

THE JOURNAL OF AGRICULTURE OF THE UNIVERSITY OF PUERTO RICO

Issued quarterly by the Agricultural Experiment Station of the University of Puerto Rico, Mayagüez Campus, for the publication of articles and research notes by staff members or others, dealing with scientific agriculture in Puerto Rico and elsewhere in the Caribbean Basin and Latin America.

VOL. 80

JANUARY AND APRIL 1996

No. 1-2

A thermodynamic evaluation of the addition of calcium and magnesium to an Ultisol: II CaSO_4 addition^{1,2}

*Gustavo A. Martínez³, Lourdes Peña-Córdova⁴
and Luis A. Figueroa⁵*

J. Agric. Univ. P.R. 80(1-2):1-12 (1996)

ABSTRACT

An experiment was conducted to evaluate the effects of CaSO_4 additions on the chemical properties of an Ultisol. Four levels of calcium and three levels of magnesium were combined in a 4×3 complete factorial experimental design. As expected, the addition of CaSO_4 resulted in significant increases in the levels of calcium in solution. Furthermore, a decrease in the amount of exchangeable magnesium was observed. This was in turn reflected in an increase in the concentration of magnesium in solution. The correlation between the amount of magnesium in the exchange phase and in solution suggests that the fixation phenomenon frequently observed in limed soils does not occur when CaSO_4 is used. To evaluate the effect of increases in pH in these samples, NaOH was added a month after CaSO_4 addition. As in the case of $\text{Ca}(\text{OH})_2$, a decrease in the levels of magnesium in solution was observed. This led us to conclude that the presence of SO_4^{2-} can not prevent the fixation of magnesium, and that aluminum and pH might be the controlling factors of said mechanism.

Key words: Mg fixation, soil acidity, CaSO_4

¹Manuscript submitted to Editorial Board 25 June 1992.

²The authors thank Eleanor Fontanet of the Statistics Section for her cooperation in the statistical analysis. This paper is lovingly dedicated to the memory of Gustavo Javier Martínez Peña, late son of the first two authors.

³Research Assistant, Agronomy and Soils Department. Agricultural Experiment Station, P.O. Box 21360, Río Piedras, P.R. 00928.

⁴Former Laboratory Technician, Agronomy and Soils Department.

⁵Assistant Technician, Agronomy and Soils Department.

RESUMEN

Evaluación termodinámica de la adición de calcio y magnesio a un Ultisol: II
 CaSO_4

Se condujo un experimento con el propósito de determinar los efectos de la aplicación de CaSO_4 a un Ultisol de la montaña. Cuatro niveles de calcio y tres niveles de magnesio se combinaron en un diseño experimental factorial completo 4×3 . La aplicación de CaSO_4 causó un incremento significativo en los niveles de calcio en solución. Esto estuvo acompañado por una disminución en los niveles de magnesio intercambiable y por un aumento significativo en los niveles de magnesio en solución. La relación entre los niveles de magnesio intercambiable y magnesio en solución sugiere que el mecanismo de fijación de magnesio típico en suelos ácidos que han sido encalados no ocurre si se utiliza CaSO_4 . Para evaluar los efectos de incrementos en pH en estas muestras, le añadimos NaOH a las mismas un mes luego de la aplicación de CaSO_4 . Los aumentos en pH observados estuvieron acompañados de una disminución en los niveles de magnesio en solución similares a los observados con Ca(OH)_2 . Por tal motivo se concluyó que la presencia de SO_4^{2-} no pudo prevenir la fijación de magnesio y que el aluminio y el pH son los factores que controlan dicho mecanismo.

INTRODUCTION

Soil acidity has long been recognized as one of the most limiting factors to crop production in highly weathered soils. Annually, several hundred million hectares produce inadequate yields because of toxic levels of aluminum, manganese or both (Cornell International Bulletin no. 34, 1979). Liming is considered the most efficient alternative in most cases. An appropriate liming program will result in adequate soil base saturation, reduction in the concentration of toxic elements, enhanced availability of most plant nutrients and higher activity of beneficial microorganisms (McLean, 1971). Despite the great success of different liming programs in the tropics, the generalization of such practice is creating concerns in the scientific community. Reports on negative impacts on nutrient availability induced by liming have prompted a detailed evaluation of the effects of liming in these soils. One of the most intensively investigated aspects in the last two decades is the problem sometimes referred to as "Mg-fixation" (Hunsaker and Pratt, 1970a, 1970b; Christenson et al., 1973; Sumner et al., 1978; Grove et al., 1981; Pavan et al., 1984; Grove and Sumner, 1985; Myers et al., 1988; Martínez et al., 1995). This phenomenon is characterized by a dramatic reduction in the levels of exchangeable Mg when acid soils are limed. Proposed mechanisms for the Mg fixation include formation of Mg-Al double hydroxides (Hunsaker and Pratt, 1970a), the coprecipitation of Mg and Al hydroxides (McBride, 1978), and the adsorption of Mg by hydroxy-Al polymers (Grove et al., 1981).

