

## SOYBEAN YIELD AND QUALITY AS A FUNCTION OF LIME AND GYPSUM APPLICATIONS

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**ABSTRACT:** Effects of lime and gypsum applications on the quality of soybeans grown under no-till (NT) are not well defined yet. A field trial established in 1998 on a dystrophic clayey Rhodic Hapludox, at Ponta Grossa, State of Paraná, Brazil, evaluated grain yield and soybean quality based on oil, protein and nutrient content, after lime and gypsum applications under NT, in a randomized complete block design (n = 3), split-plot experiment. In the main plots, the treatments with dolomitic lime were: control (no lime), split application of lime on the surface (three yearly applications of 1.5 Mg ha<sup>-1</sup>), surface lime (4.5 Mg ha<sup>-1</sup>), and incorporated lime (4.5 Mg ha<sup>-1</sup>). Subplots received four different rates of gypsum: 0, 3, 6, and 9 Mg ha<sup>-1</sup>. The soybean crop was evaluated in the agricultural years of 2002–2003 and 2003–2004. After 58 months, the correction of acidity through surface liming, with full or split rates, was more pronounced in the top layer (0–0.05 m) and there was greater reaction at the depths of 0.05–0.10 and 0.10–0.20 m when lime was incorporated. Surface or incorporated liming had no effect on grain yield, soybean oil and protein content. Gypsum improved chemical subsoil conditions, raising pH (0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>) as well as Ca<sup>2+</sup> and S-SO<sub>4</sub><sup>2-</sup> contents; it also caused exchangeable Mg<sup>2+</sup> leaching in the soil profile. The application of gypsum did not affect grain yield, yet it improved soybean quality through an increase in protein and S contents, in 2003–2004, and in grain P, K and Ca, in the two cropping years. The use of gypsum in NT soybeans can be especially important for fields of seeds production.

**Key words:** *Glycine max* (L.) Merrill, soil acidity, oil, protein, nutrient

## PRODUÇÃO E QUALIDADE DA SOJA EM FUNÇÃO DA CALAGEM E APLICAÇÃO DE GESSO

**RESUMO:** Os efeitos da aplicação de calcário e gesso na qualidade da soja cultivada em plantio direto não são muito conhecidos. O experimento foi instalado em 1998 em um Latossolo Vermelho distrófico textura argilosa, em Ponta Grossa (PR), com o objetivo de avaliar a produção de soja e a concentração de óleo, proteína e nutrientes nos grãos, após a aplicação de calcário e gesso em plantio direto. O delineamento experimental utilizado foi o de blocos completos ao acaso em parcelas subdivididas, com três repetições. Nas parcelas, os tratamentos com calcário dolomítico foram: testemunha (sem calcário), calcário parcelado na superfície (três aplicações anuais de 1,5 Mg ha<sup>-1</sup>), calcário na superfície (4,5 Mg ha<sup>-1</sup>) e calcário incorporado (4,5 Mg ha<sup>-1</sup>). As subparcelas receberam quatro doses de gesso: 0, 3, 6 e 9 Mg ha<sup>-1</sup>. A cultura da soja foi avaliada nos anos agrícolas de 2002–2003 e 2003–2004. Após 58 meses, a correção da acidez pela calagem na superfície, com ou sem parcelamento, foi mais acentuada na camada superficial do solo (0–0,05 m) e houve maior reação nas profundidades de 0,05–0,10 e 0,10–0,20 m quando o calcário foi incorporado. A calagem superficial ou incorporada não influenciou a produção de grãos e as concentrações de óleo e proteína de soja. O gesso melhorou as condições químicas do subsolo, aumentando o pH (CaCl<sub>2</sub> 0,01 mol L<sup>-1</sup>) e os teores de Ca<sup>2+</sup> e S-SO<sub>4</sub><sup>2-</sup>, e causou lixiviação de Mg<sup>2+</sup> trocável no solo. A aplicação de gesso não alterou a produção de grãos, mas melhorou a qualidade da soja, ocasionando aumento nas concentrações de proteína e de S, em 2003–2004, e de P, K e Ca nos grãos, nos dois anos de cultivo. O uso de gesso em cultivo de soja no plantio direto pode ser de grande importância para campos de produção de sementes. **Palavras-chave:** *Glycine max* (L.) Merrill, acidez do solo, óleo, proteína, nutrientes

### INTRODUCTION

Brazil has extensive pasturelands that could be

used for grain production. Crop establishment under no-till (NT) in these areas would be advantageous considering the conservation of the soil chemical and

structural properties, effective erosion control, and the economics of lime incorporation and soil tillage operations (Muzilli, 1983).

The importance of liming for soybeans is due to its effect on the increase of pH and decrease in toxic concentrations of Al and Mn (Raij et al., 1977), the increase in N, P, K and S uptake (Quaggio et al., 1993) and the supply of Ca and Mg (Mascarenhas et al., 1976). However, NT affects some chemical characteristics related to soil acidity which may influence plant development (Caires et al., 1998; Salet et al., 1999; Caires & Fonseca, 2000). Recent studies have shown high yields for soybeans grown in acidic soils under NT (Pöttker & Ben, 1998; Caires et al., 1998; 1999; 2003a; 2003b).

