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Soil fertility, plant nutrition, and grain yield of upland rice affected by surface application of lime, silicate, and phosphogypsum in a tropical no-till system

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ABSTRACT

The development of technologies that provide rapid acidity amelioration of the soil profile through the surface application of amendments and phosphogypsum, such as no-till (NT) systems, is extremely important to provide adequate chemical conditions in tropical soils with low natural fertility, which limits the grain yield of upland rice (*Oryza sativa* L.). Thus, this study aimed to evaluate the effects of surface applications of lime, silicate, and phosphogypsum, applied individually or in mixtures, on the chemical properties of the soil profile in an NT system and to determine their effects on the nutrition, yield components, and grain yield of upland rice. The experiment was designed as a completely randomized block with eight treatments replicated four times. The combination of phosphogypsum with lime and/or silicate improved the surface and subsurface soil chemical properties 12 months following application. The mixtures increased the concentrations of K, Ca, Mg, N–NO_3^-, and S–SO_4^{2-} in the subsurface layers. The sulphur concentration in the flag leaves of upland rice was higher with phosphogypsum application. The number of panicles per m^2 and grain yield of upland rice were positively influenced by the surface application of soil acidity amendments and phosphogypsum mixtures.

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1. Introduction

Rice (*Oryza sativa* L.) is an important component of the diets of approximately half of the world's population (Kumar and Ladha, 2011). This cereal is cultivated primarily in Asia under controlled flood irrigation (Farooq et al., 2009; Prasad, 2011); however, a reduction in hydric resource availability for crop irrigation, resulting from increased industrial and human consumption, has led to the search for alternative methods of rice cultivation with lower water demand (Feng et al., 2007; Qu et al., 2008). The use of soil conservation management systems for the cultivation of upland rice has been suggested as an excellent alternative to increase global rice production and to reduce water use in agriculture, especially for soils with low available water capacity (Bouman and Tuong, 2001; Nascente et al., 2013).

The benefits of no-till (NT) systems for improving soil water retention and crop yields have led to worldwide adoption (Gozubuyuk et al., 2014); NT systems are currently used over an area of approximately 157 million ha, distributed primarily in Latin America (66 million ha), the USA and Canada (36 million ha), and Australia (18 million ha) (FAO, 2015).

The continued success of NT systems has been achieved through soil fertility management (Soratto and Crusciol, 2008a). However, in several tropical regions, the benefits of these agricultural production systems are limited by soil acidity, which reduces the availability of macronutrients and results in problems associated with manganese and aluminium toxicity (Oliveira and Pavan, 1996; Caires et al., 2008b; Churka Blum et al., 2013). Limestone is a common material that is used to ameliorate soil acidity; however, due to the low solubility and mobility of carbonate in the soil profile, surface liming effects are usually limited to lime application/incorporation sites (Caires et al., 2005, 2006; Soratto and Crusciol, 2008b). Under these conditions, the development of the root system is limited to a small volume of soil in the superficial layers, which in turn negatively influences crop grain yield, mainly in regions with frequent dry spells (Caires et al., 2008a).

Among certain strategies used to ameliorate subsurface soil acidity is the replacement of lime by the surface application of more soluble

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materials (Castro and Crusciol, 2013). However, to be considered effective, these materials must contain oxides, hydroxides, or silicates as neutralizing constituents (Alcarde and Rodella, 2003). By-products such as steel industry slags (basically composed of Ca and Mg silicate) can be a good alternative to replace or increase the surface liming effect due to their higher solubility and alkalinity compared with lime, which can reduce the time associated with the liming reactions in the soil profile (Peregrina et al., 2008; Yi et al., 2012). In addition, Ca, Mg, and Si sources may be useful for crops, reducing lime consumption (Castro and Crusciol, 2013) and improving the performance of Si-accumulating crops (Liang et al., 1994; Korndörfer and Lepsch, 2001; Guntzer et al., 2011).

The surface application of soil acidity amendments (lime and silicate) with low solubility has restricted the yield potential of several crops as a result of high Al^{3+} levels and low availability of basic ions in the subsurface soil (Reeve and Sumner, 1972; Smith et al., 1994; Caires et al., 2011), which can reduce the downward movement of alkaline substances. The occurrence and reaction of free Al^{3+} species in water generates hydrogen ions in the soil solution (Lindsay, 1979), which results in high potential acidity (H + Al) levels. This effect supposedly increases the neutralizing constituents required to reduce the generated acidity.

By-products such as phosphogypsum reduce the concentration of free Al^{3+} in the soil solution (Sumner et al., 1986; Shainberg et al., 1989), especially in the subsurface soil layers (Sumner, 1993), which is favourable for the amelioration of soil profile acidity in a shorter time period. Supposedly, the phosphogypsum reaction can improve the time effects of soil acidity amendments (lime and silicate), which is related to the high solubility and mobility of Ca sulphate throughout the soil profile (Farina et al., 2000; Alcarde and Rodella, 2003). Each type of gypsum has specific chemical characteristics, but most of them are considered excellent sources of Ca^{2+} and SO_4^{2-} for subsurface soil layers, which allows greater development of deep roots in acidic soils, reducing water stress caused by drought periods (Sumner et al., 1986; Alva and Gascho, 1991; Rutherford et al., 1994; Soratto and Crusciol, 2008a; Soratto et al., 2010; Caires et al., 2011).

Although upland rice has been considered acid-tolerant, new cultivars with better genotypic performance are apparently less tolerant to high Al^{3+} toxicity and the poor chemical conditions of tropical soils (Fageria et al., 2015). In addition, some studies suggest that fertilizer application, including Si sources, significantly increases upland rice grain yield, which indicates greater nutrient demand (Seebold et al., 2000; Korndörfer and Lepsch, 2001; Crusciol et al., 2013). Therefore, the adoption of new techniques in acidic soils under NT systems is essential to provide better conditions for plant development, resulting in increases in upland rice production.

The identification of alternatives that enable the amelioration of soil acidity at depth in an NT system through surface application without the incorporation of amendments may facilitate the success and continued use of this type of agricultural system. In addition, there is limited information on the surface application of acidity amendments and phosphogypsum applied as a mixture to tropical soils, which may have potential to improve the reactions of substances with low mobility and solubility.

Thus, this study was based on the following hypotheses: a) the surface application of silicate can neutralize soil acidity and provide Ca at depth in a shorter time period compared with the application of lime only; b) the application of soil acidity amendments (silicate + lime) in a mixture is more efficient than individual applications of each amendment with respect to reducing the acidity of the soil profile; c) due to its high mobility, the addition of phosphogypsum to soil acidity amendments (silicate + lime) promotes the enrichment of bases in the soil profile in a shorter time period compared with individual or mixed applications of lime and silicate; and d) the application of soil acidity amendments mixed with phosphogypsum can increase the grain yield of upland rice.

In summary, the aims of this study were to evaluate the effects of superficially applied silicate, lime, and phosphogypsum mixtures on the amelioration of the soil profile under an NT system, and to determine their effects on the nutrition, yield components, and grain yield of upland rice crop.

2. Materials and methods

2.1. Site description

A field experiment was conducted in the Cerrado region, Selvíria, State of Mato Grosso do Sul, Brazil (51°22′ W, 20°22′ S, 335 m a.s.l.) over two growing seasons. The soil was classified as a clay-textured Typic Acrustox (USDA, 1999). The chemical properties of the soil were determined at multiple depths (0–0.05, 0.05–0.10, 0.10–0.20, and 0.20–0.40 m) prior to installing the experiment (Table 1), according to the methodologies described by van Raij et al. (1986).

