) and Rampim et al. (2011), who reported Mg^{2+} reduction to depths of 0.20 and 0.40 m, respectively. The GY effects on Mg^{2+} mobility to the subsoil have been attributed to Mg^{2+} and Ca^{2+} competition for negatively charged sites, since Ca^{2+} has a preference at soil exchange sites. After GY application, the increased Ca^{2+} content favors the displacement

of Mg^{2+} because it can form an ionic pair with $S-SO_4^{2-}$ (from GY) or is leached in the form of Mg^{2+} ions, which is the preferred form of displacement (Zambrosi et al., 2007). The preference for Mg^{2+} , relative to other cations, is due to the charge density (charge/ionic radius), whereby the higher Mg^{2+} charge density (3.07) relative to Ca (2.02) and K (0.75) results in a stronger ionic bond with oppositely charged ions. Therefore, the preference for the formation of percolable sulfates in the soil follows the order $MgSO_4^0 > CaSO_4^0 > K_2SO_4^0$ (Ramos et al., 2013). The results observed for the Mg^{2+} mobility in SL are in accordance with those obtained by Fidalski and Tormena (2005), who verified an increase in Mg^{2+} up to 0.60 m. According to those authors, the Mg^{2+} content in the soil profile was the chemical property that best described the efficiency of surface liming in the soil profile.

When GY was applied, the $S-SO_4^{2-}$ content increased consistently throughout the soil profile and was higher than the critical level of 6 and 9 $mg\ dm^{-3}$ for the 0.00-0.20 and 0.20-0.40 m layers, respectively (Pauletti and Motta, 2019) (Figure 6a). The results suggest a rapid movement of $S-SO_4^{2-}$ in the soil profile. Between the GY application and soil sampling, 798 mm of precipitation occurred, which could contribute to the $S-SO_4^{2-}$ mobility at depth. Nogueira and Melo (2003) showed that maximum levels of $S-SO_4^{2-}$ at 0.00-0.20 m were observed after 152 mm of rainfall at 21 days after GY application. According to the authors, the $S-SO_4^{2-}$ values were greater at higher rainfall rates and decreased with time; moreover, 63 days after the application, the $S-SO_4^{2-}$ content was already close to that found before GY application. Greater $S-SO_4^{2-}$ values have been observed in subsurface layers in tropical and subtropical soils. This is due to the higher anion exchange capacity (AEC) in the deepest layers resulting from the low SOM content (Fontes and Alleoni, 2006) and oxidic mineralogy of the clay fraction. Furthermore, an increase in P content at the soil surface decreases potential sites for $S-SO_4^{2-}$ adsorption because phosphate is more readily adsorbed by colloids than $S-SO_4^{2-}$ (Pias et al., 2019), leading to an increase in $S-SO_4^{2-}$ at the subsurface.

The decrease in the SOM content at the superficial depth with IL (Figure 6b) occurred because the soil aggregates were fragmented when the soil was plowed, and SOM was released to the decomposing microorganisms. Most likely, the small increment of SOM at 0.20-0.30 m (Figure 6b) is a result of both crop residue and organic matter accumulation over the years, which were incorporated into the soil. The results agreed with those of Alleoni et al. (2005), who did not observe any effect of lime rates or incorporation on SOM content at six, eighteen, and thirty months after application. However, those authors observed an effect of the method of application, with higher levels being observed at the 0.00-0.05 m layer due to surface liming and higher levels of SOM in the 0.05-0.10 m layer with lime incorporation. Soil organic matter accumulation in the soil is slow; however, it generates chemical, physical, and biological benefits.

Five months after lime reapplication, our results showed that the effect of surface liming varies according to the chemical properties and diagnostic layer (Figures 1, 2, 3, 4, 5, and 6). Despite this, the increase in pH in the 0.10-0.20 m layer provided by SL might not have agronomic effects due to the low magnitude of the increase (Figure 1c) and thus the reduction in potential acidity in the 0.10-0.20 m layer (Figure 3c). Although lime incorporation presents the fastest corrective reaction, surface liming has longer residual effects, especially in soils with high buffer capacity and with high lime doses (Rheinheimer et al., 2018a). Thus, surface liming is an effective strategy to abate the negative effects of soil acidity under long-term NT because the soil reacidification process is slow (Rheinheimer et al., 2018b). For example, Fontoura et al. (2019) observed that 11 years after lime surface application in an Oxisol, the soil had recovered 67 % of its initial potential acidity (H+Al) throughout the profile (0.00-0.60 m). In another study carried out in an Ultisol, the soil reacidification process recovered only 20 % of the initial soil acidity 24 years after liming (Rheinheimer et al., 2018b) and only 50 % of its Al^{3+} after 18 years (Rheinheimer et al., 2018a).

Grain yield

When the soil was managed under continuous NT (SL), no response to the BS% levels was observed for either corn or wheat (Figure 7). Bortolini et al. (2016) mentioned that BS% 50 must be adopted as the liming criterion for the main crops grown under consolidated NT. Thus, in our study, BS% levels under this threshold (Bortolini et al., 2016) were not sufficiently low to limit crop yield, even BS% 44. Our results show that although IL acts on the acidity at deeper soil layers, it does not influence crop yield, suggesting that continuous NT promotes benefits that were maximized with GY application. Nevertheless, an increase in corn yield was observed after lime incorporation.

