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SOIL CHEMICAL ATTRIBUTES AFTER THE SUPERFICIAL DISTRIBUTION AND WITHOUT INCORPORATION OF LIMESTONE DOSES

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ABSTRACT - Limestone, a common soil amendment in agriculture, is used to correct soil acidity by raising pH, increasing Ca and Mg levels, and neutralizing Al. This study evaluated the effectiveness of surface application of calcitic limestone doses to correct acidity at different soil depths. The research was conducted in a Eutroferric Red Latosol using a randomized block experimental design with eight repetitions in 30 m^2 plots, covering a total area of 960 m^2. Four doses of calcitic limestone (0, 3, 6, and 9 t ha^{-1}) were applied without mechanical incorporation into the soil. Evaluations were performed at 12 and 24 months after the doses were applied, at depths of 0-0.05, 0.05-0.10, and 0.10-0.20 m, measuring chemical attributes such as pH, H+Al, Al, Ca, Mg, BS, and m. As the calcitic limestone doses increased, there were improvements in pH, approaching neutrality, an increase in Ca content, and an elevation in BS, reducing Al content and potential acidity. This demonstrated the effectiveness of calcitic limestone in increasing BS and reducing m. After 2 years, liming with calcitic limestone provided improvements to the root environment up to a depth of 0.20 m, with increased pH and base saturation, as well as reduced Al and H+Al levels. Furthermore, calcitic limestone doses did not influence soil Mg levels.

Keywords: acidity correction, nutrients, soil management.

ATRIBUTOS QUÍMICOS DO SOLO APÓS APLICAÇÃO SUPERFICIAL DE DOSES DE CALCÁRIO CALCÍTICO

RESUMO - O calcário, corretivo comum na agricultura, é usado para corrigir a acidez do solo, elevando o pH, aumentando os níveis de Ca e Mg e neutralizando o Al. Este estudo avaliou a eficácia da aplicação superficial de doses de calcário calcítico para corrigir a acidez em diferentes profundidades do solo. O estudo foi desenvolvido em um Latossolo Vermelho Eutroférrico, utilizando-se de um delineamento experimental em blocos casualizados, com oito repetições, com parcelas de 30 m^2, em uma área total de 960 m^2. Os tratamentos empregados foram quatro doses de calcário calcítico (0, 3, 6 e 9 t ha^{-1}), aplicadas sem incorporação mecânica no solo. As avaliações foram realizadas aos 12 meses e 24 meses após a implantação das doses, nas profundidades de 0-0,05, 0,05-0,10 e 0,10-0,20 m e determinado os atributos químicos: pH, H+Al, Al, Ca, Mg, V e m. Com o aumento das doses de calcário calcítico, houve melhorias do pH, ficando próximo da neutralidade, aumento no teor de Ca e elevação do V reduzindo o teor de Al e da acidez potencial, evidenciando efetividade no uso do calcário calcítico, no aumento do V e redução do m. A calagem com calcário calcítico após 2 anos, proporcionando melhorias ao ambiente radicular até a profundidade de 0,20 m, com aumento do pH e saturação por bases, além da redução nos teores de Al e H+Al, além disso, as doses de calcário calcítico não influenciaram os teores de Mg no solo.

Palavras-chave: correção da acidez, nutrientes, manejo do solo.

INTRODUCTION

Brazil has a vast expanse of soils, with 70% considered acidic or facing issues of acidity and low nutrient availability (FERRARI NETO et al., 2021; SANTOS et al., 2018). The presence of hydrogen (H) and aluminum (Al) in the soil solution is responsible for its acidity, consequently leading to reduced productivity, especially in tropical and subtropical regions (FERRARI NETO et al., 2021). Acidity can be generated both by formation factors and by agricultural activity responsible for nutrient extraction and inadequate replenishment (NATALE et al., 2012; KOCHIAN et al., 2015). Acidity influences different reactions and processes in the soil, affecting the availability of macro and micronutrients, soil biological activity, and alterations in the organic matter decomposition dynamics (SCHMITT et al., 2016; FONTOURA et al., 2019).

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The practice of liming for soil correction is one of the most commonly used methods to control soil acidity. However, its effect is limited to the application site, with greater efficiency when the corrective is incorporated throughout the soil profile, providing physical and chemical improvements and higher agricultural yields (BLUM et al., 2013; HOLLAND et al., 2018; SHI et al., 2019). The application of limestone ($CaCO_3$ and $MgCO_3$) has proven effective in rehabilitating acidic soils, leading to improvements in Ca and Mg levels, pH elevation, base saturation (V%), and reducing the toxic action of Al and Mn, creating a favorable environment for root system development (HOLLAND et al., 2018). These benefits reflect on improved water retention capacity, reduced susceptibility to soil compaction and erosion, providing greater tolerance to water stress (SHI et al., 2019).

Biazatti et al. (2020), working with doses of 3 and 6 t ha^{-1} of dolomitic limestone, observed improvements in Mg and P availability. However, doses above 7 t ha^{-1} resulted in a negative impact on the Ca:Mg ratio. The authors noted an increase in Mg up to the dose of 8.8 t ha^{-1}, beyond which Mg became less soluble due to the high concentration of Ca in the soil's cation exchange capacity (CTC), interfering with the aggregation of K and Mg to soil colloids, which become easily leached (ANDA, 1971).

