Short-term effects of liming on chemical attributes of tropical sandy soil and soybean (Glycine max L.) yield

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Abstract

Lime application is the most appropriate technique to raise soil pH, decrease Al³⁺ toxicity and increase Ca²⁺ and Mg²⁺ contents in acidic tropical and subtropical moist soils. The objective of this research is to evaluate changes in chemical attributes and soybean yield in sandy soil after lime incorporation. The soil was classified as a typical Quartzipsamment cultivated with (Brachiaria decumbens Stapf) pasture, and its degradation state was classified as strong. The experimental design was a randomized block with six replicates and four lime doses (0, 2, 4 and 8 Mg ha⁻¹). The soil in the area was prepared with one plowing and two harrowings, followed by lime application and two more harrowings to incorporate the lime up to 0.2 m depth. The dependent variables analyzed were soybean yield; numbers of pods filled, pods not filled, and total pods and soil pH in water, CaC₂ and KCl. All parameters were measured at depth of 0.0-0.1, 0.1-0.2 and 0.2-0.3 m. The increase of soil pH by the different lime rates were observed just in 0.0-0.1 and 0.1-0.2 m layers. After 6 months no changes in soil pH were observed in subsoil (0.2-0.3 m). With lower H⁺ and Al³⁺ activity and higher basic cation availability, soybean yield was also changed. The maximum soybean yield of 2,929 kg ha⁻¹ was observed with 4.6 Mg ha⁻¹ lime application, although pod number per plant remained constant, independent of limestone dose.

Keywords: base saturation; grain production; lime; ΔpH; quartzipsamments.

Abbreviations: Al_aluminum, %BS_percent base saturation, Ca_calium, CEC_exchange capacity, HCO₃⁻_bicarbonate, H⁺_hydrogen, i_i ons, K_potassium, I_liquid, LQ_lime quality, Mg_magnesium, Mn_manganese, N_nitrogen, NV_neutralizing value, OH⁻_hydroxyls, pH_hydrogen potential, P_phosphorus, PZC_point of zero charge, PS_particle size distribution, s_solid, S_sulfur.

Introduction

Most Brazilian tropical soils are acidic with high toxic aluminum levels, low bases saturation and low phosphorus content (Olmos and Camargo, 1976). Soil acidity is limiting to several economic crops, including soybean grain production (Corrêa et al., 2009). Correcting the acidity in these types of soils, can double grain production (BELLINGIERI ET AL., 1992). Liming is helpful because it neutralizes active protons (H⁺) in the soil solution, alters the exchangeability and potential acidity associated with the presence of toxic Al and Mn (Raj et al., 1977) in soil solution, increase the absorption of N, P, K and S (Quaggio et al., 1993); and provides Ca and Mg as plant nutrients (Mascarenhas et al., 1976). Despite these benefits, there is no single criterion for liming, since environmental factors (temperature and precipitation) and soil attributes (pH, buffer capacity, texture, structure, organic matter content and clay mineralogy) affect the methods and the doses estimated for application, especially in regions with low availability and use of technologies. Several methodologies for determining liming recommendations have been used in Brazil; however, the most commonly used method was proposed by Catani and Gallo (1955) and adapted by Raji (1981). This method considers the principle of increasing soil pH as a result of Ca, Mg and K saturation (Sousa et al., 2007).

Lime reactions in the soil occur at a low level, depending on limestone quality (CaO and MgO content and particle size), dose, incorporation method, rainfall intensity, soil and air temperatures. Several soil attributes are amended with lime application in agricultural soils, such as: pH, CEC, Al, Ca and Mg contents (Caires et al., 1999; Moreira et al., 2001). The pH increase is due to lime reactions with free or adsorbed protons at the exchange complex, which that release OH⁻ and HCO₃⁻ ions into the soil solution, according to reactions 1 and 2 (Sousa et al., 2007):

\[ \text{CaCO}_3(s) + H_2O(l) \rightarrow \text{Ca}^{2+}(aq) + HCO_3^-(aq) + OH^-(aq) \] (Reaction 1)

\[ \text{HCO}_3^-(aq) + H_2O(l) \rightarrow C_2H_3O_2(aq) + OH^-(aq) + H_2O(l) \] (Reaction 2)

Al activity reduction in the soil is due to the increase in soil pH and the subsequent precipitation of this element, forming the solid secondary mineral gibbsite, according to reaction 3, proposed by Raji (1991):

\[ \text{Al}^{3+}(aq) + 3OH^-(aq) \leftrightarrow \text{Al(OH)}_3(s) \] (Reaction 3)

