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Biogenic, sedimentary, and metamorphic limestone: a comparative characterization of soil amendment[1]

Biogenic, sedimentary, and metamorphic limestone: a comparative characterization of soil amendments[1]

Maria Maiara Cazotti[2]* , Liovando Marciano da Costa[2], Paulo Roberto Cecon[3]

ABSTRACT

Liming acid soils is fundamental for agricultural activity such as the study and characterization of alternative liming materials. The objective of this study was to characterize biological, sedimentary, and metamorphic limestones. The following limestones were studied: biogenic (BL), sedimentary (SL), commercial (CL), and marble (ML). This study evaluated total relative neutralizing power (TRNP), chemical composition, specific surface area, and Ca^{2+} and Mg^{2+} release at concentrations of 0.10, 0.50, 1.00, and 2.00 mol L^{-1} HCl, in addition to the effects on the soil 90 days after limestone application. The Si identified contributed to the lower TRNP of BL (73.7%) and CL (74.4%). At the lowest HCl concentrations, BL was the most reactive, but with an increase in concentration, ML became the most reactive. The highest CaO (58.32%) and MgO (13.05%) levels were observed in SL and ML, respectively, which contained the highest Ca^{2+} (3.95 $cmol_c$ dm^{-3}) and Mg^{2+} (1.09 $cmol_c$ dm^{-3}) concentrations when applied to the soil. All the limestones increased pH and lowered soil H+Al. Soil Ca^{2+} and Mg^{2+} were influenced by the composition of the amendments.

Keywords: liming; lithothamnium; soil acidity.

RESUMO

Calcário biogênico, sedimentar e metamórfico: caracterização comparativa na correção de solos[1]

A correção da acidez é fundamental para a atividade agrícola em solos ácidos, assim como a caracterização e estudo do efeito no solo de fontes alternativas de corretivos. Objetivou-se caracterizar os calcários de origem biológica, sedimentar e metamórfica. Os calcários estudados foram: biogênico (CB), sedimentar (CS), comercial (CC) e o mármore (CM). Foram avaliados: poder relativo de neutralização total (PRNT); composição química; área superficial específica e liberação de Ca^{2+} e Mg^{2+} nas concentrações de 0,10; 0,50; 1,00 e 2,00 mol L^{-1} de HCl e os efeitos no solo, após 90 dias da aplicação dos calcários. O Si identificado contribuiu para o menor PRNT do CB (73,7%) e CC (74,4%). Nas menores concentrações de HCl, o CB mostrou-se mais reativo, porém com o aumento da concentração do HCl, o CM passou a ser mais reativo. Os maiores teores de CaO (58,32%) e MgO (13,05%) foram observados no CS e CM, respectivamente, que contribuíram com maiores aportes de Ca^{2+} (3,95 $cmol_c$ dm^{-3}) e Mg^{2+} (1,09 $cmol_c$ dm^{-3}), quando aplicados ao solo. Todos os calcários promoveram elevação do pH e redução do H+Al no solo. Os teores de Ca^{2+} e Mg^{2+} no solo foram influenciados pela composição dos corretivos.

Palavras-chave: lithothamnium; calagem; acidez do solo.

INTRODUCTION

Acid soils present high saturation by Al, low saturation by base, and lower availability of P (Fageria, 2011), all of which limit the development of most agricultural crops (Bortoluzzi *et al.*, 2014; Singh *et al.*, 2017). Liming stands out as an efficient and less costly practice to raise pH, contents of Ca, Mg, base saturation, and P availability and to reduce toxic Al in soil (Fageria, 2011, Rheinheimer *et al.* 2018). These effects result in a significant improvement in the production capacity of the soils, which allows better yields to the farmer in addition to avoiding the opening of new areas (Crusciol *et al.*, 2016; Inagaki *et al.*, 2016).

Although studies on the field of acidity correction and improvement in soil fertility show great progress, there is a need to seek new agricultural inputs, which are sustainable and provide greater productivity. In this context, it is important to characterize and understand the behavior of non-conventional sources for acidity correction in the soil, such as marine biogenic limestone.

Limestone produced from the extraction of calcareous algae receives the name of marine biogenic limestone or lithothamnium, alluding to the genus of Lithothamnium algae, which are the most extracted ones. The group of calcareous algae presents over 30 genera and about 500 species (Dias, 2000). Marine biogenic limestone represents a renewable short-term source. According to Dias (2000) and Melo & Moura (2009), as long as there is light, algae grow naturally in the marine environment up to approximately 200 m of depth. Since the seventeenth century, calcareous algae have been used for the correction of acid soils in Europe (Dias, 2000). However, in Brazil, its agricultural use and exploration are still incipient.

