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Reduction of Exchangeable Calcium and Magnesium in Soil with Increasing pH

Mário Miyazawa, Marcos A. Pavan*, Cláudio O. Ziglio and Júlio C. Franchini
Instituto Agronômico do Paraná (IAPAR). Caixa Postal 481, CEP 86001-970, Londrina - PR, Brasil

ABSTRACT

A laboratory study was conducted with soil samples and synthetic solutions to investigate possible mechanisms related with reduction in KCl exchangeable Ca and Mg with increasing pH. Increasing soil pH over 5.3 with $CaCO_3$ added to the soil and with NaOH solution added to soil/KCl suspension increased adsorptions of Ca and Mg. The reduction of Mg was greater than Ca and was related to the concentration of soil exchangeable Al. The decreases of soluble Ca and Mg following addition of Al in synthetic solution were at pH > 7.5. The isomorphic coprecipitation reaction with Al compounds may be the most possible mechanism responsible for the decrease of exchangeable Ca and Mg with increasing pH. Possible chemical reactions are presented.

Key words: Coprecipitation, aluminum, liming, acid soils

INTRODUCTION

Soil acidity is of major concern in cropping, horticulture, and pasture production in Brazil. Lime applications have proved to be efficient in ameliorating soil acidity. However, high rates of $CaCO_3$, $Ca(OH)_2$ or CaO caused reduction in soil exchangeable Mg (Mg_{ex}) resulting in plant nutritional unbalanced (Farina et al., 1980; Grove & Sumner, 1985; Myers et al., 1988). Laboratory studies conducted with soil column showed that although additions of $CaCO_3$ increased Mg concentration in the drainage water, the total amount of Mg leached was less than the amount of Mg reduced in soil (Pavan et al., 1984; Pavan & Roth, 1992). Field studies in apple orchard showed that lime reduced leaf-Mg and fruit yields (Pavan, 1992, 1997). The reduction in Mg_{ex} has been attributed to the exchangeable reaction between Ca and Mg following by Mg leaching out of the root zone.

Kinniburgh et al. (1976), Chan et al. (1979), Grove et al. (1981), Grove & Sumner (1985), and Myers et al. (1988) also found that lime reduced Mg_{ex} and suggested that other mechanisms are involved in Mg reduction than a simple leaching process. They identified three possible mechanisms for the effect of lime on Mg reduction. In summary these include (1) Mg adsorption in the inter layers of $Al(OH)_3$ (Kinniburgh et al., 1976); (2) coprecipitation of Mg as $MgAl(OH)_n$ (Kinnburgh et al., 1976); and (3) adsorption of $MgOH^+$ in the stern layer (Chan et al., 1979).

The objective of this study was to determine the possible mechanisms related to Mg_{ex} and Ca_{ex} reductions in Brazilian soils with increasing pH.

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[*] Author for correspondence

MATERIAL AND METHODS

Three experiments were conducted with soil samples collected from the 0-20 cm horizon. The soil samples were air dried and ground to pass through a 2mm screen before being treated. Table 1 shows the chemical characteristics of the soils. Soils 1, 2, 3, 4, 5 and 6 were LEd, PV, LEd, TRd, LRd, and LRd, respectively, in according with brazilian soil classification.

Table 1 - Chemical characteristics of the soils.

Soil Nº	pH $CaCl_2$	Ca	Mg	Al	C mg kg^{-1}
		$Cmol_ckg^{-1}$			
1	4.0	2.48	0.58	2.79	37.5
2	3.8	0.36	0.12	1.10	7.4
3	4.4	3.71	0.82	0.75	17.5
4	4.3	2.42	1.23	1.88	41.2
5	4.0	1.47	0.94	1.83	25.5
6	4.0	2.10	0.78	2.68	27.0