In a previous paper, Martínez et al. (1995) examined the effects of Ca(OH)_2 additions on the chemistry of the soil solution of an Ultisol of

Puerto Rico. Decreases in the amount of exchangeable Mg brought about by liming were accompanied by a reduction in the levels of Mg in solution, all of which confirmed the occurrence of the "fixation" phenomenon in this soil. A pH drop caused by the addition of HCl to those samples significantly increased the levels of Mg in solution, thus suggesting that the "fixation" of Mg could be a reversible process. In this work, we report the results of a similar study in which the effects of CaSO₄ addition [as opposed to Ca(OH)₂] were evaluated. CaSO₄ has been successfully used to ameliorate soil acidity problems in the tropics. CaSO₄ reduces aluminum toxicity by exchanging OH for SO₄ on aluminum and iron hydroxide surfaces, by forming aluminum hydroxysulfate minerals, by decreasing the activity of Al in solution by ion pair formation, and by displacement and subsequent leaching of soluble aluminum (Farina, 1988). It also increases the concentration of calcium in solution, which in most cases is deficient in these soils. In addition, CaSO₄ provides the system with a highly mobile anion, which allows all the benefits of its application to be encountered deep into the profile, thereby allowing the crops to utilize the water and nutrients of the subsoil.

The effects of CaSO₄ addition on the chemistry of highly weathered soils are well documented (Alva et al., 1990; Jerksak, 1989; Marcano-Martínez and McBride, 1989; Pavan et al., 1984). Evaluating this calcium source in this work pertains exclusively to the determination of its role in the magnesium fixation phenomenon. Additions of CaSO₄ are not expected to increase the pH of the soil dramatically, which may preclude the fixation of Mg. In addition, the presence of SO₄ may prevent the fixation of Mg even if the pH of the soil is increased through the formation of an ion pair with Al. To evaluate the last point, NaOH was added to samples previously equilibrated with CaSO₄ to raise their pH to near neutrality values. This strategy is analogous to that used in the Ca(OH)₂ experiment (Martínez et al., 1995), although in that case HCl was added after equilibration to evaluate the effect of lowering the pH of the samples on the chemistry of Mg.

MATERIAL AND METHODS

An Ultisol (Typic Tropohumult) from Corozal, Puerto Rico, was used. A detailed description of the experimental design and procedures used in this experiment appears elsewhere (Martínez et al., 1995). Briefly, combinations of the following calcium and magnesium treatments were applied to the soil in accordance with a 4 × 3 complete factorial experimental design.

Calcium: (CaSO ₄)	Magnesium: (MgSO ₄)
1) Control - 0 calcium added	1) Control - 0 magnesium added
2) 1x - 1 meq Ca ²⁺ /meq Al ³⁺	2) 1x - 10% of the sum of cations
3) 2x - 2 meq Ca ²⁺ /meq Al ³⁺	3) 2x - 20% of the sum of cations
4) 3x - 3 meq Ca ²⁺ /meq Al ³⁺	

Analyses for soluble and exchangeable cations were performed 48 hours after the treatments had been applied (Date 1). A month later (Date 2) the same analyses were performed. At this point NaOH was added to all the CaSO₄ treated samples to raise their pH levels to near neutrality values, and the samples were analyzed once again two months later (Date 3).

RESULTS AND DISCUSSION

Calcium in Solution - Ca-s:

The addition of CaSO₄ caused a 10-fold increase (2nd date) in the levels of Ca-s relative to those of the control (Table 1). However, no significant difference was observed among the amounts of CaSO₄ applied (1x, 2x, 3x). This finding may have been due to the formation of a solid phase (probably CaSO₄), which controlled the solubility of calcium present in the system (the K_{sp} for CaSO₄ is 2.40×10^{-5}).

The addition of NaOH significantly increased the pH of the soil measured on the third date (Table 2). A significant decrease in the levels of calcium in solution was observed (Table 1). Apparently, additional cation exchange sites created by the increase in pH were then satisfied by calcium ions originally present in solution.

If the effects of the two calcium sources [Ca(OH)₂ and CaSO₄] are compared in Figure 1, it can be seen that initially (2nd date), the levels

TABLE 1.—Effect of CaSO₄ additions on the levels of Ca-s (cmol^l/L).