According to Alvarez *et al.* (1999), the reactivity of a limestone depends somewhat on its geological nature, in which those of sedimentary origin and of a less crystalline nature are more reactive than the metamorphic ones, with a more crystalline structure. Gallo & Catani (1954) reported that sedimentary rocks are more soluble than metamorphic rocks of the same chemical composition. However, Bellingieri *et al.* (1989) reported that the efficiency of limestones in soil acidity correction is not influenced by their geological nature, provided they have the same particle size. Such information gives rise to a demand for knowledge on the performance of biogenic, sedimentary, and metamorphic limestone in agriculture.

Limestones of sedimentary origin are formed through the disintegration and decomposition of preexisting rocks by weathering agents, in which the Ca in solution is conducted to continental or marine accumulation sites. Evaporation and temperature variations can reduce the CO_2 content in the water and precipitate $CaCO_3$ due to

saturation conditions (Sampaio & Almeida, 2008). Metamorphic rocks, represented by marbles, can also be used as acidity correctives. Moreover, they are composed of calcite and/or dolomite and result from the recrystallization of limestone rocks, mostly of sedimentary nature by means of high temperatures and pressure (Sampaio & Almeida, 2008).

The objective of this study was to comparatively characterize limestone of biological, sedimentary, and metamorphic origin for use in agriculture.

MATERIAL AND METHODS

The experiment was carried out in the Geochemistry Laboratory and in a greenhouse belonging to the Department of Soils in the Universidade Federal de Viçosa, Viçosa, MG - Brazil, from March to July 2014. The limestones used in the experiment were the following: marble (ML), biogenic limestone (BL), commercial limestone (CL), and sedimentary limestone (SL). Figure 1 shows the location of the municipalities from where the corrective samples were collected.

Blocks of the studied materials were collected in each location. In the laboratory, ML and SL were washed with distilled water, broken into smaller blocks with the aid of a geological hammer, and ground in a disc mill. After that, they were standardized in the particle size of less than 0.074, for characterization and experiment assembly.

The total relative neutralizing power (TRNP) and the CaO and MgO contents were determined according to Mapa (2014), considering four replications. The determination of Ca^{2+} and Mg^{2+} elements was obtained using an atomic absorption spectrometer. Total contents of Ca, Mg, Al, K, P, Na, and Si contents were determined by the alkaline fusion method, following the procedure described by Pansu & Gautheyrou (2003), adapted by Guerra *et al.* (2013). The dosage of the above elements was performed in inductively coupled plasma - optical emission spectrometry (ICP-OES). The B.E.T. method was used to determine the specific surface area (SSA). (Brunauer, Emmett and Teller) using the NOVA instrument (Quantachrome Instruments version 10.01) (Gregg & Sing, 1982).

Regarding the solubility test in hydrochloric acid, the methodology adapted from Amaral Sobrinho *et al.* (1992) was used, which consists of weighing 1 g of limestone in 125-mL Erlenmeyer. Then, 50 mL HCl was added at the concentrations of 0.01, 0.10, 0.50, 1.00, and 2.00 mol L^{-1}, with four replicates. The reaction time was 12 h, in which the samples were shaken for 15 min every hour in a shaker of 200 oscillations per minute. After the reaction period, the solutions containing limestone samples were filtered on slow filtering quantitative filter paper. Then, contents of the Ca^{2+} and Mg^{2+} were determined in the filtrate by

atomic absorption spectroscopy. The filter papers containing the residues were taken to the muffle at 500 °C for 1 h. By mass difference before acid attack and post muffle, it was possible to determine the limestone residue for each sample.

An incubation experiment was carried out, by using samples of Red-Yellow Latosol (Embrapa, 2018), collected in the city of Viçosa, MG, in the 0-20 cm layer. The results of the soil chemical analysis were as follows: pH (H_2O), 5.24; Al^{3+} ($cmol_c$ dm^{-3}), 1.4; $H + Al^{3+}$ ($cmol_c$ dm^{-3}), 9.70; Ca^{2+} ($cmol_c$ dm^{-3}), 0.63; Mg^{+2} ($cmol_c$ dm^{-3}), 0.14; K^+ (mg dm^{-3}), 43.00; P (mg dm^{-3}), 1.2. The physical characterization indicated sand, silt, and clay contents of 130, 190, and 680 g kg^{-1}, respectively. The methods used in these analyzes are described by Embrapa (2011). Based on the results of chemical analysis of soil and limestone, the need for liming (NL) was determined for the soil, using the Al^{3+} neutralization method and raising of contents of Ca^{2+} and Mg^{2+} (Alvarez *et al.*, 1999). For the purpose of calculating the NL, the parameters of the corn crop were considered. To calculate the amount of limestone to be applied, the TRNP found for the different materials studied was considered.