Gypsum, a by-product of the phosphoric acid industry, is largely available in many parts of the world. In Brazil alone, some 4.5 million tons are produced each year (Vitti, 2000). Gypsum application to top soil results in improved root growth and increased water and nutrient uptake by plants (Sumner et al., 1986; Marsh & Grove, 1992; Carvalho & Raij, 1997) as a result of the increase in subsoil Ca content and the formation of less toxic Al species (Oates & Caldwell, 1985; Shainberg et al., 1989).

Soybeans are produced to respond to human and livestock demand for oil and protein. Changes in oil, protein and mineral composition of the grain of soybeans resulting from fertilizer management or application of lime have been reported in the literature (Tanaka et al., 1991; 1995; Spehar, 1994; Mascarenhas et al., 1996). Even so, there is little information regarding the consequences of liming and gypsum application on the quality of soybeans grown under NT.

We evaluated grain yield and soybean quality, based on oil, protein and nutrient content, after application of lime on soil surface, at full or split rates, or incorporated at 0.2 m depth, and surface application of gypsum rates under NT.

## MATERIAL AND METHODS

The experiment was carried out in Ponta Grossa, PR, Brazil (25°10'S, 50°05'W), on an Oxisol (clayey, kaolinitic, Rhodic Hapludox), previously used as pastureland. The trial area was constituted mainly by the grass species *Paspalum notatum* cv. Pensacola. The selected site did not have a history of liming and fertilizer application. At the beginning of the experiment, soil chemical (Pavan et al., 1992) and granulometric (EMBRAPA, 1997) analyses of the 0–0.20 m depth showed the following results: pH 4.6 (1:2.5 soil: 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> suspension); exchangeable Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> contents of 3, 25, 20, and

3.6 mmol<sub>c</sub> dm<sup>-3</sup>, respectively; total acidity (H<sup>+</sup> + Al<sup>3+</sup>) of 78.0 mmol<sub>c</sub> dm<sup>-3</sup>; P (Mehlich-1) of 0.3 mg dm<sup>-3</sup>; total organic matter of 53 g dm<sup>-3</sup>; and 580, 130, and 290 g kg<sup>-1</sup> of clay, silt, and sand, respectively. The subsoil (0.40–0.60 m) had 6 mmol<sub>c</sub> dm<sup>-3</sup> of Ca<sup>2+</sup>, 8 mmol<sub>c</sub> dm<sup>-3</sup> of Al<sup>3+</sup>, 35% of Al<sup>3+</sup> saturation, and 620 g kg<sup>-1</sup> of clay.

A randomized complete block design was used, with three replications in a split-plot arrangement. In the main plots, four treatments with dolomitic lime were applied: control (no lime), split application of lime on the surface (three yearly applications of 1.5 Mg ha<sup>-1</sup>), surface lime (4.5 Mg ha<sup>-1</sup>) and incorporated lime (4.5 Mg ha<sup>-1</sup>). The lime rate was calculated to raise the base saturation in the topsoil (0–0.20 m) to 70%. The dolomitic lime used contained 224 g kg<sup>-1</sup> Ca, 140 g kg<sup>-1</sup> Mg, and 89% effective calcium carbonate equivalent. In the subplots, four different rates of gypsum were surface-applied: 0, 3, 6, and 9 Mg ha<sup>-1</sup>. The gypsum, a by-product obtained from a Brazilian phosphate fertilizer industry, contained 235 g kg<sup>-1</sup> Ca, 153 g kg<sup>-1</sup> S, 3 g kg<sup>-1</sup> P, and 156 g kg<sup>-1</sup> water. Lime and gypsum were applied by hand to the soil surface in July and October 1998, respectively. In the incorporated lime plots, one-half of the lime was surface broadcasted by hand and the soil plowed down to a depth of 0.20 m with a disk plow; the remainder was added by hand to the surface, then the soil was harrowed to a depth of 0.10 m with a disk harrow. Plowing and harrowing only occurred at the beginning of the experiment in the plots with lime incorporation. In the plots with annual splitting of surface-applied lime, the second application was made in May 1999, and the third, in May 2000. The areas of each plot and subplot were 224 m<sup>2</sup> (32 × 7 m) and 56 m<sup>2</sup> (8 × 7 m), respectively. The sequence of crops was soybean (1998–1999), barley (1999), soybean (1999–2000), wheat (2000), soybean (2000–2001), corn (2001–2002), and soybean (2002–2003 and 2003–2004). No-till involved no disturbance to the soil other than the sowing operation. Residues were left on the soil surface following grain harvest. The present study addresses only the last two soybean crops, since the grain quality of these crops, based on the oil, protein and nutrient concentrations, was studied more thoroughly.

Soybean was sown on November 25th, 2002 (cv. COODETEC 206), and November 15th, 2003 (cv. BRS 133), at a seeding rate of 18 seeds m<sup>-1</sup> (inoculated with *Bradyrhizobium japonicum*), and row spacing of 0.45 m. Fertilizers were applied at rates of 200 kg ha<sup>-1</sup> of 0-20-20 (N – P<sub>2</sub>O<sub>5</sub> – K<sub>2</sub>O) at each sowing. There was no water limitation throughout the growth period of the soybean crop, for both years. Rainfall was 727 and 814 mm during the crop cycle in 2002–2003 and 2003–2004, respectively.

