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EFFECTS OF SURFACE APPLICATION OF CALCIUM-MAGNESIUM SILICATE AND GYPSUM ON SOIL FERTILITY AND SUGARCANE YIELD⁽¹⁾

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SUMMARY

Lime application recommendations for amendment of soil acidity in sugarcane were developed with a burnt cane harvesting system in mind. Sugarcane is now harvested in most areas without burning, and lime application for amendment of soil acidity in this system in which the sugarcane crop residue remains on the ground has been carried out without a scientific basis. The aim of this study was to evaluate the changes in soil acidity and stalk and sugar yield with different rates of surface application of calcium, magnesium silicate, and gypsum in ratoon cane. The experiment was performed after the 3rd harvest of the variety SP 81-3250 in a commercial green sugarcane plantation of the São Luiz Sugar Mill (47° 25' 33" W; 21° 59' 46" S), located in Pirassununga, São Paulo, in southeast Brazil. A factorial arrangement of four Ca-Mg silicate rates (0, 850, 1700, and 3400 kg ha⁻¹) and two gypsum rates (0 and 1700 kg ha⁻¹) was used in the experiment. After 12 months, the experiment was harvested and technological measurements of stalk and sugar yield were made. After harvest, soil samples were taken at the depths of 0.00-0.05, 0.05-0.10, 0.10-0.20, 0.20-0.40, and 0.40-0.60 m in all plots, and the following determinations were made: soil pH in CaCl₂, organic matter, P, S, K, Ca, Mg, H+Al, Al, Si, and base saturation. The results show that the application of gypsum reduced the exchangeable Al³⁺ content and Al saturation below 0.05 m, and increased the Ca²⁺ concentration in the whole profile, the Mg²⁺ content below 0.10 m, K⁺ below 0.4 m, and base saturation below 0.20 m. This contributed to the effect of surface application of silicate on amendment of soil acidity reaching deeper layers. From the results of this study, it may be concluded that the silicate rate recommended

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may be too low, since the greater rates used in this experiment showed greater reduction in soil acidity, higher levels of nutrients at greater depths and an increase in stalk and sugar yield.

Index terms: soil acidity correction, silicon, stalk and sugar yield, green sugarcane.

RESUMO: EFEITO DA APLICAÇÃO SUPERFICIAL DE SILICATO DE CÁLCIO-MAGNÉSIO E DE GESSO NA FERTILIDADE DO SOLO E PRODUTIVIDADE DA CANA-DE-AÇÚCAR

As recomendações de corretivos de acidez em cana-de-açúcar foram desenvolvidas em sistema de colheita com cana queimada. Hoje, a maioria das áreas é colhida sem queima. Nesse novo sistema de colheita, em que o resíduo da colheita permanece na superfície do solo, a aplicação superficial de corretivos de acidez realiza-se sem embasamento científico. O objetivo deste estudo foi avaliar a alteração da acidez do solo e a produtividade de colmos e açúcar com a aplicação superficial de doses de silicato de cálcio-magnésio e gesso agrícola em cana-soca. O experimento foi realizado após a 3ª colheita da variedade SP 81-3250, em uma plantação comercial de cana crua da Usina São Luiz (47° 25' 33" W, 21° 59' 46" S), localizada em Pirassununga, Estado de São Paulo. O experimento foi montado em um arranjo fatorial com quatro doses de silicato de cálcio-magnésio (0, 850, 1.700 e 3.400 kg ha⁻¹) e duas doses de gesso agrícola (0 e 1.700 kg ha⁻¹). Após 12 meses, o experimento foi colhido e determinada a produtividade de colmos e açúcar. Após a colheita, amostras de solo foram retiradas nas profundidades de 0,00-0,05, 0,05-0,10, 0,10-0,20, 0,20-0,40 e 0,40-0,60 m em todas as parcelas, e realizadas as seguintes determinações: pH em CaCl₂, matéria orgânica, P, S, K, Ca, Mg, H+Al, Al, Si e saturação por bases. A aplicação de gesso agrícola reduziu os teores de Al³⁺ e a saturação por Al abaixo de 0,05 m e aumentou o teor de Mg²⁺ abaixo de 0,10 m, a concentração de Ca²⁺ em todo o perfil, a concentração de K⁺ abaixo de 0,4 m e a saturação por bases abaixo dos 0,20 m. Isso contribuiu para que o efeito da aplicação superficial de silicato na alteração da acidez do solo atingisse camadas mais profundas. A partir dos resultados deste estudo, pode-se concluir que a dose de silicato recomendada pode ser insuficiente, já que as maiores doses utilizadas neste experimento propiciaram maior redução da acidez do solo, níveis mais elevados de nutrientes em profundidade e aumento na produtividade de colmos e açúcar.

Termos de indexação: correção de acidez do solo, silício, produtividade de colmos e açúcar, cana crua.

INTRODUCTION

Soils in vast regions of the world are acidic, with pH values <5.5 (von Uexküll & Mutert, 1995). Approximately 70 % of Brazilian territory is composed of acid soils, which may reduce yield potential by about 40 %, mainly due to high concentrations of soluble Al³⁺ (Quaggio, 2000). These soils are also characterized by low base saturation, low P content, and the predominance of 1:1 clay minerals. Furthermore, iron and Al oxides are present in varying degrees, which are pH dependent (Olmos & Camargo, 1976).