The limestones were applied to the dry soil and homogenized throughout the volume. The treatments, arranged in a factorial scheme $(4 \times 4) + 1$, consisted of four acidity limestones (ML, BL, CL, and SL), four NL levels (30, 60, 100 and 150%), and one control, with no limestone application, and were distributed in randomized blocks, with three replications. Each experimental unit consisted of a plastic bag, with a capacity of 1 dm^3 of soil, distributed on a bench, inside the greenhouse. The experimental units were maintained with humidity between 60 and 80% of the field capacity, through weighing and replenishment of water. The plastic bags were kept slightly open, using polypropylene tubes, to allow gas exchanges.

The sample units were incubated for 90 days. At the end of the incubation period, the fine air-dry soil of each experimental unit was obtained. From the fine air-dry soil, the following chemical and physical-chemical features were determined: pH in water, in the 1:2.5 soil:solution ratio; Ca^{2+} and Mg^{2+} contents (extraction with KCl 1 mol L^{-1}); exchangeable acidity by titration (extraction with KCl 1 mol L^{-1}); and potential acidity, also by titration (extraction with $Ca(Ac)_2$ 0.5 mol L^{-1} at pH 7, 1:15 soil:solution ratio) (Embrapa, 2011).
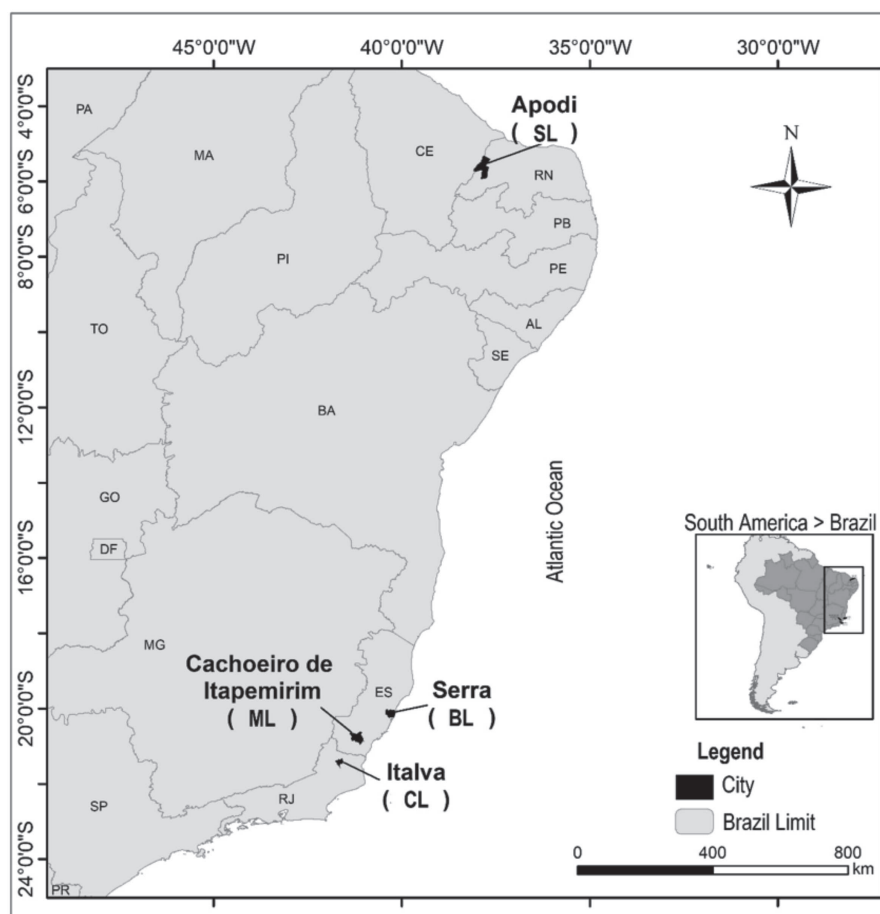

Figure 1: Location of the collection area of the different correctives. ML: metamorphic limestone; BL: biogenic limestone; CL: commercial limestone; and SL: sedimentary limestone.

The means obtained for 100% of the NL at the agronomic interest level were compared by the classification proposed by the Fifth Approximation Recommendation of Corrective and Fertilizers (Ribeiro *et al.*, 1999) to relate the results experimentally obtained for the different limestones with those targeted in the agricultural practices.

Data were subjected to analysis of variance. In relation to the qualitative factor, the means were compared using the Tukey test, adopting the 5% probability level. To compare the control to the other treatments, Dunnett's test was used, adopting the 5% probability level. For the quantitative factor, regressions were adjusted, and the models were chosen based on the significance of the regression coefficients using the t test at the 1% probability level, in the coefficient of determination (R^2 = S.S Regression/ S.S Treatment) and the behavior of the phenomenon under study. Because of the great variability, the descriptive statistical analysis was chosen for the chemical characterization of the different acidity correctives under study. SAEG 9.1 was used to support the statistical analysis (Universidade Federal de Viçosa, 2007).