Soil incubation with lime: Three soil samples (soils1, 2, and 3, Table 1) were used for this study. One kg of soil sample was incubated in plastic bag with $CaCO_3$ for 120d, moistened to field capacity (0.01MPa) at room temperature. Lime rates were 0.0, 0.25, 0.50, 1.0, and 2.0 times the amount of total acidity (H + Al) extracted by 1 mol L^{-1} $Ca(C_2H_3O_2)_2$ at pH 7. Following incubation, soil pH was measured in 0.01M $CaCl_2$ (1:2.5 soil:solution ratio) after shaking for 1h; Ca_{ex}, Mg_{ex}, and Al_{ex} were extracted with 1 mol L^{-1} KCl solution in a 1:10 soil:solution ratio and 10 minutes shaking time. Al was determined by titration with standardized 0.015 mol L^{-1} NaOH solution using bromotymol blue indicator and Ca and Mg determined by atomic absorption spectroscopy. The treatments were replicated three times in a completly randomized block design.

Addition of NaOH in KCl soil suspension: Three soil samples (soils 4, 5, and 6, Table 1) were used for this study. The procedure was as the following: 5g of soil sample was transferred to 100ml flask; 40ml of 1 mol L^{-1} KCl solution was added; pH was adjusted daily to 4, 5, 7, and 8 with NaOH solution for 7d. Then, the solution volume was diluted to 50ml with 1 mol L^{-1} KCl and pH, Ca, Mg, and Al were determined in solution by the same procedures described above.

Effect of Al on Ca and Mg: Ten of 2 x 10^{-3} mol L^{-1} Mg Cl_2 solution was transferred to 60 ml glass flask and added 10ml of 0, 1, 2, and 4 x 10^{-3} mol L^{-1} $AlCl_3$ solution. The solution pH was adjusted daily to 4, 5, 6, 7, and 8 with NaOH solution for 3d. For adjusting pH, solution was shaked with magnetic bars and boiled with N_2 gas at a flow rate of 100ml min^{-1} to avoid adsorption of atmospheric CO_2 by the solution. Then, the solution volume was diluted to 40ml with deionized water and rested for 3d. Following resting period Mg was determined in solution by atomic adsorption spectroscopy. Similar study was conducted with 2 x 10^{-3} mol L^{-1} $CaCl_2$ solution.

RESULTS

Soil incubation with lime: Table 2 shows the effect of soil incubation with $CaCO_3$ on pH, Ca_{ex}, Mg_{ex}, and Al_{ex}. Lime to pH > 5.8 reduced Mg_{ex}. At pH near to neutrality, the reduction in Mg_{ex} was 93, 67, and 55% for soils 1, 2, and 3, respectively. This reduction was related to the initial Al_{ex} content (Table 1). The higher the Al_{ex}, the greater the Mg_{ex} reduction. The reduction of Mg_{ex} at pH < 5.0 was minimal, corroborating data presented in previous study with Brazilian soils (Quaggio et al., 1982).

Increasing $CaCO_3$ rates up to pH 4.9 increased Ca_{ex} (Table 2). The reduction in Ca_{ex} increased with increasing $CaCO_3$ rates. For example, for 2.0 times H + Al rate, Ca_{ex}, reduced to 55, 69, and 83% for soils 1, 2, and 3, respectively. At the highest $CaCO_3$ rate the reduction in Mg_{ex} was higher than Ca_{ex}.

Table 2 - Exchangeable Ca, Mg, and Al and pH after soil incubation with $CaCO_3$

Soil	pH	Rates $CaCO_3$	Ca	Mg	Al
Nº	$CaCl_2$	%(H+Al)	$Cmol_c kg^{-1}$		
1	4.0	0.0	2.48	0.58	2.79
	4.5	25	6.78	0.61	0.85
	4.9	50	10.21	0.53	0.08
	5.8	100	16.25	0.32	0.0
	7.1	200	21.45	0.04	0.0
2	3.9	0.0	0.36	0.12	1.10
	4.3	25	1.77	0.12	0.40
	4.8	50	3.15	0.12	0.04
	6.0	100	5.53	0.08	0.0
	7.0	200	7.77	0.04	0.00
3	4.1	0.0	3.71	0.82	0.75
	4.4	25	5.94	0.83	0.16
	4.9	50	7.87	0.81	0.0
	5.9	100	12.11	0.74	0.0
	7.2	200	18.32	0.36	0.00