Ca and Mg contents increase depending on the chemical composition of the lime used; lime can be classified as calcitic limestone (40-45% CaO and 1-5% MgO), magnesium limestone (30-40% CaO and 6-12% MgO) and dolomitic limestone (25-30% CaO and 13-20% MgO) (Malavolta, 2002). The active acidity measured by the soil pH can be determined by potentiometric methods using different
solutions (Sousa et al., 2007). The most common potentiometric methods are the measurement of soil pH with: a) water, b) CaCl₂-2H₂O 0.01 mol L⁻¹ and c) KCl 1 mol L⁻¹. The values of pH in water show higher variability among replicates. The addition of electrolytes (CaCl₂ or KCl) might decrease this variability (Raij, 1981) and simulate the ionic strength (CaCl₂ 0.01 M) of the soil solution.

Liming soil also modifies the distribution of charges in the soil particles, especially in the Neosol soil class, which shows a predominance of electrical charges (positive or negative) depending on pH or variable charges associated with the ferro, aluminol and silanol surfaces complex groups on the surface of minerals and the carboxylic and phenolic surface complex groups on the surfaces of soil organic matter (Sposito, 2008). The predominance of electrical charges in these surface complex groups can be determined using the ΔpH value (Meurer, 2006). Mekaru and Uehara (1972) defined ΔpH as the difference between pH in KCl and pH in water. Positive or negative ΔpH values indicate, respectively, the presence of positive or negative net charges on the surfaces of colloids. In addition, it is also possible to determine soil pH value at the point of zero charge (pH_{PZC}), which is the pH value at which the total number of positive electric charges equals the total number of negative charges; that is, the soil net charge is approximately zero (Ernani, 2016).

The hypothesis of this research is that doses of lime might not only change soil pH but also alter the dynamics in the soil and affect nutrients availability to soybean plants, affecting grain and plant crop production components. Therefore, the objective of this study was to evaluate the changes in soil chemical attributes (pH and net electric charge distribution) associated with increasing lime dose incorporated into a sandy soil and in soybean yield and crop production components.

Results and discussion

**Soil pH_{H₂O}, pH_{CaCl₂} and pH_{KCl}**

Soil pH_{H₂O}, pH_{CaCl₂} and pH_{KCl} data at different depths can be observed in Figures 1A, 1B, and 1C, respectively. Significant (p<0.05) increases in pH values were observed only at the 0.0-0.1 and 0.1-0.2 m depths with increasing lime dose. At a depth of 0.0-0.1 m, a quadratic model fit the pH (independent of the method) as a function of lime doses. Maximum values of pH_{H₂O} (5.94), pH_{CaCl₂} (5.63) and pH_{KCl} (5.78) at the depth of 0.0-0.1 m were obtained at the following doses, respectively: 5.25, 6.13 and 6.72 Mg ha⁻¹ of lime. The quadratic behavior of pH variation as a function of increasing lime dose shows that, after reaching the maximum pH value, part of the lime applied does not react, since the pH equilibrium of CaCO₃ in water is 8.2 (Sposito, 2008). This remaining lime must have been protected from hydrolysis (equations 1 and 2) or by the soil components released from organic matter decomposition or mineralization in soil. Among these components, poorly crystalline forms of iron and other micronutrients (Cu, Zn, Al, etc.) may have precipitated in the form of oxides or carbonates on the surface of the granules of calcite or dolomite, making it difficult to completely hydrolyze them. At a depth of 0.1-0.2 m, regardless of the method used, a linear increase was observed with increasing lime dose, with angular coefficients of 0.08, 0.075 and 0.104 for pH_{H₂O}, pH_{CaCl₂} and pH_{KCl}, respectively. The lower response to lime application at this depth is due to the intensity and distribution of precipitation after lime incorporation. The amount of rainfall during the experiment was adequate to bring the moisture content to field capacity at 0-0.2 m depth. There would be no other way to explain the differences in pH values between the two depths, since the soil was plowed and harrowed before lime application and incorporation, homogenizing the organic matter content at this depth. As rainfall intensities were not always enough to moisten the 0-0.2 m layer evenly, the first layer, 0-0.1 m, was always the first to be moistened, favoring calcium and magnesium carbonate hydrolysis and, thus, greater pH increase.

