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ABSTRACT
The efficiency of limestone in amending soil acidity is primarily based on the particle size and the neutralization value of the ground rock, but the origin of the rock can also affect its reactivity. The aim of this work was to evaluate, under controlled conditions, the efficiency of the reactivity of sedimentary limestones of different particle sizes in neutralizing soil acidity. The experiment was conducted using a clayey and a sandy soil, and the treatments consisted of four samples of a sedimentary limestone (with the same neutralization values but different particle sizes), two metamorphic limestones and an untreated control. In the first months of incubation, the sedimentary limestones demonstrated higher soil amelioration abilities than the metamorphic limestones, but all samples used in the study achieved the goal of neutralizing soil acidity to desired values: a base saturation (BS) of ~70% and a pH > 6.0. In sedimentary limestones, the availability of calcium (Ca) and magnesium (Mg) was more closely related to the levels of Ca oxide (CaO) in the amendment than to the size of the particles. The results of this study suggest that the currently used equation may underestimate the reactivity of certain limestones.

Introduction

The use of limestone to neutralize soil acidity is a widespread agricultural practice (Conyers et al. 1996; Quaggio et al. 1995; Yang, Mitchell, and Howe 2018), and the limestone is obtained by grinding calcareous rocks that primarily consist of calcium (Ca) and magnesium (Mg) carbonates (Jones and Mallarino 2018; Lepsch, Rotta, and Kupper 1968). As rock composition is variable depending on its formation process, limestones can differ greatly in chemical composition, physicochemical properties, and mineralogical characteristics (Gallo 1954; Gallo and Catani 1954); the solubility of each liming material depends on the combined action of these factors (Gallo and Catani 1954; Jones and Mallarino 2018; Rippy et al. 2007).

The capacity and speed with which limestone ameliorates soil acidity depend on the combination of the chemical and physical attributes of the rock (Conyers et al. 1996; Jones and Mallarino 2018; Kurihara et al. 1999; Mayfield et al. 2004). The chemical attributes of limestone, which are represented by its neutralizing power (NP), depend on the type and concentration of the neutralizing agents in the material (Kurihara et al. 1999; Mayfield et al. 2004; Quaggio 2000; Yang, Mitchell, and Howe 2018) and indicate the capacity of the material to neutralize acidity but not its reactivity (Gallo and Catani 1954). The physical attributes, which are represented by its relative efficiency (RE),

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depend on the geological nature of the limestone and the extent of milling of the parent rock (Kurihara et al. 1999; Quaggio 2000); the reaction speed of a particular limestone in soil is related to its particle size (Gallo 1954; Gallo and Catani 1954; Haby and Leonard 2002; Hodge and Lewis 1994; Jones and Mallarino 2018; Lepsch, Rotta, and Kupper 1968; Viadé et al. 2011).

Several studies have evaluated the capacity of various materials to amend soil acidity, and in most cases, a decrease in particle size and the resultant increase in surface area have translated into an increased solubility of the amendment (Gallo 1954; Gallo and Catani 1954; Haby and Leonard 2002; Hodge and Lewis 1994; Lepsch, Rotta, and Kupper 1968; Meyer and Volk 1952; Shaw and Robinson 1959; Yang, Mitchell, and Howe 2018). Some authors have argued that the particle size of the liming material is more important than the composition of its parent rock in its efficiency as an acidity amendment (Alcarde, Paulino, and Dernardin 1989; Jones and Mallarino 2018; Meyer and Volk 1952; Motto and Mestead 1960), but other studies have indicated that the mineralogical characteristics and texture of the parent rock exert a greater influence (Conyers et al. 1996; Gallo 1954; Jones and Mallarino 2018; Rippy et al. 2007) and that limestones of sedimentary origin are generally more soluble than those of metamorphic origin, even when they are composed of coarser particles (Conyers et al. 1996; Gallo 1954; Gallo and Catani 1954; Kurihara et al. 1999).