The most recommended practice for amendment of soil acidity is liming. Substances capable of neutralizing protons in the soil solution are applied for this purpose. The materials used in amendment of soil acidity are basically oxides, hydroxides, silicates, and carbonates. Limestone is the material most commonly used. In addition to the use of substances for amendment of acidity, gypsum (CaSO₄·2H₂O) has been used as a soil conditioner. It exhibits high mobility

in the soil profile and is able to make Ca²⁺ and SO₄²⁻ ions available in the soil solution. It is subject to leaching, enriching the deeper subsurface soil layers with nutrients, reducing Al³⁺ saturation at these depths (Alcarde & Rodella, 2003) and reducing Al³⁺ activity in the soil solution (Alva et al., 1986).

Lime application recommendations for amendment of soil acidity in sugarcane were developed for a burnt cane harvesting system. Sugarcane harvest without burning is already a reality and has been growing significantly not only in São Paulo, the main sugarcane producer, but also in other Brazilian states. In sugarcane harvest without prior burning, a 10-20 t ha⁻¹ yr⁻¹ cover of crop residue remains on the soil surface (Trivelin et al., 1996). Lime application for amendment of soil acidity in this system in which the crop residue remains on the ground has been carried out without a scientific basis.

Studies on amendment of soil acidity in grain crops under no-tillage have shown that the effect of lime applied on the surface for subsoil amendment varies with the rate and particle size of the product,

form of application, soil type, climatic conditions (especially water regime), cropping system, and time since application (Oliveira & Pavan, 1996; Caires et al., 2000, 2003, 2005; Soratto & Crusciol, 2008a), which places the efficiency of the practice in question, particularly in amendment of subsoil acidity.

More recently, farmers and sugar mills have used silicates to amend soil acidity. Calcium and magnesium silicate is an original source from high temperature processing of the reaction of limestone with silica (SiO_2), present in Fe ore (Malavolta, 1981), with acidity amendment properties similar to those of limestone (Castro & Crusciol, 2013). Studies on silicates applied to the soil have shown increased pH and reduced H+Al (Prado & Fernandes, 2003), due to the presence of acid neutralizing agents such as SiO_3^{2-} (Alcarde & Rodella, 2003), and increases in the availability of P, Ca, Mg (Prado & Fernandes, 2003), and Si in soil (Winslow, 1992), which has been reflected in yield increases for some crops (Carvalho-Pupatto et al., 2004; Pulz et al., 2008; Crusciol et al., 2009). According to Alcarde & Rodella (2003), Ca silicate is 6.78 times more soluble than Ca carbonate, and, thus, has greater potential than limestone for amendment of subsoil acidity. In Brazilian literature, there are a few studies that address the use of silicate for amendment of acidity (Prado & Fernandes, 2003; Carvalho-Pupatto et al., 2004), but silicate was incorporated into the soil. Castro & Crusciol, (2013) observed that products from silicate dissociation 18 months after application reach deeper soil layers in comparison to liming under no-tillage.

It is known that soils after liming, upon replanting of sugarcane, have decreased base saturation and decreases in Ca^{2+} , Mg^{2+} , and K^+ throughout the cut areas (Morelli et al., 1992). It is known that there is a progressive decline in production associated with the decline in soil fertility, which, over the time of the cuttings, will culminate in the need for replanting the sugarcane, which is one of the most expensive phases of the production system. Therefore, it is necessary to verify if the application of Ca-Mg silicate and gypsum on the sugarcane residue can lead to amendment of acidity in the subsurface soil, increasing the yield and longevity of the sugarcane field.

Thus, the aim of this study was to evaluate the amendment of soil acidity, and stalk and sugar yield when differing rates of calcium and magnesium silicate and gypsum are applied on ratoon cane.

MATERIAL AND METHODS

The experiment was carried out from October 2006 to October 2007, starting in the rainy season after the 3rd harvest of the variety SP 81-3250 in a

commercial green sugarcane plantation of the São Luiz Sugar Mill (47° 25' 33" W; 21° 59' 46"), located in Pirassununga, São Paulo, in southeast Brazil. The altitude of the location is 627 m a.s.l.. The climate is Aw (Tropical Savanna, by the Köppen classification) and the area is flat. Daily rainfall was registered during the experiment, and the results showed 102 mm in October, 120 mm in November, 175 mm in December, 275 mm in January, 172 mm in February, 164 mm in March, 62 mm in April, 58 mm in May, 18 mm in June, 15 mm in July, 15 mm in August, 28 mm in September, and 84 mm in October, for a total of 1,288 mm.

The soil is classified as kaolinitic, thermic Typic Haplorthox, with a sandy loam texture. Immediately after the harvest of the 2nd ratoon and before initiating the experiment, the soil chemical and textural characteristics were determined. Thus, 10 subsamples were taken from the experimental area between the ratoon rows and combined into one composite sample with the following results for the topsoil (0.00-0.20 m) and subsoil (0.20-0.40 m): pH of 4.8 and 4.7, soil organic matter (OM) of 23.6 and 16.8 g dm^{-3} , P (resin) of 7.0 and 4.0 mg dm^{-3} , Si of 5.4 and 5.1, and S of 6.0 and 4.0, respectively. Exchangeable K, Ca, Mg, and Al, CEC (cation exchange capacity), and H+Al (total acidity pH 7.0), for the topsoil (0.00-0.20 m) and subsoil (0.20-0.40 m), were 1.7 and 1.0, 17 and 12.5, 6.15 and 4.9, 1.3 and 2.8, 53.9 and 49.0, 29.3 and 30.6 mmol $_c$ dm^{-3} , respectively. Base saturation for the topsoil (0.00-0.20 m) and subsoil (0.20-0.40 m) was 46.1 and 37.6%, respectively. Sand, silt, and clay contents for the topsoil (0.00-0.20 m) and subsoil (0.20-0.40 m) were 693 and 677, 43 and 34, and 264 and 289 g kg^{-1} , respectively.

