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Mitigation of the Gradient of Chemical Properties in the Rooting Zone of Dystrophic Oxisols by Gypsum and Lime Inputs under a No-Till System

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ABSTRACT: Improvement of soil chemical properties in dystrophic Oxisols managed under long-term no-tillage system (NTS) with surface broadcast lime has been, frequently, restricted to a shallow topsoil layer. As a consequence, a sharply-defined chemical quality gradient is created, with deterioration from the surface towards deeper layers in Oxisols in southern Brazil. The aim of this study was to assess the temporal effects of gypsum, applied alone or in combination with lime, on Ca^{2+} content and Al^{3+} saturation in the rooting zone (RZ) (0.00-0.40 m). Four experiments were conducted from 2009 to 2014 in Typic Hapludox soils with distinct chemical qualities in the RZ managed under a long-term NTS (over 20 years) in Rio Grande do Sul (subtropical region). A randomized block experimental design with three replications was used. Experiments I and II were implemented in 2009, with treatments consisting of gypsum rates ranging from 0.0 to 6.5 Mg ha^{-1}. The other two experiments were implemented in 2011. In experiment III, a split-plot design was used, with plots received gypsum rates ranging from 0.0 to 5.0 Mg ha^{-1}, and the subplots received two lime rates (0.0 and 2.0 Mg ha^{-1}). A split-plot design was also used in experiment IV, with plots receiving gypsum rates ranging from 0.0 to 6.0 Mg ha^{-1}, and subplots receiving four lime rates, ranging from 0.0 to 4.8 Mg ha^{-1}. Soil samples were stratified in layers at depth from 0.00 to 0.60 m and taken during the period of the experiment. The use of gypsum increased the Ca^{2+} and SO_4^{2-}-S contents, proportional to the rate applied, and lowered Al^{3+} saturation throughout the soil profile evaluated. However, an increase in base saturation of the subsoil (0.25-0.60 m layer) was only observed at high rates of gypsum (>5.0 Mg ha^{-1}) in the medium-term and through accumulation of a high rainfall volume. A faster and more pronounced effect of subsoil improvement was observed when the chemical quality of the topsoil layer was already high and when gypsum and lime were applied in combination. Greater improvement in subsoil chemical quality induced by gypsum, alone or in combination with lime, was found in a period exceeding 30 months (Experiments III and IV), remaining for up to 54 months (Experiments I and II). The combination of gypsum with lime was an effective strategy to increase vertical movement of bases in the RZ, mitigating the gradient of chemical quality in dystrophic Oxisol, avoiding discontinuity in the NTS.

Keywords: calcium, base saturation, Al saturation, subsoil.

INTRODUCTION

The no-tillage system (NTS), associated with cover crops and crop rotation, has been reported as one of the best alternatives for agricultural soil management in southern Brazil (Debarba and Amado, 1997). Savings in time, fuel, and labor in establishing the crop under the NTS spurred rapid adoption of this conservation system in Paraná (PR) and Rio Grande do Sul (RS), Brazil throughout the 1990s, now including around 80 % of cropland in these states (Febrapdp, 2012).

However, studies have reported that soil chemical improvements in a long-term NTS are often restricted to shallow top layers (Blanco-Canqui and Lal, 2008), creating an unfavorable profile for deepening the root system in dystrophic Oxisols (Typic Hapludox) (Caires et al., 2011a; Bortoluzzi et al., 2014). As a consequence, there is an increase in drought susceptibility and yield instability (Dalla Nora and Amado, 2013). The state of RS stands out among Brazilian states in having the highest losses in agricultural production in the last two decades due to short-term water stress (Leivas et al., 2014), highlighting the importance of developing strategies to lessen drought stress in the NTS.

Experiments carried out under the NTS in southern Brazil during the 1980s and 1990s in previously limed soils managed under conventional tillage showed limited response to lime application and the mode of application (surface-applied or incorporated) (CQFSRS/SC, 1981; Pöttker and Ben, 1998). Furthermore, gypsum application, alone or in combination with lime, was also generally not supported by the research conducted during that period (Ernani, 1986; Peruzzo et al., 1990). Therefore, the liming recommendation under the NTS in RS was set up for soil amendment of the 0.00-0.10 m layer, which has been considered as the acidity diagnosis layer. In addition, values of Al^{3+} saturation up to 10 % in the diagnosis layer could be acceptable, since the Al^{3+} has lower activity due its complexation with soil organic matter (SOM) under the NTS (Miyazawa et al., 2002). Generally, lime rates under the NTS were reduced in consideration of the shallow diagnostic layer (0.00-0.10 m) in relation to the layer previously used in conventional tillage (full rate and 0.00-0.20 m as the diagnostic layer) and upon assuming a certain tolerance of soybean and corn to the presence of Al^{3+} (CQFS-RS/SC, 2004).

Improvement in the chemical quality of subsurface layers in Oxisols under continuous NTS is improbable under low rates of lime spaced out over a long period of time (Bortoluzzi et al., 2014). In addition, mono-cropping of soybean and higher grain yields achieved in recent years have resulted in higher nutrient export (Medeiros et al., 2008). As a consequence, a sharply defined chemical quality gradient between the surface and subsurface layers in the rooting zone (RZ) has frequently been reported in southern Brazil (Dalla Nora and Amado, 2013; Zandoná et al., 2015). This gradient is characterized by an increase in Al^{3+} content and decrease in Ca^{2+} saturation in subsurface layers. This frequently causes a chemical restriction to deepening of plant roots, compromising efficient use of soil water (Pauletti et al., 2014; Zandoná et al., 2015). Farmers and technical consultants have sought alternatives to improve the subsoil layers in order to create a thicker layer (0.00-0.40 m) of high chemical quality under continuous NTS. Caires et al. (2008), evaluating improvement in subsoil chemical quality, noted that surface broadcast lime was efficient in reducing the acidity of subsoil layers only at high rates with frequent reapplication and only in the medium/long term. The use of gypsum has been recognized as an efficient alternative for chemical improvement of soil subsurface layers, particularly when combined with lime, since a synergistic effect between these inputs has been reported (Raij, 2010; Dalla Nora et al., 2014).

More recently, studies carried out since the 2000s under long-terrm NTS by Caires et al. (2005; 2008), Dalla Nora and Amado (2013), Pauletti et al. (2014), and Zandoná et al.

(2015) have reported chemical improvement of the RZ by applying gypsum, alone or in combination with lime (Soratto and Crusciol, 2008; Crusciol et al., 2016), increasing Ca^{2+} and Mg^{2+} contents and decreasing Al^{3+} activity in Oxisol subsoil in the NTS.

The state of RS has an NTS area of about 5 million ha, mostly Oxisols; however, there is little information on strategies for improvement of chemical quality in subsoil layers. Because of the importance of agriculture in RS, the second largest soybean area in Brazil, there is a need to develop site-specific fertilizer and liming recommendations. Therefore, studies with gypsum input carried out in the states of Paraná, São Paulo, or the Cerrado (Brazilian tropical savanna) regions should be extrapolated with great care to RS.

This study tests the hypothesis that combined applications of gypsum and dolomitic lime, or gypsum alone, improve subsoil chemical quality under continuous NTS. The main objective of this study was to assess the temporal effects of gypsum, applied alone or in combination with lime, on an increase in Ca^{2+} content and decrease in Al^{3+} saturation, mitigating the gradient of chemical quality in the RZ (defined in the present study as the 0.00 to 0.40 m layer) under a long-term NTS in a Typic Hapludox.

MATERIALS AND METHODS

Description of experimental areas

Four experiments were conducted in the three main small grain crop municipalities in RS (Table 1). In all experiments, the soil was classified as a Typic Hapludox (Soil Survey Staff, 2010) with loamy to clayey texture [*Latossolo Vermelho Distrófico* according to Embrapa (2006)]. Climate in the region is classified as humid subtropical (Cfa) (Köppen, 1931). Air temperature data and average annual rainfall are shown in table 1. Rainfall during the experimental period was recorded at an experimental station near the experimental sites (Figure 1).

The experimental areas had been managed under a continuous NTS for at least 15 years before the implementation of the experiments, with inputs of 2.0 Mg ha^{-1} of lime with 80 % effective $CaCO_3$ equivalent applied at 4-year intervals. The experiments were implemented when the croplands had a black oat (*Avena strigosa Schreb*) winter cover crop, which was chemically managed with glyphosate [N-(phosphonomethyl) glycine]. Two experiments had gypsum applied alone and two others had gypsum in combination with lime. Gypsum was applied in August 2009 in experiments I and II. Gypsum was applied in August 2011 and lime in April 2013 in experiment III. Gypsum and lime were applied simultaneously in experiment IV. These inputs were broadcast on the soil surface in all the experimental areas. The sequence of crops, the fertilizer inputs, and the grain yield evaluation period are shown in table 2.

The hybrids and cultivars used in this study were: Pioneer 3069 in experiments I and II, and *Dekalb* 240 in experiments 3 and 4 for maize; *Nidera* 5909 in experiments I and II,

Table 1. Location of the experiments with their coordinates, altitude, annual precipitation, and soybean acreage in Rio Grande do Sul, Brazil

Experiment	Municipality	Coordinates	Altitude	Annual rainfall	Average temperature	Soybean acreage[1]
			m	mm	°C	ha
1	Carazinho	28° 19' S - 52° 55' W	595	2,020	16	28,000
2	Carazinho	28° 17' S - 52° 47' W	617	2,020	16	28,000
3	São Miguel das Missões	28° 40' S - 54° 23' W	265	1,651	15	48,000
4	Tupanciretã	29° 00' S - 53° 94' W	507	1,766	17	116,780