Addition of NaOH in KCl soil suspension:
Figure 1 shows the effect of pH on the concentration of Ca, Mg, and Al in KCl suspension for the three soils. Increasing pH decreased KCl exchangeable Mg. The reduction in KCl-Mg at pH 7.3 was an average of 49% for the three soils. Increasing pH also decreased KCl exchangeable Ca. The reduction in KCl-Ca was higher than in KCl-Mg. At pH 7.3 the reduction in KCl-Ca was an average 54% for the three soils. As expected, KCl exchangeable Al was undetected at pH > 5.2.

Effect of Al on Ca and Mg: Figure 2 shows the effect of Al and pH on the concentrations of soluble Ca and Mg (Ca_s, Mg_s). Aluminum started to reduce Mg_s at pH higher than 8.4. This pH valuer agreed with that found in a solubility diagram for the formation of $MgAl(OH)_n$ presented by Hunsaker & Pratt
(1970). Increasing Al concentration at pH > 8.4 decreased drastically Mg_s.
The behavior of Ca_s was similar than Mg_s, except for the pH which resulted in the beginning of Ca precipitation (Figure 2). Precipitation of Ca started at pH 7.3. The reduction In Ca_s was higher than Mg_s for similar pH and Al/M molar ration, were M = Ca or Mg.