Leaf samples, composed of 30 leaves per subplot, were taken each year at flowering by collecting the third leaf from the top. The samples were washed, dried at 60°C, and ground prior to total nitrogen content analysis according to the method described by Malavolta et al. (1997).

Each year, after maturation, soybean grain was harvested from 10.8 m<sup>2</sup> (middle six rows of 4 m length). Grain yields were expressed at 130 g kg<sup>-1</sup> moisture. Grain samples were ground to determine protein and oil content. In order to estimate the content of crude protein, total nitrogen content was determined by the Kjeldahl method, the resulting value being multiplied by the conventional factor 6.25 (Lusas & Rhee, 1995). The oil content was determined gravimetrically after hot extraction of the samples with hexane, in a Soxhlet extractor, according to the method of the Association of Official Agricultural Chemists (AOAC, 1955). For the analysis of grain nutrient levels, 1.5 g of the material was weighed in a porcelain capsule and, after that, the samples were incinerated on a hot plate until carbonization. Later, the samples were transferred to a muffle furnace at 450°C for eight hours. The ashes were dissolved in concentrated nitric acid and transferred quantitatively into a 50 mL volumetric flasks. The determination of P, K, Ca, Mg, Cu, Zn, Mn and Fe was performed by inductively coupled plasma optical emission spectrometry (ICP-OES). The content of S in the grain was determined through nitric-perchloric digestion and barium sulfate turbidimetry (Malavolta et al., 1997).

Soil samples were taken after harvest, in 2002–2003, corresponding to 58 months after liming and 55 months after gypsum application. Total rainfall in the period between lime and gypsum application and soil sampling was 8200 and 7570 mm, respectively. The soil samples were collected manually with a tubular probe sampler (core diameter of 2.5 cm and open-faced corer). Twelve soil core samples per subplot were taken to constitute a composite sample of the 0–0.05, 0.05–0.10, and 0.10–0.20 m layers, and five cores of the 0.20–0.40, 0.40–0.60, and 0.60–0.80 m layers. Soil pH was determined in a 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> suspension (1:2.5 soil/solution, v/v). Total acidity (H<sup>+</sup> + Al<sup>3+</sup>) by a SMP buffer procedure described by Pavan et al. (1992). Exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup> were extracted with neutral 1 mol L<sup>-1</sup> KCl, and K<sup>+</sup> with double acid (Mehlich-1), in a 1:10 (v/v) soil/solution ratio, according to standard methods used by the Agronomic Institute of the State of Paraná (Pavan et al., 1992). Exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup> were determined by titrating with 0.025 mol L<sup>-1</sup> EDTA, and K<sup>+</sup> by flame photometry. Analyses of S–SO<sub>4</sub><sup>2-</sup> for the different soil depths were also performed through extraction by am-

monium acetate 0.5 mol L<sup>-1</sup> in acetic acid 0.25 mol L<sup>-1</sup> and later determination by the turbidimetric method described by Vitti & Suzuki (1978).

Results were submitted to variance and regression analyses. In the absence of a significant interaction lime vs gypsum on the variables studied, the effects of liming were compared by the Tukey test at 5% probability, and the effects of gypsum, through regression analyses by orthogonal polynomials, through means observations. The criterion for choosing the model was the magnitude of the significant coefficients of determination at 5% probability.

## RESULTS AND DISCUSSION

After 58 months, liming lead to a significant increase in pH, exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup> contents and soil base saturation in the 0–0.05 m soil layer, especially when lime was surface-applied, at full or split rates (Table 1). In the 0.05–0.10 and 0.10–0.20 m layers, greater lime reaction was achieved with incorporation, even though surface liming, at full or split rates, also produced, however to a lesser degree, beneficial effects on acidity correction at 0.05–0.10 m depth. Surface-applied, as well as incorporated lime, also promoted a significant increase in pH and in base saturation of the 0.20–0.40 m layer, but such effects were not accompanied by significant alterations in exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup> content at that depth – likely because of the broader variability of those attributes, as revealed by higher coefficients of variation. Surface-applied lime, at full or split rates, or incorporated, did not influence the acidity-related chemical attributes of the soil at the 0.40–0.60 and 0.60–0.80 m depths.

There are studies in the literature showing that lime does not move to deeper layers of the soil (Ritchey et al., 1980; Pavan et al., 1984), while, in other studies, considerable increases in pH were observed below the region where lime was applied in annual cropping areas under conventional tillage (Quaggio et al., 1993; Oliveira et al., 1997) or managed under NT (Oliveira & Pavan, 1996; Caires et al., 2000). The action of lime in neutralizing subsoil acidity is impaired by the low lime solubility and by the increase in cation retention which occurs as a result of the generation of variable negative charges as soil pH rises. In addition, the anions resulting from the dissolution of lime, which are responsible for the correction of acidity, are also consumed in the reactions with other acidic cations (Al<sup>3+</sup>, Mn<sup>2+</sup>, and Fe<sup>2+</sup>) in the lime deposition layer. However, the rise in pH on soil surface may increase the rate at which HCO<sub>3</sub><sup>-</sup>, along with Ca<sup>2+</sup> and Mg<sup>2+</sup>, moves toward the subsoil to neutralize acidity (Costa, 2000). Nevertheless, the results clearly

Table 1 - Changes in soil pH (0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>), exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>, and base saturation for different depths 58 months after various liming treatments.