RESULTS AND DISCUSSION

In the chemical limestone characterization (Table 1), except for Ca and Mg, the highest concentrations of Al, Na, Zn, Fe, Cu, Mn, B, K, P, and Si elements were observed in BL (Table 1). According to Melo & Moura (2009), the main characteristics that potentiate calcareous algae are attributed to the greater availability of micronutrients, adsorbed on cell walls, easily assimilated by plants and animals. In addition, Dias (2000) indicated that calcareous algae are composed mainly of $CaCO_3$ and $MgCO_3$ and varying concentrations of elements such as Fe, Mn, B, Ni, Cu, Zn, Mo, Se, and Sr.

A larger concentration of Mg and Ca was observed in CM and in SL, respectively, due to the inherent characteristics of each reserve. Jordt-Evangelista & Viana (2000) observed that the marbles that compose the collection region of the ML are predominantly composed of dolomite, with small intrusions of calcite, whereas limestones with low dolomite content compose the collection SL region.

Due to the particle size standardization in a sieve smaller than 0.074 mm, the TRNP will be equal to the NP (neutralization power). The limestone NP was: ML = 98.9%; BL = 73.7%; CL = 74.4%; and SL = 96.3%. The lowest NP values were observed in the BL and CL, a fact that may be associated with the presence of silicate minerals in the composition of the correctives. In the chemical characterization, 65.72 and 57.19 mg g^{-1} Si were observed in BL and CL correctives, respectively. The neutralizing capacity of limestones considers the chemical purity of the rock of origin and the fineness of grinding (Quaggio, 2000). For the same granulometry, the higher the chemical purity of the rock, the higher the TRNP of the corrective.

The CaO and MgO contents maintained the same behavior of the total contents of Ca and Mg in the correctives. The CaO and MgO contents were as follows: ML with 35.40% CaO and 13.05% MgO; BL with 43.90% CaO and 2.91 MgO; CL with 30.80% CaO and 6.63% MgO; and SL with 58.32% CaO and 0.51% MgO.

The largest SSA was observed in BL, with a value of 4.05 m² g^{-1}. According to Melo & Moura (2009), calcareous algae present high porosity that provides a greater surface area of action. The ML, CL, and SL presented SSA of 0.09, 1.68, and 2.08 m² g^{-1}, respectively. The smaller SSA observed in the ML and CL may be attributed to the higher crystallinity of these rocks.

According to Gonçalves *et al.* (2011) and Rodrighero *et al.* (2015), neutralization speed depends on the surface

Table 1: Average contents and standard deviations of the contents of Al, Ca, K, Mg, Na, P, Fe, Zn, Cu, Mn, B, and Si in the different acidity correctives

Acidity correctives	Al	Ca	Mg	Na	Zn	Fe
	mg g⁻¹					
ML	0.614 ± 0.022	262.694 ± 5.305	179.238 ± 3.920	0.116 ± 0.006	0.009 ± 0.001	0.375 ± 0.042
BL	10.541 ± 0.833	283.143 ± 7.760	29.960 ± 1.001	2.870 ± 0.042	0.013 ± 0.001	11.489 ± 0.235
CL	5.624 ± 0.472	274.192 ± 3.299	115.018 ± 3.274	0.119 ± 0.001	0.012 ± 0.0001	2.004 ± 0.006
SL	2.688 ± 0.787	403.464 ± 7.063	7.406 ± 0.575	0.097 ± 0.006	0.007 ± 0.0001	1.424 ± 0.036
	Cu	**Mn**	**B**	**K**	**P**	**Si**
	mg g⁻¹					
ML	0.006 ± 0.0001	0.008 ± 0.001	0.004 ± 0.0001	4.778 ± 0.898	1.406 ± 0.009	11.702 ± 0.312
BL	0.006 ± 0.0001	0.379 ± 0.005	0.012 ± 0.0001	4.158 ± 0.386	1.786 ± 0.093	65.718 ± 6.890
CL	0.008 ± 0.0001	0.064 ± 0.0001	0.005 ± 0.0001	3.544 ± 0.487	<LD	57.187 ± 1.361
SL	0.008 ± 0.0001	0.046 ± 0.001	0.004 ± 0.0001	1.773 ± 0.089	<LD	10.044 ± 0.496

<LD = below the gadget detection limit.

area of the corrective in contact with the soil and, due to the low solubility of the limestones, it requires its incorporation in the soil to promote a better reaction (Alleoni *et al.*, 2005). Acidity correctives with a large contact surface may present great potential in areas where limestone has not been incorporated such as in the no-tillage system. According to Alleoni *et al.* (2005), in the no-tillage system, as time passes by, the intervention with limestone application is necessary because there is a decrease in pH and, consequently, an increase in Al^{3+} on the superficial layer. In these cases, the use of limestones with higher reaction velocity associated with greater residual power becomes interesting. In this way, BL could be used combined with other limestones with a smaller contact surface to reduce the reaction time and to increase the residual effect.