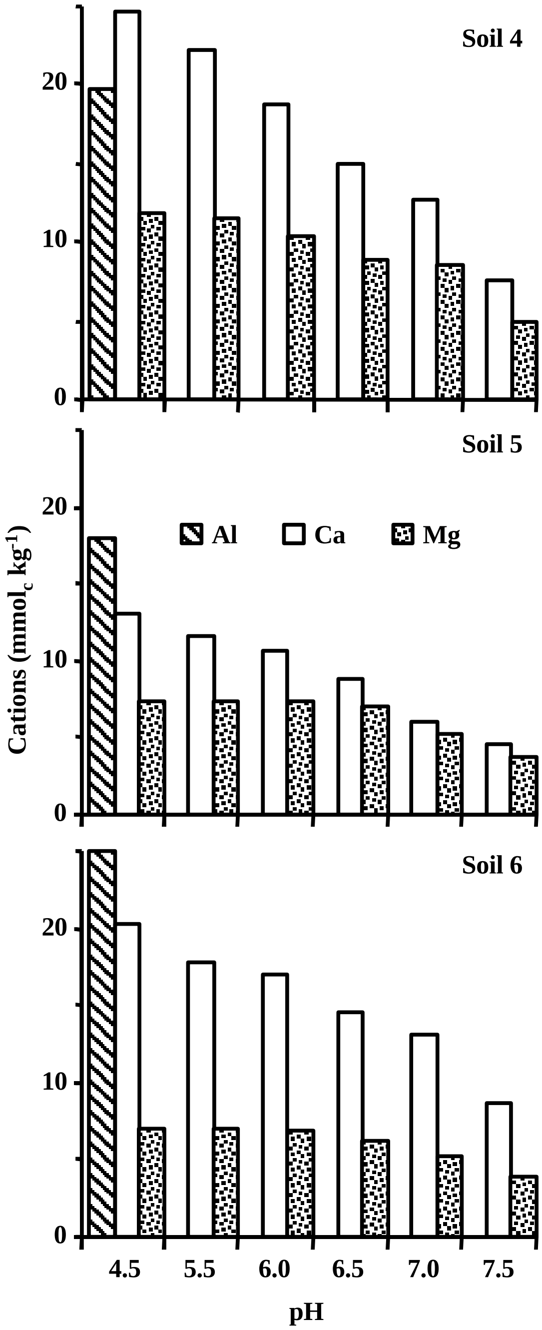

Figure 1 - Changes in KCl exchangeable Ca, Mg, and Al as function of pH

DISCUSSION

Calcium and magnesium are alkaline earth metals with different salt solubilities. In general, Ca-salts are less soluble that Mg-salts. For example pK_s for $MgCO_3$ is 5.0; $Mg(OH)_2$ is 10.7; $MgSO_4$ is soluble; $CaCO_3$ is 8.32; $Ca(OH)_2$ is 5.26 and $CaSO_4$ is 5.92 (Meites, 1963). Mg precipitates in solution only at pH > 10.5 as $Mg(OH)_2$ or at pH > 8.5 as $MgCO_3$ (Lindsay, 1979).

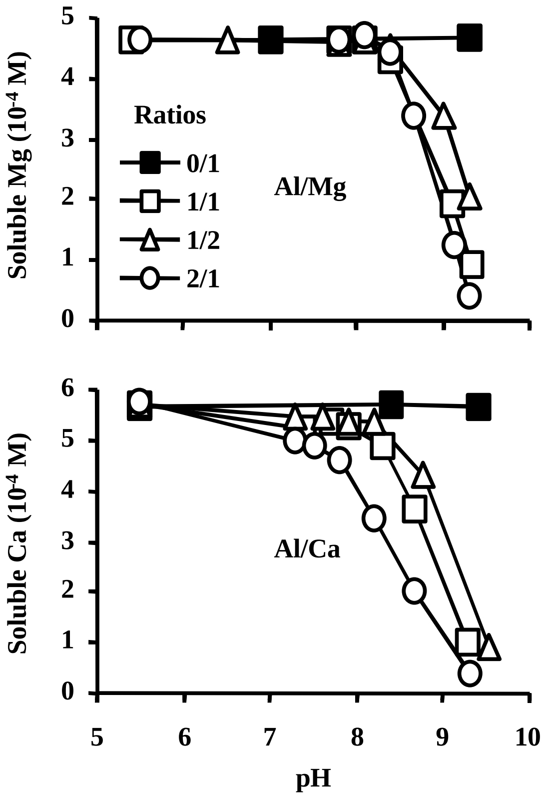

Figure 2 - Effect of Al/Mg and Al/Ca molar ratios on soluble Ca and Mg with varying pH.

On the other hand, Ca precipitates as $Ca(OH)_2$ at pH > 12.5 or as $CaCO_3$ at pH > 8.0 in an open system (0.0003 atm of CO_3). These pH values are much higher than those found for the beginning of Ca_{ex} and Mg_{ex} reductions (Table 2 and Figure 1). Therefore, the reductions in Ca_{ex} and Mg_{ex} in the present study were probably due to precipitation as $MgCO_3$ and $CaCO_3$ or $Mg(OH)_2$ and $Ca(OH)_2$. Both, Ca and Mg started to precipitate at a pH values where KCl exchangeable Al was absent (Table 2 and Figure 1). The concentration of a dissolved ion may decrease in solution due to the formation of a coprecipitate. In other words, during the formation of an insoluble compound, estrange ions may be incorporated in the precipitate (Ohlweiler, 1976). Two types of co-precipitate are characterized: (1) adsorption: estrange ions are adsorbed on the surface of the precipitate, which are easily removed from the solid surface by a simple water percolation, common in crystalline precipitate, and (2) isomorphic: estrange ions are incorporated in the precipitate structure, which are not easily removed by solvents or other ions. This type of coprecipitation is common in amorphous precipitates, formed by metal hydroxides, such as Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, and others (Ohlweiler, 1976). The solubility of Al in solution decreased with increasing pH (Table 2 and Figure 1). In the pH range from 5.5 to 7.5, $Al(OH)_3$ was the principal specie (Baes & Mesmer, 1976). The soil KCl exchangeable Ca_{ex} and Mg_{ex} started to precipitate at pH 5.2, while in pure solution, the precipitation started at pH 7.3 and 8.5 for Ca and Mg, respectively. These differences in pH which Ca and Mg started to precipitate is due to different processes in the formation of $Al(OH)_3$ amorphous precipitate in soil and in pure solution.