The long-term (1956–2006) mean temperature during the rice growing season was 26.9 °C, with a minimum of 21.4 °C and a maximum of 32.4 °C. The mean rainfall during this period was 749 mm. In addition, during the experimental period, the minimum and maximum air temperatures and rainfall were measured daily (Fig. 1).

2.2. Experimental design and treatment establishment

The experiment was designed as a randomized complete block with eight treatments and four replications. Each plot covered an area of 35 m^2 (5.0 m × 7.0 m). The following treatments were tested: (i) control (no lime, silicate, or phosphogypsum); (ii) phosphogypsum (3.0 Mg ha^{-1}); (iii) lime (2.1 Mg ha^{-1}); (iv) silicate (2.2 Mg ha^{-1}); (v) lime and silicate mix (1.05 Mg ha^{-1} + 1.1 Mg ha^{-1}); (vi) lime and phosphogypsum mix (2.1 Mg ha^{-1} + 3.0 Mg ha^{-1}); (vii) silicate and phosphogypsum mix (2.1 Mg ha^{-1} + 3.0 Mg ha^{-1}); and (viii) lime, silicate, and phosphogypsum mix (1.05 Mg ha^{-1} + 1.1 Mg ha^{-1} + 3.0 Mg ha^{-1}).

The dolomitic limestone and Ca and Mg silicate rate (R) was calculated to increase the base saturation (BS) in the topsoil (0–0.20 m) to 70%, using Eq. (1) as described by Cantarella et al. (1998).

$$R\left(\text{kg ha}^{-1}\right) = (BS_2 - BS_1)\,CEC/(ECCE/100) \qquad (1)$$

where ECCE is the effective Ca carbonate equivalent of the amendments; BS_2 is the estimated base saturation (70%); and BS_1 is the base saturation measured in the soil, calculated using Eq. (2) as described by Cantarella et al. (1998).

$$BS_1(\%) = (Ca_{ex} + Mg_{ex} + K_{ex})100/CEC \qquad (2)$$

where Ca_{ex}, Mg_{ex}, and K_{ex} are basic exchangeable cations, and CEC is the total cation exchange capacity, which was calculated using Eq. (3).

$$CEC\left(\text{mmol}_c\ \text{dm}^{-3}\right) = Ca_{ex} + Mg_{ex} + K_{ex} + \text{total acidity at pH } 7.0\ (H + Al) \qquad (3)$$

The phosphogypsum rate (GR) was calculated using Eq. (4), as recommended by van Raij et al. (1997).

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

where CL is the clay content (g kg^{-1}) in the 0.20- to 0.40-m soil layer.

The dolomitic limestone was composed of 30% Ca and 7.2% Mg with an ECCE of 86%. The Ca and Mg silicate, a by-product obtained from the steel manufacturing process, contained 23% SiO_2, 26% Ca, and 7.8% Mg with an ECCE of 82%; minor amounts of heavy metals were detected,

Table 1
Soil chemical properties of the experimental area prior to experiment initiation.

Depth	pH ($CaCl_2$)	O.M.[a]	P (resin)	S–SO_4^{2-}	Si	Al	H + Al	K	Ca	Mg	CEC	V
(cm)		(g dm^{-3})	(mg dm^{-3})			($mmol_c$ dm^{-3})						(%)
0–5	4.9	28	22	14	6.2	1.2	40	3.3	18	14	75	47
5–10	4.8	25	28	14	5.4	2.1	40	0.7	16	10	67	40
10–20	4.9	26	16	16	5.7	1.1	37	0.6	18	13	69	46
20–40	4.7	23	8	40	4.7	3.0	34	0.6	12	9	56	39
0–20	*4.9*	*27*	*20*	*16*	*5.9*	*1.1*	*40*	*1.5*	*19*	*12*	*73*	*45*

[a] O.M., organic matter.

i.e., Cd, Ni, Pb, Cr, and Hg, at concentrations of 3.1, 53.6, 12.6, 990, and <0.1 mg kg^{-1}, respectively. These are not considered pollutants according to their trace element concentrations in biosolid material (USEPA, 1994). The phosphogypsum ($CaSO_4 \cdot 2H_2O$), which is a by-product obtained from a Brazilian phosphoric acid company, was composed of 22% Ca, 17% S, and residual P and F (0.1%).

The products were dried before being mixed. A mechanical mixer was used to produce the mixtures, and all mixtures and individual products were stored in packets. Fifteen days before product application, pearl millet was dried by applying glyphosate (1800 g active ingredient ha^{-1}). The products were applied to millet straw without soil incorporation one month (October) before the upland rice was sown.

2.3. Rice cultivar characteristics and crop management

The rice cultivar BRS Primavera has a short life cycle (95–105 days), long grains and high drought tolerance. This cultivar was developed by the Rice and Bean National Research Center (EMBRAPA — Brazilian Agricultural Research Corporation) and has produced good results in several management systems (Santos et al., 2006).

Upland rice BRS Primavera cultivar seeds were planted in the fourth week of November in two growing seasons (2003–2004 and 2004–2005) at a spacing of 0.35 m between rows, with 80 seeds m^{-1} row. Base fertilization was performed using 300 kg ha^{-1} of $N–P_2O_5–K_O$ (08–28–16) + 0.4% Zn, and top dressing fertilization consisted of 60 kg of N (urea) ha^{-1} at the tillering stage, as recommended by Cantarella et al. (1997). In both growing seasons, there was homogeneous germination and no limitation of upland rice growth due to weeds or pests.

Water was not a limiting factor in the experiment because the upland rice received supplementary water when necessary. The soil matric potential was monitored inside the experimental area using 12 conventional mercury tensiometres (13-mm diameter, with a ceramic porous cup connected by tubing to a mercury manometer), which were constructed according to Richards (1941) and installed on the planting date at a depth of 0.15 m. Irrigation was performed when the mean matric potential of the soil reached −0.058 MPa (vegetative and maturity phenological phases) or −0.033 MPa (reproductive phenological phase) according to recommendations by Stone et al. (1986), and was calculated to increase the soil moisture tension to field capacity.

2.4. Soil sampling and chemical analyses

Three and twelve months after treatment establishment, eight individual soil samples were randomly collected at depths of 0.00–0.05, 0.05–0.10, 0.10–0.20 and 0.20–0.40 m from the useful area of each plot and between the rows of the previous crop to form a composite sample. The samples were dried, sieved (2-mm sieves) and analysed according to Cantarella et al. (1998) and Korndörfer et al. (1999) to determine chemical properties (pH, H + Al, Ca, Mg, K, N–NO_3^-, S–SO_4^{2-}, base saturation, and Si).

The soil pH was determined in a 0.01 mol L^{-1} $CaCl_2$ suspension (1:2.5 soil/solution). The total acidity (H, Al) was determined by extraction using calcium acetate (0.5 mol L^{-1} at pH 7.0) and titration (0.025 mol L^{-1} NaOH solution). The exchangeable Ca, Mg, and K were extracted using ion exchange resin (van Raij et al., 1986) and determined using atomic absorption spectrophotometry. Inorganic N was extracted using 1.0 mol L^{-1} KCl and distilled using Devarda's alloy (Keeney and Nelson, 1982). Soil SO_4–S analyses were performed through extraction using calcium phosphate (0.01 mol L^{-1}) in a 1:2.5 soil/solution ratio, followed by the turbidimetric method using $BaSO_4$ (Bardsley and Lancaster, 1960). The soluble Si concentration was determined using a 0.01 mol L^{-1} $CaCl_2$ solution (Korndörfer et al., 1999). Silicon determination was performed by beta-molybdosilicic complex formation (Kilmer, 1965) using a spectrophotometer at 660 nm.