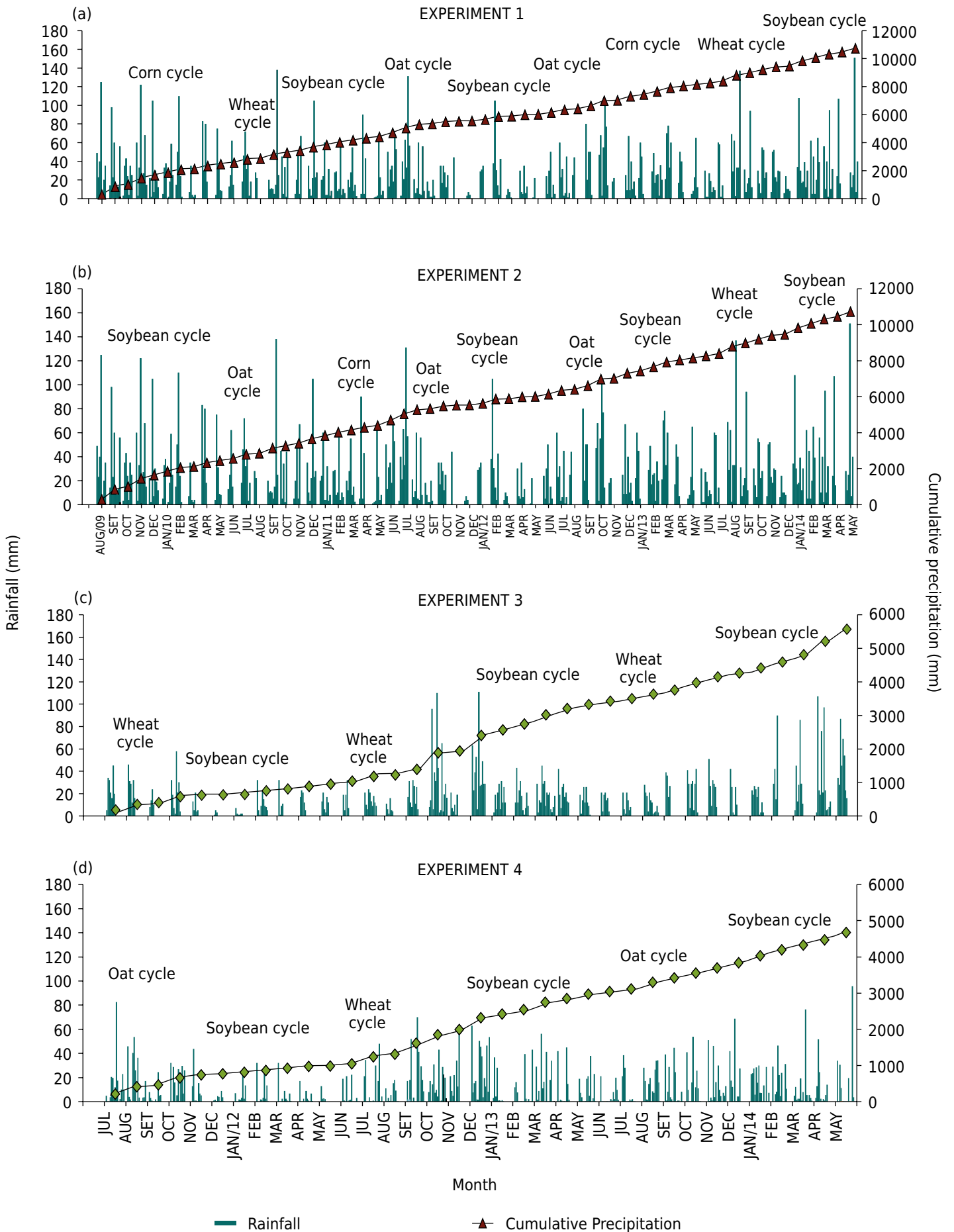[1] Main grain crops. Source: Luiz et al. (2012).

Figure 1. Daily and cumulative precipitation during the experimental period for experiments I, II, III, and IV, and crops evaluated in the experiments. Source: INMET (Instituto Nacional de Meteorologia).

Table 2. Crop sequence performed in experiments I, II, III, and IV, period of the crop cycle, fertilizer used, and the time of yield evaluation

Crop	Cycle	Fertilization	Yield measurement
		Experiment I	
Black oat	May to Sep/2009	Without fertilization	Setting up experiment
Corn	Sep/2009-Feb/2010	85.5 kg ha^{-1} of N (9 kg ha^{-1} at seeding and 76.5 kg ha^{-1} in topdress), 120 kg ha^{-1} of P_2O_5, and 120 kg ha^{-1} of K_2O; the source of N was urea, $[CO(NH_2)2]$ (45 % N)	Evaluated in February 2010
Wheat	Jul to Nov/2010	11.5 of N, 57.5 of P_2O_5, and 57.5 of K_2O (formulated fertilization N-P_2O_5-K_2O); 20.25 kg ha^{-1} of N in topdress (urea)	Not harvested, due to frost at flowering
Soybean	Nov/2010-Apr/2011	4.8 of N, 48 of P_2O_5, and 48 of K_2O (N-P_2O_5-K_2O)	Evaluated in April 2011
Black oat	May to Oct/2011	Without fertilization	Cover crop
Soybean	Nov/2011-Apr/2012	4.8 of N, 48 of P_2O_5, and 48 of K_2O (N-P_2O_5-K_2O)	Evaluated in February 2012
Black oat	May to Aug/2012	Without fertilization	Cover crop
Corn	Sep/2012-Feb/2013	85.5 kg ha^{-1} of N (urea) (9 kg ha^{-1} at seeding and 76.5 kg ha^{-1} in topdress), 120 kg ha^{-1} of P_2O_5, and 120 kg ha^{-1} of K_2O	Evaluated in February 2013
Wheat	Jul to Nov/2013	11 of N, 55 of P_2O_5, and 55 of K_2O (N-P_2O_5-K_2O) and 18 kg ha^1 of N (urea)	Evaluated in November 2013
Soybean	Nov/2013-Mar/2014	4.4 of N, 44 of P_2O_5, and 44 of K_2O (N-P_2O_5-K_2O)	Evaluated in March 2014
		Experiment II	
Black oat	May to Sep/2009	Without fertilization	Setting up experiment
Soybean	Nov/2009-Apr/2010	4.8 of N, 48 of P_2O_5, and 48 of K_2O (N-P_2O_5-K_2O)	Evaluated in April 2010
Oat/radish	May to Aug/2010	Without fertilization	Cover crop
Corn	Oct/2010-Feb/2011	85.5 kg ha^{-1} of N (urea) (9 kg ha^{-1} at seeding and 76.5 kg ha^{-1} in topdress), 120 kg ha^{-1} of P_2O_5, and 120 kg ha^{-1} of K_2O	Evaluated in February 2011
Black oat	May to Sep/2011	Without fertilization	Cover crop
Soybean	Nov/2011-Mar/2012	4.8 of N, 48 of P_2O_5, and 48 of K_2O (N-P_2O_5-K_2O)	Evaluated in March 2012
Black oat	May to Sep/2012	Without fertilization	Cover crop
Soybean	Nov/2012-Mar/2013	4.8 of N, 48 of P_2O_5, and 48 of K_2O (N-P_2O_5-K_2O)	Evaluated in March 2013
Wheat	Jul to Nov/2013	11 of N, 55 of P_2O_5, and 55 of K_2O (N-P_2O_5-K_2O) and 18 kg ha^1 of N (urea)	Evaluated in November 2013
Soybean	Nov/2013-Mar/2014	4.4 of N, 44 of P_2O_5, and 44 of K_2O (N-P_2O_5-K_2O)	Not evaluated by problems at harvest
		Experiment III	
Black oat	May to Sep/2011	Without fertilization	Setting up experiment
Soybean	Nov/2011-Mar/2012	4.2 of N, 42 of P_2O_5, and 42 of K_2O (N-P_2O_5-K_2O)	Not evaluated
Wheat	Jul to Nov/2012	10.5 of N, 52.5 of P_2O_5, and 52.5 of K_2O (N-P_2O_5-K_2O) and 18 kg ha^{-1} of N (urea)	Evaluated in November 2012
Soybean	Nov/2012-Mar/2013	4.2 of N, 42 of P_2O_5, and 42 of K_2O (N-P_2O_5-K_2O)	Evaluated in March 2013
Wheat	Jul to Nov/2013	10.5 of N, 52.5 of P_2O_5, and 52.5 of K_2O (N-P_2O_5-K_2O) and 18 kg ha^{-1} of N (urea)	Evaluated in November 2013
Soybean	Nov/2013-Mar/2014	4.2 of N, 42 of P_2O_5, and 42 of K_2O (N-P_2O_5-K_2O)	Evaluated in March 2013
		Experiment IV	
Black oat	May to Sep/2011	Without fertilization	Setting up experiment
Soybean	Nov/2011-Mar/2012	4.6 of N, 46 of P_2O_5, and 46 of K_2O (N-P_2O_5-K_2O)	Not evaluated
Wheat	Jul to Nov/2012	11 of N, 55 of P_2O_5, and 55 of K_2O (N-P_2O_5-K_2O) and 22.25 kg ha^{-1} of N (urea)	Evaluated in November 2012
Soybean	Nov/2012-Mar/2013	4.4 of N, 44 of P_2O_5, and 44 of K_2O (N-P_2O_5-K_2O)	Evaluated in March 2013
Black oat	May to Set/2013	Without fertilization	Cover crop
Soybean	Nov/2013-Mar/2014	4.6 of N, 46 of P_2O_5, and 46 of K_2O (N-P_2O_5-K_2O)	Not evaluated

The source of N was urea $[CO(NH_2)_2]$ (45 % N), P was triple superphosphate $Ca(H_2PO_4).2H_2O$ (45 % P_2O_5), and K was potassium chloride (60 % K_2O); Corn (*Zea mays* L.); Wheat (*Triticum aestivum* L.); Soybean [*Glycine max* (L.) Merr.]; Oilseed radish (*Raphanus sativus* L.); Black oat (*Avena strigosa* Schreb).

and 235RR *Coodetec* in experiments 3 and 4 for soybean; *Quartz* in Experiments I and II, and BRS *Tarumã* in experiments 3 and 4 for wheat. The soybean cultivars and maize hybrids used in the experiments were transgenic, with short-cycle and high yield potential characteristics. These genetic materials are currently the most widely cropped in RS. Maize was sown at a density of 4 seeds m[-1] and a row spacing of 0.50 m; soybean at 12 seeds m[-1] (inoculated with *Bradyrhizobium japonicum*) and row spacing of 0.50 m; and wheat at 60 seeds m[-1] and row spacing of 0.20 m.

Soil chemical characterization was performed prior to implementation of the experiments, randomly collecting five sub-samples in each experimental area at the following depths: 0.00-0.05, 0.05-0.10, 0.10-0.15, 0.15-0.25, 0.25-0.40, and 0.40-0.60 m. The chemical properties from the first characterization of the experimental areas are shown in table 3.