Soil pH was determined in 0.01 mol L^{-1} CaCl_2 (Raij et al., 2001), SOM (soil organic matter) by the colorimetric method (Raij et al., 2001), P from extraction by ion exchange resin and determination by colorimetry (Raij et al., 2001), S by 0.5 mol L^{-1} NH_4OAc in 0.25 mol L^{-1} HOAc (Vitti, 1988), K from extraction by ion exchange resin and determination by flame photometry (Raij et al., 2001), Ca and Mg from extraction by ion exchange resin and determination by atomic absorption spectrometry (Raij et al., 2001), H+Al (total acidity at pH 7.0) from determination by a potentiometer in SMP-buffer solution (Raij et al., 2001), Al^{3+} by 1 mol L^{-1} KCl (Raij et al., 2001), and Si from extraction by 0.5 mol L^{-1} acetic acid and determination by a spectrophotometer at 660 nm (Korndörfer et al., 1999).

A randomized block experimental design was used in a factorial arrangement, with four replications. Treatments consisted of four Ca-Mg silicate rates (0; 850; 1,700; and 3,400 kg ha^{-1}) and two gypsum rates (0 and 1,700 kg ha^{-1}). Each plot consisted of eight sugarcane rows of 12 m length, spaced at 1.4 m.

Calcium-magnesium silicate composition was 39.8 % CaO, 12.0 % MgO, 23 % SiO₂, and 88 % effective Ca carbonate equivalence (ECCE). The composition of gypsum (CaSO₄·2H₂O), a by-product obtained from a Brazilian phosphoric acid industry, was 20 % Ca, 16 % S, and a small residue of 0.1 % of P and F.

The Ca-Mg silicate rate (SR) was calculated so as to increase the soil base saturation (0.00-0.40 m) to 60 % according to Spironello et al. (1996). For this purpose, the soil chemical characteristics determined in the topsoil (0.00-0.20 m) were used, and the result obtained from the amount of Ca-Mg silicate is multiplied by two (Spironello et al., 1996), as shown in equation 1:

$$SR \text{ (kg ha}^{-1}\text{)} = \{[(BS_2 - BS_1) \times CEC] / (ECCE \times 10)\} \times 2 \quad (1)$$

where BS₂ is the estimated base saturation (60 %) and BS₁ is the base saturation measured in soil analysis, as in equation 2:

$$BS_1 \text{ (}\%) = [(Ca^{2+} + Mg^{2+} + K^+) / CEC] \times 100 \quad (2)$$

where Ca²⁺, Mg²⁺, and K⁺ are exchangeable base cations and CEC is the total cation exchange capacity, calculated according to equation 3:

$$CEC \text{ (mmol}_c \text{ dm}^{-3}\text{)} = \frac{Ca^{2+} + Mg^{2+} + K^+}{\text{total acidity at pH 7.0 (H+Al)}} \quad (3)$$

Thus, the Ca-Mg silicate application rates were defined as the control (0 kg ha⁻¹), half the recommended rate (850 kg ha⁻¹), the recommended rate (1,700 kg ha⁻¹), and double the recommended rate (3,400 kg ha⁻¹). Before application of the products, silicate and gypsum were mixed, according to the treatments, and they were packed in plastic bags.

The gypsum rate (GR) was calculated through equation 2:

$$GR \text{ (kg ha}^{-1}\text{)} = 6 \text{ CL} \quad (4)$$

where CL is the clay content (g kg⁻¹) in the 0.20-0.40 m soil layer.

Thus, products were applied over the sugarcane harvest residue layer (12.2 t ha⁻¹) without previous burning or soil incorporation, according to the treatments. Topdressing fertilization on the sugarcane ratoon was performed with 70 kg ha⁻¹ of N in the form of ammonium nitrate and 80 kg ha⁻¹ of K₂O in the form of potassium chloride.

After 12 months, the experiment was harvested and soil samples were taken at the depths of 0.00-0.05, 0.05-0.10, 0.10-0.20, 0.20-0.40, and 0.40-0.60 m in all plots. Seven subsamples were taken at random from each plot between the rows and combined into one composite sample. Soil samples were chemically analyzed for pH, OM, H+Al, and P, exchangeable Al, Ca, Mg, and K (Raij et al., 2001), Si (Korndorfer et al., 1999), and S (Vitti, 1988). Using the results of exchangeable bases and total acidity at pH 7.0 (H+Al), base saturation values were calculated (Raij et al., 2001).

Stalk yield at harvest was determined in the four central rows, with two rows of plants being used for

technological measurements (sugar concentration, purity, fiber, and reducing sugar). One meter was established at random in both plant rows; the stalks were collected, topped at apical bud height, defoliated and then sent to the sugarcane technology laboratory, São Luiz Sugar Mill, to be processed according to the method defined in the Sucrose Content-Based Sugarcane Payment System, in accordance with Consecana's semiannual updates for technological evaluations described in Fernandes (2003), considering the sugarcane total reducing sugar parameter. Using the results of stalk yield and sugar concentration, the sugar yield values were calculated.