Depth	Treatment	pH CaCl <sub>2</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Base saturation
m			----- mmol <sub>c</sub> dm <sup>-3</sup> -----			%
0-0.05	No lime	4.8	44.0	21.0	5.8	50
	Surface-applied lime <sup>a</sup>	5.9	69.3	40.7	5.7	77
	Surface-applied lime <sup>b</sup>	5.9	68.4	37.8	5.1	76
	Incorporated lime	5.5	57.7	32.7	6.0	69
	LSD <sub>0.05</sub> <sup>c</sup>	0.3	12.5	8.9	2.0	6
	CV (%)	4.0	14.7	19.0	25.5	5.8
0.05-0.10						
0.05-0.10	No lime	4.6	27.4	12.7	3.8	35
	Surface-applied lime <sup>a</sup>	5.1	38.0	23.6	3.3	52
	Surface-applied lime <sup>b</sup>	5.2	37.3	23.3	3.1	53
	Incorporated lime	5.4	48.6	26.4	3.9	63
	LSD <sub>0.05</sub> <sup>c</sup>	0.2	7.2	8.1	1.6	9
	CV (%)	3.8	13.4	26.6	32.8	12.5
0.10-0.20						
0.10-0.20	No lime	4.6	16.0	11.9	2.0	28
	Surface-applied lime <sup>a</sup>	4.7	19.1	14.7	1.8	33
	Surface-applied lime <sup>b</sup>	4.7	18.9	14.2	1.8	33
	Incorporated lime	5.2	30.1	18.9	2.2	49
	LSD <sub>0.05</sub> <sup>c</sup>	0.4	7.9	8.8	1.5	14
	CV (%)	5.4	26.8	41.5	31.7	27.6
0.20-0.40						
0.20-0.40	No lime	4.5	14.4	10.4	1.8	25
	Surface-applied lime <sup>a</sup>	4.7	19.1	13.8	1.8	34
	Surface-applied lime <sup>b</sup>	4.8	18.6	12.1	1.3	33
	Incorporated lime	4.9	19.4	16.1	1.9	38
	LSD <sub>0.05</sub> <sup>c</sup>	0.2	5.7	6.5	1.2	6
	CV (%)	3.1	22.4	34.9	36.9	13.6
0.40-0.60						
0.40-0.60	No lime	4.7	11.9	10.1	1.1	26
	Surface-applied lime <sup>a</sup>	4.8	14.4	14.0	1.2	34
	Surface-applied lime <sup>b</sup>	4.9	13.7	10.9	0.8	30
	Incorporated lime	4.8	13.5	12.0	1.3	32
	LSD <sub>0.05</sub> <sup>c</sup>	0.2	3.5	6.5	1.1	8
	CV (%)	3.1	18.5	39.2	35.5	17.7
0.60-0.80						
0.60-0.80	No lime	4.8	10.0	10.7	0.8	28
	Surface-applied lime <sup>a</sup>	4.9	11.0	11.6	0.8	31
	Surface-applied lime <sup>b</sup>	4.9	11.5	11.2	0.8	31
	Incorporated lime	4.9	11.0	12.2	1.0	32
	LSD <sub>0.05</sub> <sup>c</sup>	0.3	1.7	5.1	1.0	7
	CV (%)	4.1	10.5	31.5	35.8	16.5

<sup>a</sup>1/3 of the lime rate applied on the surface per year for 3 years. <sup>b</sup>Full-rate lime on the surface in a single application. <sup>c</sup>Least-significant difference by Tukey test at  $P = 0.05$ .

indicate that surface liming, at full or split rates, provided greater efficiency in the correction of topsoil acidity (0–0.05 m), while incorporated lime produced greater reaction at 0.05–0.10 and 0.10–0.20 m depths, as compared to surface liming.

After 55 months, the application of gypsum did not influence soil acidity at 0–0.05, 0.05–0.10, 0.10–0.20, and 0.20–0.40 m depths (Table 2). It only produced a significant increase in pH and base saturation in subsoil layers (0.40–0.60 and 0.60–0.80 m). An increase in subsoil pH through gypsum application has been found in other studies (Alva et al., 1990; Carvalho & Raij, 1997; Caires et al., 1999; 2003a), and it was

due to a reaction of ligand substitution on the surface of soil particles, involving iron and aluminum hydrated oxides,  $\text{SO}_4^{2-}$  displacing  $\text{OH}^-$ , thus promoting a partial neutralization of acidity (Reeve & Sumner, 1972). There was a linear increase in exchangeable  $\text{Ca}^{2+}$  content as a function of the gypsum rates, at all depths. In addition to  $\text{Ca}^{2+}$ , gypsum also promoted  $\text{Mg}^{2+}$  downward movement the soil. Exchangeable  $\text{Mg}^{2+}$  leaching occurred down to 0.40 m, and an increase in the content of this nutrient in the 0.60–0.80 m layer. Exchangeable  $\text{Mg}^{2+}$  leaching has been a frequent response in studies involving gypsum application on soils (Syed-Omar & Sumner, 1991; Oliveira & Pavan, 1996; Caires

Table 2 - Regression equations and coefficients of determination between some soil chemical characteristics ( $\hat{y}$ ), for different depths, and gypsum rate (x), 55 months after application.