Calcareous rocks of a sedimentary origin have been favored as acidity amendments because of their high friability; i.e., they do not require the same level of milling as metamorphic limestones (Kurihara et al. 1999). However, when a sedimentary limestone that has been crushed into coarser particles is submitted to particle size analysis, the larger particles that do not pass through the set of sieves required by the regulatory standards (MAPA-SDA 2006) reduce the calculated effective Ca carbonate ($CaCO_3$) equivalence (ECCE) value of the material, so the actual neutralizing capacity of the material in the soil may be underestimated (Kurihara et al. 1999). Therefore, evaluations of the amelioration capacity of these limestones based on only particle size and the total amount of neutralization agent present in the ground rock (i.e., NP) may not accurately reflect all the characteristics of the material (Gallo 1954).

As suggested by several studies (Alcarde, Paulino, and Dernardin 1989; Meyer and Volk 1952; Motto and Mestead 1960; Verlengia and Gargantini 1972), Brazilian law requires that 100% of the particles of a soil acidity amendment pass through a 2.00-mm sieve [Associação Brasileira de Normas Técnicas (ABNT) no. 10 or 9 mesh]; 70% must pass through a 0.84-mm sieve (ABNT no. 20 or 20 mesh); and at least 50% must pass through a 0.30-mm sieve (ABNT no. 50 or 48 mesh) (MAPA-SDA 2006). Using these standards, the RE of particles with a size between 2.00 and 0.84 mm is 20%; that of particles between 0.83 and 0.30 mm is 60%; and that of particles smaller than 0.30 mm is 100% in the soil (MAPA-SDA 2006). However, because the RE values of sedimentary and metamorphic limestones continue to be evaluated based on the NP of the milled rock and the particle size of the material (i.e., RE) and because there is evidence that sedimentary limestones are more soluble even when milled into larger particles (Gallo 1954; Gallo and Catani 1954; Kurihara et al. 1999), we believe that the present methods of evaluating the RE of sedimentary limestones underestimate the real reaction capacities of these amendments in soils.

Therefore, the objective of this work was to evaluate the RE of sedimentary limestone of different particle sizes in the amelioration of soil acidity.

Materials and methods

The limestones were sampled, dried in a forced-air oven at 105 ± 5ºC until they reached a constant weight, and analyzed for their characteristics (BRASIL 2014). Calcium oxide (CaO) and Mg oxide (MgO) concentrations were determined according to the atomic absorption spectrometry method (BRASIL 2014). The RE and NP values also were determined according to procedure described by MAPA-SDA (2006) and BRASIL (2014), and so the ECCE values were calculated, as follows and the results are shown in Table 1.

$$ECCE\,(\%) = (RE \times NP)/100$$

Table 1. Granulometric and chemical characteristics of the studied limestones.

Limestone	Moisture	CaO	MgO	n° 10 (2 mm)	n° 20 (0.84 mm)	n° 50 (0.30 mm)	RE[a]	NP[b]	ECCE[c]
					(%)				
Sedimentary 1 (S1)	1.0	23.6	15.2	99.9	99.9	99.0	99.6	83.8	83.5
Sedimentary 2 (S2)	1.1	27.0	12.0	99.7	93.0	78.2	90.3	85.3	77.0
Sedimentary 3 (S3)	3.9	28.6	11.4	100.0	93.1	30.8	69.6	85.6	60.0
Sedimentary 4 (S4)	6.8	27.2	11.0	97.9	76.5	12.0	54.9	85.6	47.0
Metamorphic 1 (M1)	1.1	38.7	13.1	99.7	98.2	85.7	93.5	101.2	94.6
Metamorphic 2 (M2)	0.2	29.4	22.7	99.9	88.1	66.1	81.6	108.1	88.3
Efficiency (%)				20.0	60.0	100.0			
Legislation (%)				100.0	70.0	50.0			

[a]RE: reactivity.
[b]$NP_{(\%ECaCO3)}$: neutralizing power.
[c]ECCE: effective calcium carbonate equivalence, calculated according to BRASIL (2014).

Two Red Oxisols (EMBRAPA 2006) of different textures, one clayey and one sandy, were used in the experiment. Soil samples were collected from the 0–20-cm layer, air dried and sieved through a 4-mm mesh sieve and then passed through 2-mm sieves and submitted to chemical (Raij et al. 2001) and particle size (EMBRAPA 1997) analyses (Table 2).