2.5. Leaf sampling and chemical analysis methods

When 50% of the panicles of the rice plants in each plot were at the flowering stage, 50 flag leaf samples were collected for nutrient concentration determination (Cantarella et al., 1997). The leaves were dried in a forced air oven at 65 °C for 72 h, ground to pass through a 40-mesh stainless steel screen and analysed for nutrient concentration.

Analyses of P, K, Ca, Mg, and S concentrations were performed after nitric-perchloric acid digestion and were determined using atomic absorption spectrophotometry (Malavolta et al., 1997). Nitrogen was analysed using sulphuric acid digestion and the semi-micro Kjeldahl method (Malavolta et al., 1997).

The Si concentration in the flag leaves was assayed based on the procedure recommended by Elliott and Snyder (1991), adapted by Korndörfer et al. (1999). Plant tissue samples (0.1 g) were placed in polyethylene tubes and wetted using 2 mL of 50% H_2O_2. Then, 3 mL of 50% NaOH at room temperature was added to each tube. The tubes were placed in a double boiler for 1 h and then in an autoclave at 138 kPa for 1 h. After atmospheric pressure was reached, the tubes were removed, and 45 mL of water was added. After a 12-h period, a 1-mL aliquot of the supernatant was set aside, and 15 mL of water, 1 mL of HCl (500 g L^{-1}), and 2 mL of ammonium molybdate were added. After 5 to 10 min, 2 mL of oxalic acid (500 g L^{-1}) was added. The silicon concentration was determined at a wavelength of 410 nm using a spectrophotometer.

2.6. Yield components and grain yield measurements

When approximately 90% of the panicles had grains with a typical mature colouration, the following parameters were evaluated: the number of panicles m^{-2} (calculated by counting the number of panicles in an area of 2.0 m in the two central rows from the usable area of each plot), total number of spikelets $panicle^{-1}$ (calculated by counting the number of spikelets in 20 panicles in the useable area), spikelet fertility [calculated using the following function: (number of grain-bearing spikelets/total number of spikelets per panicle) × 100], and weight of 1000 grains (evaluated by randomly collecting and weighing four samples of 1000 grains from each plot (the values were adjusted to a moisture content of 130 g kg^{-1})). A manual harvest was conducted,

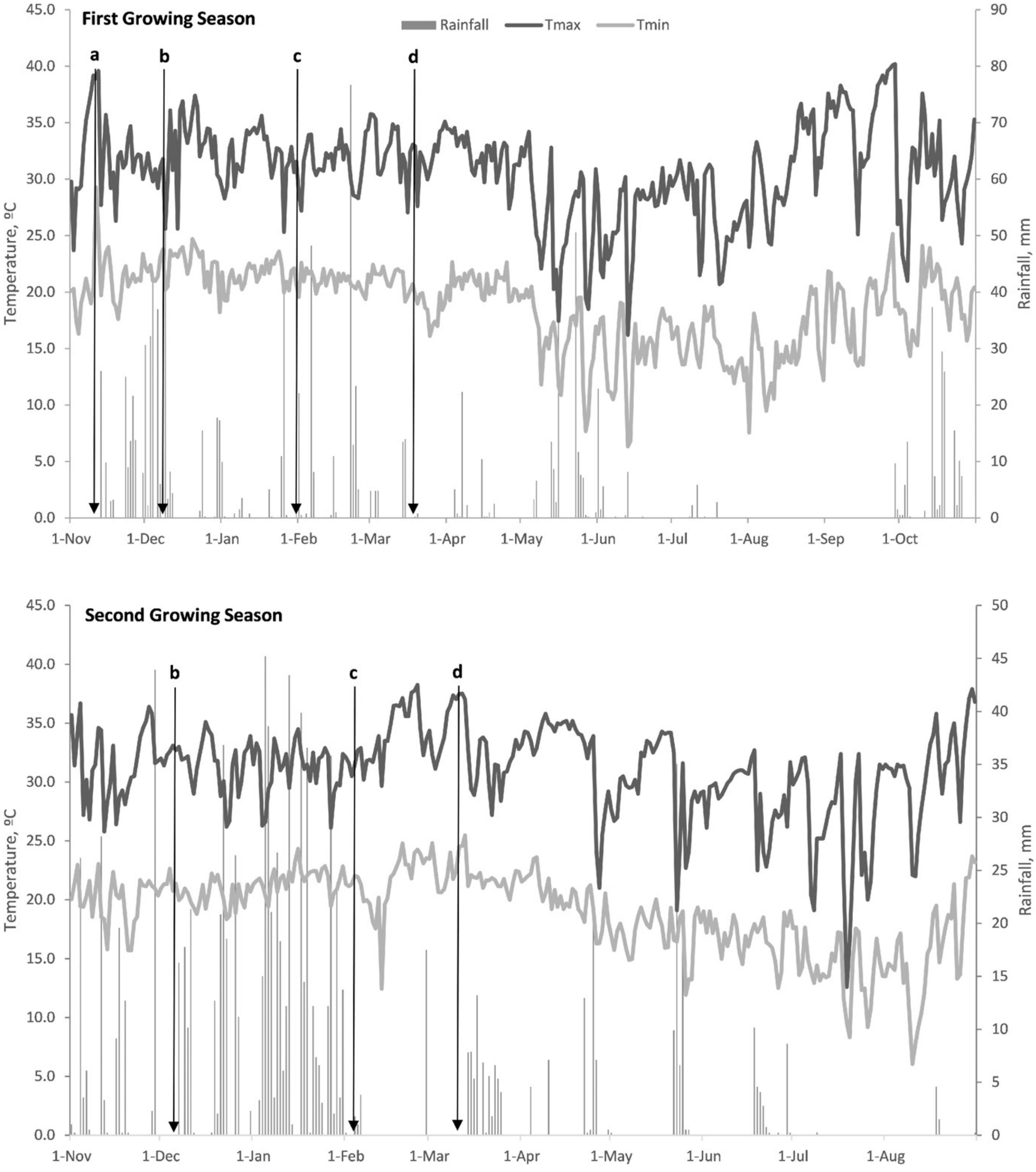

Fig. 1. Rainfall (▮) and maximum (▬) and minimum temperature (▬) at Selvíria, Mato Grosso do Sul State, Brazil, during the experimental period. a → treatment application; b → emergence; c → flowering; d → harvest.

and the panicles were dried in the sun for 1 to 2 days and later subjected to mechanical threshing using a research plot thresher. The grain yield (calculated from the weight of unhulled grain collected from the three central rows spanning five metres in each plot, eliminating 2.5 m on each side) and the values were adjusted to a moisture content of 130 g kg^{-1} and converted to kg ha^{-1}.

2.7. Statistical analysis

All data were analysed using two-way ANOVA in the statistical software package SAS®. The treatments and growing seasons (plant results only) were considered fixed effects. Significant differences between the means were determined using Fisher's protected LSD test. Effects were

Table 2
The pH and H + Al values of the soil samples collected from four depths 3 and 12 months after the surface application of lime, silicate, and phosphogypsum. ANOVA results are also shown.