Table 3. Soil chemical properties before implementation of the treatments in the four experimental areas in dystrophic Oxisols managed under a no-tillage system in RS, Brazil

Experiments with Crop Rotation in summer													
Depth	**pH(H$_2$O)**	**Al^{3+}**	**Ca^{2+}**	**Mg^{2+}**	**K$^+$**	**Ca/Mg**	**CEC$_{pH7,0}$**	**P**	**S**	**V**	**m**	**Clay**	**SOM**
m		——— cmol$_c$ dm^{-3} ———					cmol$_c$ dm^{-3}	— mg dm^{-3} —		——— % ———		— g kg^{-1} —	
Experiment I (August 2009)													
0.00-0.05	5.6	0.0	6.7	3.5	0.18	1.9	15.6	28.3	8.6	68.2	0.0	530	3.9
0.05-0.10	5.6	0.0	6.1	3.5	0.13	1.7	14.9	10.1	17.3	67.6	0.0	600	3.4
0.10-0.15	5.4	0.2	5.4	3.2	0.07	1.7	14.8	5.0	12.9	59.9	1.8	670	2.8
0.15-0.25	5.2	0.4	4.3	3.0	0.05	1.4	15.2	2.6	10.8	49.5	4.6	680	2.0
0.25-0.40	4.9	0.8	2.5	2.6	0.04	1.0	15.6	1.1	14.0	34.8	16.1	700	1.6
0.40-0.60	4.5	0.9	2.1	2.3	0.03	0.9	15.3	0.8	15.1	30.9	23.9	740	1.1
Experiment II (August 2009)													
0.00-0.05	5.9	0.0	4.9	2.2	0.40	2.2	11.6	62.8	16.9	65.6	0.0	240	3.6
0.05-0.10	5.7	0.0	4.2	2.0	0.36	2.1	10.3	27.0	14.5	64.9	0.0	320	2.3
0.10-0.15	5.7	0.0	3.3	2.0	0.35	1.6	9.7	16.6	10.4	59.1	0.0	370	1.7
0.15-0.25	5.4	0.1	2.6	1.8	0.33	1.4	9.4	4.07	8.05	51.4	1.3	460	1.3
0.25-0.40	5.1	0.4	2.5	1.3	0.25	1.9	11.4	2.40	9.6	37.8	8.1	500	1.3
0.40-0.60	4.8	1.2	1.8	0.7	0.17	2.5	12.2	0.97	7.2	22.3	30.9	520	0.7
Experiments without Crop Rotation in summer													
Experiment III (August 2011)													
0.00-0.05	5.0	0.5	4.5	2.8	0.46	2.0	16.2	29.2	4.9	54.4	5.6	420.0	3.9
0.05-0.10	4.6	1.2	3.1	3.1	0.23	1.0	13.4	6.8	2.3	43.1	15.3	600.0	1.5
0.10-0.15	4.3	1.8	1.9	1.2	0.15	0.9	14.8	3.6	1.1	27.7	29.9	650.0	0.9
0.15-0.25	4.2	2.5	1.5	1.7	0.09	0.9	13.2	2.4	6.2	21.0	42.3	770.0	0.9
0.25-0.40	4.2	2.4	1.4	1.6	0.06	0.9	11.6	1.6	4.7	23.3	43.2	750.0	0.6
0.40-0.60	4.2	2.1	1.2	1.4	0.06	0.8	11.5	1.8	1.6	23.8	43.3	650.0	0.7
Experiment IV (August 2011)													
0.00-0.05	6.2	0.0	6.5	3.5	0.37	1.9	12.5	14.7	5.2	82.2	0.0	295.0	3.3
0.05-0.10	6.1	0.0	4.7	2.3	0.23	2.0	10.5	2.7	5.2	68.4	0.0	335.0	2.6
0.10-0.15	5.0	0.5	2.3	2.2	0.15	1.1	12.5	10.7	4.2	37.0	9.9	400.0	2.5
0.15-0.25	4.7	1.3	1.7	1.8	0.11	0.9	13.0	4.0	2.4	28.0	25.7	440.0	2.3
0.25-0.40	4.4	2.9	1.4	1.1	0.10	1.2	20.0	2.3	5.7	13.4	52.6	500.0	1.9
0.40-0.60	4.2	4.3	1.1	0.5	0.08	1.1	22.3	0.9	12.1	9.6	66.9	610.0	1.2

Al^{3+}: extracted with 1 mol L^{-1} KCl and titrated with 0.0125 mol L^{-1} NaOH; Ca^{2+} and Mg^{2+}: extracted with 1 mol L^{-1} KCl and determined by atomic absorption spectrophotometry; P and K: extracted with Mehlich-1 solution; CEC$_{pH7.0}$: cation exchange capacity in pH 7.0; S: extraction with Ca(H$_2$PO$_4$)$_2$ (500 mg L^{-1} P) and determined by turbidimetry; V: base saturation; m: aluminum saturation; SOM: soil organic matter, extracted by wet combustion.

Experimental design

A randomized block design with three replications was used in all experiments, with temporal assessments of soil chemical properties. Each plot had an area of 64 m^2 (8.0 × 8.0 m). The treatments assessed in experiments I and II consisted of gypsum rates of 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.5 Mg ha^{-1}, applied in August 2009. In experiment III, a split-plot design was used, with plots receiving gypsum rates of 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 Mg ha^{-1}, applied in August 2011. Two years before, lime application of 2.0 Mg ha^{-1} occurred at this site. After 22 months (April 2013) of the experiment, the main treatments were subdivided and the split-plots received dolomitic lime rates of 0.0 and 2.0 Mg ha^{-1}. In experiment IV, a 4 × 4 factorial design was used, consisting of four gypsum rates (0.0, 2.0, 4.0, and 6.0 Mg ha^{-1}) and four lime rates (0.0, 2.4, 3.6, and 4.8 Mg ha^{-1}), applied simultaneously in August 2011. The mean lime rate (3.6 Mg ha^{-1}) was set up in order to achieve 70 % of BS in the 0.00-0.20 m soil layer. A mean gypsum rate was set up according to Equation 1, reported by Quaggio and Raij (1996). Equation 1 has been recommended for calculation of gypsum application in soils of the Cerrado region and Central Brazil.

$$GR = \text{clay content} \times 60 \qquad \qquad \text{Eq. 1}$$

where GR is the gypsum rate (kg ha^{-1}) and clay content is in g kg^{-1} in the 0.20-0.40 m soil layer.

The agricultural gypsum ($CaSO_4.2H_2O$) used in the experiments consisted of 210.0 g kg^{-1} of Ca^{2+}, 155.0 g kg^{-1} of SO_4^{2-}-S, 0.024 g kg^{-1} of F$^-$, and 9.0 g kg^{-1} of P_2O_5. The dolomitic lime consisted of 30 % CaO and 20 % MgO, with total relative neutralizing power of 75 % and reactivity of 85 %.

Sampling and main assessments

Soil samples in experiments I and II were taken at 6, 14 (only in experiment I), 22, 32, 44, and 56 months after application of treatments. Soil samples in experiments III and IV were taken 15 and 30 months after application. Soil samples in experiment III were taken 30 months after gypsum application and eight months after the lime split-plot was set up. The soil was sampled with three replicates to form a composite sample for each of the following depths: 0.00-0.05, 0.05-0.10, 0.10-0.15, 0.15-0.25, 0.25-0.40, and 0.40-0.60 m, manually opening sampling pits with dimensions of 0.3 × 0.3 × 0.6 m. Soil samples were collected with a spatula at the front wall of the trench; they were dried in a forced-air laboratory oven and roots and plant residues were removed.

The chemical properties were analyzed following the methods described in Tedesco et al. (1995). Chemical evaluations were performed of Al^{3+} content extracted with 1 mol L^{-1} KCl and titrated with 0.0125 mol L^{-1} NaOH, and Ca^{2+} content extracted with 1 mol L^{-1} KCl and determined by atomic absorption spectrophotometry. The SO_4^{2-}-S was extracted by $Ca(H_2PO_4)_2$ (500 mg L^{-1} of P) and determined by turbidimetry (Beaton et al., 1968). The Ca^{2+} saturation was obtained by calculating the percentage of Ca^{2+} participation in CTC at pH 7.0.

Statistical analysis

The data were subjected to analysis of variance using the PROC GLM procedure in the SAS (Statistical Analysis Systems Institute Inc., 2009) in a randomized block experimental model. Regression analysis were performed in experiments I and II when the results exhibited significant effects between treatments and BS, Al^{3+} saturation, and Ca^{2+} saturation over time. Means of the treatments were subjected to the F test and compared by the Tukey test ($p<0.05$) for experiments III and IV. The temporal effect of gypsum applied alone on these chemical properties was characterized by selecting three treatments for each experimental area: a) control, b) treatment with an intermediate rate of gypsum, c) treatment with a high rate of gypsum. When there was an interaction between gypsum and lime, the effect

on the chemical properties was exhibited by the rate of gypsum in combination with the rate of lime that had the biggest effect on the chemical property investigated.

RESULTS AND DISCUSSION

Characterization of soil chemical properties at the beginning of the experiments

Relevant chemical quality differences in the RZ were found among the experimental areas (Table 3). In general, the topsoil layer from 0.00-0.10 m, suggested as the diagnostic layer (CQFS-RS/SC, 2004), had chemical quality at the beginning of the experiments that not require lime application, except for experiment III (Table 4). This result supports the treatments of gypsum input alone in experiments I and II. Regarding SO_4^{2-}-S, a nutrient added by gypsum, half of the experimental areas (III and IV) required input for soybean cultivation. Chemical quality transition from the topsoil layer towards the subsurface layers in the RZ was observed in all experimental areas, however, at different depths (Table 4). Deterioration in chemical quality of the subsoil layer has been reported in Oxisols managed under the NTS that had low lime input (Amado et al., 2009).

Experimental areas I and II had the strongest transition of chemical quality among the areas investigated, which was noted in the 0.25-0.40 m and 0.40-0.60 m layers, respectively (Table 3 and 4). Thus, in experiment I, the BS decreased by 42.2 % and the Al^{3+} saturation (m) increased by 250.0 % in the 0.25-0.40 m layer compared to the adjacent upper layer (0.15-0.25 m). In experiment II, the decrease in BS and increase in Al^{3+} saturation were 69.5 and 281.5 %, respectively, in the 0.40-0.60 m layer compared to the adjacent upper layer (0.25-0.40 m). The experimental sites with a thicker layer of high chemical quality had adoption of a crop rotation program rotating soybean with maize and the use of winter cover crops in common. In both, the soil amendment program adopted was effective in maintaining chemical quality favorable to plant root growth in medium (0.00-0.25 m) and deep (0.00-0.40 m) soil layers (Table 4).