$\hat{y}$	Unit	Depth m	Equation	R <sup>2</sup>
pH	-	0-0.05	$\hat{y} = \bar{y} = 5.5$	-
		0.05-0.10	$\hat{y} = \bar{y} = 5.1$	-
		0.10-0.20	$\hat{y} = \bar{y} = 4.8$	-
		0.20-0.40	$\hat{y} = \bar{y} = 4.8$	-
		0.40-0.60	$\hat{y} = 4.72 + 0.02x$	0.99**
$\text{Ca}^{2+}$	$\text{mmol}_c \text{ dm}^{-3}$	0.60-0.80	$\hat{y} = 4.75 + 0.03x$	0.99**
		0-0.05	$\hat{y} = 52.62 + 1.61x$	0.98**
		0.05-0.10	$\hat{y} = 32.76 + 1.13x$	0.94**
		0.10-0.20	$\hat{y} = 18.16 + 0.64x$	0.88**
		0.20-0.40	$\hat{y} = 15.00 + 0.64x$	0.97**
$\text{Mg}^{2+}$	$\text{mmol}_c \text{ dm}^{-3}$	0.40-0.60	$\hat{y} = 9.35 + 0.89x$	0.99**
		0.60-0.80	$\hat{y} = 7.12 + 0.89x$	0.87**
		0-0.05	$\hat{y} = 37.53 - 0.99x$	0.82**
		0.05-0.10	$\hat{y} = 26.22 - 1.05x$	0.99**
		0.10-0.20	$\hat{y} = 17.02 - 0.47x$	0.89**
$\text{K}^+$	$\text{mmol}_c \text{ dm}^{-3}$	0.20-0.40	$\hat{y} = 14.83 - 0.39x$	0.53*
		0.40-0.60	$\hat{y} = \bar{y} = 11.8$	-
		0.60-0.80	$\hat{y} = 10.30 + 0.25x$	0.65*
		0-0.05	$\hat{y} = \bar{y} = 5.7$	-
		0.05-0.10	$\hat{y} = \bar{y} = 3.6$	-
Base saturation	%	0.10-0.20	$\hat{y} = \bar{y} = 2.1$	-
		0.20-0.40	$\hat{y} = \bar{y} = 1.8$	-
		0.40-0.60	$\hat{y} = \bar{y} = 1.1$	-
		0.60-0.80	$\hat{y} = \bar{y} = 0.9$	-
		0-0.05	$\hat{y} = \bar{y} = 68$	-
Base saturation	%	0.05-0.10	$\hat{y} = \bar{y} = 51$	-
		0.10-0.20	$\hat{y} = \bar{y} = 36$	-
		0.20-0.40	$\hat{y} = \bar{y} = 33$	-
		0.40-0.60	$\hat{y} = 26.90 + 0.80x$	0.98**
		0.60-0.80	$\hat{y} = 25.16 + 1.19x$	0.99**

\*significant at  $P < 0.05$ , \*\*significant at  $P < 0.01$ .



et al., 1999; 2003a). Thus, when gypsum is applied at high rates, strategies must be developed in order to minimize the loss of exchangeable  $Mg^{2+}$ . For that reason, the use of gypsum alone has not been recommended, rather a combination with dolomitic lime. Soil exchangeable  $K^+$  content were not influenced by gypsum application. Although  $K^+$  leaching from the use of gypsum may occur according to the soil type (Sousa & Ritchey, 1986; Sumner, 1995),  $K^+$  loss by leaching with the application of gypsum to soils with high buffer capacity under NT have been very small (Caires et al., 1998; 2001).

The lime treatments, after 58 months, did not cause significant alterations in soil  $S-SO_4^{2-}$ , and, down to 0.80 m, mean concentrations of 9.2 (0–0.05 m), 9.1 (0.05–0.10 m), 11.1 (0.10–0.20 m), 15.9 (0.20–0.40 m), 7.8 (0.40–0.60 m) and 4.3 (0.60–0.80 m)  $mg\ dm^{-3}$  were found. The decline in sulfate content in deeper layers of the soil derives from the lack of previous S-containing fertilizer amendments. After 55 months, gypsum application increased soil  $S-SO_4^{2-}$  levels at all depths (Figure 1). There was sulfate movement in the soil, proportional to the rates of gypsum applied, after total rainfall of 7570 mm. Sulfate is more strongly retained in soils which are more acidic and have a lower negative charge (Raij & Peech, 1972). This fact, and the repulsion of the sulfate by phosphate, account for the lower content of  $S-SO_4^{2-}$  on the soil surface. In the deeper layers (0.40–0.60 and 0.60–0.80 m), sulfate build-up was more pronounced, indicating that the effect might have extended to even greater depths. These results are in line with the observations of Raij et al. (1998), and it is clear that the ion  $S-SO_4^{2-}$  is strongly adsorbed in the subsoil, where it remains for many

years – information of paramount importance regarding the diagnosis of sulfur availability in soils. It must be taken into consideration, however, that the rate at which sulfate moves is variable in different soils (Quaggio et al., 1993; Caires et al., 1998), and is expected to be lower in soils with higher clay content.