There are numerous benefits to using limestone as a soil amendment, as it not only corrects acidity and neutralizes the toxic effect of Al but also provides greater availability of Ca and Mg, crucial for the maximum expression of crop productivity. However, the use of high doses of the amendment can lead to nutritional imbalance. Therefore, the hypothesis is that increasing limestone doses may result in negative effects on soil chemical attributes. Thus, the objective of the study was to evaluate the effectiveness of surface application of calcitic limestone doses to correct acidity at different soil depths.

MATERIAL AND METHODS

This study was conducted under field conditions in the years 2017, 2018, and 2019 at the "Professor Antônio Carlos dos Santos Pessoa" Experimental Farm, owned by the State University of West Paraná, located in Marechal Cândido Rondon (Paraná), at coordinates 24º31'58.24" S and 54º01'11.08" W, with an altitude of 390 m.

According to the Köppen classification, the region's climate is type *Cfa*, humid subtropical mesothermal with a dry winter, featuring well-distributed rainfall throughout the year and hot summers. The average annual temperature ranges between 22 and 23ºC, with an average annual precipitation of 1600 to 1800 mm (ALVARES et al., 2014). Meteorological data for the experimental periods were obtained from the Automatic Climatological Station of the Unioeste Experimental Stations Unit, located near the experimental area (Figure 1 and Figure 2).

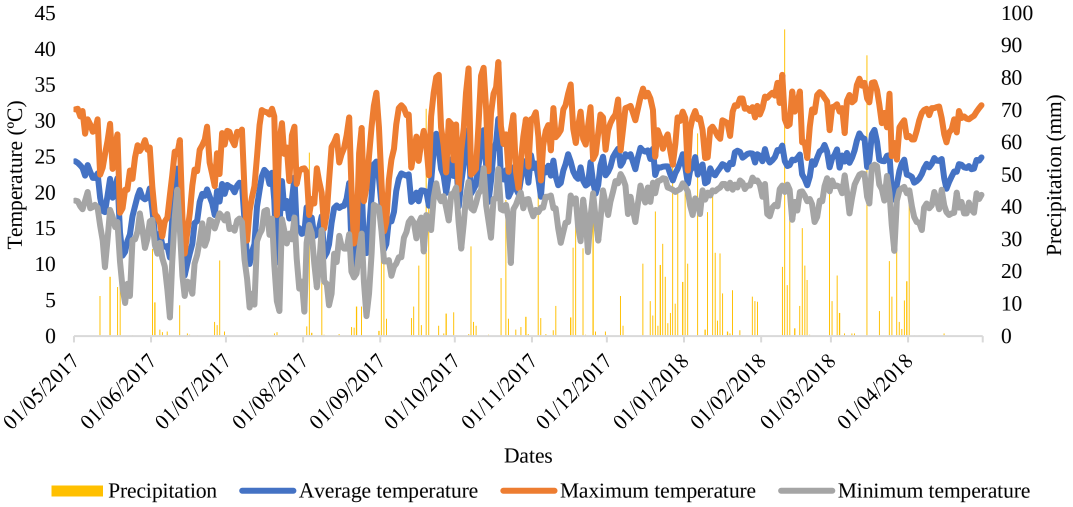

FIGURE 1 - Averages of accumulated rainfall, average air temperature, maximum, and minimum temperatures occurring during the first year after the application of treatments.

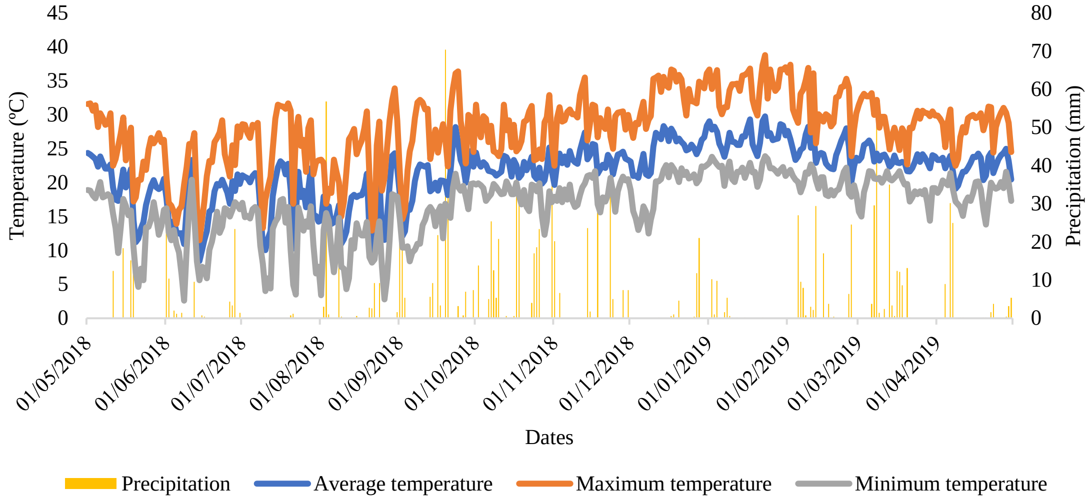

FIGURE 2 - Averages of accumulated rainfall, average air temperature, maximum, and minimum temperatures occurring during the second year after the application of treatments.

The soil in the experimental area is classified as Eutroferric Red Latosol (LVef) (SANTOS et al., 2018) and has a clayey texture, with a clay content of 585.50 g kg^{-1}. The area was under no-till management.