On the other hand, GY application strongly increased $S-SO_4^{2-}$ levels in the soil and was the main factor related to the increase in crop yields in our study (Figures 8 and 9). As a result, we assume that the addition of GY in association with liming is effective for increasing $S-SO_4^{2-}$ levels and crop yields in Oxisols under NT conditions. The strong dependence of yield on the levels of $S-SO_4^{2-}$ is in accordance with the results of Pias et al. (2019), who, after evaluating 58 harvests, proposed that the critical levels of S in the soil surface (0.00-0.20 m) and subsurface layer (0.20-0.60 m) are 7, 5, and 8.5 $mg\ dm^{-3}$. Before growing corn and wheat in our study, the levels of S (Table 2) were below the critical level established by Pias et al. (2019), and the application of GY increased the levels of $S-SO_4^{2-}$ in the soil (Figure 6a) and consequently the yield (Figures 7 and 9). According to Pias et al. (2019), the main factor that controls the crop response to S fertilization in NT soils in Brazil is the $S-SO_4^{2-}$ content available in the soil, with 50 % of crops showing an increase in yield when the levels of $S-SO_4^{2-}$ were below the mentioned critical level. Among the positive responses to S fertilization, corn exhibited the greatest increase in yield (6-36 %, mean = 19 %) (Pias et al., 2019). In our study, treatments with limestone and GY increased the productivity of corn by 7.66 % on average and wheat by 4.16 % compared to BS% 44 SL.

However, it is worth noting that similar results could have been obtained with lower GY doses, and thus, it is necessary to understand better whether the benefits of GY occur due to the chemical improvement of deep layers, the supply of S, or both factors. In our study, relative yields near 100 % were obtained at SO_4^{2-} content values higher than 40 $mg\ dm^{-3}$, whereas nonapplication of GY resulted in content values lower than 10 $mg\ dm^{-3}$ but a relative yield still above 95 %. Therefore, lower rates of GY should be tested to achieve higher yields with the correct supply of SO_4^{2-} . According to Tiecher et al. (2018), studies using lower rates of gypsum application ($<1\ Mg\ ha^{-1}$) as an S source are needed because gypsum rates $\geq 2\ Mg\ ha^{-1}$ decrease soil subsurface acidity.

The yields of wheat and corn were also associated with increases in Ca at 0.00-0.20 and 0.20-0.60 m, respectively (Figure 8). In a recent study, Tiecher et al. (2018) observed that applying GY in soils with high acidity and/or lower levels of Ca^{2+} at the deeper layers increased corn yield by 14 % (85 % of the cases) and increased the yield of winter crop grain by 20 % (75 % of the cases). Our results corroborated those from Tiecher et al. (2018), who proposed that the critical level to recommend GY for grasses in subtropical Oxisol under NT is 3.0 $cmol_c\ dm^{-3}$ of Ca^{2+} at the 0.20-0.40 m layer (or Al saturation greater than 10 %). In a meta-analysis evaluating the responses of crops to GY in South America, Pias et al. (2020) observed that for cereals, the application of GY is recommended in soils with Al³⁺ saturation $>5\ %$ in the 0.20-0.40 m layer. In our study, the aluminum saturation of the control (BS 44 SL) was 25 %, and after GY + lime application, it was reduced to 15 %. According to the previous recommendations, our results and those reported by Tiecher et al. (2018) and Pias et al. (2020) show that positive responses to GY are more frequent than expected.

The relationship between SOM and wheat productivity demonstrates the importance of management practices that contribute to an increase in SOM. Increasing SOM on the surface is important because organic carbon may associate with Al³⁺, reducing its

toxicity to plants (Miotto et al., 2020) and because increasing SOC in clay soils with oxidic mineralogy (Ciotta et al., 2003) reduces the leaching of nutrients. These findings reveal that management practices, such as lime incorporation, that reduce SOM levels in established NT fields should be avoided.

CONCLUSIONS

Lime incorporation was more effective in reducing Al^{3+} and increasing pH, Ca, and Mg levels. Furthermore, lime incorporation acts at greater depths than surface application but contributes to reducing SOM levels at the surface layers. Therefore, when lime and phosphogypsum (GY) were applied to the soil surface, higher wheat and corn yields were obtained. Phosphogypsum increased Ca and $S-SO_4^{2-}$ levels at deeper layers. However, high GY rates (7.42 Mg ha^{-1}) should be avoided because they reduce the availability of Mg^{2+} at the soil surface. Our results demonstrate that GY in association with liming is effective in reducing soil acidity and increasing the supply of $S-SO_4^{2-}$ while maintaining the benefits of continuous NT in crop yields.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data for this article can be found online at https://www.rbcjournal.org/wp-content/uploads/articles_xml/1806-9657-rbcs-45-e0200135/1806-9657-rbcs-45-e0200135-suppl01.pdf.

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