After the characterization of the soil and limestone, the experiment was set up according to a randomized design with four replications in the controlled environment of a greenhouse at the Department of Crop Science, College of Agricultural Sciences of São Paulo State University in Botucatu, SP, Brazil. The lime treatments consisted of four samples of a sedimentary limestone denominated sedimentary 1 (S1), sedimentary 2 (S2), sedimentary 3 (S3), and sedimentary 4 (S4) [with similar NP values and different particle sizes (Table 1)]; two metamorphic limestones denominated metamorphic 1 (M1) and metamorphic (M2); and a control without liming. For treatments S1, M1, and M2, the limestone addition rates were based on the ECCE values and calculated according to Raij et al. (1997) (Tables 1 and 3), as follows:

$$\text{Limestone rate for treatments S1, M1, and M2} \left(\text{t ha}^{-1}\right) = (CEC \times (BS_2 - BS_1))/(ECCE \times 10)$$

where CEC is cation exchange capacity in $mmol_c \ dm^{-3}$, BS_2 is the expected base saturation (70%), and BS_1 is the base saturation measured in soil analysis before the experiment (Table 2).

Table 2. Soil chemical and textural characteristics before the experiment.

	Soil	
Soil characteristics	Clayey	Sandy
pH (1:2.5 soil/CaCl$_2$ suspension 0.01 mol L^{-1})	3.8	3.8
Soil organic matter (g dm^{-3})	27	14
P$_{resin-extractable}$ (mg dm^{-3})	3	1
Al^{3+} (mmol$_c$ dm^{-3})	13.8	12.4
H + Al (mmol$_c$ dm^{-3})	113	76
K$^+$ (mmol$_c$ dm^{-3})	0.2	0.1
Ca^{2+} (mmol$_c$ dm^{-3})	2	1
Mg^{2+} (mmol$_c$ dm^{-3})	1	0
Cation exchange capacity (mmol$_c$ dm^{-3})	116	77
Base saturation (%)	3	1
Sand (g kg^{-1})	160	598
Silt (g kg^{-1})	160	197
Clay (g kg^{-1})	680	205

Table 3. Limestone rates calculated to increase the base saturation values to 70% according to the ECCE values of the limestones and used for Red Oxisols of clayey and sandy textures in the present experiment.

Limestone	Rate calculated[c] (t ha^{-1})	Rate used[c]		CaCO$_{3\text{-Eq}}$[d] (mmol$_c$ kg^{-1})
		(t ha^{-1})	(g 0.3 kg^{-1} soil)	
		Clayey soil		
S1[a]	9.5	9.5	1.418	79
S2[b]	10.4	9.5	1.418	81
S3[b]	13.7	9.5	1.418	81
S4[b]	18.0	9.5	1.418	81
M1[a]	8.4	8.4	1.251	84
M2[a]	9.0	9.0	1.340	97
		Sandy soil		
S1[a]	6.4	6.4	0.965	54
S2[b]	7.0	6.4	0.965	55
S3[b]	9.2	6.4	0.965	55
S4[b]	12.1	6.4	0.965	55
M1[a]	5.7	5.7	0.852	58
M2[a]	6.0	6.0	0.905	65

[a]Rate calculated according to the ECCE and expressed on a wet basis.
[b]The limestone rates used for the sedimentary limestones S2, S3, and S4 in the incubation were the same as used for limestone S1; i.e., their respective ECCE values were not considered.
[c]Rates expressed on a dry basis, i.e., without moisture.
[d]Neutralization required to increase the base saturation to 70%: 79 mmol$_c$ kg^{-1} and 54 mmol$_c$ kg^{-1} for clayey and sandy soils, respectively.

Considering that the arable soil layer (0–20-cm depth) contains 2×10^9 g of soil, the limestone rates in g 0.3 kg^{-1} soil were calculated (Table 3). For treatments S2, S3, and S4, the RE and ECCE values of the limestone samples were not considered; instead, these treatments used the same rates calculated for the S1 treatment even using limestones with different ECCE values (Table 1), i.e., 1.418 g 0.3 kg^{-1} soil (equivalent to 9.5 t ha^{-1}) for clayey soil and 0.965 g 0.3 kg^{-1} soil (equivalent to 6.4 t ha^{-1}) for sandy soil (Table 3). For all treatments, the limestone rates refer to the dry basis, i.e., discounting moisture levels (Tables 1 and 3), since the RE, NP, and ECCE of the limestones were determined using dry samples (BRASIL 2014).