Before the experiment was implemented, a composite soil sample was collected for chemical characterization (Table 1).

TABLE 1 - Chemical and granulometric attributes of the experimental soil in the 0-0.20 m layer

Layer	pH	P	K	Ca	Mg	Al	H+Al	SB	CEC
(m)	$CaCl_2$	mg dm^{-3}	---------------------------------- cmol$_c$ dm^{-3} ----------------------------------						
0-0.20	5.03	34.29	0.44	2.94	1.28	0.15	6.29	4.66	11.35
Layer	BS	m	OM	Clay	Silt	Sand			
(m)	----------- % -----------		g dm^{-3}	----------------- g kg^{-1} ----------------					
0-0.20	41.06	3.12	32.81	585.5	361.61	52.79			

P e K = Mehlich^{-1} extractor, Al, Ca e Mg = KCl extractor (1 mol L^{-1}), H+Al = pH SMP (7.5). Source: Laboratory of Environmental and Instrumental Chemical Analysis (Unioeste).

The experimental design was a randomized block design, with the treatments being doses of calcitic limestone (48% CaO and 3% MgO), with a PRNT of 75%, at 0, 3, 6, and 9 t ha^{-1}, and eight replications. The experimental plot had dimensions of 7.5 m in length x 4 m in width (30 m^2), with a total area of 960 m^2. The limestone was applied on May 10, 2017, without mechanical incorporation. Following that, black oat (*Avena strigosa* Schreb), cv. BRS 139, was sown as a cover crop, and after 30 days, broadcast fertilization with ammonium sulfate (250 kg ha^{-1}) was applied to the entire area.

Soil samples were collected 12 months and 24 months after the treatment implementation (May 10, 2018, and May 10, 2019), using a Dutch auger, with 5 single samples to compose a representative composite sample within each plot, at depths of 0-0.05, 0.05-0.10, and 0.10-0.20 m. Subsequently, the soil was air-dried, sieved through 2.0 mm mesh, placed in plastic bags, and sent to the Laboratory of Environmental and Instrumental Chemical Analysis at Unioeste, Campus Marechal Cândido Rondon. In the composite samples, chemical attributes such as hydrogen potential (pH) in $CaCl_2$, calcium (Ca), magnesium (Mg), potassium (K), potential acidity (H+Al), and exchangeable aluminum (Al) were determined according to the methodology described by Pavan et al. (1992). Based on these data, base saturation (BS) and aluminum saturation (m) were calculated according to Ronquim (2010).

The data were subjected to tests for homogeneity of variance, normal distribution, additivity, and independence of errors. Following this step, they underwent analysis of variance using the F-test ($p<0.05$) and were analyzed through a joint analysis of the experiment within the crop years. In cases of significance for the variation source "year," the Tukey test ($p<0.05$) was used for mean comparison, and when the dose or dose x year interaction was significant, regression analysis was performed using the statistical program SISVAR® (FERREIRA, 2011).

RESULTS AND DISCUSSION

A significant interaction between year and dose was observed only for pH in the 0.00-0.05 m layer (Table 2). Regarding isolated effects, variables such as pH, Al, H+Al, Ca, BS, and m were found at doses in the

0.00-0.05 and 0.05-0.10 m layers, and for pH in the 0.10-0.20 m layer. For crop years, in the 0.00-0.05 m depth, there were significant effects for pH, Al, H+Al, and BS; in the 0.05-0.10 m layer, effects were observed for pH, Al, H+Al, BS, and m; and in the 0.10-0.20 m layer, there were significant effects for pH, Al, H+Al, Ca, and BS. For pH values, there was no adjustment for the first year, but there was an interaction for dose and year, with a significant linear adjustment for the second year in the 0.00-0.05 m layer (Figure 3A) and a significant effect for doses in the 0.05-0.10 and 0.10-0.20 m layers (Figures 3B and 3C), respectively.

The increase in calcium carbonate concentration in the soil due to the increase in limestone doses, coupled with the low solubility of the amendment, linearly raised the pH only after 24 months of application (Figure 3A). This pH increase confirms results presented by Biazatti et al. (2020) and Meert et al. (2016), where increasing limestone doses led to pH increase in subsoil layers after a certain period. A linear increase in pH was observed with increasing limestone doses in the 0.05-0.10 and 0.10-0.20 m layers, justifying the reduction in Al (Table 4), corroborating Holland et al. (2018), who stated that pH elevation reduces the toxic action of Al.

For Al and m, a significant effect of limestone doses was observed at depths of 0-0.05 m and 0.05-0.10 m (Figure 4). With increasing limestone doses, there was a reduction in Al and m content up to 6.26 ton ha^{-1}, neutralizing at the 0-0.05 m depth but losing neutralization power later. At the 0.05-0.10 m depth, there was a reduction in Al and m content up to 5.93 ton ha^{-1}, with total neutralization of the element. Limestone doses influenced m in the 0-0.05 and 0.05-0.10 m layers, exhibiting quadratic behavior in both, with total m neutralization at 0-0.05 m, at a dose of 6.2 ton ha^{-1} (Figure 4C), and maximum reduction up to 5.9 ton ha^{-1}, in the 0.05-0.10 m layer, with m of 0.7% (Figure 4D).