Solubility of the different limestones in hydrochloric acid

Among the evaluated limestones (Table 2), BL was more reactive at the concentrations of 0.01 and 0.1 mol L^{-1} HCl; however, as the HCl concentration was increased, the carbonate consumption occurred, providing greater residue generation in BL as well as in CL treatments as both limestones presented the lowest NP values among them. The ML and SL presented higher chemical purity, consequently, higher NP values and a smaller amount of residue.

By using the adjusted equation of the variable limestone residue as a function of the concentration (Figure 2A), it was observed that concentrations greater than 0.31 mol L^{-1} HCl solubilize the carbonates present in BL. In CL, values greater than 0.29 mol L^{-1} HCl were obtained, that is, from those concentrations, the concentration does not affect the generation of limestone residue anymore. A likely influence of the specific surface area was observed in ML and SL. In SL, the surface area is 30 times larger than in ML, with a faster consumption of carbonates. On the other hand, because ML is a more crystalline rock and, consequently, presents a smaller SSA, HCl found greater difficulty to solubilize the carbonates. The lower solubility of ML may also be related to its chemical constitution; when a change occurs in the crystalline structure of limestones, through the substitution of Ca ions with Mg ions, the solubility of limestones decreases (Grunwaldt *et al.*, 2016). Rodrighero *et al.* (2015) observed that the solubility of limestones containing a large Ca content was higher than that of dolomitic limestones with the same particle size.

In relation to Ca^{2+} release, it was observed that at the concentration of 0.01 mol L^{-1}, the correctives ML, CL, and SL presented a greater release of Ca^{2+} in relation to BL; at the concentration of 0.10 mol L^{-1} HCl, the limestones that

Table 2: Average values of limestone residue, Ca^{2+}, and Mg^{2+} release for the different acidity correctives and evaluated concentrations of HCl

HCl concentration	Limestone residue				Ca^{2+} release				Mg^{2+} release			
	ML	BL	CL	SL	ML	BL	CL	SL	ML	BL	CL	SL
mol L^{-1}					mg mg^{-1}							
0.01	0.940a	0.904b	0.937a	0.954a	14.279b	15.347b	18.559a	16.448a	1.756a	1.239b	0.802bc	0.518c
0.10	0.741a	0.686c	0.714b	0.720b	83.501c	102.990b	117.760a	124.876a	15.104a	5.854b	4.782c	1.004d
0.50	0.033c	0.187b	0.217a	0.033c	321.431a	307.110b	267.132c	323.534a	63.810a	16.761c	46.229b	3.089d
1.00	0.036c	0.165b	0.232a	0.034c	345.076c	420.121b	321.298d	500.081a	82.796a	16.997c	47.007b	3.227d
2.00	0.034c	0.165b	0.237a	0.030c	385.651c	434.528b	353.970d	574.958a	88.921a	17.184c	48.730b	3.417d

Means followed by the same letter in the row are not different from each other at the 5% probability level by the test of Tukey

released more Ca²⁺ to the solution were CL and SL; and at the concentration of 0.50, the limestones ML and SL stood out. Only at the 1.00 and 2.00 mol L⁻¹ HCl concentrations, the Ca²⁺ release followed the same trend observed in the chemical characterization. The limestones presented CaO percentage and Ca²⁺ release in the following order: SL> BL> ML> CL. In relation to the release of Mg²⁺, it followed the same trend observed in the chemical characterization, in which the limestones ML and CL presented the greatest percentages of MgO and greater release of Mg to the solution (Table 2).

For the adjusted values of Ca²⁺ release (Figure 2B), it was observed that as HCl concentration increased, a greater Ca²⁺ release occurred in limestones with higher CaO, SL followed by BL. Similar behavior was observed for Mg²⁺ release when ML and CL also released more Mg²⁺ since they presented a higher percentage of MgO (Figure 2C).

Effects of limestones on soil physicochemical characteristics

It was observed with the analysis of variance that only the levels of NL had a statistically significant influence

on soil pH (p <0.05), whilst the variables H+Al, Ca²⁺, and Mg²⁺ were statistically influenced by the different sources of limestone and liming levels.

It was observed that the adjusted pH values as a function of NL increased linearly as the levels of NL increased (Figure 3A). Similar results were also observed by Kurihara *et al.* (1999), in which at the end of 100 days of incubation, the increase in pH was similar between sedimentary and metamorphic limestones with a particle size within the 50-70 mesh interval. The treatments that received acidity correctives showed significant (p<0.05) and greater results than the control by the Dunnett test (Table 3). The pH of the control was classified as low (4.5-5.4); however, regardless of the soil acidity corrective applied to the soil at the level of agronomic interest, the pH reached values classified as good (5.5-6.0), and at the level of 150% of liming requirement, it reached values classified as high (6.1-7.0).