In addition to receiving less water, the 0.1-0.2 m depth also has less gas exchange, lower oxygen content, and consequently, less biological activity necessary for the decomposition and mineralization of soil organic matter (Stevenson, 1994). At the 0.2-0.3 m depth, there was no significant response to pH, regardless of the method. The trends seen in the 0.1-0.2 m layer are accentuated here due to the smaller amount of water available for the hydrolysis of (CaMg)CO₃, in addition to the aggravating factor of having even lower organic matter content.

The time required for the complete lime hydrolysis in soil varies due to a series of factors, although generally, it is considered to be 100 days (Sousa et al., 2007). The lower values of pH_{CaCl₂} and pH_{KCl} are due to the change in the ionic strength of the soil solution, which affects H⁺ ion activity coefficient. In electronegative soils, pH decreases with increasing soil solution salt concentration, due to ion exchange between salt cations and the H⁺ and Al³⁺ ions of the exchange complex (Sousa et al., 2007).

**ΔpH and pH_{PZC}**

Significant variations in ΔpH values were observed at the 0.0-0.1 and 0.1-0.2 m depths (Figure 1D). Positive or negative ΔpH values indicate, respectively, the presence of positive or negative net charges in colloids (Uehara and Gillman, 1981).

At all evaluated depths, negative ΔpH was observed, that is, cation exchange capacity prevailed in all treatments. With increasing lime dose, decreasing ΔpH values were observed. However, this result does not necessarily imply that increasing lime dose decreased soil CEC, in contrast to the majority of authors (Alleoni et al., 2005; Santos et al., 2010; Briedis et al., 2012; Calonego et al., 2012). This finding is due to the short period of time (180 days) allowed for lime hydrolysis before soil sampling and subsequent analysis. The precipitation amounts were insufficient for lime hydrolysis to be completed and reach equilibrium among the different phases of the soil after lime incorporation, which would allow appropriate use of the ΔpH equation as mentioned by Mekaru and Uehara (1972).

For ΔpH measurement, ion H⁺ activity is measured in a soil mixture, and this solution can vary from 1:1 to 1:2.5 (v/v). In the lime reaction, protons (H⁺-indicator) and Al (exchangeable and potential) are consumed and form water and gibbsite [Al(OH)₃], respectively.
Table 1. Soil chemical attributes and particle size distributions at different depths before the experiment.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>pH&lt;sub&gt;CaCl&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;</th>
<th>H+Al</th>
<th>Al&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Ca&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Mg&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>K&lt;sup&gt;+&lt;/sup&gt;</th>
<th>BS</th>
<th>CEC</th>
<th>%BS</th>
<th>P (g kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0-0.20</td>
<td>4.60</td>
<td>3.69</td>
<td>0.31</td>
<td>0.83</td>
<td>0.62</td>
<td>0.16</td>
<td>1.61</td>
<td>5.30</td>
<td>30</td>
<td>2.5</td>
</tr>
<tr>
<td>0.2-0.40</td>
<td>4.20</td>
<td>4.61</td>
<td>0.77</td>
<td>0.43</td>
<td>0.36</td>
<td>0.13</td>
<td>0.92</td>
<td>5.53</td>
<td>17</td>
<td>2.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>C</th>
<th>S-SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</th>
<th>B</th>
<th>Fe</th>
<th>Zn</th>
<th>Cu</th>
<th>Mn</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0-0.20</td>
<td>10.30</td>
<td>5.4</td>
<td>0.29</td>
<td>58.59</td>
<td>3.06</td>
<td>0.91</td>
<td>15.18</td>
<td>780</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>0.2-0.40</td>
<td>9.57</td>
<td>10.2</td>
<td>0.25</td>
<td>96.01</td>
<td>0.56</td>
<td>0.68</td>
<td>10.87</td>
<td>780</td>
<td>100</td>
<td>120</td>
</tr>
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</table>

pH<sub>CaCl<sub>2</sub></sub> ratio; 1:2.5 soil:CaCl<sub>2</sub> solution (0.01 mol L<sup>-1</sup>); Al, Ca and Mg were extracted by KCl (1 mol L<sup>-1</sup>); base saturation (BS = Ca + Mg + K); cation exchange capacity (CEC = BS + H+Al); percent base saturation (%BS = BS/CEC × 100); P, K, Cu, Fe, Mn and Zn were extracted by Mehlich I (H<sub>2</sub>SO<sub>4</sub> 0.0125 mol L<sup>-1</sup> + HCl 0.05 mol L<sup>-1</sup>); C (Walkley and Black), B (hot water), S (monocalcium phosphate) and particle size distribution (Bouyoucos hydrometer method).