Treatments	Soil depth			
	0–0.05 m	0.05–0.10 m	0.10–0.20 m	0.20–0.40 m
	pH ($CaCl_2$)			
	3 months			
Control	4.9c[†]	4.8b	4.8a	4.6a
Phosphogypsum	5.2b	4.9b	4.9a	4.7a
Lime	5.5a	5.1a	4.8a	4.7a
Silicate	5.5a	5.1a	4.8a	4.6a
Lime + Silicate (mix)	5.6a	5.1a	4.8a	4.7a
Lime + Phosphogypsum (mix)	5.5a	5.1a	4.8a	4.7a
Silicate + Phosphogypsum (mix)	5.6a	5.1a	4.8a	4.7a
Lime + Silicate + Phosphogypsum (mix)	5.6a	5.1a	4.9a	4.6a
ANOVA (*F probability*)				
Blocks	0.266	0.279	0.414	0.387
Treatments	0.030	0.046	0.294	0.416
Orthogonal contrast (WG × G)[‡]	0.444	0.605	0.707	0.653
	12 months			
Control	4.8c	4.6c	4.8b	4.7c
Phosphogypsum	4.8c	4.6c	4.8b	4.8bc
Lime	5.2b	4.8b	4.9b	4.8bc
Silicate	5.2b	4.8b	4.9b	4.9b
Lime + Silicate (mix)	5.2b	4.8b	4.9b	4.9b
Lime + Phosphogypsum (mix)	5.4a	5.0a	5.1a	5.0ab
Silicate + Phosphogypsum (mix)	5.4a	5.0a	5.1a	5.0ab
Lime + Silicate + Phosphogypsum (mix)	5.4a	5.0a	5.2a	5.1a
ANOVA (*F probability*)				
Blocks	0.099	0.081	0.153	0.836
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	<0.001
	H + Al ($mmol_c\ dm^{-3}$)			
	3 months			
Control	39a	41a	42a	39a
Phosphogypsum	38a	42a	42a	39a
Lime	32b	40a	43a	37a
Silicate	32b	40a	42a	36a
Lime + Silicate (mix)	28b	40a	42a	36a
Lime + Phosphogypsum (mix)	32b	40a	43a	36a
Silicate + Phosphogypsum (mix)	28b	38a	43a	37a
Lime + Silicate + Phosphogypsum (mix)	27b	39a	42a	37a
ANOVA (*F probability*)				
Blocks	0.195	0.389	0.543	0.500
Treatments	0.042	0.219	0.583	0.602
Orthogonal contrast (WG × G)[‡]	0.421	0.612	0.635	0.696
	12 months			
Control	42a	46a	39a	36a
Phosphogypsum	38b	45a	39a	36a
Lime	33c	42a	37a	33a
Silicate	31c	42a	38a	33a
Lime + Silicate (mix)	32c	42a	38a	32a
Lime + Phosphogypsum (mix)	30c	40a	30a	30a
Silicate + Phosphogypsum (mix)	30c	40a	31a	30a
Lime + Silicate + Phosphogypsum (mix)	30c	40a	30a	30a
ANOVA (*F probability*)				
Blocks	0.323	0.093	0.106	0.770
Treatments	<0.001	0.092	0.103	0.113
Orthogonal contrast (WG × G)[‡]	0.004	0.047	<0.001	0.003

[†] Values followed by the same letter within a column are not significantly different at $p \le 0.05$ according to the LSD test.

[‡] Orthogonal contrast analysis between treatments with (G) and without (WG) phosphogypsum ($p \le 0.05$).

considered significant at $P \le 0.05$ for the soil chemical parameters, yield components and grain yield data. Orthogonal contrast analyses were performed to compare treatments with (G) and without (WG) phosphogypsum (soil and plant results) and with (S) and without (WS) silicate (plant results only); these effects were considered significant at $P \le 0.05$.

3. Results and discussion

3.1. Soil chemical characteristics

The pH in the 0–0.05 and 0.05–0.10-m soil layers increased three months after amendment application (Table 1). This result is attributed to the low solubility and mobility of the carbonate- and silicate-based inputs. According to Pavan et al. (1984), the surface application of soil acidity amendments, such as Ca carbonate, increased the pH only in the surface soil layers; little or no change in pH occurred below a depth of 0.20 m. In addition, these authors also found that phosphogypsum had little or no effect on soil pH.

Although phosphogypsum is not considered an effective material for ameliorating soil acidity (Smith et al., 1994), we noticed that the individual addition of 3.0 Mg ha^{-1} of this by-product led to an increase of 0.3 pH units in the 0–0.05-m soil layer (Table 2). In areas of Peninsular Malaysia, Ismail et al. (1993) also reported increases in soil solution pH (from 4.2 to 4.5) resulting from the application of 4 Mg ha^{-1} of phosphogypsum. It is likely that these reactions result from anion

Table 3.
N-nitrate and S-sulfate concentrations of soil samples collected from four depths 3 and 12 months after the surface application of lime, silicate, and phosphogypsum. ANOVA results are also shown.

Treatments	Soil depth			
	0–0.05 m	0.05–0.10 m	0.10–0.20 m	0.20–0.40 m
	$N–NO_3^-$ (mg dm^{-3})			
	3 months			
Control	12c[†]	12b	12b	11b
Phosphogypsum	14c	12b	12b	12b
Lime	19b	12b	13b	11b
Silicate	18b	13b	13b	11b
Lime + Silicate (mix)	18b	13b	12b	12b
Lime + Phosphogypsum (mix)	26a	17a	15a	16a
Silicate + Phosphogypsum (mix)	23a	18a	16a	16a
Lime + Silicate + Phosphogypsum (mix)	24a	18a	16a	17a
ANOVA (*F probability*)				
Blocks	0.375	0.417	0.393	0.557
Treatments	0.023	0.015	0.049	0.049
Orthogonal contrast (WG × G)[‡]	<0.001	0.039	0.036	0.048
	12 months			
Control	10 g	12e	11e	8b
Phosphogypsum	13f	13e	14d	15a
Lime	14e	16d	16c	15a
Silicate	19c	18c	17bc	17a
Lime + Silicate (mix)	16d	17 cd	16c	16a
Lime + Phosphogypsum (mix)	23b	19bc	18ab	18a
Silicate + Phosphogypsum (mix)	29a	21a	19a	18a
Lime + Silicate + Phosphogypsum (mix)	22b	20ab	18ab	17a
ANOVA (*F probability*)				
Blocks	0.477	0.715	0.563	0.739
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	<0.001
	$S–SO_4^{-2}$ (mg dm^{-3})			
	3 months			
Control	13c	15d	19b	36b
Phosphogypsum	39a	65a	82a	91a
Lime	12c	13d	20b	35b
Silicate	14c	14d	19b	37b
Lime + Silicate (mix)	15c	14d	21b	40b
Lime + Phosphogypsum (mix)	30b	28c	76a	80a
Silicate + Phosphogypsum (mix)	27b	43b	76a	79a
Lime + Silicate + Phosphogypsum (mix)	23b	44b	78a	90a
ANOVA (*F probability*)				
Blocks	0.459	0.516	0.406	0.616
Treatments	0.027	0.033	0.043	0.047
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	<0.001
	12 months			
Control	31f	17e	33e	84e
Phosphogypsum	40d	67c	92b	173b
Lime	32f	21e	48d	84e
Silicate	37e	57d	88b	148c
Lime + Silicate (mix)	34ef	52d	65c	120d
Lime + Phosphogypsum (mix)	63c	73c	135a	173b
Silicate + Phosphogypsum (mix)	76b	113a	133a	208a
Lime + Silicate + Phosphogypsum (mix)	118a	79b	134a	203a
ANOVA (*F probability*)				
Blocks	0.228	0.515	0.153	0.186
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	<0.001

[†] Values followed by the same letter within a column are not significantly different at $p \leq 0.05$ according to the LSD test.
[‡] Orthogonal contrast analysis between treatments with (G) and without (WG) phosphogypsum ($p \leq 0.05$).

exchange mechanisms, which involve the replacement of OH^- by SO_4^{2-} in the colloidal soil complex, a process referred to as "self-liming" (Reeve and Sumner, 1972; Soratto and Crusciol, 2008a; Churka Blum et al., 2013).