In relation to the active acidity, ML and BL reduced Al³⁺ from 1.23 cmol_c dm⁻³, observed in the control, to 0.48 cmol_c dm⁻³ at 30% of NL. The value observed when the CL and SL were applied was 0.58 cmol_c dm⁻³. At 60% of NL, values of Al³⁺ observed with the application of the BL
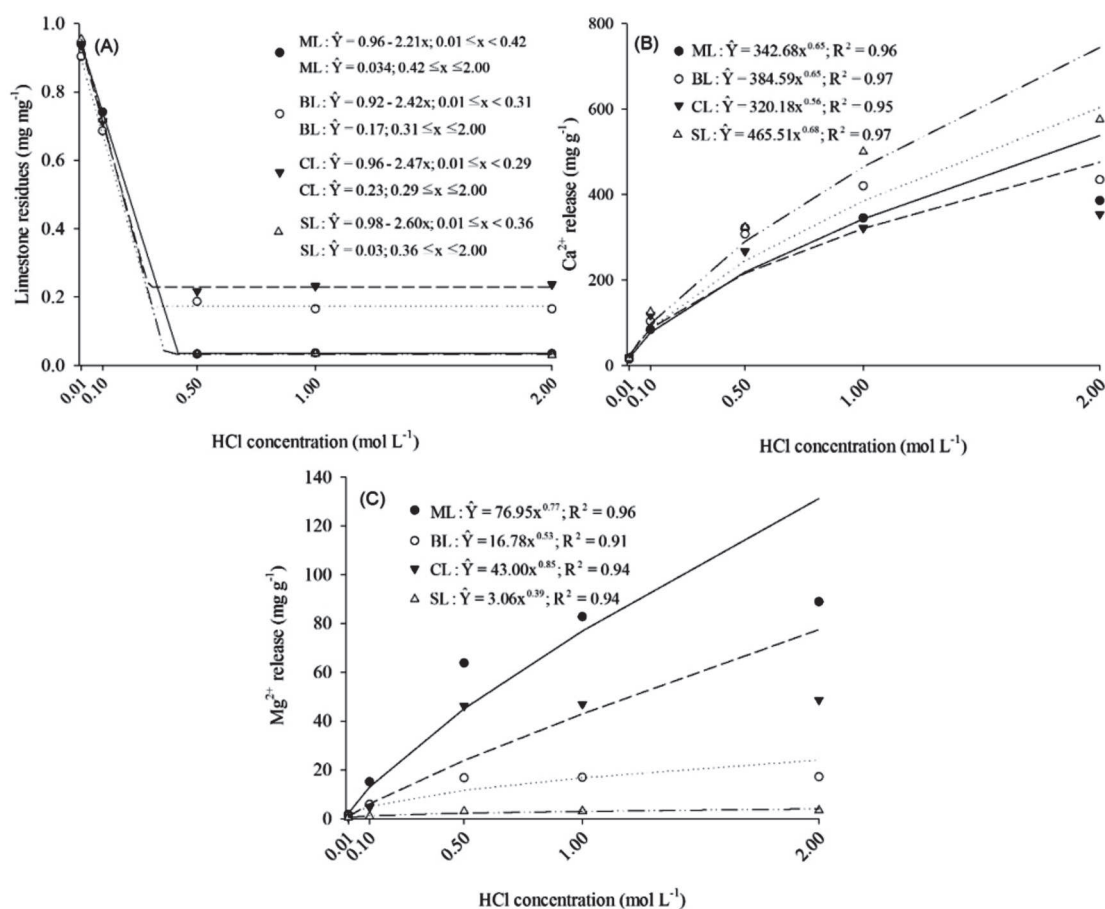

Figure 2: Values of the limestone residues, Ca²⁺, and Mg²⁺ release as a function of HCl concentration for the different acidity correctives.

and SL correctives were 0.10 $cmol_c\ dm^{-3}$, ML of 0.19 $cmol_c\ dm^{-3}$, and CL of 0.29 $cmol_c\ dm^{-3}$. The pH range reached at 100 and 150% of liming requirement, regardless of the limestone applied, was sufficient to reduce Al^{3+} to zero. The exchangeable acidity has an inverse relationship with soil pH; therefore, the rise in pH is one of the alternatives to reduce the toxic effect of Al (Sousa *et al.*, 2007). According to the same authors, when the pH of the soil, determined in water, is close to 5.5, Al^{3+} is reduced to almost zero.

The application of increasing levels of limestone promoted a reduction in values of H + Al (Figure 3B). In relation to the behavior of the different limestones within each liming level (Table 3), at the 30% level, the BL acidity corrective presented the lowest average H + Al values. At 60 and 100% levels, the lowest mean values were observed in ML-treated samples. At the 150% level, there was no statistical difference between limestones. Regardless of the evaluated limestone, at the liming level of agronomic interest, limestones were effective in reducing the potential acidity of the very high level presented in the control (> 9.00 $cmol_c\ dm^{-3}$) for values classified as medium (2.51-5.00 $cmol_c\ dm^{-3}$). According to Dunnett's test, all treatments that received lime presented lower and statistically significant H + Al values ($p<0.05$) compared with the control (Table 3).