The soil of experimental site III already had low chemical quality in the topsoil layers (Table 3 and 4). Thus, the 0.05-0.10 m layer had a decline in BS of 26.1 % and an increase in Al^{3+} saturation of 57.7 % compared to the adjacent upper layer (0.00-0.05 m). The 0.10-0.15 m layer had a decline in BS of 55.6 % and an increase in Al^{3+} saturation of 95.4 % compared to the 0.05-0.10 m layer. These results indicate that this experimental area had an inefficient soil amendment program, characterized by a low rate of lime input and a large time interval between applications. The chemical quality of the 0.00-0.10 m layer served as an effective diagnosis layer of the RZ only for this experimental site.

Table 4. Response probability classes of liming, gypsum, and sulfur for the four experiments and depth of transition of chemical quality

Inputs	Probability of response to inputs investigated in experiment			
	I	II	III	IV
Lime[1]	Low	Low	High	Low
Sulfur[2]	Low	Low	High	High for soybean; Low for corn and wheat
Gypsum[3]	Low	Low	High according to Al saturation	High according to Al saturation
Transition depth of chemical quality[4]	0.25-0.40 m	0.40-0.60 m	0.05-0.10 m	0.10-0.15 m

[1] Criteria for response to liming: pH >5.5; base saturation >65 %, Al saturation <10 % according to CQFS-RS/SC (2004);
[2] Critical limit for sulfur for legumes (soybean) is 10.0 mg dm^{-3} and for grasses (wheat and corn) is 5.0 mg dm^3 according to CQFS-RS/SC (2004);
[3] Gypsum in RS/SC, Brazil is not recommended, the criteria for the *Cerrado* are Al saturation >20 % and Ca <0.5 $cmol_c$ dm^{-3};
[4] Transition from chemical quality according to Al saturation and base saturation.

Experimental area IV had satisfactory chemical quality in the surface layer (BS >65 % and Al^{3+} saturation <0.0 % in the 0.00-0.10 m layer). However, it showed a sharp decrease in BS and marked increase in Al^{3+} saturation in the middle depth soil layer (0.10-0.15 m) (Table 3 and 4); in relation to the adjacent upper layer (0.05-0.10 m) there was a decrease in BS of 84.9 % and increase in Al^{3+} saturation from 0.0 % to 9.9 %, reaching a critical value [BS <65 % and Al^{3+} saturation >10 % (CQFS-RS/SC, 2004)]. In addition, in the 0.15-0.25 m soil layer, there was a decrease in BS of 32.1 % and an increase in Al^{3+} saturation of 159.6 % compared to the 0.10-0.15 m layer. This gradient was even more significant in the 0.25-0.40 m layer, with a decrease in BS of 108.9 % and an increase in Al^{3+} saturation of 104.7 %. This deterioration in chemical quality from the topsoil toward deeper layers (Table 4), especially the sharp increase in Al^{3+} saturation, has a negative effect on plant root growth and grain yields (Farina et al., 2000). Therefore, the liming program adopted in this experimental area was effective only in amending the shallow 0.00-0.10 m topsoil layer. In this case, the 0.00-0.10 m layer was not a proper soil layer to diagnostic the chemical quality of the RZ. The liming program at a rate of 2.0 Mg ha^{-1}, applied every four years in a cropping system with soybean monoculture, resulted in limited lime vertical displacement (Caires et al., 2005; Bortoluzzi et al., 2014). Therefore, in order to determine the chemical quality of the RZ in this experimental area, soil sampling of subsurface layers (0.10-0.20 or 0.20-0.40 m) would be required similar to what is recommended in the Brazilian Cerrado region (Quaggio and Raij, 1996; Oliveira et al., 2007), or, alternatively, sampling a much thicker layer, such as the 0.00-0.20 m layer recommended in the state of Paraná.

The use of gypsum as a soil amendment for the NTS in southern Brazil has increased over the last decade; however, there is still no specific criterion for purposes of recommendation. For gypsum recommendation for the Cerrado region of Brazil, Oliveira et al. (2007) suggested the critical contents of Ca^{2+} <0.5 $cmol_c\ dm^{-3}$ or Al^{3+} saturation >10.0 % at a depth of 0.20-0.40 m as criteria. The soils in experimental areas III and IV meet this criterion of Al^{+3} saturation (Table 3), but none of the experimental areas exhibited Ca^{2+} content below the critical values (Ca^{2+} <0.5 $cmol_c\ dm^{-3}$) at the beginning of the experiment. However, this critical Ca^{2+} content was proposed for Cerrado soils, which usually have low CEC ($\cong6.0\ cmol_c\ dm^{-3}$), whereas the soils of the present study had moderate CEC ($\cong12.0\ cmol_c\ dm^{-3}$).

Improvement in chemical properties in the RZ associated with lime and gypsum input

Significant (p<0.05) increases in Ca^{2+} and SO_4^{2-}-S contents were observed in the gypsum and lime treatments investigated, regardless of the experimental area, with increases throughout the soil profile (Figure 2). Overall, vertical displacement of SO_4^{2-}-S in the RZ was rapid and followed by downward movement of Ca^{2+} in all gypsum treatments. Agricultural soils generally have negative charges, which adsorb Ca^{2+} with a positive charge. In addition, SO_4^{2-}-S mobility is greater, due to its negative charge (Raij, 2010). Furthermore, low initial Ca^{2+} content and SO_4^{2-}-S content accelerate the dissociation of gypsum (Quaggio et al., 1993).

Fast vertical mobility of SO_4^{2-}-S is supported by the slight increase in SO_4^{2-}-S content in the topsoil layers (0.00-0.05 and 0.05-0.10 m) at 56 (experiments I and II) and 30 months (experiments III and IV) from the beginning of the experiments (Figure 2). This result is explained by this nutrient in the gypsum being in an oxidized form (SO_4^{2-}), which is repelled by the negative charges of clay minerals, thus remaining in the soil solution and susceptible to displacement by draining water (Farina et al., 2000; Caires et al., 2011a; Nava et al., 2012). Previously, Caires et al. (2011a) reported a strong displacement of SO_4^{2-}-S from the topsoil to deeper soil layers in gypsum improved Oxisols. In this study, 56 (experiments I and II) and 30 months (experiment III) after the beginning of the experiments, the SO_4^{2-}-S content in the topsoil layer (0.00-0.10 m) (Figure 2) remained lower than the critical values (10.0 mg dm^{-3}) proposed by Fontes et al. (1982) for the
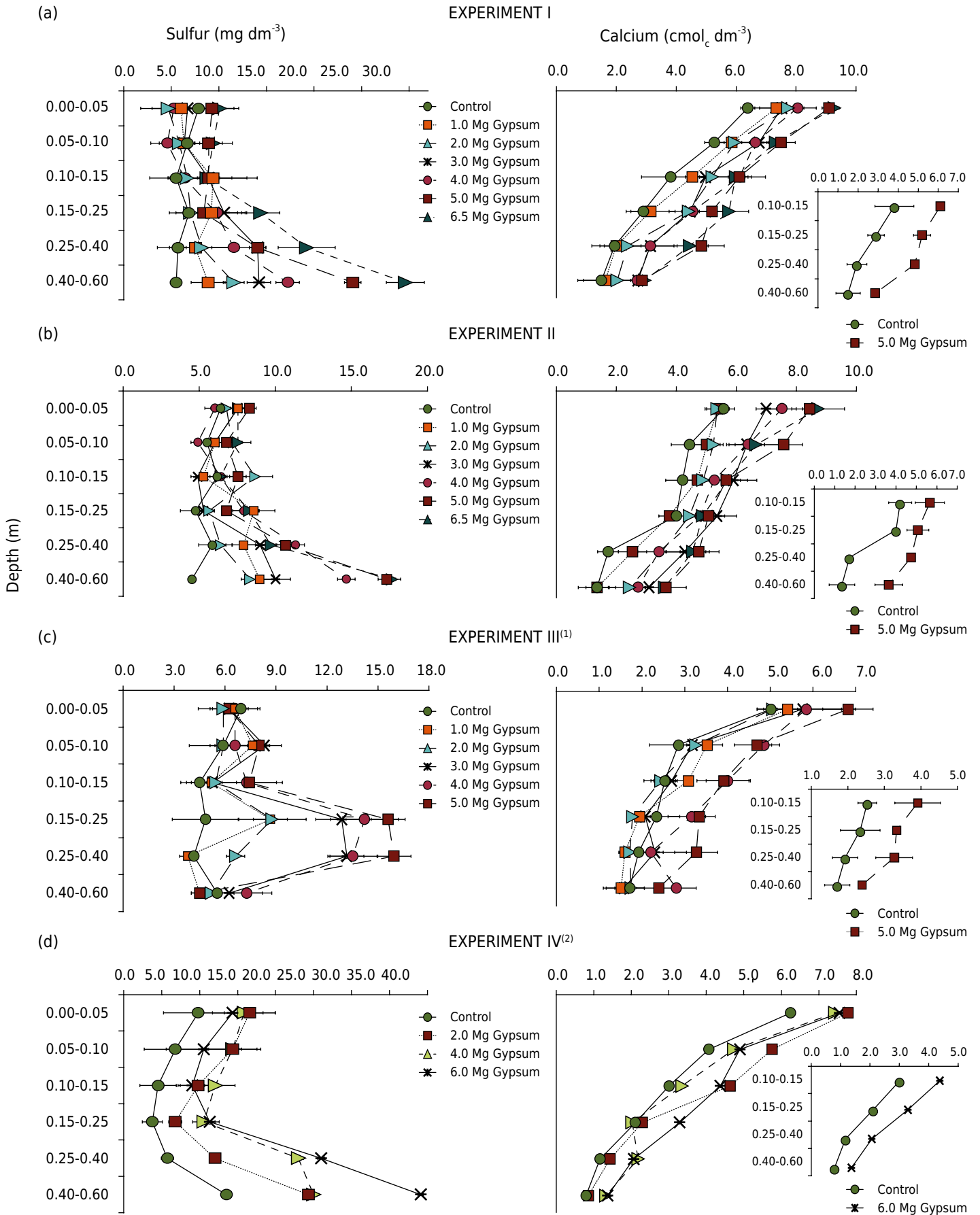
Figure 2. Effect of gypsum rates on calcium and sulfur in experiment I at 56 months after application of treatment (a), in experiment II at 56 months (b), in experiment III at 30 months (c), and experiment IV at 30 months (d). [1] Average of sulfur and calcium among treatments with lime, and the treatments that did not receive inputs due to the significant interaction between rates of gypsum and lime. [2] Averages of sulfur and calcium for gypsum rates combined with 3.6 Mg ha^{-1} of lime due to the interaction between rates of gypsum and lime. Error bars represent 95 % confidence limits for the average.