Several studies address the effect of liming under different soil conditions and the replacement of Al by Ca ions, causing calcium carbonate ions to react with the soil solution, promoting an excess of hydroxide ions (OH), which react with H to form water (FLORES et al., 2008; FREIRIA et al., 2008; CRAVO et al., 2012; PAULETTI et al., 2014; MEERT et al., 2016). According to Malavolta (1985), water is responsible for removing bases from exchange complexes, allowing the exchange for H ions, favoring the physicochemical transformation of clay minerals, causing the appearance of Al, and consequently, soil acidification. Thus, it is inferred that the high limestone dosage applied (9 ton ha^{-1}) may have promoted an excess of OH ions, leading to base leaching, resulting in increased Al content.

TABLE 1 - Mean square of variance analysis for pH, Al, H+Al, Ca, Mg, K, BS and m, in different soil layers, after application of calcitic limestone on the surface

					Layer of 0-0.05 m				
SV	DF	pH	Al	H+Al	Ca	Mg	K	BS	m
Blocks	14	0.06	0.03	0.58	1.74	0.61	0.11	78.65	15.01
Doses	3	0.79**	0.23**	4.74**	16.48**	0.33	0.05	616.81**	96.59**
Year	1	10.17**	0.18*	154.23**	2.26	0.001	1.23**	3651.18**	46.72
Year*Doses	3	0.35*	0.03	0.13	16.05	0.17	0.12	26.77	9.05
Error	42	0.12	0.040	0.63	11.74	0.21	0.06	67.11	17.98
CV (%)		6.89	221.46	16.33	21.83	24.22	37.43	13.42	248.16
Average		5.07	0.09	4.87	4.96	1.88	0.68	61.05	1.70
					Layer of 0.05-0.10 m				
SV	DF	pH	Al	H+Al	Ca	Mg	K	BS	m
Blocks	14	0.05	0.05	0.74	1.15	0.66	0.21	104.96	21.03
Doses	3	1.01**	0.44**	5.12**	8.47**	0.12	0.32	532.07**	157.43**
Year	1	7.59**	0.57**	160.97**	2.60	0.001	2.66**	3790.40**	126.31*
Year*Doses	3	0.33	0.02	0.08	0.77	0.21	0.31	46.06	8.59
Error	42	0.16	0.08	0.76	0.94	0.26	0.11	76.70	29.36
CV (%)		8.23	147.45	17.24	21.8	28.36	48.42	15.05	153.56
Average		4.99	0.19	5.05	4.43	1.80	0.67	58.19	3.52
					Layer of 0.10-0.20 m				
SV	DF	pH	Al	H+Al	Ca	Mg	K	BS	m
Blocks	14	0.10	0.12	0.94	1.93	0.49	0.27	114.16	59.30
Doses	3	0.49*	0.04	2.04	2.42	0.05	0.07	208.98	22.84
Year	1	3.48**	0.81**	141.46**	11.39**	0.001	1.59**	2316.02**	191.96
Year*Doses	3	0.19	0.15	0.59	1.79	0.15	0.16	151.90	98.32
Error	42	0.15	0.11	0.83	1.63	0.24	0.07	112.25	51.38
CV (%)		8.08	112.97	16.96	31.82	30.96	47.78	19.74	128.32
Average		4.84	0.28	5.38	4.01	1.59	0.57	53.66	5.58

SV = source of variation, DF = degrees of freedom, CV = coefficient of variation, pH = hydrogen potential, Al = aluminum, H+Al = potential acidity, Ca = calcium, Mg = magnesium, K = potassium, BS = base saturation, m = aluminum saturation. *Significant at 5% probability of error by the F-test. **Significant at 1% probability of error by the F-test.

Another issue that could explain the increase in Al and m values above 6 ton ha^{-1} may be related to the soil analysis extractor, which tends to overestimate the soil sample. According to Cunha et al. (2015), the potassium chloride (KCl 1 mol L^{-1}) used as an extractor can overestimate Al levels, extracting other forms of this element besides the exchangeable one, favored by the increasing doses of limestone. Furthermore, as stated by Cunha et al. (2015), not all Al determined by KCl (1 mol L^{-1}) is part of the exchange bonds in the soil colloidal system, causing exchangeable Al to be overestimated and consequently, aluminum saturation.

Another assumption is that, due to the study area being managed under a straw seeding system and having 32.81 g dm^{-3} of organic matter (OM), the use of limestone may have favored the availability of greater activity, intensifying the decomposition of OM, releasing ammonia (NH^3), later converted into nitrate (NO^{3-}), releasing a higher quantity of H^+ (CANELLAS; SANTOS, 2005), increasing Al levels.

For potential acidity (H+Al), there was significance in the limestone doses, observing a linear reduction in potential acidity in the 0-0.05 m layer up to the maximum dose used (Figure 5A), and a reduction in the 0.05-0.10 m layer up to the dose of 6.9 ton ha^{-1} (Figure 5B), with increasing doses. This increase in potential acidity concentration may be related to the behavior exhibited by Al and the sum of Al and H adsorbed to soil colloids (EBELING et al., 2008). Potential acidity (H+Al) was influenced by corrective doses, as limestone corrects the soil by releasing hydroxide, which reacts with hydrogen to form water and reduce soil acidity levels (BIAZATTI et al., 2020). This reduction is related to the increase in pH, as observed in Figure 4, and the increase in Ca levels (Figure 6), emphasizing the efficiency of liming in reducing potential acidity, corroborating Alleoni et al. (2009) and Kaminski et al. (2005).