The amounts of each limestone to be added according to the treatment parameters were weighed (Table 3), and samples of 0.3 kg of soil and the respective amount of limestone for each experimental unit (350-mL pot) were placed in a plastic bag and manually shaken to promote proper soil and amendment mixing. After returning the mixture, the plastic pots were closed with loose caps perforated with holes to allow gas exchange. There were 224 pots for each soil type (seven treatments × eight periods of incubation × four replications), so 448 pots were prepared.

The maximum water retention capacity of both dry soils was determined according to the method of Richards (1949) and Topp et al. (1993). Deionized water was added in equal amounts to pots containing soils of the same texture with the objective of reaching 80% of the maximum water retention capacity of each soil. Every 15 days, the pots were weighed, and when necessary, the amount of water needed to maintain soil moisture was added.

Soil evaluations were performed at eight time points: 30, 60, 90, 120, 180, 240, 300, and 360 days after the start of incubation. For each incubation interval, the entire soil in each plastic pot was air dried and sieved through a 2-mm mesh sieve, and the soil of each plastic pot was then sampled and analyzed for pH(CaCl$_2$), aluminum (Al), Ca, Mg, and BS according to the methodologies described by Raij et al. (2001). The soil pH was determined in a 0.01 mol L^{-1} Ca dichloride (CaCl$_2$) suspension (1:2.5 soil/solution) with an AJ Micronal model AJX-522 pH meter (Micronal S.A., São Paulo, SP, Brazil). According to Raij et al. (2001), pH(CaCl$_2$) is more accurate than pH in water, which is greatly affected by small amounts of salts in the soil and 0.6 units higher on average. Theoretical values of pH(CaCl$_2$) expected according to the applied rates and respective ECCE values of the

limestones (Tables 1 and 3) were estimated using the equation for the relation between pH and BS proposed by Quaggio, Dechen, and Raij (1982), as follows:

$$pH = 3.66 + 0.027BS$$

Exchangeable Al was extracted with neutral 1 mol L^{-1} potassium chloride (KCl) in a 1:10 soil/solution ratio and determined by titration with 0.025 mol L^{-1} sodium hydroxide (NaOH) solution. Exchangeable Ca and Mg were extracted with ion exchange resin and determined by atomic absorption spectrophotometry. The BS values were calculated using the exchangeable bases and total acidity at pH 7.0 [hydrogen (H) + Al] results (Raij et al. 2001).

The results for each soil type and incubation time were analyzed with an individual ANOVA. Differences between the treatment means were assessed using Tukey's test at the 5% level of probability.

Results and discussion

The pH values of both soils were low prior to the limestone application (Table 2), but after only 30 days of incubation, liming significantly elevated soil pH values, regardless of the type of limestone used (Table 4). In a study carried out under controlled conditions, Verlengia and Gargantini (1972) also reported increased pH value compared to those established before the amelioration with only 35 days of incubation, and Mayfield et al. (2004) found a significant increase in soil pH at 1 day of incubation after dolomitic lime application. This increase in pH values with the application of limestones is due to an increase in hydroxyl concentration, a reduction of the H$^+$ concentration in the solution and precipitation of Al in the form of Al hydroxide [Al(OH)$_3$] (Mayfield et al. 2004; Pavan and Oliveira 1997; Quaggio 2000).

In general, treatments with sedimentary limestone, regardless of particle size, more efficiently increased the pH of both soils in the first months of incubation compared to those with metamorphic limestones (M1 and M2) (Table 4). During the first 180 days of incubation, all treatments with sedimentary limestone in the clayey soil, regardless of particle size, showed pH values 0.3 to 0.4 units higher than those obtained with metamorphic limestones. Furthermore, the acidity neutralizing capacities were similar among the treatments with sedimentary limestones of

Table 4. Soil pH values estimated and obtained in response to application of sedimentary and metamorphic limestones to clayey and sandy soils incubated for different time periods.