Treatment	12/90 ¹	1/91 ²	3/91 ³
Control	0.36a	0.26a	0.34a
1x Ca	2.14b	2.64b	1.08ab
2x Ca	2.08b	2.64b	1.82bc
3x Ca	2.16b	2.66b	2.02c
	b > a 1%	b > a 1%	c > a 1%
			c > ab 5%
			bc > a 5%

¹48 hrs after sample treatment.

²One month after sample treatment.

³Two months after NaOH addition.

TABLE 2.—pH values measured at different dates.

Treatments	12/90 ¹	1/91 ²	3/91 ³
Control	4.25	4.25	4.27
1x Ca	3.91	3.91	6.31
2x Ca	3.88	3.89	5.79
3x Ca	3.89	3.89	6.21

¹48 hours after sample treatment.

²One month after sample treatment.

³Two months after NaOH addition.

of Ca-s obtained with CaSO_4 were much higher than those obtained with $\text{Ca}(\text{OH})_2$. This was possibly a manifestation of the different effects of the two calcium sources on pH-dependent sites of the soil. The addition of $\text{Ca}(\text{OH})_2$ caused an increase in the pH of the soil which in turn increased the number of sites available for cation exchange (Martínez et al., 1995). On the other hand, CaSO_4 caused a small decrease in the pH of the soil, all of which may have decreased the number of sites available for cation exchange (Table 2). As expected, the soil with a larger number of exchange sites had the lowest concentration of calcium in solution.

At the third date (3/91), both sources experienced dramatic changes in their respective levels of Ca-s as expected (Figure 1). Again, this was the stage at which NaOH was added to the CaSO_4 samples to raise their pH to near neutrality values, and HCl was added to the $\text{Ca}(\text{OH})_2$ samples to lower their pH to natural levels. A significant increase in Ca-s was observed in the $\text{Ca}(\text{OH})_2$ treated samples (after HCl addition), whereas a decrease was observed in the CaSO_4 samples (after NaOH addition). This is consistent with the hypothesis that Ca-s concentrations vary inversely with pH-induced surface charge. However, it is important to notice that the final concentration of Ca-s observed for the $\text{Ca}(\text{OH})_2$ samples is almost twice the initial level present in the CaSO_4 samples (2nd date). This finding again points to the presence of a solid phase controlling the solubility of calcium in the CaSO_4 samples.

Exchangeable calcium- (Ca-e):

A gradual increase in Ca-e was observed as a result of the calcium addition (Table 3). A slight decrease in Ca-e was observed on the 2nd date relative to the first. This was probably the result of a more complete reaction of the source (CaSO_4), one month after the application. On the third date, a slight increase (not statistically significant) in the levels of Ca-e was observed. This was probably due to a small increase