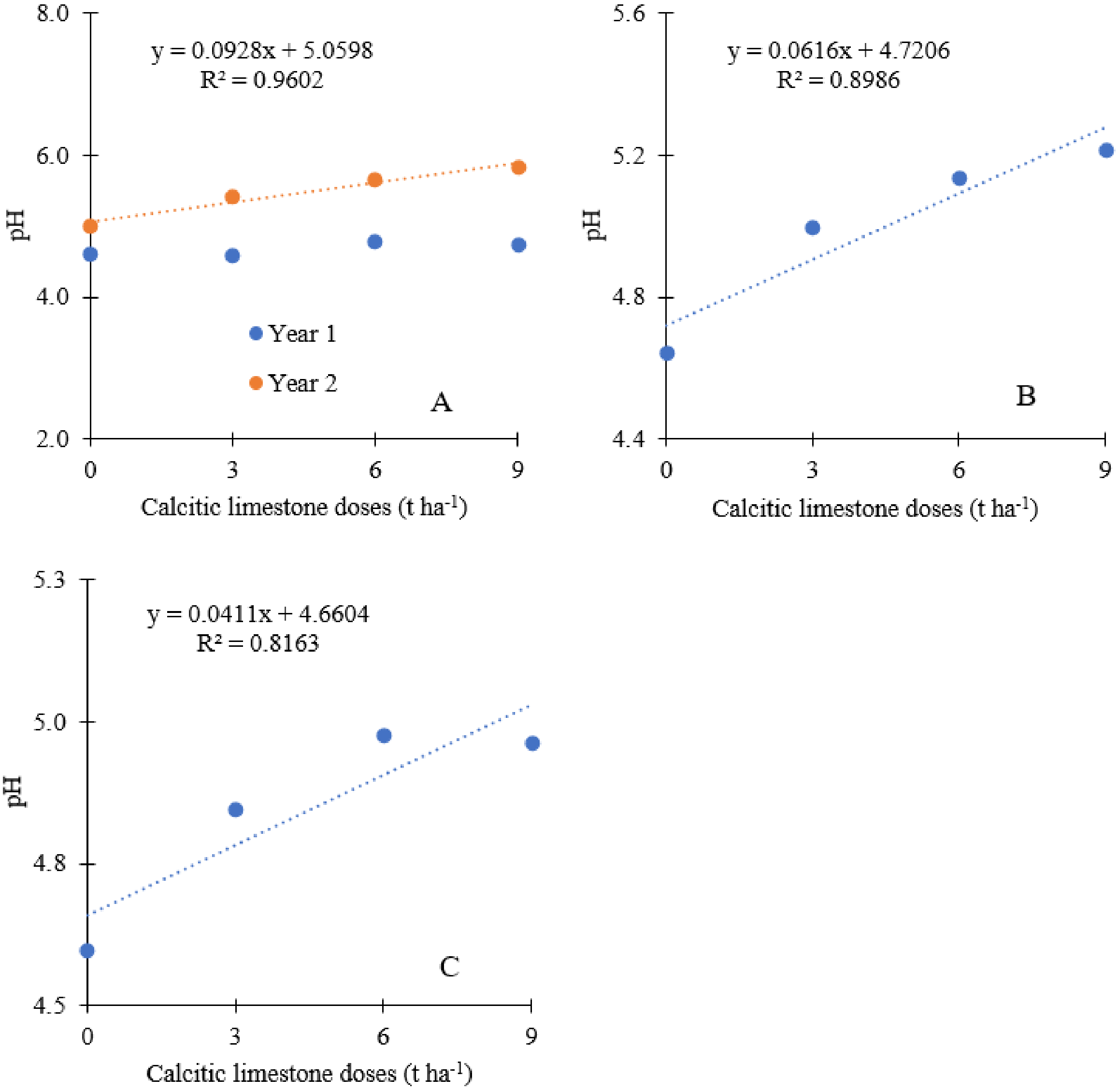

FIGURE 3 - pH values in the soil after surface application of doses of calcitic limestone in the layers 0-0.05 m (A), 0.05-0.10 m (B), and 0.10-0.20 m (C).