Limestone	pH estimated[a]	pH(CaCl$_2$) obtained after incubation (days)								
		0	30	60	90	120	180	240	300	360
					Clayey soil					
S1	5.6	3.8	6.3a	6.3b	6.4a	6.4ab	6.3a	6.5ab	6.0a	6.2a
S2	5.4	3.8	6.4a	6.4a	6.3a	6.6a	6.4a	6.4ab	6.2a	6.1a
S3	5.0	3.8	6.4a	6.4a	6.2ab	6.6a	6.3a	6.7a	6.2a	6.1a
S4	4.7	3.8	6.4a	6.4a	6.3ab	6.4ab	6.4a	6.5ab	6.2a	6.1a
M1	5.6	3.8	6.0b	6.0c	6.1bc	6.2c	6.0b	6.1bc	6.0a	6.1a
M2	5.6	3.8	5.9b	5.9c	6.0c	6.0c	6.0b	6.0c	6.3a	6.0a
Control	-	3.8	4.0c	4.0d	3.9d	4.0d	4.0c	3.9d	4.1b	4.1b
LSD Tukey			0.16	0.14	0.18	0.18	0.21	0.34	0.36	0.23
					Sandy soil					
S1	5.6	3.8	6.3b	6.4abc	6.1c	6.2d	6.2b	6.0c	5.8b	6.3b
S2	5.4	3.8	6.6a	6.5ab	6.4a	6.6a	6.4a	6.3ab	6.1a	6.4ab
S3	5.0	3.8	6.5a	6.6a	6.4a	6.6a	6.5a	6.3ab	6.1a	6.5a
S4	4.7	3.8	6.6a	6.5ab	6.5a	6.7a	6.5a	6.4a	6.1a	6.6a
M1	5.6	3.8	6.1c	6.2c	6.2b	6.5bc	6.4a	6.2ab	6.1a	6.5ab
M2	5.6	3.8	6.0d	6.2c	6.2bc	6.4c	6.4a	6.1bc	6.2a	6.4b
Control	-	3.8	3.9e	4.0d	4.0d	4.0e	4.0c	3.9d	4.1c	4.1c
LSD Tukey			0.17	0.31	0.13	0.17	0.20	0.22	0.23	0.15

Means followed by the same letter in the columns within each soil do not differ according to Tukey's test ($p \leq 0.05$).
[a]Theoretical values of pH(CaCl$_2$) expected according to the applied rates and respective ECCE values of the limestones (Tables 1 and 3) using the equation for the relation between pH and base saturation (pH = 3.66 + 0.027BS) proposed by Quaggio, Dechen, and van Raij (1982).

different particle sizes, with pH values of 6.3–6.4 (Tables 1 and 4). From 240 days onward, treatments with metamorphic limestones exhibited pH values similar to those with sedimentary limestones, indicating that the reaction of the metamorphic limestones in the soil was slower than that of the sedimentary limestones, even though the sedimentary limestones had larger particle sizes (lower RE).

In the sandy soil, the capacity of all limestones to neutralize soil acidity was similar after 180 days of incubation, regardless of the origin of the material and its RE (Tables 1 and 4). At the end of 250 days of incubation, Kurihara et al. (1999) observed that the soil pH obtained with metamorphic sources with smaller particle sizes was equivalent to that of sedimentary sources with larger particle sizes, but greater initial increases in soil pH values occurred when using sedimentary limestones than when using metamorphic limestones.

In the control treatments with clayey and sandy soils, the exchangeable Al concentrations during the incubation period were, on average, 15.3 and 13.4 $mmol_c$ dm^{-3}, respectively (Figure 1). However, in the treated soils that received liming, the exchangeable Al concentrations were reduced to zero due to the increase in soil pH regardless of the limestone used.

In both soils, the exchangeable Ca concentrations increased in all treatments that received liming (Figure 1), and the highest concentrations occurred in the sedimentary limestone treatments S2, S3 and S4 as well as in the M1 metamorphic limestone treatment. The lowest soil concentrations of exchangeable Ca were observed for S1 in the sedimentary limestone group and M2 among the metamorphic limestones. Despite having a Ca concentration similar to those of the sedimentary limestones S2, S3, and S4, the metamorphic limestone M2 resulted in lower concentrations of exchangeable Ca in the soil, indicating that this nutrient was released faster from the sedimentary limestones (Figure 1 and Table 1). The exchangeable Mg concentrations of the two studied soils also increased with liming application, and higher Mg concentrations were observed in the treatments containing metamorphic (M2) and sedimentary (S1) limestones. These results indicated that the release of Ca and Mg from the limestones was affected by both the concentrations of these elements in the amendments, as found by Conyers et al. (1996), and by the origin of the material.