Fig 1. Effects of different lime doses on soil pH<sub>H<sub>2</sub>O</sub> (A), pH<sub>CaCl<sub>2</sub></sub> (B), pH<sub>KCl</sub> (C), ΔpH (D) and pH<sub>PZC</sub> (E) at different depths.
When equilibrium is attained, the balance of the charges associated with the cations and anions present in the soil solution with the negative and positive charges on the surface functional groups of soil colloids is always zero. Consumption of $\mathbf{H}^+$ and exchangeable $\mathbf{Al}^{3+}$ from the soil solution must always be balanced by the release of lime bases. In this experiment, given the conditions of moisture and reaction time, some lime particles were not hydrolyzed and remained in the solid phase of the soil, releasing bases and consuming protons and aluminum without attaining complete chemical equilibrium. This situation resembles the reactions shown above, but progressing only toward the right side. The nonhydrolyzed lime particles have a $\mathbf{pH}_{\text{zpc}}$ above eight (Somasundaran and Agar, 1967), and thus, they affect the $\mathbf{pH}_{\text{zpc}}$ value of soil, making it less negative, with an apparent CEC reduction. At the 0.0-0.1 m depth, the quadratic model fit the $\mathbf{pH}_{\text{zpc}}$ as lime dose increased (Figure 1E). The maximum value of $\mathbf{pH}_{\text{zpc}}$ at the 0.0-0.1 m depth was obtained with a lime dose of 7.36 Mg ha$^{-1}$, which generated pH 5.50. At the 0.1-0.2 m depth, a linear increase was observed with increasing lime dose. For each ton of lime added, $\mathbf{pH}_{\text{zpc}}$ increased by 0.128 units. At the 0.2-0.3 m depth, there was no significant response to $\mathbf{pH}_{\text{zpc}}$. Thus, the $\mathbf{pH}_{\text{zpc}}$ values had exactly the same behavior as the pH values as a function of lime dose observed previously.

Gonçalves et al. (2015), working with liming in Plintossolo, also showed that $\mathbf{pH}_{\text{zpc}}$ increased with liming from 3.14 to 6.46 and from 3.24 to 4.68 in two different samples. Another hypothesis for this soil chemical behavior, and especially its $\mathbf{pH}_{\text{zpc}}$ values, would be associated with accelerated organic matter decomposition and mineralization due to lime incorporation and the subsequent Ca and Mg adsorption that would promote an increase in positive charge on the solid surfaces of soil, thereby reducing negative net load (Albuquerque et al., 2000).

**Pod formation and soybean yield**

No significant responses ($p>0.05$) were observed at different lime doses for the crop variables: pods filled, pods not filled and total pods, which presented average values of 186.25; 68.15 and 254.40, respectively (Figure 2A).

The crop yield data (Figure 2B) were adjusted to a second-order polynomial equation where the maximum yield was reached at a lime dose of 4.6 Mg ha$^{-1}$, and a productivity of 2,929 kg ha$^{-1}$. This dose corresponds to % a BS (the standard method used for liming recommendations in the state of Mato Grosso do Sul) of 76%, considering LQ equal to 75% and a reactivity of 70% in the 6 months of the experiment. The recommended LQ value for soybean in sandy soils is 60% (Embrapa, 2011). $\mathbf{LQ} = (\mathbf{N} \times \mathbf{P}) / 100$, where $\mathbf{N}$ represents the percentage of CaCO$_3$ in the lime, which is proportional to the amount of acid the lime can neutralize.

These results are associated with Al activity reduction in the upper soil layer, in which lime incorporation was more effective (0.0-0.2 m), resulting in an environment more favorable to root system development, biological nitrogen fixation and greater water and nutrient absorption. However, excessive lime doses increase the ionic strength of the soil solution, because of the higher amounts of Ca and Mg from lime; this effect might have decreased the availability of micronutrients such as Cu, Fe, Zn and even B, since the organic matter contents were also low. This outcome might have occurred in this study, because yield decreased at the highest dose of lime (8 Mg ha$^{-1}$). Gonzalez-Erico et al. (1979) showed that lime incorporation in acid soils resulted in higher yields, and this finding was attributed to Al saturation reduction and increased pH in a larger volume of soil. Furthermore, in the same study, the authors observed that, after the third crop year, lime incorporation had no effect on yield. Alleoni et al. (2005) showed that lime incorporation corrected soil acidity and increased the availability of soil bases to a depth of 0.2 m in Cerrado soil. Miranda et al. (2005) studying liming effects on soil acidity correction and corn and soybean yield in a Red Latosol, observed that, in soils with high acidity, incorporated lime promoted higher soybean and corn yields than nonincorporated lime, in a no-tillage system. Due to the relatively low solubility of lime, higher liming efficiency is generally observed when this additive is applied in advance and incorporated into soil to reach the effective depth of the crop root system.
Materials and methods