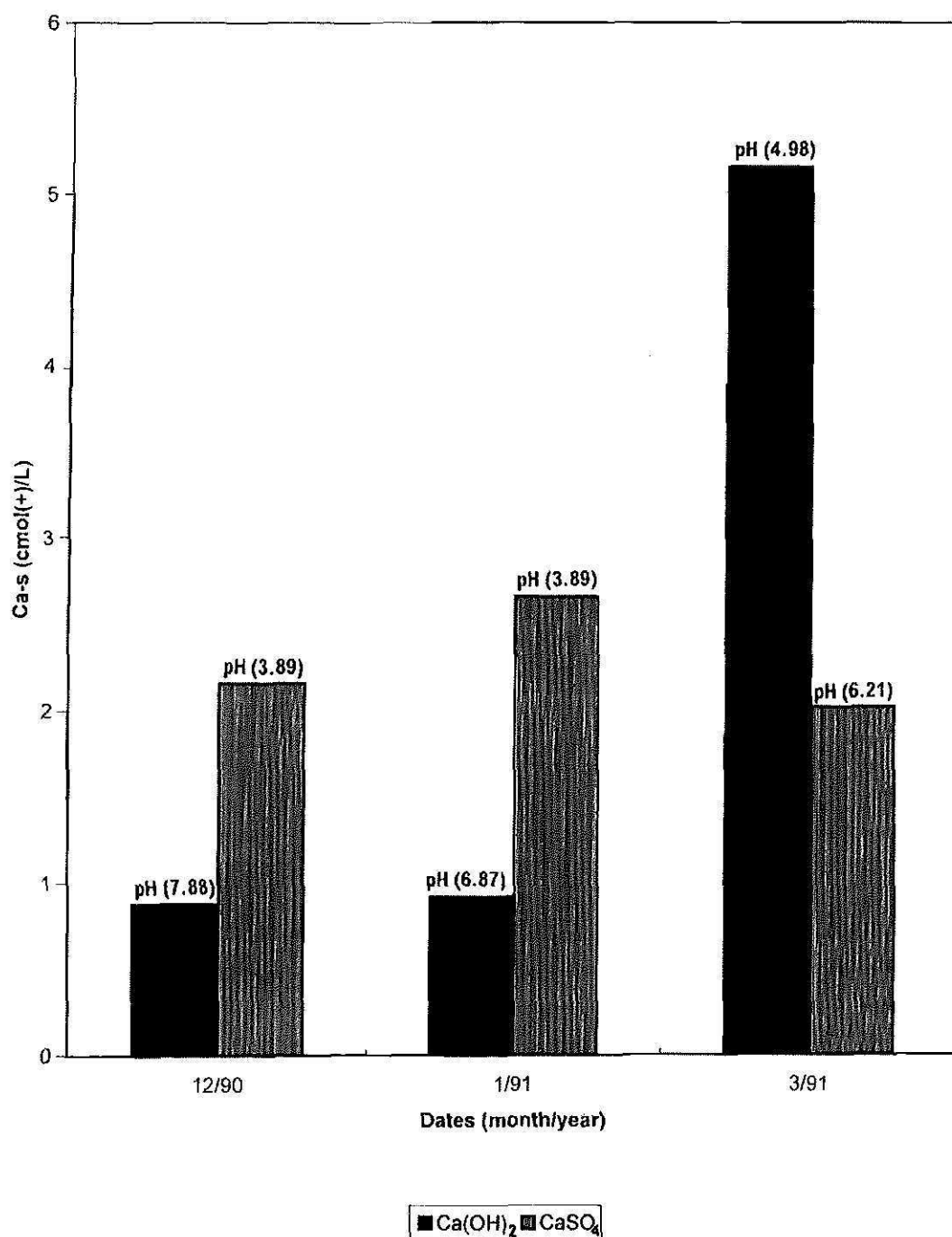


FIGURE 1. Effect of two calcium sources and soil pH on the levels of calcium in solution (Ca-s). Data from the calcium treatment - 3X Ca/meq Al.

in the number of exchange sites caused by the increase in pH due to NaOH addition. However, the increase in the number of exchange sites observed was less than expected if we compare that increase to the results observed in the Ca(OH)₂ samples. Lower pH values achieved through the NaOH addition, as well as the presence of SO₄ and proba-

TABLE 3.—*Effects of CaSO₄ additions on the levels of Ca-e (cmol⁺/kg).*

Treatments	12/90 ¹	1/91 ²	3/91 ³
Control	3.79a	3.68a	3.57a
1x Ca	10.79b	8.34b	9.88b
2x Ca	15.13c	11.42c	12.26c
3x Ca	18.33d	13.85d	13.43c
	b,c,d > a 1%	b,c,d > a 1%	b,c > a 1%
	d > c 1%, > c 5%	c,d > b 1%	c > b 5%
	c > b 5%	d > c 5%	

¹48 hrs after sample treatment.

²One month after sample treatment.

³Two months after NaOH addition.

bly of a solid phase controlling the solubility of Ca in the CaSO₄ samples, may have been the reason for it.

Figure 2 shows the effects of the two calcium sources applied to the soil. The addition of Ca(OH)₂ resulted in more Ca-e present in the soil (1st and 2nd Date). Again this fact is due to the effect of both sources on the pH dependent sites. In the case of Ca(OH)₂ the sites created should disappear as the pH returns to normal levels.

Magnesium in solution (Mg-s):

As expected, an increase in Mg-s resulted from the additions of CaSO₄ (Table 4). This increase presumably resulted from a displacement of Mg present in exchange sites by calcium. It is important to keep in mind that CaSO₄ does not increase the number of exchange sites present in the system as does Ca(OH)₂; therefore, the addition of the competing cation (Ca) probably saturated the exchange sites, displacing cations previously present in the exchange phase. Also important is that the fixation of magnesium encountered in the case of Ca(OH)₂ treatment (Martínez et al., 1995) does not appear to be present in the case of CaSO₄.

The addition of NaOH caused a significant decrease in the levels of Mg-s by the 3rd date (Table 4; Figure 3). This decrease came without a subsequent increase in the levels of exchangeable magnesium, all of which suggests that magnesium was being fixed. Thus, SO₄ does not seem to prevent the fixation of Mg, since a similar pattern to that observed with Ca(OH)₂ was observed with these samples when the pH was raised to near neutrality.

Table 5 shows the overall effect of the addition of magnesium at each calcium level. As expected, there was a significant increase in Mg-s with the addition of Mg. Moreover, the addition of calcium resulted in a significant increase in the levels of Mg-s.