Liming increased the BS of the two soils (Table 5). In the first months of incubation, treatments S2, S3, and S4 (sedimentary) yielded higher BS values than those with metamorphic limestones, but after 180–240 days of incubation, the differences between the types of limestone disappeared.

The sedimentary limestone S1 and the metamorphic limestones M1 and M2 were applied to the soil at rates defined by the ECCE according to the liming recommendation standards used in Brazil (Raij et al. 1997). In the clayey soil, higher pH values due to liming were observed for sedimentary limestone S1 up to 180 days of incubation, but in the sandy soil, these values continued to change for up to 60 days (Table 4). The effect on pH of different limestones applied at the same rate as defined by the ECCE continued only up to 30 days, and in this case, only the metamorphic limestone M2 presented significantly lower pH values than those obtained with limestones S1 and M1. The small-scale effect observed only with shorter incubation on measurements of BS is most likely due to the composition of the limestones; limestones with higher Mg carbonate (dolomitic) concentrations generally have slower reaction rates than those containing Ca carbonate (calcitic) due to their lower solubility (Conyers et al. 1996; Jones and Mallarino 2018; Rippy et al. 2007). In a study of different liming materials, Gallo and Catani (1954) observed that dolomitic limestones with higher Mg concentrations had a less pronounced reaction with a 1% acetic acid solution, while limestones with high Ca concentrations demonstrated higher solubilities. Jones and Mallarino (2018) found similar results in an incubation experiment and also verified that the increase in the solubility of the smaller-sized particles of the amendments was greater for limestones with high Mg concentrations than for those with high Ca concentrations, which is consistent with the results of the present study (Tables 1 and 4 and Figure 1).