The lime and gypsum treatments did not cause significant alterations in soybean grain yield (Table 3). Leaf N concentration was only increased with the incorporation of lime, and only in the agricultural year 2002–2003. There was effective biological fixation of  $N_2$  and high grain yield, despite the presence of soil acidity (Table 1). The importance of acidity correction for improving the symbiotic fixation of  $N_2$  and the yield of soybeans grown under a conventional tillage system was demonstrated by Mascarenhas et al. (1996). In acidic soils under NT in southern Brazil, adequate N uptake by soybeans and high crop yields have been recorded, even without acidity correction (Pöttker & Ben, 1998; Caires et al., 1998; 1999; 2003a; 2003b; Caires & Fonseca, 2000). This behavior of soybeans grown under NT may be associated with a lower concentration of toxic species ( $Al^{3+}$  and  $AlOH^{2+}$ ) and a higher concentration of Al complexed with organic ligands (Salet et al., 1999), along with greater availability of soil exchangeable  $Ca^{2+}$  and  $Mg^{2+}$  (Caires et al., 1998). It is worth noting that greater soybean responses to liming, regardless of the management system, have been observed in soils with lower levels of exchangeable  $Mg^{2+}$  (Mascarenhas et al., 1996; Oliveira & Pavan, 1996).

Absence of soybean response to the application of gypsum (Table 3) has also been reported in other studies (Quaggio et al., 1993; Oliveira & Pavan, 1996; Caires et al., 1998; 1999; 2003a) and may be related to the fact that soybean root growth, under no water deficit conditions, is not influenced by the decrease in Al saturation in the subsoil (Caires et al., 2001). Hydroponic study of soybean seedling root response to various levels of Al and Ca as gypsum in solution has shown the importance of an appropriate calcium-aluminum balance for adequate initial soybean root growth in the presence of solution aluminum (Noble et al., 1988). However, the toxicity of Al for the plants grown under NT seems to be quite dependent on the water regime occurring during the growth cycle of the plants.

Soybean oil and protein levels were not affected by the lime treatments in the two years of cropping (Table 4). The content of soybean oil was reduced with incorporated lime under a conventional tillage system (Tanaka et al., 1991; Mascarenhas et al., 1996), but such effect was not observed in the present study. Smaller amounts of soybean oil were found under conditions of extreme acidity or soil acidity correction in

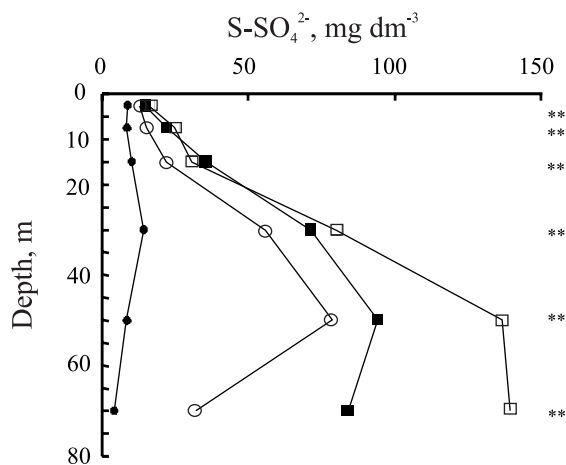


Figure 1 - Soil  $SO_4^{2-}$  levels, extracted by ammonium acetate  $0.5\ mol\ L^{-1}$  in acetic acid  $0.25\ mol\ L^{-1}$ , 55 months after surface gypsum application at the rates of (●) 0, (○) 3, (■) 6, and (□)  $9\ Mg\ ha^{-1}$ . \*\*significant at  $P < 0.01$  by linear regression.

Table 3 - Soybean grain yield and leaf-N concentration after various liming and gypsum treatments.

Treatment	Grain yield		Leaf-N	
	2002-2003	2003-2004	2002-2003	2003-2004
	----- kg ha <sup>-1</sup> -----		----- g kg <sup>-1</sup> -----	
<b>Liming</b>				
No lime	3,441	3,663	52.2	53.8
Surface-applied lime <sup>a</sup>	3,478	3,735	52.8	54.9
Surface-applied lime <sup>b</sup>	3,474	3,922	52.6	55.7
Incorporated lime	3,478	3,713	53.8	54.0
LSD <sub>0.05</sub> <sup>c</sup>	313	514	1.5	4.2
CV (%)	6.4	9.7	2.0	5.4
<b>Gypsum, Mg ha<sup>-1</sup></b>				
0	3,384	3,738	52.6	54.5
3	3,448	3,722	52.8	56.2
6	3,491	3,726	53.3	54.0
9	3,547	3,846	52.7	53.8
Effect <sup>d</sup>	ns	ns	ns	ns
CV (%)	8.1	6.1	4.9	4.1

<sup>a</sup>1/3 of the lime rate applied on the surface per year for 3 years. <sup>b</sup>Full-rate lime on the surface in a single application. <sup>c</sup>Least-significant difference by Tukey test at  $P = 0.05$ . <sup>d</sup>ns: non-significant by polynomial regression.

Table 4 - Soybean oil and protein concentration after various liming and gypsum treatments.