In addition, phosphogypsum application may have reduced the chemical activity of Al^{3+}, which reduces the Al hydrolysis process and consequently, the displacement of H^+ ions to solution, which is responsible for soil pH reduction (Shainberg et al., 1989; Alva and Gascho, 1991). This reaction can explain the positive effects of phosphogypsum when applied in mixtures with lime and/or silicate; these effects were observed 12 months after treatment establishment (Table 2), as confirmed by contrast orthogonal analysis. Results from tropical regions with high annual rainfall suggest that soil acidity amendments and phosphogypsum have positive effects on the amelioration of subsurface acidity in a relative short period of time. In a trial conducted in New South Wales, Australia, contradictory results was observed by Smith et al. (1994) in a region where the mean annual rainfall is approximately 800 mm. These authors reported that surface liming combined with phosphogypsum did not increase soil pH below a depth of 0.05 m 18 months after application. In addition to the intrinsic characteristics of this product, these results suggest that the action of acidity amendment materials in subsurface soil layers may vary depending on soil type, water availability (Oliveira and Pavan, 1996; Caires et al., 2005) and the presence of other substances, such as Ca sulphate.

Silicate is 6.78 times more soluble than Ca carbonate (Alcarde and Rodella, 2003), and silicate did not have a positive effect on soil pH

Table 4
Exchangeable Ca^{2+}, Mg^{2+}, and K^+ concentrations of soil samples collected from four depths 3 and 12 months after the surface application of lime, silicate, and phosphogypsum. ANOVA results are also shown.

Treatments	Soil depth			
	0–0.05 m	0.05–0.10 m	0.10–0.20 m	0.20–0.40 m
	Exchangeable Ca^{2+} ($mmol_c\ dm^{-3}$)			
	3 months			
Control	20d[†]	19c	18a	11a
Phosphogypsum	31c	25b	20a	12a
Lime	40b	24b	18a	11a
Silicate	42b	25b	19a	12a
Lime + Silicate (mix)	42b	30a	19a	12a
Lime + Phosphogypsum (mix)	50a	31a	19a	13a
Silicate + Phosphogypsum (mix)	51a	30a	20a	13a
Lime + Silicate + Phosphogypsum (mix)	52a	31a	21a	13a
ANOVA (*F probability*)				
Blocks	0.141	0.200	0.355	0.297
Treatments	<0.001	0.039	0.125	0.227
Orthogonal contrast (WG × G)[‡]	<0.001	0.023	0.157	0.172
	12 months			
Control	18f	16c	15f	12c
Phosphogypsum	18f	18c	17e	15b
Lime	24d	21b	20d	16b
Silicate	22e	19bc	22c	17b
Lime + Silicate (mix)	25c	20bc	21 cd	16b
Lime + Phosphogypsum (mix)	37b	27a	24b	18ab
Silicate + Phosphogypsum (mix)	43a	28a	28a	20a
Lime + Silicate + Phosphogypsum (mix)	44a	27a	25b	19ab
ANOVA (*F probability*)				
Blocks	0.137	0.110	0.083	0.392
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	<0.001
	Exchangeable Mg^{2+} ($mmol_c\ dm^{-3}$)			
	3 months			
Control	12c	9c	12a	8 a
Phosphogypsum	10c	10c	12a	9 a
Lime	28a	17a	10a	9 a
Silicate	28a	17a	10a	9 a
Lime + Silicate (mix)	29a	17a	10a	8 a
Lime + Phosphogypsum (mix)	23b	14b	11a	9 a
Silicate + Phosphogypsum (mix)	22b	14b	11a	8 a
Lime + Silicate + Phosphogypsum (mix)	23b	15b	12a	8 a
ANOVA (*F probability*)				
Blocks	0.144	0.100	0.257	0.227
Treatments	0.032	0.040	0.430	0.501
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	0.633	0.508
	12 months			
Control	10.7d	7.3e	9.4a	9.0a
Phosphogypsum	10.3d	5.9f	10.6a	10.0a
Lime	19.7a	11.5a	10.4a	9.1a
Silicate	17.0b	10.3bc	9.8a	9.8a
Lime + Silicate (mix)	19.0a	11.2ab	10.0a	9.4a
Lime + Phosphogypsum (mix)	12.1c	9.2d	11.5a	11.0a
Silicate + Phosphogypsum (mix)	12.4c	7.8e	10.7a	12.1a
Lime + Silicate + Phosphogypsum (mix)	11.6 cd	9.4 cd	11.0a	11.0a
ANOVA (*F probability*)				
Blocks	0.115	0.051	0.473	0.315
Treatments	<0.001	<0.001	0.423	0.077
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	0.036	<0.001
	Exchangeable K^+ ($mmol_c\ dm^{-3}$)			
	3 months			
Control	3.2a	1.4a	1.2a	0.8a
Phosphogypsum	3.0a	1.4a	1.1a	0.8a
Lime	3.2a	1.6a	1.2a	1.0a
Silicate	3.0a	1.5a	1.2a	0.9a
Lime + Silicate (mix)	2.9a	1.6a	1.1a	0.8a
Lime + Phosphogypsum (mix)	2.9a	1.5a	1.2a	1.0a
Silicate + Phosphogypsum (mix)	3.0a	1.4a	1.1a	0.9a
Lime + Silicate + Phosphogypsum (mix)	3.0a	1.4a	1.2a	0.9a
ANOVA (*F probability*)				
Blocks	0.222	0.177	0.200	0.585
Treatments	0.203	0.193	0.196	0.275
Orthogonal contrast (WG × G)[‡]	0.429	0.376	0.312	0.479
	12 months			
Control	3.9a	2.5a	2.4a	2.5a
Phosphogypsum	1.9d	1.1f	1.5b	1.3b
Lime	2.5b	2.3b	1.1e	0.8d

(continued on next page)

Table 4 (*continued*)

Treatments	Soil depth			
	0–0.05 m	0.05–0.10 m	0.10–0.20 m	0.20–0.40 m
Silicate	2.6b	2.0c	1.3c	0.9d
Lime + Silicate (mix)	2.6b	2.1c	1.2d	0.8d
Lime + Phosphogypsum (mix)	1.9d	1.5d	1.5b	1.1c
Silicate + Phosphogypsum (mix)	2.2c	1.2e	1.5b	1.3b
Lime + Silicate + Phosphogypsum (mix)	2.1c	1.3e	1.5b	1.1c
ANOVA (*F probability*)				
Blocks	0.246	0.011	0.099	0.653
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	0.316

[†] Values followed by the same letter within a column are not significantly different at $p \leq 0.05$ according to the LSD test.

[‡] Orthogonal contrast analysis between treatments with (G) and without (WG) phosphogypsum ($p \leq 0.05$).

compared with lime (Table 2). Despite its ineffectiveness, silicate is considered a good alternative to replace lime, mainly in regions with extensive agriculture where the cost of lime is high (Smith et al., 1994). In a trial conducted in an Oxisol without supplementary irrigation, Castro and Crusciol (2013) reported that lime and silicate increased the pH in the topsoil layer. However, 12 months after treatment establishment, liming only influenced the pH above a depth of 0.10 m, while Ca and Mg silicate increased pH to a depth of up to 0.2 m.

In the present study, changes in potential acidity (H + Al) occurred exclusively in the 0–0.05-m layer from the third month after the surface application of the treatments (Table 2). The neutralization of acidity and the increase in pH can be explained by an increase in the amount of hydroxyls (OH^-), which resulted from the application of the amendments, such as lime and silicate (McLean, 1982). The phosphogypsum application decreased H + Al only after 12 months following treatment establishment. Despite the reactions described previously, the fluoride in phosphogypsum can bond with free Al^{3+}, forming an Al–F complex that can reduce exchangeable Al and, consequently, H + Al (Alva et al., 1988). The effect of the combination with respect to reducing the acidity potential was small and was not detected by Fisher's LSD test; however, orthogonal contrast analysis confirmed that phosphogypsum decreased H + Al. This reaction involves the displacement of free Al^{3+} by the Ca^{2+} from the exchange complex and consequently the formation of the $AlSO_4^+$ ion pair, a species form that decreases free Al^{3+} in soil solution (Sumner, 1993; Peregrina et al., 2006, 2008). Similar effects were reported by Caires et al. (2006) 11 months after surface liming. In a subtropical Oxisol previously used as pastureland, these authors observed small effects of Ca carbonate on H + Al reduction in the uppermost soil layer, and no effects below a depth of 0.05 m.