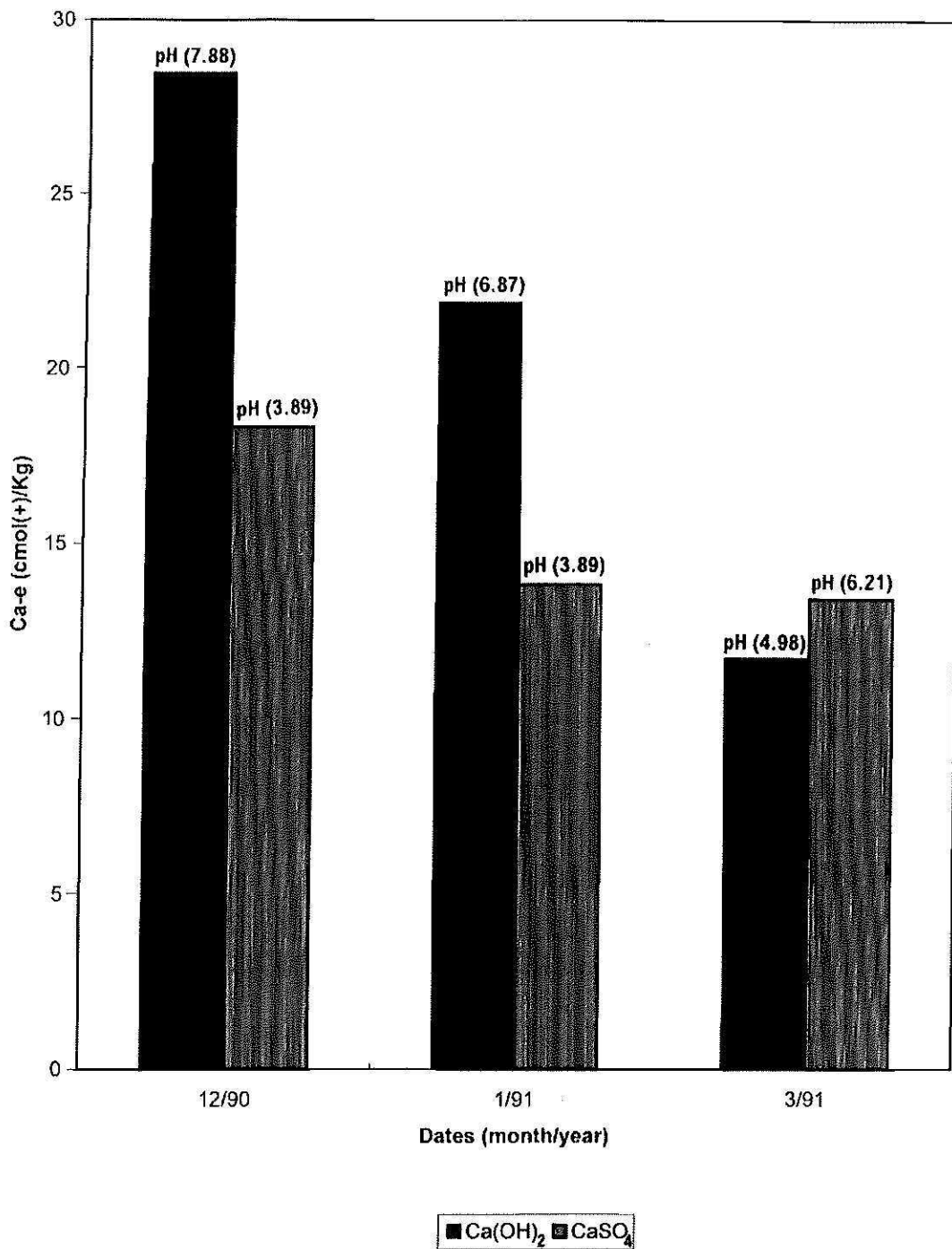


FIGURE 2. Effect of two calcium sources and soil pH on the levels of exchangeable calcium (Ca-e). Data from the calcium treatment - 3X Ca/meq Al.

Exchangeable magnesium (Mg-e):

A significant decrease in Mg-e came as a result of the CaSO₄ additions (Table 6). As mentioned earlier, this decrease is due to the displacement of the Mg-e by the added calcium. With both calcium

TABLE 4.—*Effects of CaSO₄ additions on the levels of Mg-s (cmol⁺/L).*

Treatments	12/90 ¹	1/91 ²	3/91 ³
Control	0.16a	0.14a	0.12a
1x Ca	0.28b	0.30b	0.10a
2x Ca	0.30bc	0.32bc	0.14a
3x Ca	0.32c	0.34c	0.14a
	b,c,bc > a 1% c > b 5%	c,bc,b > a 1% c > b 5%	

¹48 hrs after sample treatment.