Treatment	Oil		Protein	
	2002-2003	2003-2004	2002-2003	2003-2004
	----- g kg <sup>-1</sup> -----		----- g kg <sup>-1</sup> -----	
<b>Liming</b>				
No lime	176.9	166.3	367.2	333.3
Surface-applied lime <sup>a</sup>	187.1	151.7	370.1	342.7
Surface-applied lime <sup>b</sup>	179.7	166.9	370.8	346.1
Incorporated lime	182.8	164.4	369.5	335.3
LSD <sub>0.05</sub> <sup>c</sup>	10.9	29.3	17.9	29.4
CV (%)	4.2	12.8	3.4	6.1
<b>Gypsum, Mg ha<sup>-1</sup></b>				
0	181.4	164.4	368.0	324.6
3	186.0	163.1	369.8	340.1
6	177.4	158.9	370.8	346.5
9	181.7	162.9	369.0	346.1
Effect <sup>d</sup>	ns	ns	ns	L*
CV (%)	5.2	10.6	2.6	7.7

<sup>a</sup>1/3 of the lime rate applied on the surface per year for 3 years. <sup>b</sup>Full-rate lime on the surface in a single application. <sup>c</sup>Least-significant difference by Tukey test at  $P = 0.05$ . <sup>d</sup>L: Linear effect by polynomial regression, ns: non-significant, and \*significant at  $P < 0.05$ .

NT (Caires et al., 2003b), which did not occur in the present study (Table 1).

Liming usually increases the concentration of protein in soybeans (Tanaka et al., 1991; 1995; Mascarenhas et al., 1996) by improving the conditions for biological N<sub>2</sub> fixation as a result of a decline in soil acidity and an increase in Mo availability (Quaggio et

al., 1998). However, for soybeans grown under NT, acidity correction through the application of lime (Table 1) did not alter the effectiveness of biological fixation of N<sub>2</sub> evaluated through the concentration of N in the leaves (Table 3) and, consequently, soybean protein content (Table 4), in accordance to the results obtained by Caires et al. (2003b).

The application of gypsum did not influence the soybean oil content in the two years of cropping (Table 4). Gypsum increased soybean protein content in 2003–2004 (cv. BRS 133), but such effect was not observed in 2002–2003 (cv. CODETEC 206), probably due to genetic differences of cultivars (Table 4). Even though the negative correlation is known between oil content and protein content in soybeans (Brim, 1973), the increase in protein content through the application of gypsum was not sufficient to bring about a significant decline in soybean oil content. The protein/oil ratio in the two years of soybean crops was of the order 2.0 (Table 4), very close to the ratio obtained in other studies (Tanaka et al., 1995; Mascarenhas et al., 1996; Caires et al., 2003b).

Nutrient concentrations in the soybean grain were little influenced by the lime treatments (Table 5). Incorporated lime provided greater P content in the grain than the no-lime treatment, in 2002–2003. With the application of lime, there was a reduction in Zn levels in 2002–2003, and Mn in the two years of cropping, regardless of the application method. An increase in P and a decrease in Zn in the soybean grain with liming were also observed by Caires et al. (2003b). In a study conducted with lime rates (1 and 4 Mg ha<sup>-1</sup>) and 45 soybean varieties in a Brazilian savannah soil (Spehar, 1994), it was observed that the increase in lime rates did not affect Ca and Mg levels and resulted in lower concentrations of P, K, Cu, Fe, Zn, and Mn in the seeds. Considering the existing genetic variability for the accumulation of mineral elements in soy-

bean germplasms (Spehar, 1994), the results showed that the increase in P (Caires & Fonseca, 2000; Caires et al., 2001) and the decline in Zn (Mascarenhas et al., 1988; Caires & Fonseca, 2000) and Mn (Caires & Fonseca, 2000) absorbed by the soybean plants, with liming, could influence the levels of those nutrients in the grain.

The concentrations of P, K and Ca in the soybean grain in the two years of cropping, and S, in 2003–2004, increased linearly with the applied gypsum rates (Table 6). It is important to note that such effects were observed some five years after the application of gypsum. The content of Mg in the grain decreased linearly with the gypsum rates only in 2002–2003. This decrease in Mg in the soybean grain with the application of gypsum is likely due to leaching of exchangeable Mg<sup>2+</sup> caused by the gypsum (Table 2). A decline in Mg uptake by the soybeans as a consequence of leaching of soil exchangeable Mg<sup>2+</sup> due to the use of gypsum has been reported in a number of studies (Oliveira & Pavan, 1996; Caires et al., 1998; 1999; 2003a). Cationic micronutrient amounts (Cu, Fe, Zn, and Mn) in the soybean grain were not affected by gypsum application, in the two years of cropping. In another study, concentrations of Cu, Fe, Zn, and Mn in soybean seeds were also not affected by gypsum application at the rates of 16 and 67 kg S ha<sup>-1</sup> (Chen et al., 2005). Caires et al. (2003a) found that soybean leaf Mn content increased with the application of gypsum only when high sulfate concentrations were found in the superficial soil layers.

Table 5 - Soybean grain nutrient concentration after various liming treatments.