The surface application of acidity amendments increased available N–NO_3^- in the 0–0.05 m soil layer (Table 3); however, higher levels were observed when phosphogypsum was added as a mixture. Sierra et al. (2001) suggested that the nitrification process can be affected by factors that influence soil electrochemical properties, mainly those that influence soil pH (Chung and Zasoski, 1993). In a trial conducted in an acid soil (initial pH 4.8) with an organic matter content of 3.5% and a clay content of 22%, Dancer et al. (1973) confirmed a positive correlation between soil pH and NO_3^- levels ($r = 0.92$). These authors reported that a pH change from 4.8 to 6.5 resulted in a fivefold increase in the soil NO_3^- content. In this context, we suggest that lime and silicate application may have a strong influence on soil NO_3^-.

For both soil sampling periods, the ability of phosphogypsum to increase the N–NO_3^- concentration compared with the application of individual soil acidity amendments is supposedly related to the anion-exchange phenomenon. Kinjo and Pratt (1971) studied the competitive effects of SO_4^{2-} and NO_3^- adsorption and concluded that the amount of NO_3^- in the soil solution increased linearly with the addition of SO_4^{2-} sources because of higher energy retention in the positively charged colloidal complexes. This competitive adsorption effect can explain the positive effect of phosphogypsum on available N–NO_3^-. Phosphogypsum is a good alternative that can increase the amount of N in the soil profile. Furthermore, Crusciol et al. (2011) reported that higher N–NO_3^- levels in soil may reduce the negative effects caused by free Al^{3+}.

Regardless of the soil sampling time and type of mixture, the phosphogypsum-based treatments resulted in higher S–SO_4^{2-} concentrations in all soil layers (Table 3), which confirms the results obtained in several studies (Reeve and Sumner, 1972; Farina et al., 2000; Caires et al., 2011). It is important to emphasize that three months after treatment establishment, the individual application of phosphogypsum resulted in higher S–SO_4^{2-} concentrations in the topsoil layers (0–0.10 m). In addition to the effect of the acidity amendments, i.e., increasing the negative charges in soils with variable charges (Ji, 1997), the application of lime and/or silicate combined with Ca sulphate increased the amount of Ca and Mg in the soil solution, which resulted in a greater downward movement of SO_4^{2-} and consequently, neutral species formation ($CaSO_4^0$ and $MgSO_4^0$). This phenomenon can result in the removal of considerable quantities of Ca, Mg and K from the soil surface layers (O'Brien and Sumner, 1988; Churka Blum et al., 2013), making them more available at depths below 0.20 m, as was observed in this study. The phosphogypsum and silicate mixture provided more S–SO_4^{2-} in the soil surface layers (0–0.05 and 0.05–0.10 m) 12 months after treatment establishment (Table 3). It is likely that this effect is related to sulphate release, which was increased by silicate adsorption (Rãjan and Fox, 1975). Interactive effects between inorganic anions and soil colloids were reported by Haynes (1982). Castro and Crusciol et al. (2013) observed higher PO_4^{2-} availability in a Brazilian Oxisol after the surface application of Ca and Mg silicate.

Regardless of the type of material used, the levels of exchangeable Ca increased in the soil surface layers (0–0.05 and 0.05–0.10 m) in the third month after treatment establishment (Table 4). However, at the 12th month, the concentrations of Ca increased in all layers, but higher concentrations were observed when phosphogypsum was associated with the acidity amendments. The mixture reaction proved satisfactory in improving the chemical properties of the soil subsurface layers. Similar positive effects of phosphogypsum were observed by Caires et al. (2011) nine months after surface application (in this case, Ca sulphate was not mixed with the soil acidity amendments). According to Caires et al. (2008a), the ability of phosphogypsum to increase the Ca levels in the lowest acidic soil layers can result in greater proliferation of roots at greater depths, increasing the efficiency of nutrient and water absorption by plants.

For both soil sampling periods, the surface application of lime and/or silicate resulted in a larger amount of exchangeable Mg present in the shallowest layers (0–0.05 and 0.05–0.10 m) (Table 4). The use of phosphogypsum combined with the soil acidity amendments reduced the available Mg in the uppermost soil layers. Other studies have confirmed that phosphogypsum application increased the downward movement of exchangeable Mg to the deeper layers (Oliveira and Pavan, 1996; Soratto and Crusciol, 2008a), but in this scenario, i.e., a tropical region under irrigation, the movement of Mg through the soil

Table 5
Base saturation and Si concentration of soil samples collected from four depths 3 and 12 months after the surface application of lime, silicate, and phosphogypsum. ANOVA results are also shown.

Treatments	Soil depth			
	0–0.05 m	0.05–0.10 m	0.10–0.20 m	0.20–0.40 m
	Base saturation (%)			
	3 months			
Control	47c[†]	42b	43a	34a
Phosphogypsum	56b	46b	44a	36a
Lime	69a	52a	40a	36a
Silicate	70a	53a	42a	38a
Lime + Silicate (mix)	73a	55a	42a	37a
Lime + Phosphogypsum (mix)	70a	54a	42 a	39a
Silicate + Phosphogypsum (mix)	73a	54a	43 a	37a
Lime + Silicate + Phosphogypsum (mix)	74a	55a	45 a	37a
ANOVA (*F probability*)				
Blocks	0.101	0.135	0.197	0.563
Treatments	0.027	0.031	0.251	0.305
Orthogonal contrast (WG × G)[‡]	0.166	0.209	0.256	0.363
	12 months			
Control	44d	35c	41c	40c
Phosphogypsum	44d	36c	44b	42bc
Lime	58c	45b	46b	44b
Silicate	57c	43b	46b	45b
Lime + Silicate (mix)	59c	44b	46b	45b
Lime + Phosphogypsum (mix)	63b	49a	55a	50a
Silicate + Phosphogypsum (mix)	67a	49a	57a	53a
Lime + Silicate + Phosphogypsum (mix)	66a	49a	56a	51a
ANOVA (*F probability*)				
Blocks	0.087	0.020	0.151	0.841
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	<0.001	<0.001	<0.001	<0.001
	Si (mg dm^{-3})			
	3 months			
Control	4.1d	4.0e	4.0a	4.1a
Phosphogypsum	5.1c	4.8d	4.1a	4.0a
Lime	5.9b	5.7c	4.2a	4.0a
Silicate	7.3a	8.0a	4.4a	4.1a
Lime + Silicate (mix)	6.8a	7.1b	4.3a	4.2a
Lime + Phosphogypsum (mix)	6.0b	6.1c	4.1a	4.0a
Silicate + Phosphogypsum (mix)	7.0a	7.9a	4.3a	4.2a
Lime + Silicate + Phosphogypsum (mix)	7.3a	7.0b	4.4a	4.1a
ANOVA (*F probability*)				
Blocks	0.123	0.175	0.444	0.511
Treatments	0.016	0.039	0.284	0.312
Orthogonal contrast (WG × G)[‡]	0.136	0.164	0.419	0.469
	12 months			
Control	5.5d	5.7d	5.1e	4.5e
Phosphogypsum	6.1d	5.7d	6.0d	4.6e
Lime	6.9c	5.7d	6.3 cd	5.5d
Silicate	12.5a	11.9a	11.9a	9.0a
Lime + Silicate (mix)	8.1b	7.0bc	6.8bc	6.2c
Lime + Phosphogypsum (mix)	6.8c	6.6c	6.2 cd	5.4d
Silicate + Phosphogypsum (mix)	8.6b	7.5b	7.4b	7.0b
Lime + Silicate + Phosphogypsum (mix)	7.2c	6.7c	6.5 cd	6.0c
ANOVA (*F probability*)				
Blocks	0.472	0.123	0.291	0.110
Treatments	<0.001	<0.001	<0.001	<0.001
Orthogonal contrast (WG × G)[‡]	0.123	0.093	0.158	0.242

[†] Values followed by the same letter within a column are not significantly different at $p \le 0.05$ according to the LSD test.