²One month after sample treatment.

³Two months after NaOH addition.

TABLE 5.—*Interaction effects of Ca and Mg additions on the levels of Mg-s (cmol⁺/L).*

Treatments	Control (Mg)	1x Mg	2x Mg
Control (Ca)	0.02a	0.12a	0.28a
1x Ca	0.08bc	0.22b	0.28b
2x Ca	0.08bc	0.26c	0.42c
3x Ca	0.12c	0.30d	0.40bc
	bc,c > a 1%	b,c,d > a 1% c > b 5% d > b 1%, d > c 5%	b,c > a 1% c > b 5%

sources [Ca(OH)₂ and CaSO₄] there was an initial decrease in the levels of Mg-e as a result of the addition of Ca. However, in the case of CaSO₄ this decrease was accompanied by an increase in Mg-s. On the other hand, in the case of Ca(OH)₂, the reduction in Mg-e did not result in an increase in Mg-s, thus suggesting the presence of a fixation mechanism.

TABLE 6.—*Effects of CaSO₄ additions on the levels of Mg-e (cmol⁺/kg).*

Treatments	12/90 ¹	1/91 ²	3/91 ³
Control	1.03a	1.09a	0.88a
1x Ca	0.67b	0.70b	0.75b
2x Ca	0.63b	0.75b	0.71b
3x Ca	0.76b	0.80b	0.71b
	a > b 1%	a > b 1%	a > b 1%

¹48 hrs after sample treatment.

²One month after sample treatment.

³Two months after NaOH addition.