0.00-0.20 m soil layer. The SO_4^{2-}-S content in the topsoil layer had a significant (p<0.05) increase only in the treatment with the highest gypsum rate, except for experiment IV, in which all gypsum treatments had higher SO_4^{2-}-S content than the control. These results are similar to those previously reported by Caires et al. (2011a), who did not observe increases in SO_4^{2-}-S in the 0.00-0.10 m topsoil layer even with 9.0 Mg ha^{-1} of gypsum input. According to these authors, a long time period after application, the presence of negative charges on soil colloids, and high cumulative volume of rainfall were associated with intense downward mobility of SO_4^{2-}-S. Thus, in this study, the increase in SO_4^{2-}-S content in the topsoil layer after gypsum input was observed only for the short term.

In experiment I, there were increases in SO_4^{2-}-S content of 147.2 % (0.25-0.40 m) and 338.2 % (0.40-0.60 m) 56 months after input of 5.0 Mg ha^{-1} of gypsum, compared to the control. In experiment II, these increases were 84.5 % (0.25-0.40 m) and 284.4 % (0.40-0.60 m) (Figure 2b). The increases in SO_4^{2-}-S content in experiment IV, with a gypsum rate of 6.0 Mg ha^{-1} combined with lime, 30 months after the input, were 356.1 % (0.25-0.40 m) and 189.6 % (0.40-0.60 m). The increase in SO_4^{2-}-S content in deeper layers of the soil profile after gypsum application has generally been reported in other studies with Oxisols (Quaggio et al., 1993; Caires et al., 2011a; Rampim et al., 2011; Pauletti et al., 2014). In a recent study in a clayey Oxisol in the state of Paraná, Pauletti et al. (2014) reported an increase in SO_4^{2-}-S content in the 0.80-1.00 m depth layer already at 30 months after 12.0 Mg ha^{-1} gypsum input. Improvement in soil structure and an increase in the infiltration rate after gypsum application has been reported in studies conducted in the United States (Torbert and Watts, 2014; Watts and Dick, 2014). This result was associated with an increase in Ca^{2+} content, which enhances soil aggregation (Shainberg et al., 1989) and development of the plant root system in deep soil layers. This improvement in soil hydrophysical properties may contribute to the vertical mobility of SO_4^{2-}-S in the soil profile.

In experimental site III, increases in SO_4^{2-}-S content, with a gypsum rate of 5.0 Mg ha^{-1} 30 months after application, were 271.4 % (0.15-0.25 m) and 189.1 % (0.25-0.40 m), compared to the control (Figure 2c). In area III, this increase in SO_4^{2-}-S content occurred to a lesser degree compared to the other experimental areas (Table 3), probably due to the high clay content and low pH and low SO_4^{2-}-S content (Quaggio et al., 1993; Caires et al., 2003). These conditions favor chemical adsorption of anions such as SO_4^{2-}-S in positively charged clay minerals and are contrary to its downward movement (Pozza et al., 2007).

Experiments I and II, 56 months after lime and gypsum application, and experiments III and IV, 30 months after, showed increases in Ca^{2+} content throughout the soil profile. This result can be attributed to formation of the ion pair $CaSO_4^0$, which has a neutral charge, and since it is not attracted by the negative charges on the surface of clay minerals, it enhances the downward movement in the soil profile along with water flow (O'Brien and Sumner, 1988; Sumner, 1995; Nava et al., 2012). Therefore, the application of gypsum alone in soils with high chemical quality, or combined with lime in acid soils, was an efficient alternative for improving the NTS in the state of RS.

The increases in Ca^{2+} content in the 0.00-0.05 m layer with a gypsum rate of 5.0 Mg ha^{-1} were 42.2, 50.0, and 36.4 % for experiments I, II, and III, respectively, compared to the control treatment. The increase in Ca^{2+} content in the 0.00-0.05 m layer in experiment IV, with a gypsum rate of 6.0 Mg ha^{-1} combined with the lime, was 20.1 % in relation to the control (Figure 2d). In contrast, the increases in Ca^{2+} content in the subsurface layers with at a gypsum rate of 5.0 Mg ha^{-1} were 152.3 and 90.0 % in experiment I (Figure 2a), 175.6 and 170.3 % in experiment II (Figure 2b), and 68.4 and 41.2 % in experiment III (Figure 2c) in the 0.25-0.40 and 0.40-0.60 m layers, respectively, compared to the control. In experiment IV, the increases in Ca^{2+} content in the 0.25-0.40 and 0.40-0.60 m subsurface layers, at a gypsum rate of 6.0 Mg ha^{-1} combined with lime, were 75.0 and 71.2 % (Figure 2d), respectively, compared to the control. These results confirm the

role of gypsum in increasing Ca^{2+} content, most notably in the Oxisol subsurface layers managed under the NTS, in agreement with Rampim et al. (2011), who reported increases in Ca^{2+} content to a depth of 0.40 m six months after gypsum application rates up to 5.0 Mg ha^{-1} in an Oxisol.

This increase in Ca^{2+} content in the RZ is important, especially in the deepest and more acidic layers, due to its role in enhancing root growth by stimulating cell division (Hawkesford et al., 2012). The Ca^{2+} needs to be in the soil solution near root tips, since its uptake is almost exclusively in the root cap (Taiz and Zeiger, 2009). In addition, Ca^{2+} is practically immobile in the phloem, so its uptake by the roots in topsoil does not meet the demand for root growth in deeper soil layers (Taiz and Zeiger, 2009). In our study, high rates of gypsum alone (5.0 Mg ha^{-1}) (Experiments I, II, and III) or combined with lime (6.0 Mg ha^{-1} of gypsum + 3.6 Mg ha^{-1} of lime) (Experiment IV) were required to increase Ca^{2+} content in deep soil layers (Figure 2). This result is associated with higher SO_4^{2-}-S leaching and accumulation in these deep layers. Thus, improvement in chemical properties in subsoil with application of gypsum and lime will be achieved under high rates; i.e., lower rates of gypsum and lime application in clay Oxisols from RS did not result in improvement in deeper layers (Figure 2).

Temporal evolution of soil chemical properties in the RZ by gypsum and lime input

Interaction ($p<0.05$) between the time period since gypsum and lime application and BS, Ca^{2+} saturation, and Al^{3+} saturation was observed in all four experiments investigated. The gypsum rates selected for experiments I, II, and III were 3.0 (b) and 5.0 Mg ha^{-1} (c) (Figures 3, 4, and 5). The temporal effect of gypsum combined with lime in experiment IV was characterized in selecting the treatments with 6.0 Mg ha^{-1} of gypsum, and 6.0 Mg ha^{-1} of gypsum combined with 3.6 Mg ha^{-1} of lime (Figure 6).

As expected, the temporal effect in the control treatment caused only minor changes in the BS, Ca^{2+} saturation, and Al^{3+} saturation properties, regardless of the experiment (Figures 3, 4, 5, and 6). Therefore, 54 months after implementation of the experiments, there was little increase in Al^{3+} saturation in experiments I (Figure 3c) and II (Figure 4c). This result may be attributed to the natural process of soil acidification, the low rates of lime (2 Mg ha^{-1}), and the long time elapsed (four years) before implementation of the experiments. Similar results were presented by Caires et al. (2005), who reported a decrease in pH after 10 years without liming, followed by an increase in Al^{3+} saturation, in an Oxisol.

In experiment I, the treatment with a gypsum rate of 5.0 Mg ha^{-1}, the temporal effect exhibited a quadratic response to BS (Figure 3a) and Ca^{2+} saturation (Figure 3b) in the 0.00-0.05, 0.05-0.10, and 0.10-0.15 m layers (Figure 2a). This quadratic response suggests that the gypsum effect reaches a maximum point and then decreases after a certain time. The maximum effect in increasing BS decreased after 30 (0.00-0.05 m), 23 (0.05-0.10 m), and 27 (0.10-0.15 m) months after gypsum application (Figure 3a). In part, this result can be attributed to dislocation of Ca^{2+} from the topsoil to deeper soil layers (Caires et al., 2011a; Dalla Nora and Amado, 2013; Pauletti et al., 2014). The intermediate gypsum rate did not affect BS in layers below 0.15 m.