The average content of Ca^{2+} in the soil increased linearly as the levels of the applied liming requirement levels increased (Figure 3C). The BL and SL presented a tendency to contribute with more Ca^{2+} in relation to ML and CL. It is likely that such behavior is related to the fact that SL presents a greater percentage of CaO and second largest specific surface. Although ML presented TRNP very close to SL, which results in the application of very close acidity corrective amounts, the ML contributed with less Ca^{2+} in the soil. Similar behavior was observed between BL and CL, although the TNRP was very close, BL displayed a larger CaO percentage, which resulted in a greater release of Ca^{2+} in contact with the soil. Despite presenting a higher percentage of CaO in relation to CL, in the soil, ML behaved in an opposite manner, possibly due to the largest specific surface area of CL, 18 times larger than ML, which promoted the highest Ca^{2+} release.

In relation to the behavior of the different limestones within each liming level, at the 30% level, BL and SL were more efficient in releasing Ca^{2+} to the soil, while for the other evaluated liming levels, SL offered a greater release of this nutrient to the soil. The limestones ML and CL presented similar behavior at the 60% liming requirement level, with a lower contribution of Ca^{2+} to the soil. At the 100 and 150% liming levels, the smallest mean values of Ca^{2+} release were observed in ML (Table 3).
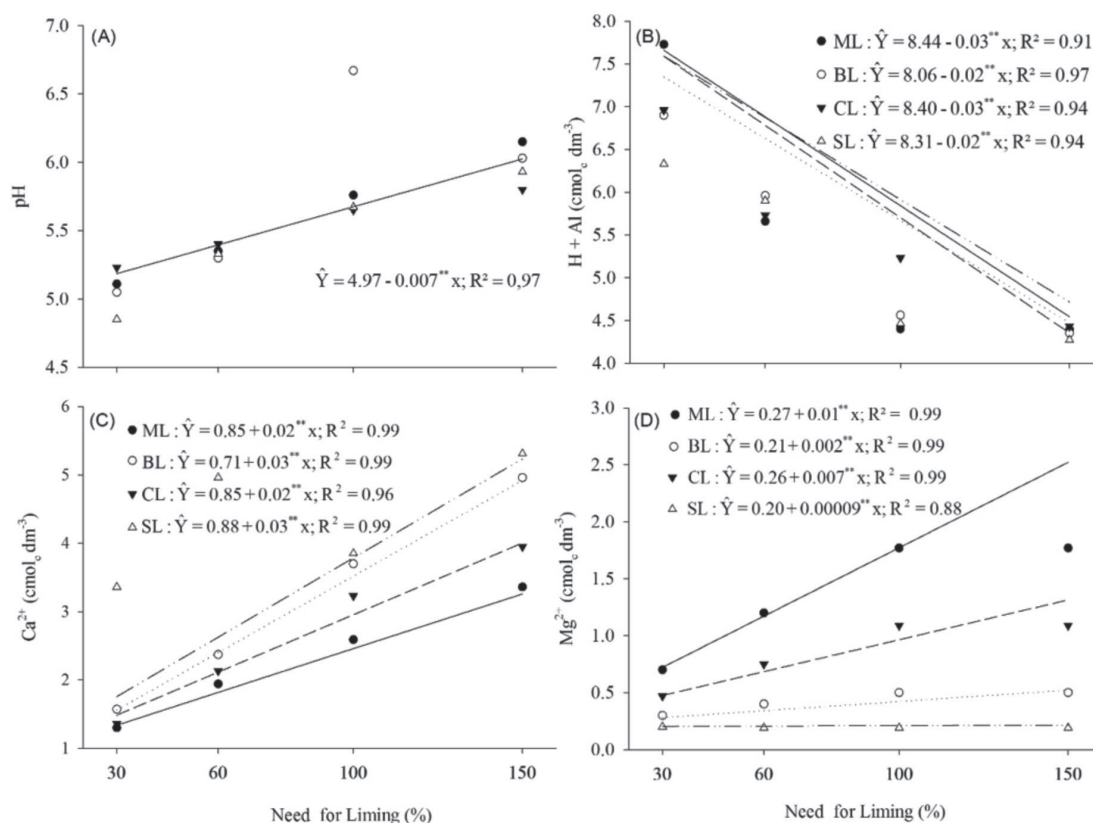

Figure 3: pH values in the soil as a function of liming requirement and H + Al, Ca^{2+}, and Mg^{2+} in the soil as a function of different acidity correctives and the need for liming. ** significant at the 1% probability level by the t test.