Data were subjected to ANOVA using SAS (SAS, 1997). Mean values of gypsum application were compared by Fisher's protected LSD test at the 0.05 significance level. Calcium-magnesium silicate rates were analyzed through regression analysis, adopting the magnitude of the regression coefficients that were significant at the 0.05 significance level by the *t* test as the criterion for choosing the model.

RESULTS AND DISCUSSION

Increasing silicate application rates led to a linear increase in pH(CaCl₂) in the soil and led to a linear reduction in potential acidity (H+Al), exchangeable Al³⁺ and Al saturation from the surface to a depth of 0.60 m (Table 1). Castro & Crusciol (2013), in an experiment at 18 months after application of silicate on the surface of an Oxisol under no-tillage, also observed an increase in pH up to 0.40 m. Correa et al. (2007), at three months after application of steel slag on the surface of an Oxisol under no-tillage, also observed an increase in pH to a depth of 0.40 m with increasing rates. This higher concentration of compounds resulting from the neutralization reaction at higher silicate rates allows the soil negative charges, originating from increasing pH, to be filled by providing excess cations to the soil solution in a shorter time interval, which makes displacement of the alkaline front in the subsurface possible, confirming the assertion of Caires et al. (2004) for applying soil amendments for acidity on the soil surface. In addition, the silicate has six to seven times greater solubility than limestone, which facilitates its mobility in the soil profile (Quaggio, 2000).

The physical movement of the silicate by biopores and planes of weakness in the soil itself (Amaral et al., 2004) has been identified as the main factor that contributes to amendment of acidity at soil depths. Furthermore, in this experiment, high rainfall in the months following the application of silicate may have contributed to soil amendment in the 0.0-0.6 m depth layer.

No effect from the application of gypsum was observed for pH and H+Al. However, the application

Table 1. Values of pH in CaCl₂, total acidity at pH 7.0 (H+Al), exchangeable Al (Al³⁺), and Al saturation (m) of soil samples taken 12 months after Ca-Mg silicate and gypsum surface application on green sugarcane, and ANOVA significance at five soil depths

Silicate	Gypsum, kg ha ⁻¹							
	0		1,700		0		1,700	
	pH(CaCl ₂)		H+Al		Al ³⁺		m	
kg ha ⁻¹	mmol _c dm ⁻³				%			
	0.00-0.05 m							
0	4.8	4.9	30.9	30.1	1.5	1.2	5.4	4.1
850	5.3	5.4	25.0	24.3	1.4	1.1	3.1	2.6
1,700	5.9	5.9	19.5	17.6	1.2	1.1	1.7	1.4
3,400	6.0	6.0	17.1	15.7	1.2	0.9	1.2	0.9
Mean	5.4 a	5.6 a	23.1 a	21.9 a	1.3 a	1.1 a	2.8 a	2.3 a
Effect ⁽¹⁾	L*		L*		L**		L*	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		<0.0001	
Gypsum (G)	0.1724		0.3278		0.3866		0.2991	
S*G	0.4144		0.4009		0.4151		0.4111	
	0.05-0.10 m							
0	4.7	4.8	29.3	28.4	1.7	1.1	6.8	4.1
850	5.0	5.0	28.1	26.1	1.5	1.2	4.7	3.7
1,700	5.5	5.4	22.9	22.1	1.3	1.0	2.6	2.3
3,400	5.7	5.6	21.5	20.6	1.3	1.0	2.4	2.0
Mean	5.3 a	5.2 a	25.4 a	24.3 a	1.4 a	1.1 b	4.1 a	3.0 b
Effect	L**		L**		L**		L*	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		0.0371		<0.0001	
Gypsum (G)	0.2833		0.2764		<0.0001		<0.0001	
S*G	0.3012		0.3137		0.3278		0.3159	
	0.10-0.20 m							
0	4.8	4.9	26.9	26.5	1.3	1.0	5.3	3.7
850	5.0	5.1	25.9	25.4	1.3	1.0	4.7	3.2
1,700	5.3	5.4	24.1	24.1	1.2	0.9	3.8	2.7
3,400	5.4	5.5	22.6	21.9	1.0	0.8	2.9	1.8
Mean	5.2 a	5.3 a	24.9 a	24.5 a	1.2 a	0.9 b	4.2 a	2.8 b
Effect	L*		L**		L**		L**	
	ANOVA (F probability)							
Silicate (S)	<0.0001		0.0404		0.0279		<0.0001	
Gypsum (G)	0.2465		0.2399		<0.0001		<0.0001	
S*G	0.2652		0.2774		0.2709		0.2687	
	0.20-0.40 m							
0	4.7	4.7	30.6	29.0	3.0	1.8	14.6	7.7
850	4.8	4.9	29.0	27.7	2.3	1.7	10.2	6.0
1,700	4.9	4.9	27.3	27.1	1.9	1.6	7.6	5.2
3,400	5.0	5.0	26.9	25.0	1.8	1.2	6.7	3.7
Mean	4.9 a	4.9 a	28.4 a	27.2 a	1.2 a	1.6 b	9.7 a	5.7 b
Effect	L**		L**		L**		L**	
	ANOVA (F probability)							
Silicate (S)	0.0217		0.0194		<0.0001		<0.0001	
Gypsum (G)	0.3608		0.3003		<0.0001		<0.0001	
S*G	0.3855		0.3829		0.3899		0.3601	
	0.40-0.60 m							
0	4.3	4.3	35.3	34.0	4.7	3.3	26.4	17.5
850	4.4	4.4	33.4	33.4	3.7	2.8	19.9	13.0
1,700	4.6	4.6	30.9	30.6	3.6	2.6	17.9	10.5
3,400	4.7	4.7	30.2	29.3	3.5	2.4	15.3	9.3
Mean	4.5 a	4.5 a	32.5 a	31.8 a	3.8 a	2.8 b	19.9 a	12.6 b
Effect	L**		L**		L*		L*	
	ANOVA (F probability)							
Silicate (S)	<0.0001		0.0449		<0.0001		<0.0001	
Gypsum (G)	0.4111		0.4058		<0.0001		<0.0001	
S*G	0.4475		0.4501		0.4497		0.4566	