[‡] Orthogonal contrast analysis between treatments with (G) and without (WG) phosphogypsum ($p \le 0.05$).

profile was minimal, which resulted in a small increase in exchangeable Mg in the lower layers (0.10–0.20 m and 0.20–0.40 m), as confirmed by orthogonal contrast analysis. It is important to emphasize that even with the use of phosphogypsum combined with the soil acidity amendments, the treatments provided sufficient levels of exchangeable Mg above a depth of 0.20 m (> 8 $mmol_c$ dm^{-3}) (Caires et al., 2011).

Three months after treatment establishment, the soil exchangeable K content was not influenced by the surface application of lime, silicate, or phosphogypsum, which shows that K leaching did not occur in a short period of time (Table 4). However, Oates and Caldwell (1985) reported that this effect can vary with the amount of phosphogypsum. Furthermore, the fertilizer added one month after the application of the Ca, Mg, and sulphate sources, which may have masked the influence of these materials on the soil K content. Some studies have emphasized the K leaching effect caused by phosphogypsum application (Alva and Gascho, 1991; O'Brien and Sumner, 1988); however, Caires et al. (2011) showed that K losses can be low and vary according to the soil type. A lower K availability in the surface layers (0–0.05 and 0.05–0.10 m) was only observed 12 months after treatment application. This can be explained by the action of SO_4^{2-} and NO_3^- through the formation of ionic complexes, which occurs with Ca and Mg, and the water infiltration rate during the period between soil sampling (Farina et al., 2000; Qafoku and Sumner, 2001).

An increase in the base saturation values above a 0.10-m depth was observed three months after treatment establishment, which is related to increasing Ca and Mg levels in the soil surface layers, as discussed

Table 6

Macronutrients (N, P, K, Ca, Mg, and S) and Si concentration in the flag leaves of upland rice as affected by the surface application of lime, silicate, and phosphogypsum. ANOVA results are also shown.

	N	P	K	Ca	Mg	S	Si
	(g kg^{-1})						
Treatments							
Control	31a[†]	1.8a	17a	4.6a	1.8a	2.8b	19c
Phosphogypsum	32a	1.9a	17a	4.6a	1.8a	3.5a	19c
Lime	32a	1.9a	17a	4.7a	1.8a	2.9b	20bc
Silicate	33a	1.9a	16a	4.9a	1.9a	2.7b	29a
Lime + Silicate (mix)	33a	1.9a	16a	4.8a	1.9a	2.7b	24b
Lime + Phosphogypsum (mix)	33a	1.9a	16a	4.9a	1.8a	3.4a	21bc
Silicate + Phosphogypsum (mix)	34a	1.9a	15a	4.9a	1.9a	3.5a	22bc
Lime + Silicate + Phosphogypsum (mix)	33a	1.9a	16a	5.0a	1.8a	3.5a	22bc
Growing season							
First	35a	1.7b	15b	4.4b	1.6b	3.1a	20b
Second	30b	1.9a	17a	5.1a	1.9a	3.1a	24a
ANOVA (F probability)							
Blocks	0.323	0.184	0.061	0.967	0.002	0.099	0.852
Treatments (T)	0.083	0.189	0.100	0.834	0.970	<0.001	<0.001
Growing season (GS)	<0.001	<0.001	<0.001	<0.001	<0.001	0.721	<0.001
T × GS	0.933	0.999	0.922	0.905	0.722	0.506	0.092
Orthogonal contrast (WG × G)[‡]	0.250	0.529	0.086	0.434	0.788	<0.001	0.111
Orthogonal contrast (WS × S)[§]	0.087	0.117	0.124	0.247	0.286	0.538	<0.001

[†] Values followed by the same letter within a column are not significantly different at $p \leq 0.05$ according to the LSD test.

[‡] Orthogonal contrast analysis between treatments with (G) and without (WG) phosphogypsum ($p \leq 0.05$).

[§] Orthogonal contrast analysis between treatments with (S) and without (WS) silicate ($p \leq 0.05$).

previously (Table 5). Although phosphogypsum is also considered a source of Ca, the effect of its individual application was lower compared with the other treatments, except control. However, at the second soil sampling, the action of phosphogypsum combined with lime and silicate led to higher base saturation values in all soil layers, indicating that the combination of these materials is a good alternative method by which to increase base saturation in soil subsurface layers through superficial application in an NT system. These results can be attributed to phosphogypsum, which promotes increased mobility of ionic bases throughout the soil profile (Peregrina et al., 2008; Caires et al., 2011). In a Brazilian Oxisol, Soratto and Crusciol (2008b) reported that the benefits of phosphogypsum for increasing base saturation only occurred in the soil surface layers (above a depth of 0.10 m), but in this case, Ca sulphate was not combined with lime in the mixtures.

A possible deleterious effect of phosphogypsum on the leaching of basic cations, particularly losses of Mg and K, was suggested by Alva and Gascho (1991). However, the downward movement of basic cations to subsurface soil layers is interesting in Oxisols and Ultisols, which are naturally nutrient poor, mainly in basic cations such as Ca^{2+}, Mg^{2+} and K^{+}. Therefore, the movement through the soil profile may increase the growth and development of the root system into the higher base-rich subsurface, with added benefits in crop systems. The results observed by Caires et al. (2011) considered the more probable positive effect of phosphogypsum because they reported low losses of exchangeable K and economic return as a result of increased cumulative grain yield of a crop rotation system over a period of four years.

The use of soil acidity amendments increased available Si in the shallow (0–0.05 and 0.05–0.10 m) and deep soil layers (0.10–0.20 and

Table 7

Panicles per metre^2 (P), spikelets per panicle (SP), spikelet fertility (SF), weight of 1000 grains (W1000), and grain yield (GY) of upland rice as affected by the surface application of lime, silicate, and phosphogypsum. ANOVA results are also shown.

	P (no. m^{-2})	SP (no. panicle^{-1})	SF (%)	W1000 (g)	GY (kg ha^{-1})
Treatments					
Control	191d[†]	174a	79a	23.3a	3197e
Phosphogypsum	198 cd	179a	79a	23.5a	3484de
Lime	200c	181a	82a	23.8a	3591cd
Silicate	223a	188a	81a	24.1a	4101ab
Lime + Silicate (mix)	212b	183a	80a	23.9a	3909b
Lime + Phosphogypsum (mix)	205bc	182a	81a	23.9a	3801bc
Silicate + Phosphogypsum (mix)	225a	191a	83a	24.3a	4362a
Lime + Silicate + Phosphogypsum (mix)	213b	185a	80a	24.0a	3957b
Growing season					
First	206a	158b	79b	23.3b	3525b
Second	211a	208a	83a	24.5a	4075a
ANOVA (F probability)					
Blocks	0.785	0.147	0.445	0.222	0.615
Treatments (T)	<0.001	0.696	0.642	0.564	<0.001
Growing season (GS)	0.127	<0.001	<0.001	<0.001	<0.001
T × GS	0.930	0.997	0.230	0.999	0.246
Orthogonal contrast (WG × G)[‡]	0.206	0.503	0.871	0.540	0.061
Orthogonal contrast (WS × S)[§]	<0.001	0.107	0.456	0.071	<0.001

[†] Values followed by the same letter in the column are not significantly different at $p \leq 0.05$ according to the LSD test.