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Table 3: Mean values of pH, H+Al, Ca^{2+}, and Mg^{2+} obtained for the samples of soils treated with different acidity correctives within different levels of liming 90 days after reaction

Acidity corrective	Test[1]	30	60	100	150	Test[1]	30	60	100	150
			pH					H + Al		
			cmol$_c$ dm^{-3}							
ML	4.61	5.11a*	5.35a*	5.76a*	6.15a*	9.03	7.73a*	5.66d*	4.40a*	4.39a*
BL	4.61	5.05a*	5.30a*	6.67a*	6.03a*	9.03	6.90c*	5.96a*	4.56b*	4.35a*
CL	4.61	5.23a*	5.40a*	5.65a*	5.80a*	9.03	6.96b*	5.73c*	5.23a*	4.43a*
SL	4.61	4.85a*	5.33a*	5.67a*	5.93a*	9.03	6.33d*	5.90b*	4.46c*	4.27a*
			Ca^{2+}					Mg^{2+}		
	mol$_c$ dm^{-3}		cmol$_c$ dm^{-3}							
ML	0.68	1.30b*	1.94c*	2.59d*	3.36d*	0.14	0.70a*	1.20a*	1.77a*	1.77a*
BL	0.68	1.57a*	2.37b*	3.70b*	4.96b*	0.14	0.30a*	0.40ab*	0.50b*	0.50b*
CL	0.68	1.36b*	2.13c*	3.23c*	3.85c*	0.14	0.47a*	0.75ab*	1.09ab*	1.09ab*
SL	0.68	1.72a*	2.71a*	3.95a*	5.31a*	0.14	0.20a	0.19b	0.19b	0.19b

[1]: Control.

Means followed by one same letter, at least, in the column are not different from each other by the 5% probability level by the test of Tukey. Means followed by an asterisk in the row are not different from control at the 5% probability level by the test of Dunnett.

A linear increase occurred in the average content of Mg^{2+} in the soil as the liming requirement levels increased (Figure 3D). The b$_1$ values of the equations presented in this figure indicate that each unit of liming requirement applied to the soil causes an increase of 0.01, 0.002, 0.007, and 0.00009 cmol$_c$ dm^{-3} of Mg^{2+} when the soils were incubated with ML, BL, CL, and SL. The largest contribution of ML and CL of Mg^{2+} was expected since, among the evaluated limestones, they were those with the largest percentages of MgO.

For the variable Mg^{2+}, it was observed that at the 30% NL level, no difference was found between the application of the different limestones. At the 60% NL level, the application of ML, BL, or CL resulted in a higher Mg^{2+} input to the soil when compared with SL. At the levels of 100 and 150% NL, ML and CL contributed with the largest input of Mg^{2+} to the soil (Table 3).

Treatments that received limestone presented higher and statistically significant (p<0.05) average values of Ca^{2+} and Mg^{2+} levels than the control by Dunnett's test (Table 3), except for the variable Mg^{2+} in the soil that received SL, a fact attributed to chemical characteristics of the rock that has been previously discussed.

Regarding the NL level of agronomic interest, the evaluated limestones increased the level of Ca^{2+} from very low (0.41-1.20 cmol$_c$ dm^{-3}) to the good level (2.41-4.00 cmol$_c$ dm^{-3}). For Mg^{2+}, although its level in the soil was very low (d" 0.15 cmol$_c$ dm^{-3}), the incubation with ML increased it to a very good level (> 1.50 cmol$_c$ dm^{-3}). Biological and commercial limestones were used for the good level (0.91-1.50 cmol$_c$ dm^{-3}), while SL increased it to 0.20 cmol$_c$ dm^{-3}, classified as low level of Mg^{2+} (0.16-0.45 cmol$_c$ dm^{-3}).

Limestones should be chosen not only for their acid neutralization power but mainly for the Ca:Mg ratio in the material. Among the limestones of acidity under study, the Ca:Mg ratio was 3:1 for ML, 15:1 for BL, 4:1 for CL, and 114:1 for SL. Currently, most studies consider Ca:Mg ratios between 4:1 for most cultivated plants and 8:1 as adequate for some less-demanding plants (Medeiros *et al.*, 2008). Excess of Ca^{2+} in relation to Mg^{2+} in the soil solution may impair the absorption of the later (Malavolta *et al.*, 1997). The interrelationship between nutrients in plant nutrition is related to their close chemical properties, such as ionic radius, valence, degree of hydration, and mobility, causing competition for soil adsorption sites and root absorption (Medeiros *et al.*, 2008; Júnior *et al.*, 2013). Medeiros *et al.* (2008) observed the influence of the high Ca:Mg ratio of the correctives on nutritional imbalance, through a reduction in the growth and productivity of forage plants.

CONCLUSIONS

When applied to soil, biogenic, metamorphic, and sedimentary limestones are able to correct the soil acidity. The increase in the levels of Ca^{2+} and Mg^{2+} in the soil are influenced by the chemical composition of the limestones. The limestones of sedimentary and metamorphic origin account for the greater concentration of Ca^{2+} and Mg^{2+} in the soil.

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