The Al^{3+} saturation (Figure 3c) was affected only in the 0.40-0.60 m layer ($p<0.05$) at an intermediate gypsum rate. The effect of gypsum on this deep soil layer was due to SO_4^{2-}-S accumulation in the layer (Figure 2a), carrying the Ca^{2+} ion with it (Figure 2b). That way, the participation of Al^{3+} in the CEC in the subsoil was reduced, due to an increase in Ca^{2+} content in this layer (Caires et al., 2011a). According to the equation fitted, the most pronounced effect was at 32 months after gypsum application, resulting in a decrease of 32.8 % in Al^{3+} saturation compared to time zero. This pronounced effect in the deepest layer of the soil profile is probably associated with the high rainfall volume (5,892 mm)
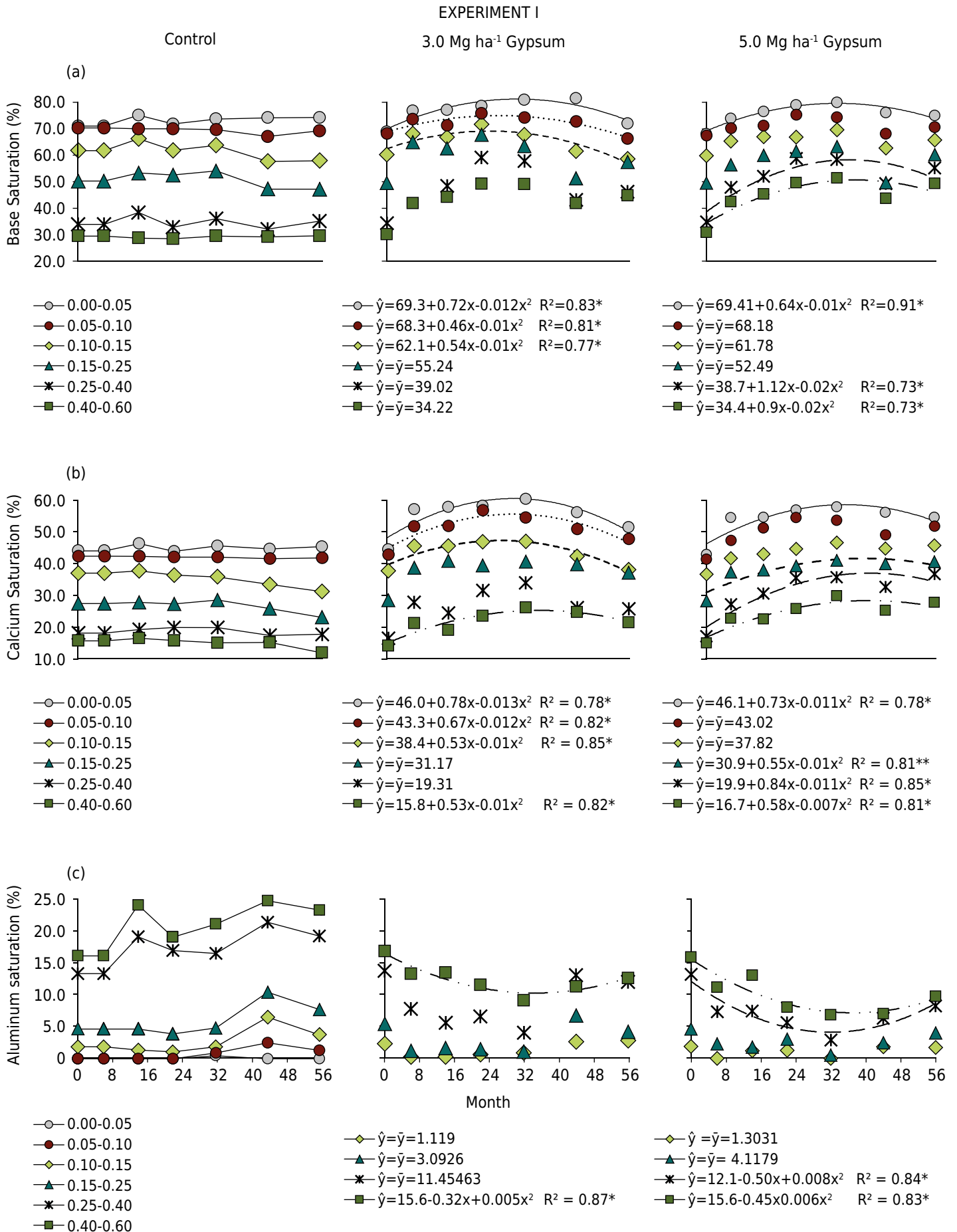
EXPERIMENT I

Control   3.0 Mg ha⁻¹ Gypsum   5.0 Mg ha⁻¹ Gypsum

(a)

Base Saturation (%)

— 0.00-0.05
— 0.05-0.10
— 0.10-0.15
— 0.15-0.25
— 0.25-0.40
— 0.40-0.60

3.0 Mg ha⁻¹ Gypsum:
- $\hat{y}=69.3+0.72x-0.012x^2$ $R^2=0.83*$
- $\hat{y}=68.3+0.46x-0.01x^2$ $R^2=0.81*$
- $\hat{y}=62.1+0.54x-0.01x^2$ $R^2=0.77*$
- $\hat{y}=\bar{y}=55.24$
- $\hat{y}=\bar{y}=39.02$
- $\hat{y}=\bar{y}=34.22$

5.0 Mg ha⁻¹ Gypsum:
- $\hat{y}=69.41+0.64x-0.01x^2$ $R^2=0.91*$
- $\hat{y}=\bar{y}=68.18$
- $\hat{y}=\bar{y}=61.78$
- $\hat{y}=\bar{y}=52.49$
- $\hat{y}=38.7+1.12x-0.02x^2$ $R^2=0.73*$
- $\hat{y}=34.4+0.9x-0.02x^2$ $R^2=0.73*$

(b)

Calcium Saturation (%)

— 0.00-0.05
— 0.05-0.10
— 0.10-0.15
— 0.15-0.25
— 0.25-0.40
— 0.40-0.60

3.0 Mg ha⁻¹ Gypsum:
- $\hat{y}=46.0+0.78x-0.013x^2$ $R^2 = 0.78*$
- $\hat{y}=43.3+0.67x-0.012x^2$ $R^2 = 0.82*$
- $\hat{y}=38.4+0.53x-0.01x^2$ $R^2 = 0.85*$
- $\hat{y}=\bar{y}=31.17$
- $\hat{y}=\bar{y}=19.31$
- $\hat{y}=15.8+0.53x-0.01x^2$ $R^2 = 0.82*$

5.0 Mg ha⁻¹ Gypsum:
- $\hat{y}=46.1+0.73x-0.011x^2$ $R^2 = 0.78*$
- $\hat{y}=\bar{y}=43.02$
- $\hat{y}=\bar{y}=37.82$
- $\hat{y}=30.9+0.55x-0.01x^2$ $R^2 = 0.81**$
- $\hat{y}=19.9+0.84x-0.011x^2$ $R^2 = 0.85*$
- $\hat{y}=16.7+0.58x-0.007x^2$ $R^2 = 0.81*$

(c)

Aluminum saturation (%)

Month

— 0.00-0.05
— 0.05-0.10
— 0.10-0.15
— 0.15-0.25
— 0.25-0.40
— 0.40-0.60

3.0 Mg ha⁻¹ Gypsum:
- $\hat{y}=\bar{y}=1.119$
- $\hat{y}=\bar{y}=3.0926$
- $\hat{y}=\bar{y}=11.45463$
- $\hat{y}=15.6-0.32x+0.005x^2$ $R^2 = 0.87*$

5.0 Mg ha⁻¹ Gypsum:
- $\hat{y}=\bar{y}=1.3031$
- $\hat{y}=\bar{y}= 4.1179$
- $\hat{y}=12.1-0.50x+0.008x^2$ $R^2 = 0.84*$
- $\hat{y}=15.6-0.45x0.006x^2$ $R^2 = 0.83*$

Figure 3. Time effect of the rates of 0.0, 3.0, and 5.0 Mg ha⁻¹ of gypsum on Ca saturation (a), base saturation (b), and Al saturation (c) for Experiment I. * and **: significant at 5 and 1 % probability of error, respectively.
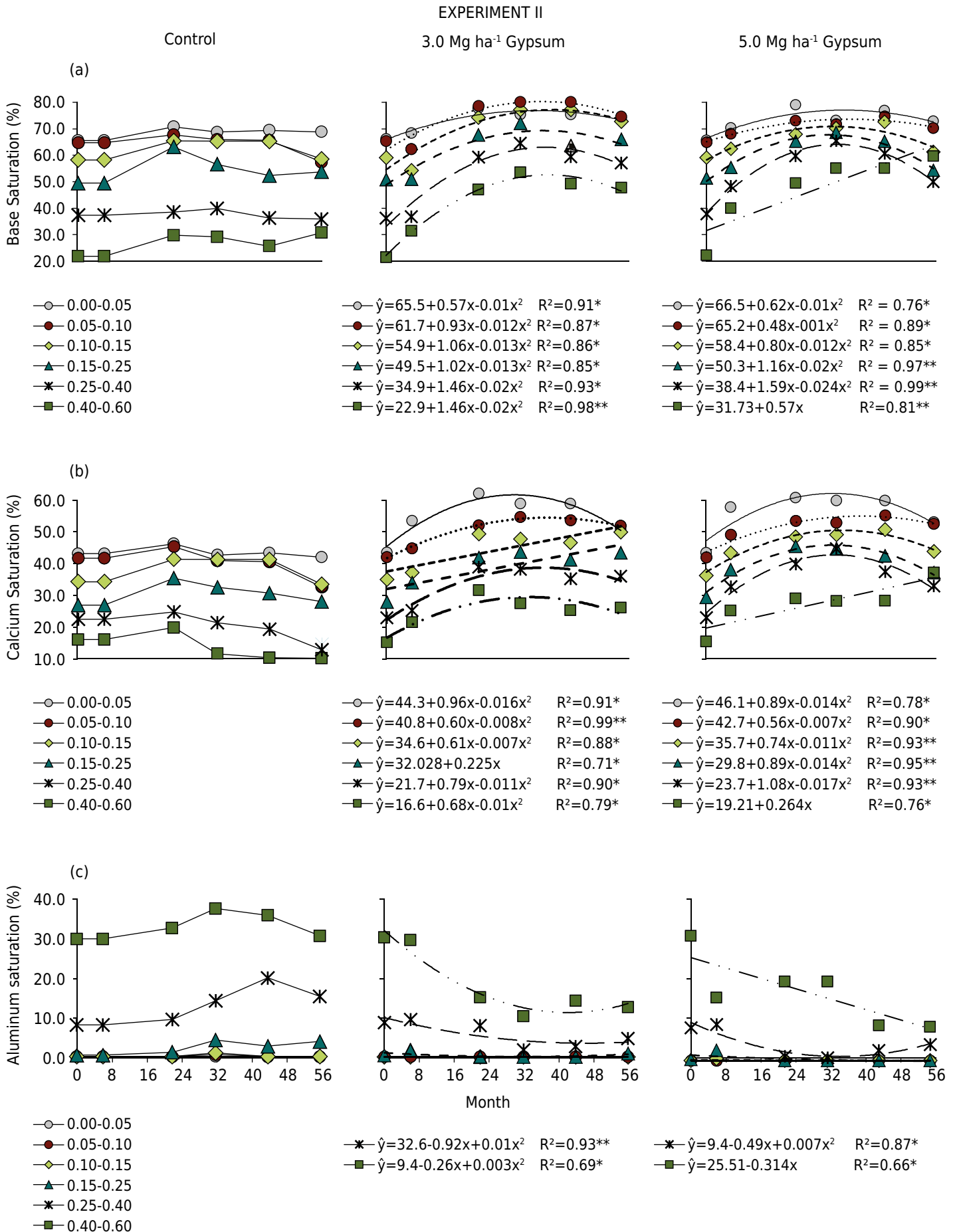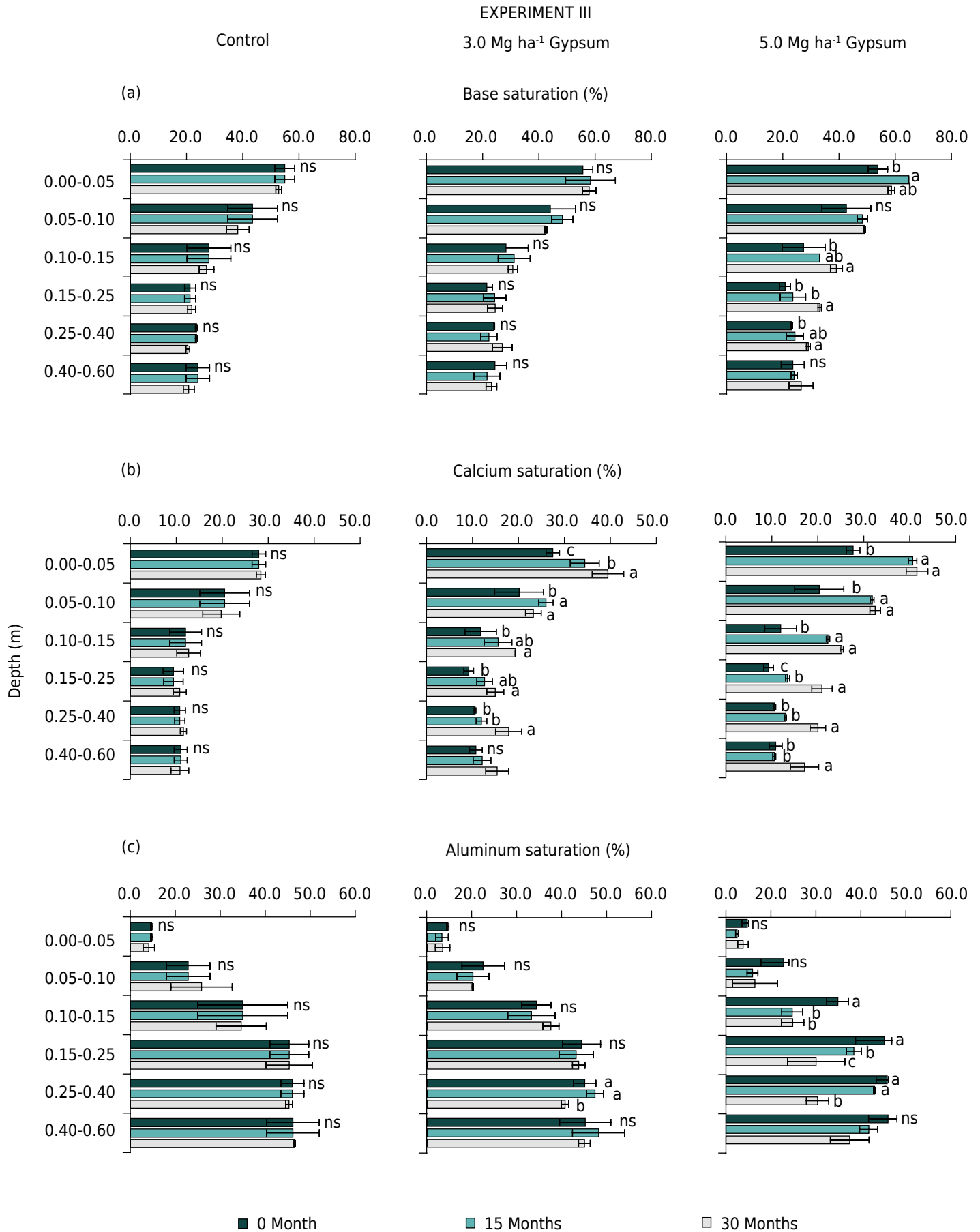
EXPERIMENT II