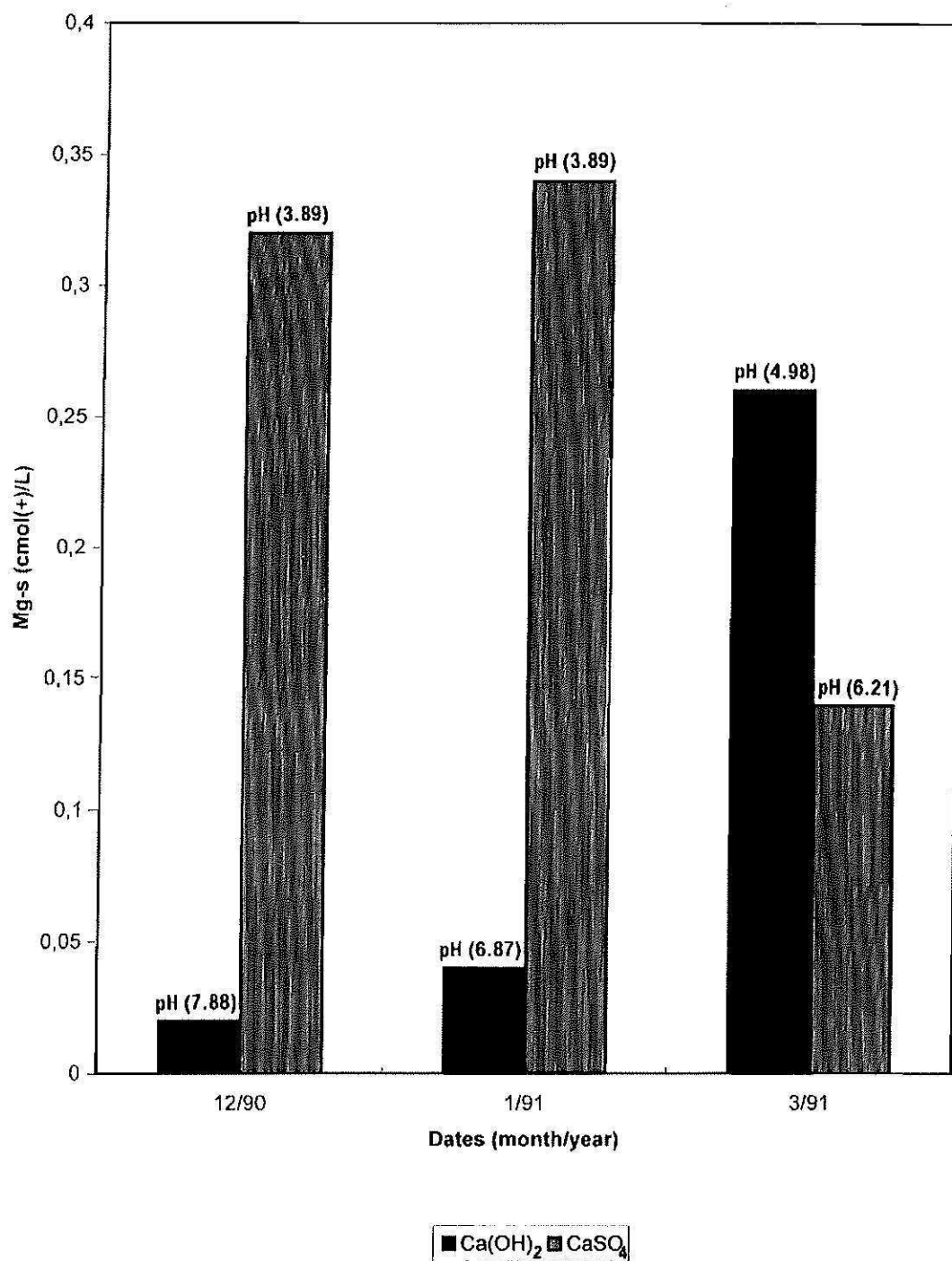


FIGURE 3. Effect of two calcium sources and soil pH on the levels of magnesium in solution (Mg-s). Data from the calcium treatment - 3X Ca/meq Al.

CONCLUSIONS

The addition of CaSO₄ caused a dramatic increase in the levels of Ca-s in the soil. This increase was intensified by the lack of available

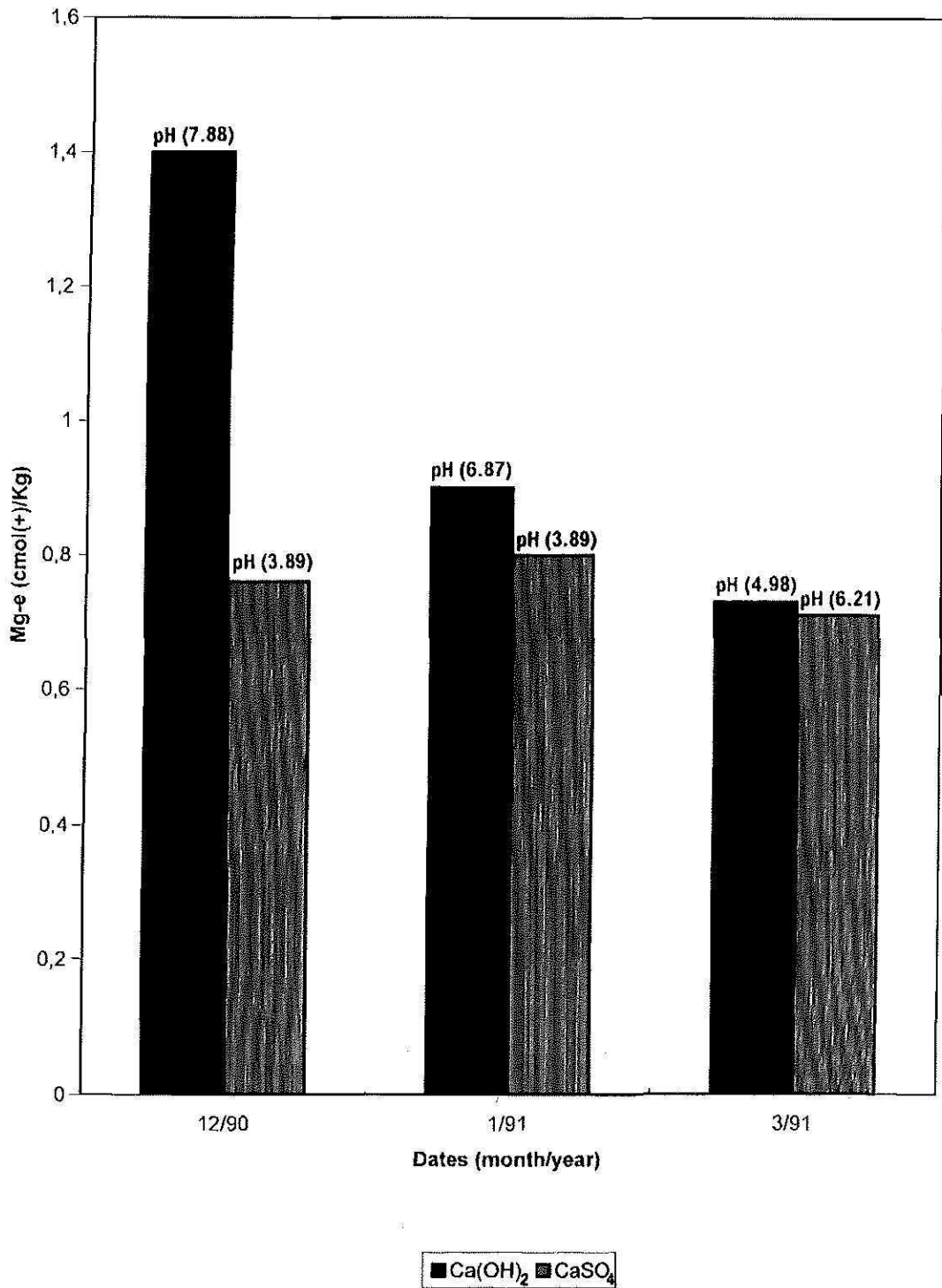


FIGURE 4. Effect of two calcium sources and soil pH on the levels of exchangeable magnesium (Mg-e). Data from the calcium treatment - 3X Ca/meq Al.