Treatment	P	K	Ca	Mg	S	Cu	Fe	Zn	Mn
	----- g kg <sup>-1</sup> -----					----- mg kg <sup>-1</sup> -----			
2002-2003									
No lime	4.6	13.9	1.7	2.0	3.0	12.0	93.2	37.2	16.5
Surface-applied lime <sup>a</sup>	4.9	13.8	1.8	2.1	3.0	12.3	105.4	34.2	15.2
Surface-applied lime <sup>b</sup>	4.9	14.0	1.7	2.1	3.0	12.3	96.8	34.3	15.1
Incorporated lime	5.0	13.7	1.8	2.1	3.0	12.4	91.3	34.9	14.7
LSD <sub>0.05</sub> <sup>c</sup>	0.3	1.0	0.1	0.1	0.4	0.7	36.8	1.1	0.9
CV (%)	5.0	5.2	3.3	4.3	9.6	4.2	26.9	2.2	4.0
2003-2004									
No lime	4.4	15.4	1.5	1.5	2.8	11.9	92.7	36.2	18.1
Surface-applied lime <sup>a</sup>	4.6	15.4	1.5	1.6	2.8	12.3	85.9	34.6	16.9
Surface-applied lime <sup>b</sup>	4.6	15.3	1.5	1.6	2.7	12.4	106.5	34.9	16.8
Incorporated lime	4.5	15.3	1.6	1.6	2.9	12.1	104.5	35.9	16.5
LSD <sub>0.05</sub> <sup>c</sup>	0.3	0.2	0.2	0.1	0.8	1.0	40.1	2.3	1.0
CV (%)	4.0	1.1	7.3	1.1	20.9	5.6	29.1	4.6	4.3

<sup>a</sup>1/3 of the lime rate applied on the surface per year for 3 years. <sup>b</sup>Full-rate lime on the surface in a single application. <sup>c</sup>Least-significant difference by Tukey test at  $P = 0.05$ .



Table 6 - Regression equations and coefficients of determination between soybean grain nutrient concentration ( $\hat{y}$ ) and gypsum rate (x).

$\hat{y}$	Unit	Year	Equation	R <sup>2</sup>
P	g kg <sup>-1</sup>	2002-2003	$\hat{Y} = 4.70 + 0.03x$	0.98**
		2003-2004	$\hat{Y} = 4.37 + 0.03x$	0.61**
K	g kg <sup>-1</sup>	2002-2003	$\hat{Y} = 13.67 + 0.04x$	0.84**
		2003-2004	$\hat{Y} = 15.19 + 0.04x$	0.69**
Ca	g kg <sup>-1</sup>	2002-2003	$\hat{Y} = 1.67 + 0.02x$	0.99**
		2003-2004	$\hat{Y} = 1.47 + 0.01x$	0.90**
Mg	g kg <sup>-1</sup>	2002-2003	$\hat{Y} = 2.12 - 0.01x$	0.88**
		2003-2004	$\hat{Y} = \bar{y} = 1.6$	-
S	g kg <sup>-1</sup>	2002-2003	$\hat{Y} = \bar{y} = 3.0$	-
		2003-2004	$\hat{Y} = 2.58 + 0.04x$	0.91*
Cu	mg kg <sup>-1</sup>	2002-2003	$\hat{Y} = \bar{y} = 12.3$	-
		2003-2004	$\hat{Y} = \bar{y} = 12.0$	-
Fe	mg kg <sup>-1</sup>	2002-2003	$\hat{Y} = \bar{y} = 96.7$	-
		2003-2004	$\hat{Y} = \bar{y} = 97.4$	-
Zn	mg kg <sup>-1</sup>	2002-2003	$\hat{Y} = \bar{y} = 35.1$	-
		2003-2004	$\hat{Y} = \bar{y} = 35.4$	-
Mn	mg kg <sup>-1</sup>	2002-2003	$\hat{Y} = \bar{y} = 15.4$	-
		2003-2004	$\hat{Y} = \bar{y} = 17.1$	-

\*significant at  $P < 0.05$ , \*\*significant at  $P < 0.01$ .

Phosphorus, present in gypsum as an impurity, can be important for plant nutrition when high gypsum rates are applied (Sumner et al., 1986). Increases in leaf P content in three soybean crops, accompanying the gains in the availability of the nutrient in the soil with the application of high gypsum rates, were obtained by Caires et al. (2003a). The higher P uptake by the soybeans with the use of gypsum had an effect on the content of P in the grain (Table 6). The increase in the concentration of Ca in the soybean grain (Table 6) resulted from the increase in soil exchangeable Ca<sup>2+</sup> levels provided by the application of gypsum (Table 2). The content of K in the soybean grain raised with the application of gypsum (Table 6), probably due to the release of K<sup>+</sup> from the exchange sites into soil solution, due to the increase in soil exchangeable Ca<sup>2+</sup> levels (Nogueira & Mozeto, 1990). Such effects of the application of gypsum can be particularly important for fields of seed production.

Soybean protein concentration was correlated with the content of S in the grain. According to data obtained by Hitsuda et al. (2004), S levels in the soybean grain were adequate ( $\geq 2.3$  g kg<sup>-1</sup>) in the two crops, even without gypsum application (Table 6). This shows that concentrations of the order of 10 mg dm<sup>-3</sup> S-SO<sub>4</sub><sup>2-</sup> in the soil (0-0.20 m), extracted by ammonium acetate 0.5 mol L<sup>-1</sup> in acetic acid 0.25 mol L<sup>-1</sup> (Figure 1), were sufficient for the supply of S to soybeans grown under NT.

## ACKNOWLEDGEMENTS

We are grateful to CNPq for the financial support and scholarships.

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Received November 01, 2005

Accepted May 19, 2006