⁽¹⁾ L: represents linear effect by polynomial regression. Values in the rows, within each variable, followed by the same letter are not significantly different at p≤0.05 according to the LSD test. * and **: significant at the 0.05 and 0.01 level, respectively.

of gypsum decreased the concentration of exchangeable Al^{3+} and Al saturation for the 0.05-0.10, 0.10-0.20, 0.20-0.40, and 0.40-0.60 m layers. Some hypotheses have been suggested to explain the mechanism involved, as described by Raij (2008). One would be the release of OH^- by SO_4^{2-} through ligand exchange, with the formation of hydroxylated Al structures, a mechanism called the “self liming” effect (Reeve & Sumner, 1972). The precipitation of Al with formation of minerals (Adams & Rawayfih, 1977) has also been indicated. Another possibility would be leaching of Al along with gypsum, which may partly be favored by the formation of ion pairs or complexes, such as AlSO_4^+ or Al fluoride (Oates & Caldwell, 1985).

The silicate rates increased Ca^{2+} and Mg^{2+} contents and base saturation in a positive linear manner in all the layers evaluated, regardless of the application of gypsum (Table 2). These results corroborate those found by Correa et al. (2007), who also observed higher values of Ca, Mg, and base saturation to a depth of 0.40 m with the increase in rates at three months after application of silicate on the surface of an Oxisol under no-tillage. The displacement of the Ca- and Mg-binding ligand to subsurface layers occurs when the stability constant of the complex is greater than the stability constant for Ca and Mg in the soil (Amaral et al., 2004). The movement of Ca^{2+} and Mg^{2+} in the soil profile by silicate may be attributed to their high concentration, especially for Ca^{2+} in the surface layers since it is well above the range of 4.0 to 7.0 $\text{mmol}_c \text{ dm}^{-3}$, considered adequate (Raij et al., 1996). The silicate was effective in raising base saturation to levels recommended for sugarcane (60 %) in the 0.00-0.05 m layer at the lower rate (850 kg ha^{-1}), the rate recommended by Spironello et al. (1996), in the 0.05-0.10 m layer at the 1,700 kg ha^{-1} rate, and in the 0.10-0.20 m layer at the highest rate (3,400 kg ha^{-1}), proving that the silicate application rate directly affects the leaching of ions and affects soil acidity at greater depths. Furthermore, the results indicate that the use of rates higher than those recommended by Spironello et al. (1996) were more effective in amendment of soil acidity in the 0.0-0.20 m layer after 12 months.

The binding energy of the Ca^{2+} , Mg^{2+} , and K^+ to soil colloids depends on the valence and size of the hydrated ion, such that, in well-drained soils, leached quantities of K^+ are relatively larger than those of divalent cations (Raij, 2008). For K^+ , it was observed that the application of increasing rates of silicate reduced the levels of this nutrient in the whole profile, regardless of the use of gypsum (Table 2). These results may have occurred because, with the addition of Ca and Mg silicate in a soil where the concentrations of Ca^{2+} and Mg^{2+} were already high (Raij et al., 1996), there was displacement of K^+ beyond the 0.6 m evaluated.

Gypsum increased the Ca^{2+} content in all soil layers studied (Table 2). In relation to Mg^{2+} , it was found

that higher contents gradually appeared in the deeper layers, with a lower surface content. Exchangeable Mg^{2+} leaching has been a frequent response in studies with the application of gypsum in soils (Oliveira & Pavan, 1996; Silva et al., 1997; Caires et al., 1999). Thus, when gypsum is applied at high rates on the soil, strategies must be developed to minimize losses of exchangeable Mg^{2+} . For that reason, the use of gypsum has not been recommended in isolation, but rather in combination with dolomitic lime or silicates that have Mg in their composition.

Gypsum promoted reduction in the K^+ contents up to the 0.40 m depth. In the 0.40-0.60 m layer, an increase in the K^+ contents from the addition of gypsum was observed (Table 2). According to Pavan & Roth (1992), the use of gypsum causes leaching of K^+ ions, due to the formation of ion pairs with SO_4^{2-} ions from the dissociation of gypsum in the soil solution.

Silicate application increased the concentration of Si in all the layers evaluated in a linear manner (Table 3). The increase in the Si contents in the soil is due to the presence of Si in the silicate (23 % SiO_2). Furthermore, the solubility of Si increases along with increased pH (Oliveira et al., 2007). In acid soils, the monomer (H_4SiO_4) polymerizes to form amorphous precipitated silica (Iler, 1979), which can result in loss of soluble Si. This mainly occurs when the Si content is high and the pH is low. Another factor that may be occurring is the adsorption of Si by Fe and Al oxides and hydroxides; the lower the pH, the more intense the adsorption (Jackson, 1964).