sites for cation exchange in this soil under natural conditions, as well as by the inability of this source to create those sites. The levels of exchangeable magnesium in the soil decreased as a result of the CaSO_4

additions. This decrease was reflected in an increase in the levels of magnesium in solution. Such pattern contrasts with the one observed in the case of $\text{Ca}(\text{OH})_2$ (Martínez et al., 1995), where a decrease in Mg-e did not result in an increase in Mg-s. Instead, a small decrease was observed in that case, indicating that magnesium was being fixed as the pH of the soil increased. Although the complexation of Al by SO_4 may reduce the extent of the fixation of Mg, the evidence suggests that this anion does not preclude the fixation.

LITERATURE CITED

- Alva, A. K., M. E. Sumner and W. P. Miller, 1990. Reactions of gypsum or phosphogypsum in highly weathered acid subsoils. *Soil Sci. Soc. Am. J.* 54:993-98.
- Christenson, D. R., R. P. White and E. C. Doll, 1973. Yields and magnesium uptake by plants as affected by soil pH and calcium levels. *Agron. J.* 43:301-4.
- Cornell International Bulletin no. 34. 1979. The influence of subsoil acidity on crop yield potential. Cornell Univ., Ithaca, New York.
- Farina, M. P. W., 1988. Acid subsoil amelioration. II Gypsum effects on growth and subsoil chemical properties. *Soil Sci. Soc. Am. J.* 52:175-80.
- Grove, J. H. and M. E. Sumner, 1985. Lime induced magnesium stress in corn: Impact of magnesium and phosphorus availability. *Soil Sci. Soc. Am. J.* 49:1192-96.
- Grove, J. H., M. E. Sumner and J. K. Syers, 1981. Effect of lime on exchangeable magnesium in variable surface soils. *Soil Sci. Soc. Am. J.* 45:497-500.
- Hunsaker, V. E. and P. F. Pratt, 1970a. The formation of mixed magnesium-aluminum hydroxides in soil materials. *Soil Sci. Soc. Am. Proc.* 34:813-16.
- Hunsaker, V. E. and P. F. Pratt, 1970b. The solubility of mixed magnesium-aluminum hydroxide in various aqueous solutions. *Soil Sci. Soc. Am. Proc.* 34:823-25.
- Jerksak, J. M. and J. G. McColl, 1989. Aluminum release from solid phase components of forest soils leached with citric acid. *Soil Sci. Soc. Am. J.* 53:550-55.
- Marcano-Martínez, E. and M. B. McBride, 1989. Calcium and Sulfate retention by two Oxisols of the Brazilian Cerrado. *Soil Sci. Soc. Am. J.* 53:63-9.
- Martínez, G. A., L. Peña-Córdova and L. A. Figueroa, 1995. A thermodynamic evaluation of the addition of calcium and magnesium to an Ultisol: I $\text{Ca}(\text{OH})_2$ effects. *J. Agric. Univ. P.R.* 78(3-4):99-110.
- McBride, M. B., 1978. Retention of Cu^{2+} , Ca^{2+} , Mg^{2+} , and Mn^{2+} by amorphous alumina. *Soil Sci. Soc. Am. J.* 42:27-31.
- McLean, E. O., 1971. Potentially beneficial effects from liming: Chemical and Physical. *Soil and Crop Sci. Soc. Florida Proc.* 31:189-195.
- Myers, J. A., E. O. McLean and J. M. Bigham. 1988. Reductions in exchangeable magnesium with liming of acid Ohio soils. *Soil Sci. Soc. Am. J.* 52:131-36.
- Pavan, M. A., F. T. Bigham and P. F. Pratt, 1984. Redistribution of exchangeable Ca^{2+} , Mg^{2+} , and Al^{3+} following lime or gypsum applications to a brazilian Oxisol. *Soil Sci. Soc. Am. J.* 48:33-8.
- Sumner, M. E., P. M. W. Farina and V. J. Hurst, 1978. Magnesium fixation - a possible cause of negative yield responses to lime applications. *Commun. Soil Sci. Plant Anal.* 9:995-1007.