Experimental location and procedure

The experiment was carried out in the municipality of Tacuru-MG, Brazil. The geographical coordinates of the site are 23° 46' 23.9" S, 54° 54' 48.08" W and 332 m altitude. The soil was classified as a typical Quartzipsamment (Embrapa, 2013) (Entisol), with a sandy-loam texture, smooth-wavy relief, a 6% slope and low natural fertility (exchangeable bases and soil phosphorus).

The experimental area was previously cultivated with pasture (Brachiaria decumbens Stapf), and its degradation state was classified as strong (Embrapa, 2014). Soil preparation was carried out in a conventional manner, with two plows (grid of 20 discs x 20 inches) and later a harrowing with a leveling grid. Then, the area was kept fallow until the experiment was installed 6 months later. Soil samples for physical and chemical characterization were removed from the 0-0.2 and 0.2-0.4 m layers according to Embrapa (1997). The data from these analyses can be seen in Table 1.

Based on Table 1, the fertilization recommendation for a soybean crop was 144 kg ha\(^{-1}\) of \(P_2O_5\) (800 kg ha\(^{-1}\) of simple superphosphate fertilizer), which was incorporated with a leveling harrow. NP fertilizers 02-24-12 at a dose of 400 kg ha\(^{-1}\) was used for in-furrow fertilization. At 25 days after of seedling emergence, potassium fertilization was performed in cover, using 100 kg ha\(^{-1}\) of KCl. The seeded soybean cultivar was BMX-Potencia RR, with a density of 17 seeds per linear meter.

Experimental design and evaluated variables

A completely randomized design with four calcitic lime doses (0, 2, 4 and 8 Mg ha\(^{-1}\)) and six replicates were used. Each plot consisted of eight by ten m\(^2\) area with a spacing of 0.45 m. Yield was obtained by harvesting 7.2 m\(^2\) of useful area. The three outermost rows were disregarded, as well as 1 m from each end of the central rows; only the two central rows of each experimental unit were harvested. Number of pods per plant, pods filled and pods not filled were obtained by counting these components from 5 plants in the R8 soybean stage in the useful area.

After the harvest, ten soil samples were randomly collected in the plot at three depths (0.0-0.1, 0.1-0.2 and 0.2-0.3 m) to form a composite sample to be analyzed. The pH values in H\(_2\)O, KCl and CaCl\(_2\) were determined according to Camargo et al., (2009). First, 10 cm\(^3\) of air-dried fine soil (ADFS, diameter less than 2 mm) was placed in a 50 ml disposable plastic cup. For pH in water, 25 ml of deionized water was added, pH in KCl used 25 ml of 1 M KCl and to pH in CaCl\(_2\) used 25 ml of 1 M CaCl\(_2\) solution. The samples were shaken for 15 minutes, and then rested for 30 minutes for later reading with a pH meter (Hanna pH 21). ΔpH was obtained by the difference between pH\(_{KCl}\) and pH\(_{CaCl_2}\). pH\(_{CaCl_2}\) was calculated according to Keng and Uehara (1974): pH\(_{CaCl_2}\) = 2pH\(_{KCl}\) - pH\(_{H_2O}\).

Statistical analysis

All data were analyzed by the Shapiro-Wilk (deviation from normality) and Bartlett (variance homogeneity) tests (p<0.01). Afterwards, the data were submitted to analysis of variance by the F test (p<0.05); when significant linear regression models were adjusted, the significance of the model parameters was verified by t test at each soil depth (Zimmermann, 2014).

Conclusion

Measured soil pH values became less acidic with increasing lime dose at the 0.0-0.1 and 0.1-0.2 m depths. The soil surface layer (0.1-0.2 m) showed the highest variations in pH values. ΔpH values decreased with increasing lime dose. This decrease was more evident at 0.0-0.1 m depth. The pH\(_{CaCl_2}\) increased up to the 0.2 m depth.

No crop component variables related to pods were influenced by lime dose. However, the maximum soybean yield was obtained at a dose of 4.6 Mg of lime ha\(^{-1}\), corresponding to a yield of 2,929 kg ha\(^{-1}\) and a pH\(_{CaCl_2}\) value of 5.5 at the 0.1 m depth.

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