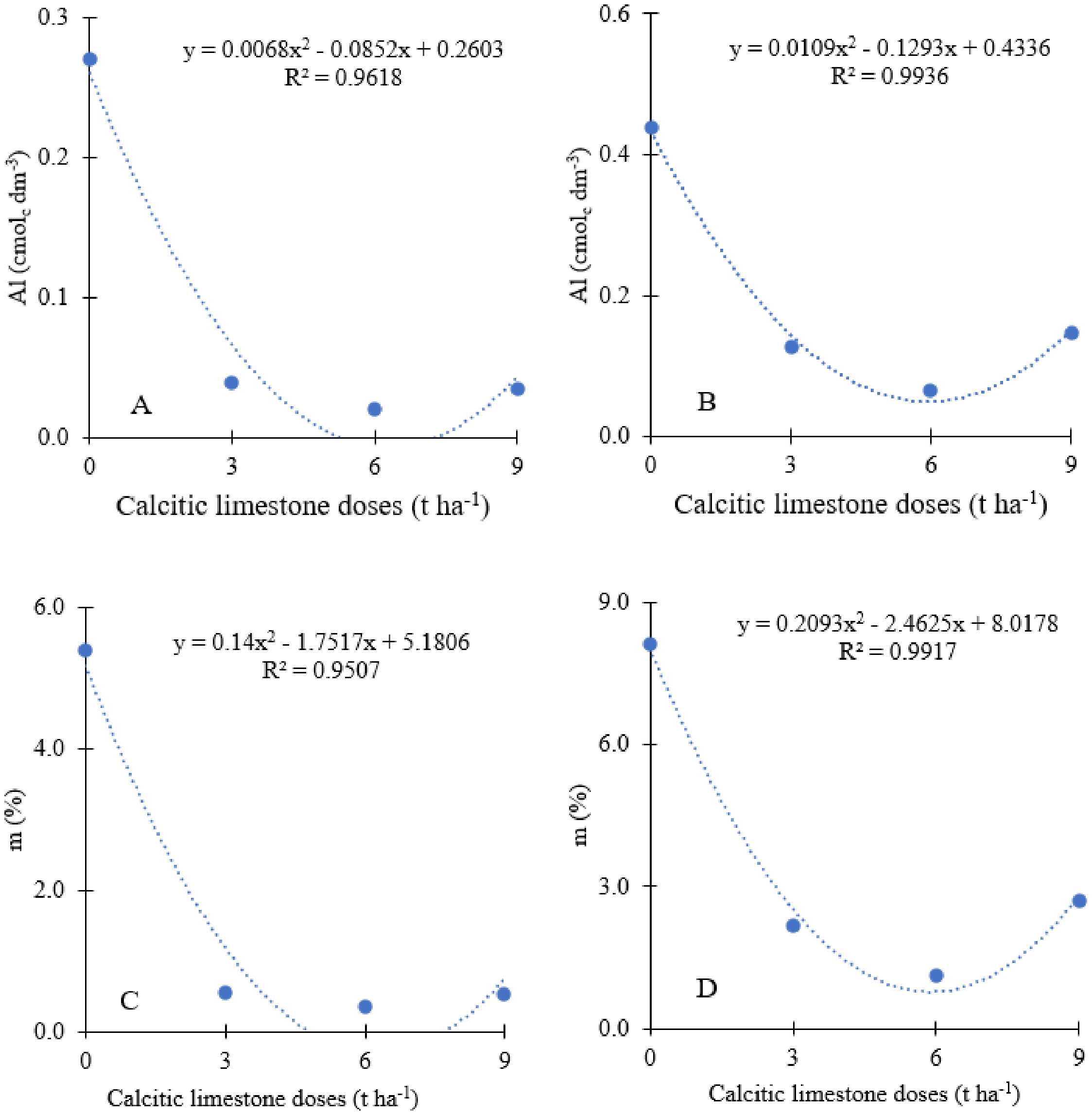

FIGURE 4 - Aluminum levels and Aluminum saturation (m) in the soil after surface application of doses of calcitic limestone in the layers 0-0.05 m (A, C) and 0.05-0.10 m (B, D).

The soil Ca levels showed a linear increase, according to the doses applied in the first two analyzed layers, related to the type of corrective used, with a concentration of 48% CaO (Figures 6A and 6B). This linear increase in Ca levels is consistent with Bambolim et al. (2015), who used increasing doses of limestone and observed nutrient content increments.

Maraschin et al. (2020), when evaluating the chemical attributes of sandy and clayey textured soils, also found increases in Ca levels with the increasing doses of limestone. The values ranged from 0.18 to 3.05 cmol_c dm^{-3} for sandy soil and 0.00 to 4.15 cmol_c dm^{-3} for clayey soil, respectively, with doses ranging from 0.0 to 20.0 t ha^{-1}. Flores et al. (2008) reported the liming effect 12 months after application up to a depth of 0.25 m, with significant modification up to 24 months, demonstrating the positive impact of increasing limestone doses on Ca levels.