In general, the metamorphic limestones, even though they produced lower pH values than those of the sedimentary limestone S1 in the first months of the incubation, satisfactorily produced the expected effects; i.e., they ameliorated soil acidity, increasing soil pH values from 3.8 to close to 6.0
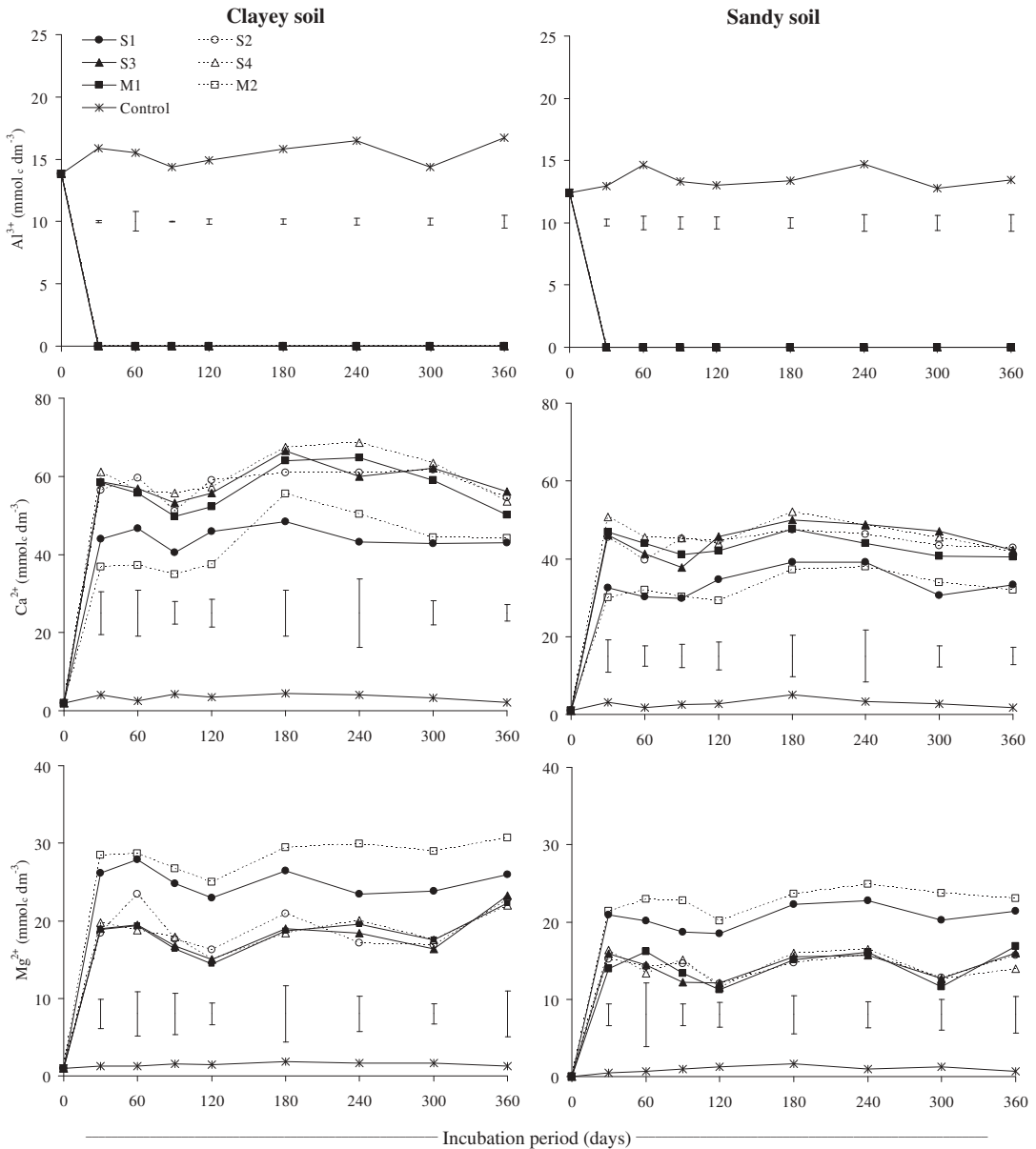
Figure 1. Effect of application of sedimentary limestones with different granulometries (S1, S2, S3, and S4) and metamorphic limestones (M1 and M2) on concentrations of Al^{3+}, Ca^{2+}, and Mg^{2+} in clayey and sandy soils during the incubation period. Vertical bars indicate the LSD values according to Tukey's test at 5% of probability.

and increasing BS to values ≥70% over a maximum period of 60 days (Tables 4 and 5). According to current Brazilian legal standards, RE expresses the proportion of the liming material that must react in the soil within 3 months (MAPA-SDA 2006). In addition, all limestones completely neutralized the exchangeable Al present in the original soils (Figure 1).

The treatments S2, S3, and S4 had the same limestone rates as S1, but the materials consisted of coarser particles with ECCE values of 77%, 60%, and 47%, respectively, compared to 84% for limestone S1 (Table 1). Thus, it was expected that the ameliorating effects of limestones S2 to S4 would be significantly slower than those of limestone S1 and limestones M1 and M2, but this did

Table 5. Base saturation (BS) values estimated and obtained in response to the application of sedimentary and metamorphic limestones to clayey and sandy soils incubated for different time periods.

Limestone	BS estimated[a]	BS obtained after incubation (days)								
		0	30	60	90	120	180	240	300	360
		(%)								
					Clayey soil					
S1	70	3	72ab	75ab	74ab	73b	72b	74a	78a	75b
S2	65	3	74a	79a	76a	77a	76a	78a	78a	78a
S3	51	3	74a	78a	75a	77a	77a	77a	79a	79a
S4	40	3	75a	79a	75a	76ab	78a	77a	81a	78a
M1	70	3	70b	76ab	71bc	73b	75ab	77a	78a	77ab
M2	70	3	65c	72b	69c	69c	75ab	75a	80a	77ab
Control	-	3	5d	4c	6d	5d	6c	5b	5b	4c
LSD Tukey			4.0	4.2	2.6	3.4	4.2	7.0	4.2	2.3
					Sandy soil					
S1	70	1	70b	75cd	72b	73cd	76ab	73a	79b	78b
S2	65	1	75a	78abc	78a	78abc	79ab	75a	83ab	80ab
S3	51	1	75a	79ab	74b	80a	79ab	76a	82ab	81a
S4	40	1	77a	80a	79a	79ab	80a	77a	84a	80ab
M1	70	1	71b	77bcd	74b	74bcd	75b	74a	80ab	80ab
M2	70	1	65c	74d	73b	71d	76ab	73a	81ab	79ab
Control	-	1	5d	3e	5c	6e	9c	6b	6c	4c
LSD Tukey			3.8	3.4	3.0	5.6	4.0	6.1	3.6	2.6