There was also a linear increase in the P contents in the soil with the application of increasing rates of silicate (Table 3). The use of silicate assisted in desorption of P for, according to Casagrande & Camargo (1997), the increase of pH led to an increase in the solubility of Fe and Al phosphates, and an increase in the concentration of OH^- in the soil solution, thus reducing the adsorption of phosphate in the solid phase of the soil. Furthermore, the silicate anions are considered as competitors with phosphate for the same adsorption sites in soil (Fassbender, 1987) such that silicon can displace (desorb) phosphate, or be displaced by it, from the solid phase to the liquid phase (Carvalho et al., 2000). Thus, amendment of soil acidity with silicates, in addition to reducing phosphate adsorption, increases P availability through the additional effect of displacing the P adsorbed to the solution (Pulz et al., 2008).

The application of increasing rates of silicate led to a linear increase in SO_4^{2-} content at all soil depths (Table 3). An increase in pH occurs with application of silicate (Table 1), which promotes an increase in the availability of SO_4^{2-} both by reducing its adsorption (Casagrande et al., 2003) and by increasing the release of the adsorbed quantity. Moreover, there is also greater mineralization from the increase in soil pH (Alvarez V. et al., 2007).

Table 2. Values of exchangeable Ca²⁺, Mg²⁺, and K⁺, and base saturation (BS) of soil samples taken 12 months after Ca-Mg silicate and gypsum surface application on green sugarcane, and ANOVA significance at five soil depths

Silicate	Gypsum, kg ha ⁻¹							
	0	1,700	0	1,700	0	1,700	0	1,700
	Ca ²⁺		Mg ²⁺		K ⁺		BS	
kg ha ⁻¹	mmol _c dm ⁻³				%			
	0.00-0.05 m							
0	18.5	21.2	7.2	6.2	0.76	0.55	46.1	48.1
850	26.7	30.4	15.9	10.0	0.63	0.50	63.4	62.7
1,700	38.9	52.5	31.9	24.8	0.54	0.46	78.5	81.5
3,400	64.7	64.8	35.1	34.2	0.51	0.40	85.5	86.4
Mean	37.2 b	42.2 a	22.5 a	18.8 b	0.61 a	0.48 b	68.4 a	69.7 a
Effect ⁽¹⁾	L*		L*		L*		L*	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		<0.0001	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.2207	
S*G	0.1850		0.2066		0.1919		0.2594	
	0.05-0.10 m							
0	16.6	19.7	6.2	5.6	0.47	0.31	44.3	47.4
850	20.3	23.7	9.6	7.5	0.45	0.30	51.9	54.7
1,700	29.4	31.0	18.3	11.7	0.38	0.28	67.7	66.0
3,400	31.9	34.8	20.5	14.6	0.32	0.16	71.0	70.6
Mean	24.6 b	27.3 a	13.6 a	9.9 b	0.40 a	0.26 b	58.7 a	59.7 a
Effect	L*		L*		L**		L*	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		<0.0001	
Gypsum (G)	0.1435		0.0481		<0.0001		0.1885	
S*G	0.2375		0.2467		0.2496		0.3003	
	0.10-0.20 m							
0	17.9	18.8	5.1	5.9	0.32	0.22	46.4	48.5
850	19.0	21.5	7.0	7.4	0.28	0.17	50.4	53.4
1,700	22.3	22.5	8.0	9.1	0.26	0.14	55.9	56.8
3,400	24.1	31.0	9.4	13.3	0.22	0.10	59.9	67.0
Mean	20.8 b	23.5 a	7.4 b	8.9 a	0.27 a	0.16 b	53.1 a	56.4 a
Effect	L*		L*		L*		L**	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		<0.0001	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.1792	
S*G	0.1725		0.2209		0.2313		0.2564	
	0.20-0.40 m							
0	12.5	15.9	4.9	5.5	0.20	0.13	36.5	42.6
850	14.7	18.7	5.5	7.7	0.16	0.11	41.2	48.9
1,700	15.7	20.3	7.2	8.5	0.17	0.10	45.8	51.6
3,400	17.6	20.3	7.5	10.7	0.14	0.10	48.8	55.4
Mean	15.1 b	18.8 a	6.3 b	8.1 a	0.17 a	0.10 b	43.0 b	49.6 a
Effect	L*		L*		L*		L**	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		<0.0001	
Gypsum (G)	<0.0001		<0.0001		<0.0001		<0.0001	
S*G	0.1861		0.1922		0.1909		0.1811	
	0.40-0.60 m							
0	9.6	11.0	3.2	4.0	0.32	0.59	27.1	31.4
850	10.0	12.0	4.7	6.6	0.15	0.18	30.8	36.0
1,700	11.3	15.1	5.1	7.0	0.06	0.08	34.8	42.0
3,400	13.0	15.2	6.3	8.0	0.06	0.09	39.1	44.3
Mean	11.0 b	13.3 a	4.8 b	6.4 a	0.15 b	0.24 a	32.9 b	38.4 a
Effect	L*		L*		L*		L**	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		<0.0001	
Gypsum (G)	<0.0001		<0.0001		<0.0001		<0.0001	
S*G	0.2621		0.2436		0.2385		0.2497	

⁽¹⁾ L: represents linear effect by polynomial regression. Values in the rows, within each variable, followed by the same letter are not significantly different at p≤0.05 according to the LSD test. * and **: significant at the 0.05 and 0.01 level, respectively.