[‡] Orthogonal contrast analysis between treatments with (G) and without (WG) phosphogypsum ($p \leq 0.05$).

[§] Orthogonal contrast analysis between treatments with (S) and without (WS) silicate ($p \leq 0.05$).

0.20–0.40 m) three and 12 months after surface application, respectively (Table 5). The use of silicate has resulted in higher Si levels in Oxisols. This represents a good alternative for acid soils deficient in Si, particularly Oxisols, which are typically low in Si (Korndörfer and Lepsch, 2001; Tavakkoli et al., 2011). Winslow et al. (1997) suggested sufficient Si values for rice soil, i.e., greater than 6 mg kg^{-1}. It is important to emphasize that even though lime is not considered as a source of Si, the application of Ca carbonate increased the available Si in the soil profile 12 months after application. This effect can be related to the formation of silica precipitates, commonly observed under acid conditions, which reduce plant Si availability. For this reason, the higher pH resulted in greater Si solubility in the soil (Oliveira et al., 2007).

3.2. Leaf nutrients and Si concentrations

The N, P, K, Ca, and Mg concentrations in the flag leaves were not affected by the application of amendments and phosphogypsum, applied individually or as a mixture (Table 6). Similar results were observed by Soratto and Crusciol (2008b), who reported that dolomite and phosphogypsum, applied separately, did not affect the foliar N, P, and K concentrations. However, these authors observed a linear effect of the dolomite rate on the Ca and Mg concentrations in upland rice leaves. In general, the absence of a similar effect in this study is assumed to be due to variations in dilution/concentration, which is a direct consequence of upland rice crop development.

The concentrations of Si and of all macronutrients, except N and S, were higher in the second growing season than in the first, which demonstrates the positive effects of the treatments on the nutritional aspects of the crop (Table 6). The lower N concentration observed in the second growing season is probably related to some edaphoclimatic factor; however, it is important to emphasize that the N, P, K, Ca, and Mg concentrations in upland rice leaves in both growing seasons remained within a range considered adequate for rice (Cantarella et al., 1997).

The surface application of phosphogypsum (as a mixture and without amendments) only influenced the leaf S concentration (Table 6). This is in accordance with the results observed by Soratto and Crusciol (2008b) and Crusciol et al. (2013), who reported that the use of S sources directly influences the uptake of S by upland rice. In both cases, the increase in the S concentrations in the flag leaves as a response to the elevated levels of sulphate in the soil was evident (Table 3). Despite the increase in leaf concentrations, all treatments, even those without soil acidity amendments, resulted in high S concentrations (1.4–3.0 g kg^{-1}) in the flag leaves according to Cantarella et al. (1997).

The Si concentration in the rice flag leaves was higher only when silicate was exclusively applied (Table 6), although the mixture with lime had potential for improving Si uptake by upland rice. The treatments that contained silicate led to higher Si concentrations in the leaves compared with the other treatments, as indicated by the orthogonal contrast analysis; this is a requirement for consideration as an important Si source (Oliveira et al., 2007). With respect to the effect of liming on Si solubilization, Castro and Crusciol (2013) verified that silicate is relatively more efficient than lime in increasing the Si content in upland rice flag leaves. Given the amount of Si extracted by the plant, which is several times higher than that of some essential macronutrients, such as P, K, Ca, Mg and S, using silicate as an important Si source is advantageous because rice is considered to be a Si accumulator (Yoshida et al., 1962; Guntzer et al., 2011). Seebold et al. (2000) reported that the foliar Si concentration of upland rice cultivars increased by 65 and 90% at Si application rates of 500 and 1000 kg ha^{-1}, respectively. In this study, the highest Si concentrations, i.e., 3.5 and 4.1 mg kg^{-1} for the Santa Rosa and La Libertad cultivars, respectively, resulted from a Si application of 1000 kg ha^{-1}.

3.3. Yield components and grain yield of upland rice

The surface application of silicate and carbonate influenced the number of panicles per m^2 (Table 7). Furthermore, the use of silicate, either exclusively or mixed with phosphogypsum, resulted in a higher number of panicles per m^2 compared with the other treatments, which clearly shows the effect of Si on crop yield. Although less noticeable, lime application also favoured the formation of panicles, demonstrating that the use of soil acidity amendments benefits the reproductive development of the crop. However, little is known about the influence of Si on this yield component, and the results presented in the literature are contradictory. For example, Takahashi (1995) observed an increase in the number of panicles, whereas Mauad et al. (2003) did not detect positive effects.

None of the treatments affected the total number of spikelets per panicle, spikelet fertility, or the weight of 1000 grains (Table 7). Similarly, when assessing the effects of lime and phosphogypsum surface application on the yield components of traditional rice cultivars, Soratto et al. (2010) did not detect any effects of dolomite and phosphogypsum application on these variables. However, these authors noticed a dolomite and phosphogypsum interaction effect on the number of panicles per m^2 and the number of spikelets per panicle. Increases in grain yield have been reported irrespective of the type or application method of soil acidity amendments.

The use of silicate as a soil acidity amendment is advantageous for improving upland rice grain yield, as confirmed by the orthogonal contrast analysis (Table 7). Increases in upland rice grain yield in response to Si have also been observed by Deren et al. (1994) and Liang et al. (1994) in traditional cultivars. Si has been hypothesized to be agronomically important for rice cultivation because of the range of benefits provided by this element. These benefits include increased growth and yield (Savant et al., 1997; Seebold et al., 2000), positive interactions with P- and N-based fertilizers (Sumner and Farina, 1986; Mauad et al., 2003; Lee and Kim, 2007), increased resistance to biotic (diseases and pests) and abiotic (drought, salinity, and lodging) stresses, and improved yield in problematic soils, such as acidic soils (Korndörfer and Lepsch, 2001).

The positive effect of silicate on panicle development and consequently grain yield may be related to the higher Si concentration in upland rice leaves observed in the second growing season (Table 7). Normally, *Poaceae* species adequately supplied with Si exhibit greater accumulation of Si in the leaf structures, which improves plant architecture and allows higher light absorption and synthesis of organic substances, with positive effects on plant productivity (Deren et al., 1994; Gao et al., 2004). Because of the intrinsic characteristics of these products, a delayed effect occurs when applying soil acidity amendments to improve soil chemical properties. Therefore, a higher grain yield was observed in the second growing season. Although cultivars of upland rice has been considered to be tolerant of soil acidity (Fageria et al., 2015), the development of modern cultivars, such as BRS Primavera, and our current results suggest that high acidity level reduces its productive potential.

4. Conclusions

The combination of soil acidity amendments (lime and silicate) and phosphogypsum improved the surface and subsurface soil chemical properties in an NT system. The surface application of phosphogypsum combined with lime and/or silicate improved the chemical properties of the deepest soil layers 12 months after surface application. The mixtures increased the concentrations of K, Ca, Mg, N–NO_3^-, and S–SO_4^{2-} in the soil subsurface, which improved conditions for upland rice development.

The sulphur concentration in the flag leaves of upland rice was highest in response to phosphogypsum application, demonstrating this material as a source of S for upland rice crop production.

The upland rice crop was influenced by the surface application of soil acidity amendments, irrespective of whether these products were combined with phosphogypsum, which resulted in positive effects on the number of panicles per m^2 and, consequently, on the grain yield of upland rice.

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