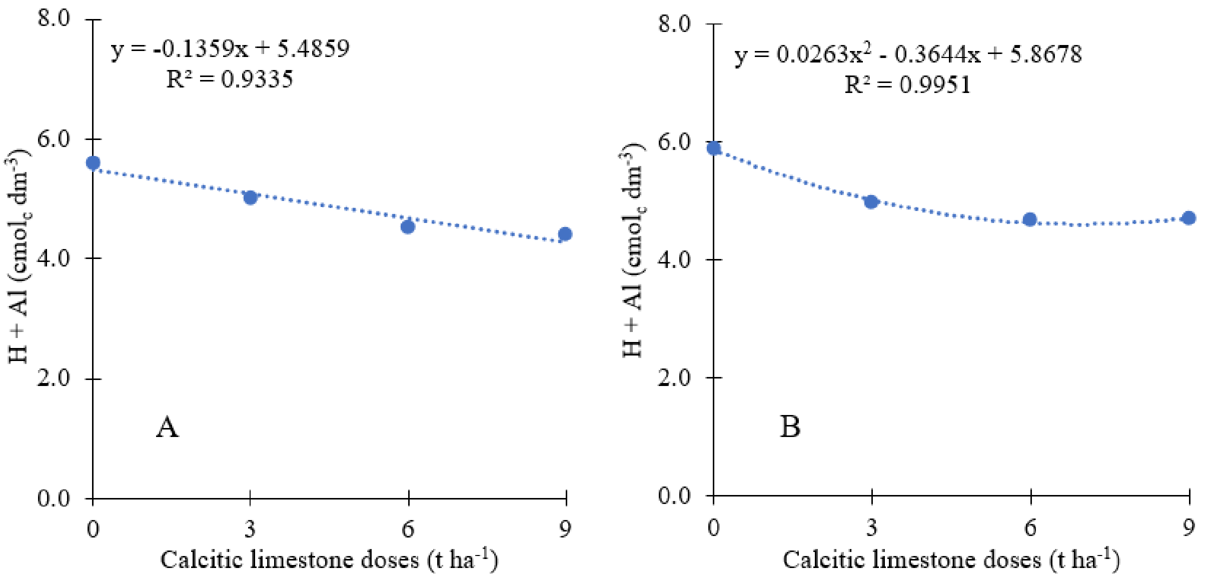

FIGURE 5 - Potential acidity values (H+Al) in the soil after the application of doses of calcitic limestone, in the layers 0-0.05 m (A) and 0.05-0.10 m (B).

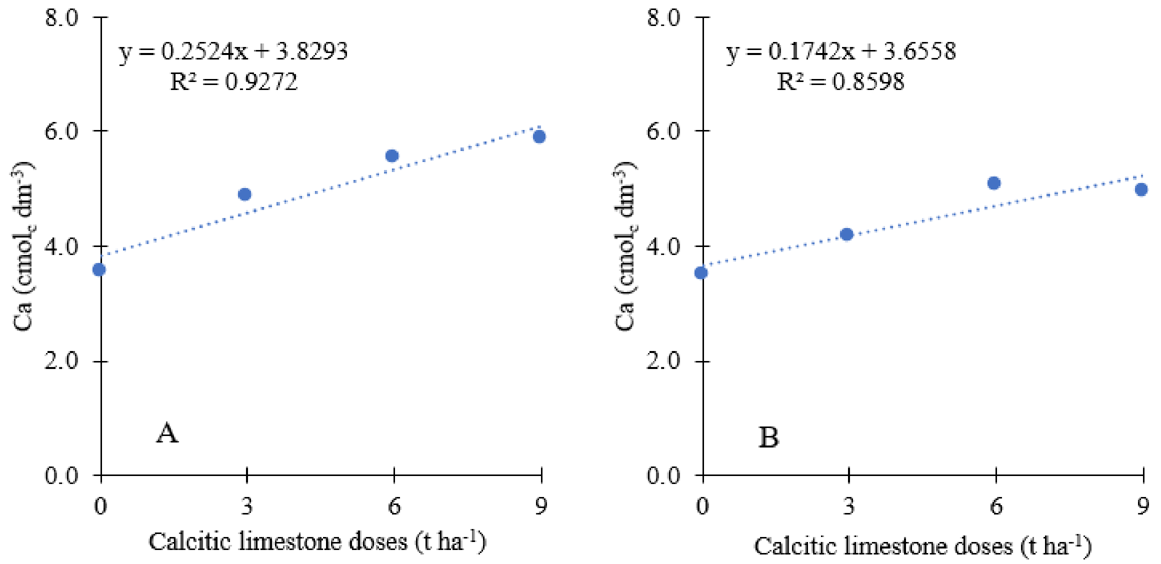

FIGURE 6 - Calcium levels in the soil after surface application of doses of calcitic limestone, in the layers 0-0.05 m (A) and 0.05-0.10 m (B).

In the present study, Mg levels did not show significant differences for year and doses, nor interaction between doses and years, which may be linked to the type of corrective used (3% MgO), as observed in the analysis of variance. The means found for Mg levels at doses of 0, 3, 6, and 9 t ha^{-1} were 1.72, 1.87, 1.78, and 1.67 cmol$_c$ dm^{-3}, respectively, considered high according to the Manual de Adubação e Calagem do Paraná (1.1-2.0 cmol$_c$ dm^{-3}) (PAVINATO et al., 2017).

For BS, there was a significant effect for doses, with a linear increase as the limestone doses increased in the 0-0.05 m layer (Figure 7A). In the 0.05-0.10 m layer, a quadratic behavior was observed, with a maximum BS at the dose of 6.8 tons per hectare, reaching 62.8% (Figure 7B). The addition of limestone increased Ca levels (Figures 7A and B) and reduced H+Al (Figures 7A and B), positively influencing the results within the soil base saturation.

Regarding the annual effect, the average values obtained for pH, Al, H+Al, K, and BS are presented in Table 3 for 1 and 2 years after the application of limestone doses. As the soil pH increased in all three evaluated layers from the first to the second year, a reduction in Al was also observed in the soil layers in the second year of the study, corroborating Zandoná et al. (2015) and Holland et al. (2018), where an increase in pH reduced the toxic action of Al. A similar pattern was observed for H+Al, meaning that the corrective had a positive effect on potential acidity by releasing hydroxide, reacting with hydrogen to form water and reducing soil acidity (KAMINSKI et al., 2005; ALLEONI et al., 2009; BIAZATTI et al., 2020).

For BS, there was an increase in values from the first to the second year of evaluation. This increase may be related to the higher concentration of K, one of the bases positively influenced by the addition of limestone, remembering that high doses can lead to an imbalance in the availability of soil chemical elements (NOLLA et al., 2020). For K, an increase in its concentration was observed from one year to another. Nolla et al. (2020) reported that higher limestone doses promoted an increase in K availability, which can be justified by the neutralization of Al toxicity, resulting in greater K adsorption in the colloidal system (BISSANI et al., 2008).