Figure 4. Time effect of the rates of 0.0, 3.0, and 5.0 Mg ha^{-1} of gypsum on Ca saturation (a), base saturation (b), and Al saturation (c) for Experiment II. [*] and [**]: significant at 5 and 1 % probability of error, respectively.

Figure 5. Time effect of the rates of 0.0, 3.0, and 5.0 Mg ha^{-1} of gypsum on calcium saturation (a), base saturation (b), and aluminum saturation (c) for Experiment III. [ns]: not significant at 5 % probability of error; the same letters on the bars for the same depth do not differ significantly at 5 % probability of error.

during this 32-month period (Figure 1). In addition, gypsum increased SO_4^{2-}-S concentration and promoted formation of the ion pair $AlSO_4^0$ and, above all, increased Ca^{2+} saturation in the subsoil. The soil with the gypsum treatment of 5.0 Mg ha^{-1} exhibited increases in BS (p<0.05) and Ca^{2+} saturation (p<0.05), especially in the deepest layers (0.25-0.40 and 0.40-0.60 m). The decrease in Al^{3+} saturation in these two layers followed the quadratic response, with decreases of 35.4 and 45.9 %, respectively, compared to time zero. Furthermore, the maximum effect on those layers was reached at 32.0 and 37.5 months after gypsum application, respectively (Figure 3c). In short, for this experimental area, the highest gypsum rate induced an improvement in the deepest layers and lasted for a longer time.

Experimental area II had more pronounced changes in chemical properties induced by gypsum application than experimental area I. This result can be explained by the lower clay content, higher SO_4^{2-}-S content, higher pH, and lower Al^{3+} saturation at implementation of the experiment (Table 3). In the treatment with the gypsum rate of 3.0 Mg ha^{-1}, an increase in BS and Ca^{2+} saturation over time was observed throughout the soil profile, with a quadratic response for most of the soil layers investigated. The increases in BS and Ca^{2+} saturation after 35.5 months in the 0.40-0.60 m layer were 46.3 and 59.0 %, respectively, compared to time zero. Similarly, Al^{3+} saturation followed the quadratic response, with decreases of 37.6 % (after 46 months) and 42.9 % (after 43 months) in the 0.25-0.40 and 0.40-0.60 m depth layers (Figure 4c), respectively.

In experiment II, with a gypsum rate of 5.0 Mg ha^{-1}, Al^{3+} saturation in the 0.40-0.60 m layer showed a linear decrease in response to application time, suggesting that in soils with better chemical quality in the topsoil layer, the effect of gypsum input is greater, lasts for a longer period of time (Figure 4c), and reaches deeper soil layers (Raij, 2010; Caires, 2011a). Thus, increases in BS of 63.7 % (Figure 4a) and in Ca^{2+} saturation of 56.5 % (Figure 4b), and a decrease in Al^{3+} saturation of 322.0 % (Figure 4c) were observed in the 0.40-0.60 m depth layer 56 months after gypsum application, compared to time zero. Caires et al. (2011b) reported that gypsum application in an Oxisol without the presence of Al^{3+} promotes a rapid effect on movement of bases.

Experiments I and II showed temporal evolution of chemical properties in a more detailed way (six soil samplings) after gypsum application than the other experiments. Although some improvement in chemical quality of the RZ was already observed six months after gypsum application, it was more noticeable after 32 months, when accumulated rainfall reached 5,635 mm. Therefore, improvement in the deepest layers required a longer time and higher application rates.

The soil of experimental area III had the lowest chemical quality in relation to the other sites investigated, expressed by higher acidity levels in the RZ (Table 3). No increase in BS in any of the soil layers sampled was observed at 15 and 30 months after gypsum application (3.0 Mg ha^{-1}) (Figure 5a). This result reinforces that, for acidic soils, there is the need for lime combined with gypsum input in order to increase the BS. In studies conducted by Caires et al. (2008), the authors found movement of bases through high application rates of lime, with frequent reapplications. However, the application of gypsum accelerates the nutrient leaching process for the deeper soil layers (Dalla Nora et al., 2014).

Gypsum input provided for a gradual increase in Ca^{2+} saturation, and after 30 months, this effect was noted in all layers up to the 0.40 m depth compared to time zero (Figure 5b). The increase in Ca^{2+} content throughout the RZ provided by gypsum application in acidic soils is an important result, since lime applied on the surface seldom offers improvement in deep layers (Bortoluzzi et al, 2014; Dalla Nora, et al, 2014.). Nevertheless, Oliveira and Pavan (1996), Caires et al. (2008), and Caires (2013) reported an increase in Ca^{2+} content a long time after high rates of lime application on the surface or through application of lime on already amended soil. According to those authors, surface lime application on already improved soil could enhance the vertical movement of fine lime particles in the

soil profile. A decrease in Al^{3+} saturation (14.3 %) was observed only in the 0.25-0.40 m layer ($p<0.05$) 30 months after gypsum application (Figure 5c). This layer exhibited the largest increase in SO_4^{2-}-S content (Figure 2c), probably favoring the formation of $AlSO_4^+$, which is displaced to deeper layers (Raij, 2010).

The gypsum rate of 5.0 Mg ha^{-1} promoted increases in BS ($p<0.05$) in all layers, except in the 0.05-0.10 and 0.40-0.60 m at 30 months after application, with the most pronounced increases in the 0.15-0.25 (59.5 %) and 0.25-0.40 m (26.2 %) layers compared to time zero (Figure 5a). However, no increases in BS were observed 15 months after application in any layer, compared to time zero. These results suggest that increasing BS in acidic soils by gypsum applications requires a high rate (5.0 Mg ha^{-1}) and a medium term (30 months). This treatment also increased Ca^{2+} saturation ($p<0.05$) in the whole soil profile (Figure 5b), results similar to those observed in experiments I and II. Increases in the surface layers (0.00-0.05, 0.05-0.10, and 0.10-0.15 m) were observed after 15 months, reaching the deepest layers after 30 months, with increases of 126.8 % (0.15-0.25 m), 87.8 % (0.25-0.40 m), and 57.7 % (0.40-0.60 m). A pronounced decrease in Al^{3+} saturation was observed in the 0.10-0.15, 0.15-0.25, and 0.25-0.40 m layers (Figure 5c), which had the highest Al^{3+} content. This decrease was 68.4 % (0.10-0.15 m), 76.2 % (0.15-0.25 m), and 76.3 % (0.25-0.40 m) at 30 months after application, compared to time zero. These 0.15-0.25 and 0.25-0.40 m layers exhibited the highest increases in SO_4^{2-}-S content (Figure 2c).