Table 3. Values of Si, P, sulfate and soil organic matter (SOM) of soil samples taken 12 months after Ca-Mg silicate and gypsum surface application on green sugarcane, and ANOVA significance at five soil depths

Silicate	Gypsum, kg ha ⁻¹							
	0		1,700		0		1,700	
	Si		P		S-SO ₄ ⁻²		SOM	
kg ha ⁻¹	mg dm ⁻³				g dm ⁻³			
	0.00-0.05 m							
0	6.2	11.7	3.9	6.8	5.9	7.9	23.4	26.3
850	9.3	14.4	7.3	7.5	6.1	12.6	27.3	28.0
1,700	9.9	14.7	9.4	9.6	6.5	14.3	28.2	26.6
3,400	11.7	15.7	11.7	12.7	6.7	14.9	27.5	28.7
Mean	9.3 b	14.1 a	8.1 b	9.2 a	6.3 b	12.4 a	26.6 a	27.4 a
Effect ⁽¹⁾	L*		L*		L*		-	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		0.3867	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.3584	
S*G	0.2262		0.2593		0.4215		0.3909	
	0.05-0.10 m							
0	5.5	5.9	3.0	5.0	4.7	8.0	23.4	24.4
850	7.2	7.6	5.4	5.7	6.0	10.6	23.9	25.0
1,700	7.8	10.6	6.2	6.3	6.1	14.2	25.3	26.0
3,400	12.9	13.2	7.0	9.1	7.4	15.1	25.5	25.3
Mean	8.3 b	9.3 a	5.4 b	6.5 a	6.0 b	12.0 a	24.5 a	25.2 a
Effect	L*		L*		L*		-	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		0.2458	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.2209	
S*G	0.1923		0.1869		0.1944		0.2615	
	0.10-0.20 m							
0	5.7	6.3	2.8	4.6	4.6	12.1	21.8	22.8
850	6.6	6.9	4.6	5.0	6.0	13.1	22.3	23.8
1,700	7.4	7.7	5.6	5.6	7.2	13.2	23.2	24.4
3,400	7.7	10.1	5.8	5.9	11.8	19.6	23.2	23.4
Mean	6.9 b	7.7 a	4.7 b	5.3 a	7.4 b	14.5 a	22.6 a	23.5 a
Effect	L*		L*		L*		-	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		0.2686	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.2511	
S*G	0.2021		0.2178		0.2199		0.2987	
	0.20-0.40 m							
0	5.7	7.0	2.0	2.9	5.9	28.9	19.7	21.1
850	5.8	7.1	2.6	3.4	7.4	30.8	21.0	22.6
1,700	6.1	7.5	2.8	3.4	9.6	42.4	21.7	22.3
3,400	6.6	9.1	2.8	3.9	10.8	47.0	23.0	23.0
Mean	6.0 b	7.7 a	2.5 b	3.4 a	8.4 b	37.3 a	21.3 a	22.2 a
Effect	L*		L*		L*		-	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		0.1766	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.2356	
S*G	0.1682		0.1875		0.1586		0.2735	
	0.40-0.60 m							
0	5.6	7.0	1.1	2.3	10.8	35.6	19.8	20.9
850	5.6	7.1	2.0	2.4	11.9	40.2	19.7	21.8
1,700	6.1	7.2	2.1	2.6	21.1	44.5	20.8	21.4
3,400	6.5	7.7	2.1	3.0	24.2	47.2	22.8	22.2
Mean	6.0 b	7.2 a	1.8 b	2.6 a	17.0 b	41.9 a	20.8 a	21.6 a
Effect	L**		L*		L**		-	
	ANOVA (F probability)							
Silicate (S)	<0.0001		<0.0001		<0.0001		0.1477	
Gypsum (G)	<0.0001		<0.0001		<0.0001		0.2851	
S*G	0.1605		0.1811		0.1676		0.3004	

⁽¹⁾ L: represents linear effect by polynomial regression, and – represents no effect. Values in the rows, within each variable, followed by the same letter are not significantly different at p≤0.05 according to the LSD test. * and **: significant at the 0.05 and 0.01 level, respectively.

The application of gypsum significantly increased the P levels in the soil throughout the profile. Despite the small amount of P present in gypsum (1 %), it was able to raise the P levels by about 1 mg dm⁻³. Other authors, such as Caires et al. (2003), also observed an increase in P uptake through the application of gypsum.

An increase in the Si contents was also observed when gypsum was applied (Table 3). With the application of gypsum, sulfate concentrations in the soil were increased, which may have displaced silicate from the adsorption sites, increasing the availability of that nutrient.

Gypsum promoted an increase in the SO₄⁻² levels in all the layers, but it was observed that the greatest concentration of SO₄⁻² was in the deeper layers, 0.20-0.40 and 0.40-0.60 m, indicating percolation of this nutrient in the soil profile (Table 3). Low retention of S-SO₄⁻² in the surface layers of the soil may be attributed to the higher pH values observed in these layers. The increase in pH promotes the predominance

of negative charges, which favor the movement of S-SO₄⁻² (Soratto & Crusciol, 2008b).