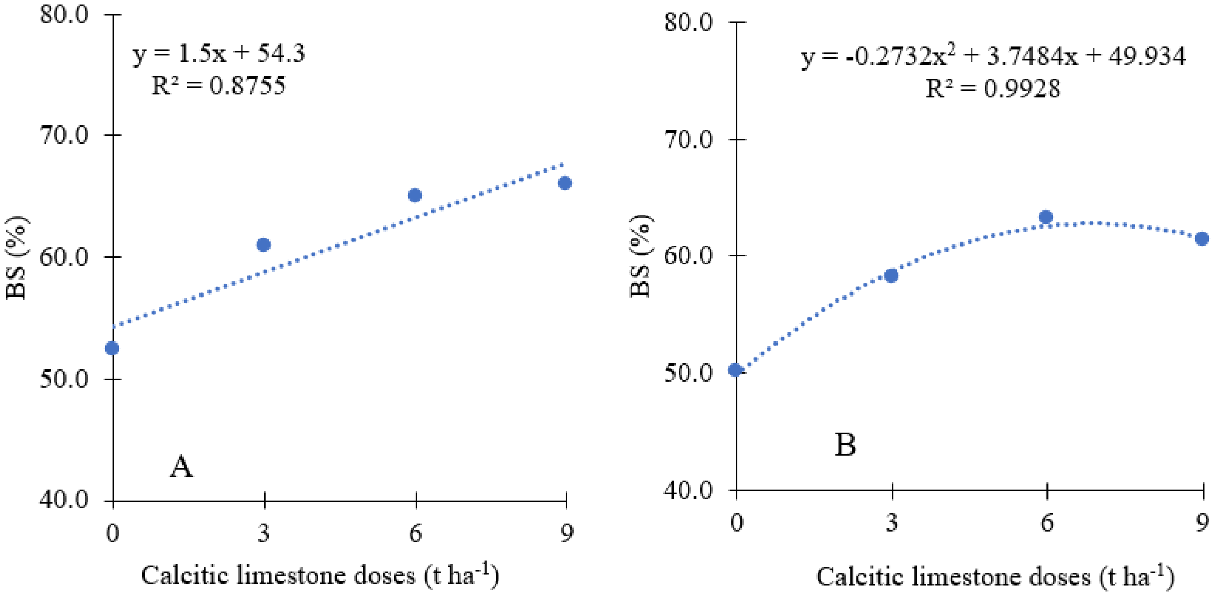

FIGURE 7 - Base saturation values (V%) in the soil after surface application of doses of calcitic limestone in the layers 0-0.05 m (A) and 0.05-0.10 m (B).

TABLE 3 - Average values of soil chemical attributes under the influence of liming in the layers 0-0.05, 0.05-0.10, and 0.10-0.20 m, one and two years after the surface application of calcitic limestone

Year	pH	Al	H + Al	K	BS
	$CaCl_2$	---------------cmol$_c$ dm^3---------------			%
			Layer of 0-0.05 m		
1	4.68b*	0.14a	6.43a	0.55b	53.50b
2	5.48a	0.04b	3.32b	0.82a	68.60a
			Layer of 0.05-0.10 m		
1	4.65b	0.29a	6.64a	0.47b	50.50b
2	5.34a	0.10b	3.47b	0.88a	65.89a
			Layer of 0.10-0.20 m		
1	4.61b	0.40a	6.87a	0.42b	47.65a
2	5.08a	0.18b	3.90b	0.73a	59.69b

*Means followed by the same lowercase letter in the column and 'a' in the row do not differ statistically according to the Tukey test (5%).

The Ca levels in the 0-0.05 m and 0.05-0.10 m layers did not show significant effects for the year, with an average of 4.96 and 4.44 cmolc dm^{-3}, respectively, for year 1 and 2. However, it had an effect in the 0.10-0.20 m layer, where in the second year, there was a decrease in concentration compared to the first year (4.43 to 3.58 cmol$_c$ dm^{-3}). This fact is related to the slow reaction of limestone that occurs over time after application, due to the low solubility of the corrective in the soil profile (PAULETTI et al., 2014; MEERT et al., 2016), which may have been accentuated in this study by the application method and the limestone's PRNT.

To achieve promising results with liming, it is necessary to understand the characteristics of the type of corrective used, the required dose, as well as managing the best application method and the ideal time for application, always considering the crop to be planted and the soil type. In this way, plants have conditions to express their maximum productive potential through better utilization of available nutrients, without the risk of toxicity (MARASCHIN et al., 2020).

Considering the obtained results, significant increases in soil calcium levels and neutralization of different types of acidity were identified. These findings demonstrate the effectiveness of the proposed liming application. Although the comparison between layers was not the focus, changes in chemical attributes were observed up to a depth of 20 cm when limestone incorporation was not performed. This opens opportunities for future research aimed at understanding the mechanisms that contributed to such effects.

CONCLUSIONS

Liming with calcitic limestone after 2 years provided improvements to the root environment up to a depth of 0.20 m, with an increase in pH and base saturation, as well as a reduction in aluminum and potential acidity.

Calcitic limestone doses did not influence soil magnesium levels.

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