Means followed by the same letter in the columns within each soil do not differ according to Tukey's test ($p \leq 0.05$).
[a]Expected values according to the applied rates and respective ECCE values of the limestones (Tables 1 and 3).

not occur. Even at 30 days of incubation, limestones that had been more coarsely milled had effects on pH, BS and exchangeable Ca and Mg availability similar to or greater than those of meta-morphic limestones (Tables 4 and 5; Figure 1), indicating that current standards may be under-estimating the RE of sedimentary limestones similar to those used in the present study. The amounts of carbonates added to the soils in all treatments, expressed in pure $CaCO_3$ equivalents, were always higher than those stoichiometrically required to increase the BS to 70% (Table 3).

It is important to note that the soils used in the present study were very acidic with a pH of 3.8 and a BS of less than 3% (Table 2), values that are uncommon in agricultural soils. The high acidity is convenient for studying limestone reactions but may also promote the solubilization of limestones, which may have caused the faster reactions of the coarsest limestones in this experiment. As there were no treatments with lower rates for metamorphic limestones, as calculated without correcting for ECCE values, than those that occurred with treatments S2, S3, and S4, it remains unknown whether the RE values calculated for metamorphic limestones were underestimated. However, data from this study combined with that of previous authors (Conyers et al. 1996; Gallo 1954; Gallo and Catani 1954; Kurihara et al. 1999) suggest that coarser particles of sedimentary limestone have a higher reactivity than currently considered, indicating that the standards for limestone character-ization should be revised. However, further testing is required, especially under field conditions. If it is found that sedimentary and possibly metamorphic limestones do not require fine milling, the costs of these amendments can be reduced to the benefit of farmers. In addition, limestones of coarser particle sizes are easier to apply because they have less of a problem with drift. Using metamorphic limestones under field conditions, Quaggio et al. (1995) demonstrated that fine limestone (NP: 101% $CaCO_3$-eq) and traditional limestone (NP: 77% $CaCO_3$-eq) had similar effects on soybean yield over three years and on sorghum yield over one year, although the authors also found that fine limestone reacted faster in the soil.

Limestones, even those of a coarser particle size such as the sedimentary limestones studied here, that rapidly react in soil can have comparative advantages due to their lower costs, but the coarse particles of limestones with less reactivity generally increase the residual liming effect. The upward correction of limestone rates by the ECCE provided in the current legislation ensures that the amount

of liming material applied will be sufficient to neutralize the acidity to the desired level, but the presence of coarse material with slow reactivity could cause an increase in the limestone rates. On the one hand, these increased rates represent a larger investment in limestone than would be required by a finer material or a sedimentary limestone, but on the other, the more rapidly reactive limestones will have a smaller residual effect (Quaggio et al. 1995). For long-cycle crops such as sugarcane, for which limestone is incorporated at intervals of several years, the residual effect may be an advantage. For crops that receive lime more often, the residual effect is less relevant, and the questions of material costs and material application may be the main factors in usage decisions by farmers.

Conclusions

In the first months of incubation, sedimentary limestones had higher soil amendment abilities than metamorphic limestones; although all the studied limestones achieved the goal of neutralizing soil acidity to the desired values. For the sedimentary limestones, the availability of Ca and Mg was more closely related to the levels of CaO in the amendment than to the particle size, which did not interfere with their acid amelioration capacity. Therefore, evaluations that use the particle size of the ground rock to calculate the reactivity of sedimentary limestone underestimate its capacity to neutralize soil acidity. However, further testing is required, especially under field conditions.

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