Organic matter (OM) was not affected by application of silicate and gypsum in any of the layers evaluated (Table 3). According to Rosolem et al. (2003), amendment of acidity can accelerate mineralization of OM through increasing the pH, and this may reduce the OM content in the soil. In this study, however, there was no change in the OM content in the soil profile through surface application of silicate and gypsum, indicating that the change in OM content may take longer. However, these data corroborate with data from Zambrosi et al. (2007) for an area under no-tillage with surface application of lime and gypsum.

For sugar concentration, purity, fiber, and reducing sugars (Table 4), there were no effects from the application of silicate and gypsum. In sugarcane, Prado et al. (2001) applied different rates of Ca silicate to raise base saturation to 50, 75 and 100 %, and they also did not observe changes in these attributes. These authors report that the lack of response from

Table 4. Values of sugar concentration, purity, fiber, reducing sugar, and stalk and sugar yield taken 12 months (at harvest time) after Ca-Mg silicate and gypsum surface application on green sugarcane, and ANOVA significance

Silicate	Gypsum, kg ha ⁻¹					
	0	1,700	0	1,700	0	1,700
	Sugar concentration		Purity		Fiber	
kg ha ⁻¹	%					
0	18.0	17.8	91.5	92.0	12.5	12.5
850	18.5	17.9	91.8	91.7	12.5	12.0
1,700	18.0	17.8	92.8	91.0	13.0	12.0
3,400	17.8	17.8	92.6	91.4	12.8	11.8
Mean	18.1 a	17.8 a	92.2 a	91.5 a	12.7 a	12.1 a
Effect ⁽¹⁾	-		-		-	
	ANOVA (F probability)					
Silicate (S)	0.5252		0.4957		0.4183	
Gypsum (G)	0.5861		0.5005		0.5077	
S*G	0.5899		0.5206		0.5361	
	Reducing sugar		Stalk yield		Sugar yield	
	%		t ha ⁻¹			
0	0.41	0.40	63.0 b	72.1 a	11.2 b	13.0 a
850	0.40	0.42	73.8 a	76.6 a	13.2 b	14.2 a
1,700	0.40	0.42	81.7 a	83.0 a	14.5 a	14.9 a
3,400	0.41	0.44	85.6 a	86.4 a	15.2 a	15.4 a
Mean	0.40 a	0.42 a				
Effect	-		L*	Q**	Q**	Q**
	ANOVA (<i>F</i> probability)					
Silicate (S)	0.6898		<0.0001		<0.0001	
Gypsum (G)	0.5915		0.0114		0.0150	
S*G	0.7502		0.0388		0.0350	

⁽¹⁾ L and Q represent linear and quadratic effect by polynomial regression, and – represents no effect. Values in the rows, within each variable, followed by the same letter are not significantly different at p≤0.05 according to the LSD test. * and **: significant at the 0.05 and 0.01 level, respectively.

sugarcane to the application of lime in the soil for such technological characteristics possibly occurs because of the dilution effect through the growth of the sugarcane plant. For gypsum application in ratoon cane without burning, Carvalho et al. (2013) also noted the lack of response from sugarcane for such technological features.

In contrast, for stalk and sugar yield, there was a linear and quadratic increase, respectively, from application of silicate (Table 4). Likewise, when gypsum associated with silicate was applied, a quadratic increase was observed for both stalk yield and sugar yield. According to Datnoff et al. (2001), increases in sugarcane production ranged from 11 to 16 % in plant cane and from 11 to 20 % in ratoon cane with the application of differing rates of Ca and Mg silicate ranging from 0.7 to 5.2 t ha⁻¹. In both cases, the highest yield was obtained at the highest rate of silicate. These findings may be related to amendment of soil acidity (Table 1) and nutrient availability in the soil profile (Tables 2 and 3) caused by the application of higher rates of silicate. These results indicate the use of higher rates of silicate so as to amend soil acidity at greater depths, increase nutrient availability, and increase stalk and sugar yields. Corroborating these results, Raij (2008) analyzed several results of experiments with limestone and gypsum in sugarcane and concluded that official recommendations for lime and gypsum application given by Spironello et al. (1996), considered as the “official recommendations for the State of São Paulo”, are too low.

The application of gypsum resulted in an increase in stalk yield when applied in isolation (Table 4). Furthermore, in the application rate for soil amendment recommended by Spironello et al. (1996), it was observed that gypsum promoted an increase in sugar yield, and its use associated with silicate was indicated under these conditions. At high rates of silicate, no effect of gypsum was observed on stalk and sugar yield. These results may be associated with amendment of acidic soil (Table 1) and nutrient availability in the soil profile (Tables 2 and 3) caused by application of high rates of silicate, thereby reducing the effects of gypsum in the first year of growth after application on sugarcane.

CONCLUSIONS

1. Gypsum application reduced the values of exchangeable Al³⁺ and Al saturation below the soil depth of 0.05 m, and increased Ca²⁺ throughout the profile, Mg²⁺ below 0.10 m, K⁺ below 0.40 m, and base saturation below 0.20 m. This contributes to the effect of the surface application of silicate in amendment of soil acidity reaching deeper layers.

2. Isolated application of gypsum is not recommended, because it promotes leaching of Mg and K⁺ from surface soil layers. The application of gypsum increased the contents of S-SO₄²⁻, Si, and P throughout the soil profile evaluated. For S-SO₄²⁻, the greatest accumulation was observed below 0.20 m.

3. The recommended silicate application rate may be being too low since the greater rates used in this experiment showed greater reduction in soil acidity, higher levels of nutrients at greater depths, and an increase in stalk and sugar yield.

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