A precipitate with net negative charge is probably formed due to hydrolysis of the Al_{ex} with increasing pH as shown by the following reaction:

$$(Soil\text{-}Al)^{2+} + 30H^- \leftrightarrow [Soil\text{-}Al(OH)_3]^- \qquad (1)$$

Reaction (1) favours adsorption of Ca, Mg, or other metallic cation (M^{++}) on the surface of the precipitate. Therefore, isomorphic coprecipitate of Ca or Mg is formed in soil. Although Al in pure solution was also precipitated in the pH range from 5.5 to 7.5, Ca and Mg reductions were not detected (Figure 2). This result indicated that both cations did not form coprecipitate with amorphous $Al(OH)_3$ $3H_2O$. The electrostatic attraction with cations was extremely low due to the neutral charge of the Al amorphous precipitate.

Increasing pH > 7.5 species with net negative charger are formed in solution, such as $Al(OH)^-_4$, $Al(OH)^{2-}_5$, and $Al(OH)^{3-}_6$. These Al species adsorb positive cations on the surface of the precipitate reducing Ca_s and Mg_s. The following reactions are proposed for the reduction of Mg.

$$Al(OH)^-_4.2H_2O + Mg_s^{2+} \rightarrow [MgAl\,(OH)_4.2H_2O]^+ \qquad (2)$$

or

$$Al(OH)^-_4.2H_2O + Mg_s^{2+} \rightarrow \{Mg[Al(OH)^-_4.2H_2O]_2\} \qquad (3)$$

Therefore, isomorphic coprecipitation reactions of Mg with Al-compounds are suggested to explain the reduction of Mg_{ex} with increasing pH reported for brazilian soils (Chaves et al., 1988; Pavan et al., 1984; Pavan & Roth, 1992). Similar reaction is believed to occur with Ca.

Other metals (Fe^{3+}, Zn^{2+}, Mg^{2+}, and Cu^{2+}) also may form isomorphic coprecipitate with Ca and Mg as suggested by Ohlweiler (1976). However, the concentrations of these metals in soil are so low that their contributions for Ca and Mg reductions are minimal.

CONCLUSION

The reductions of KCl exchangeable Ca and Mg with increasing pH were due to isomorphic coprecipitation with Al in soil as illustrate by the following reaction:

$$[\text{Soil-Al}^{3+}.5H_2O]^{2+} + 30H^- \leftrightarrow$$
$$[\text{Soil-Al}(OH)_3.2H_2O]^- + \tfrac{1}{2}\,M^{2+} \leftrightarrow$$
$$[\text{soil-Al}(OH)_3.\ \tfrac{1}{2}\,M.2H_2O]$$

where M = Ca or Mg

RESUMO

Foram conduzidos experimentos de laboratório com amostras de solo e soluções sintéticas para investigar os possíveis mecanismos de reduções do Ca e Mg trocáveis com o aumento de pH. Os aumentos no pH > 5,3 pelas adições de $CaCO_3$ no solo e NaOH na suspensão solo/KCl aumentaram as adsorções de Ca e Mg. A redução de Mg foi superior a de Ca, sendo relacionada com a concentração de Al trocável do solo. Em soluções sintéticas cotendo Al, as reduções de Ca e Mg ocorreram em pH > 7,5. Atribuíram-se às reações de coprecipitação isomórfica com compostos de Al, como o provável mecanismo de reduções de Ca e Mg com o aumento de pHs. São propostas as prováveis reações químicas responsáveis pelas reduções de Ca e Mg com o aumento de pH.

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