In experiment IV, the treatment with the gypsum rate of 6.0 Mg ha^{-1} increased the BS compared to time zero ($p<0.05$) from the 0.10-0.15 m layer to the deepest layer investigated at 30 months after application (Figure 6a), and the most pronounced increases were observed in the 0.15-0.25 m (38.5 %) and 0.25-0.40 m (50.7 %) layers. This result was probably related to the sharply defined transition in chemical quality at the beginning of the experiment, exhibiting satisfactory quality in the 0.00-0.10 m layer and low quality in the others. Increases in Ca^{2+} saturation were observed, as in the other experiments, throughout the soil profile at 30 months after gypsum application, except in the deepest layer (Figure 6b), with increases of 146.7 % in the 0.15-0.25 m layer and 188.3 % in the 0.25-0.40 m layer compared to time zero. The Al^{3+} saturation was practically zero up to 0.15 m at 30 months after gypsum input, and decreases were observed in the 0.25-0.40 m (30.5 %) and 0.40-0.60 m (20.1 %) layers compared to time zero (Figure 6c). Therefore, based on the results found in experiments II and IV, the effect of gypsum in increasing BS and Ca^{2+} saturation and decreasing Al^{3+} saturation was enhanced when the shallow soil layer had high quality at the beginning of the experiment. This result supports the general recommendation for acidic soils of first applying lime for the purpose of improving the chemical quality of the topsoil layer of the NTS, and after this improvement, applying gypsum to improve the chemical quality of the subsoil layers.

The treatment with 6.0 Mg ha^{-1} of gypsum combined with 3.6 Mg ha^{-1} of lime at 30 months after application showed increases in BS ($p<0.05$) throughout the soil profile, except in the 0.00-0.05 m layer, which was already slightly higher than 80 % at the beginning of the experiment (Figure 6a). The 0.25-0.40 and 0.40-0.60 m soil layers had increases of 141.4 and 144.7 %, respectively, compared to time zero. The Ca^{2+} saturation had a pronounced increase ($p<0.05$) in the RZ (0.00-0.40 m) (Figure 6b), with increases of 136.3 % (0.25-0.40 m) and 152.0 % (0.40-0.60 m) compared to time zero. However, Ca^{2+} saturation increases were similar in the treatments of gypsum applied alone and of gypsum combined with lime. Decreases in Al^{3+} saturation were observed ($p<0.05$) in all layers evaluated, and Al^{3+} was fully neutralized up to a depth of 0.15 m (Figure 6c). In addition, the 0.15-0.25, 0.25-0.40, and 0.40-0.60 m layers had Al^{3+} saturation decreases of 228.2, 47.7, and 34.0 %, respectively. Therefore, decreases in Al^{3+} saturation in subsurface layers were more pronounced when gypsum was combined with lime compared to when gypsum was applied alone.
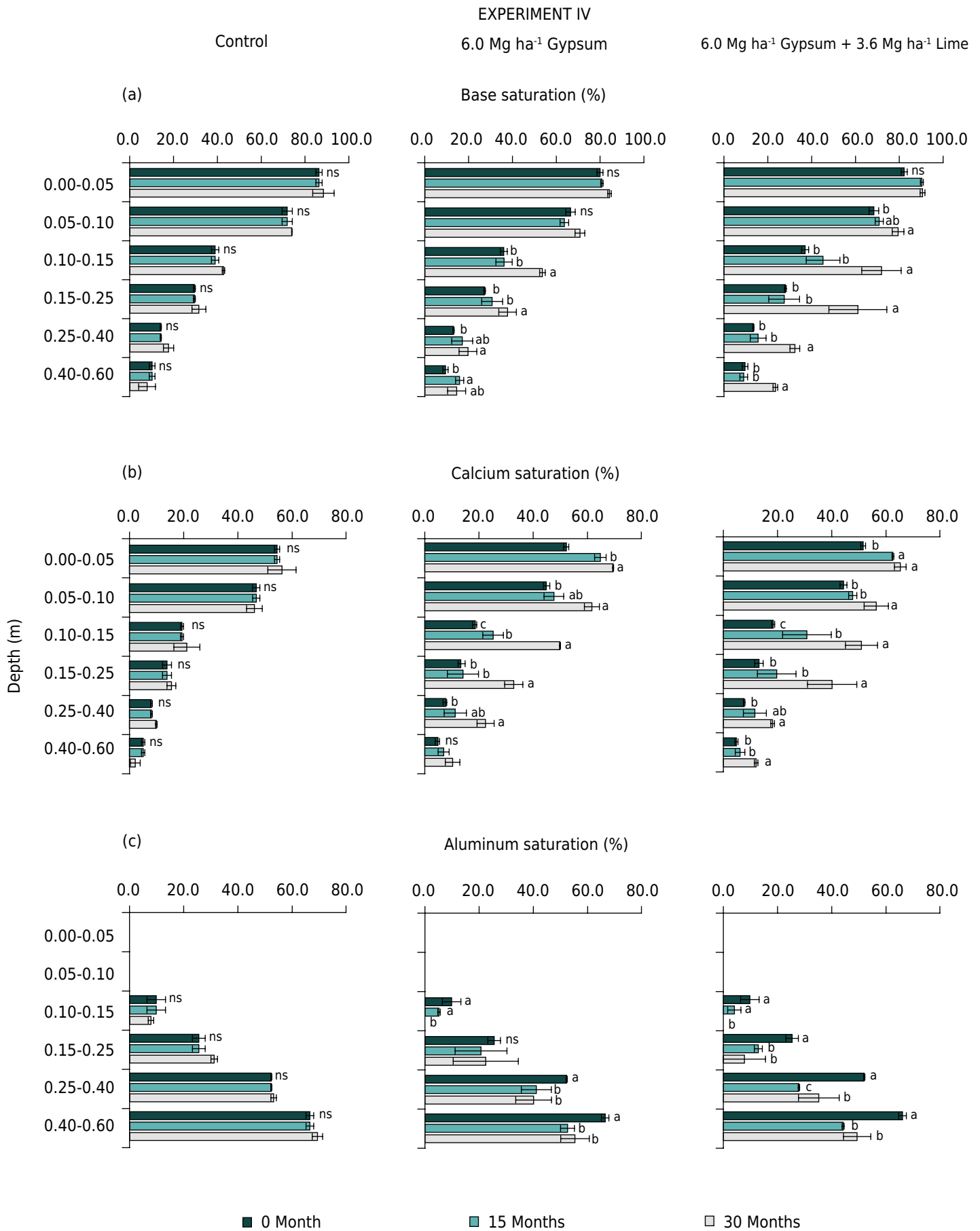
EXPERIMENT IV

Control

6.0 Mg ha^{-1} Gypsum

6.0 Mg ha^{-1} Gypsum + 3.6 Mg ha^{-1} Lime

Figure 6. Time effect of the rates of 0.0 Mg ha^{-1} of gypsum, 6.0 Mg ha^{-1} of gypsum, and 6.0 Mg ha^{-1} of gypsum + 3.6 Mg ha^{-1} of lime on calcium saturation (a), base saturation (b), and aluminum saturation (c) for Experiment IV. ^{ns}: not significant at 5 % probability of error; the same letters on the bars for the same depth do not differ significantly at 5 % probability of error.

In our study, intermediate rates of gypsum (3.0 Mg ha^{-1}) alone did little to improve soil chemical properties over time. However, higher rates of gypsum alone (experiments I, II, and III) or gypsum combined with lime (experiment IV) resulted in an improvement in soil chemical properties throughout the RZ. In experiment I, the most pronounced effect was observed in deep layers at 30 months after the application of 5.0 Mg ha^{-1} of gypsum (Figure 3). As for experiment II, the most pronounced effect in increasing BS and Ca^{2+} saturation, in addition to a decrease in Al^{3+} saturation, was noted in the 0.40-0.60 m layer at 56 months after the chemical inputs (Figure 4). This result was associated with the lower clay content and better chemical properties of experiment II compared to I (Table 3), accelerating downward movement of the Ca^{2+} ion in the RZ. Experiment III, which had the lowest chemical quality among the sites investigated (Table 3), showed an increase in BS and reduction in Al^{3+} saturation in the 0.25-0.40 m layer (Figure 5) at 30 months after input of 5.0 Mg ha^{-1} of gypsum. For experiment IV (Figure 6) greater increases in Ca^{2+} saturation and BS, and a decrease in Al^{+3} saturation was observed at 30 months after combined input of gypsum and lime, highlighting the synergistic effect of these inputs.

The positive effect of lime interaction with gypsum on improving soil chemical properties was also reported by studies conducted in Oxisols (Caires et al., 2008; Raij, 2010; Dalla Nora et al., 2014; Pauletti et al., 2014). The condition of a sharply defined chemical quality gradient from the surface toward the deepest layers, as observed in experiment IV, has frequently been reported in soils managed under long-term NTS with surface lime application (Bortoluzzi et al., 2014). In order to resolve this problem, temporarily interrupting the NTS through conventional tillage (CT) for the purpose of lime incorporation in the RZ and promotion of vertical redistribution of immobile nutrients has been recommended (CT) (Bortoluzzi et al., 2014). In the four experiments investigated in the present study, the chemical quality gradient in the RZ was mitigated by surface application of gypsum alone, especially under the condition of high chemical quality of topsoil, and an even more pronounced effect was achieved through combined application with lime, avoiding interruption in the NTS, which could deplete soil organic matter, decrease soil aggregation, and interrupt the continuity of the pore system.

The downward movement of bases in the soil profile, induced by gypsum combined with lime or gypsum alone, was related to total rainfall (Figure 1). Therefore, complementary soil management practices that improve soil hydrophysical properties that govern water infiltration rate, such as SOM content, biological pores, macro aggregates, and soil cover, are important for enhancing the effect of gypsum and lime in improving subsoil layers under a continuous NTS (Shainberg et al., 1989; Torbert and Watts, 2014; Watts and Dick, 2014).

CONCLUSIONS

Surface application of gypsum increases Ca^{2+} content and decreases Al^{3+} saturation throughout the soil profile in proportion to the application rate, especially in the rooting zone (0.00-0.40 m). This improvement was associated with downward movement of SO$_4^{2-}$-S in the soil profile. High chemical quality in the topsoil accelerated and intensified the subsoil improvement process induced by gypsum application.

The maximum effect of gypsum input in improving chemical quality was observed in a period exceeding 30 months, lasting for up to 54 months. The increase in BS and decrease in Al^{3+} saturation in subsoil are enhanced by combination with lime or by applying a high rate of gypsum (5.0 Mg ha^{-1}) alone.

The combination of lime with gypsum exhibited a complementary effect and was more efficient than applying gypsum alone. In this case, the gradient of chemical properties in the rooting zone of a dystrophic Oxisol was mitigated, avoiding the discontinuity of the no-tillage system.

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