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Do Rates and Splitting of Phosphogypsum Applications Influence the Soil and Annual Crops in a No-Tillage System?

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ABSTRACT: Applications of phosphogypsum (PG) provide nutrients to the soil and reduce Al^{3+} activity, favoring soil fertility and root growth, but allow Mg^{2+} mobilization through the soil profile, resulting in variations in the PG rate required to achieve the optimum crop yield. This study evaluated the effect of application rates and splitting of PG on soil fertility of a Typic Hapludox, as well as the influence on annual crops under no-tillage. Using a (4 × 3) + 1 factorial structure, the treatments consisted of four PG rates (3, 6, 9, and 12 Mg ha^{-1}) and three split applications (P1 = 100 % in 2009; P2 = 50+50 % in 2009 and 2010; P3 = 33+33+33 % in 2009, 2010 and 2011), plus a control without PG. The soil was sampled six months after the last PG application, in stratified layers to a depth of 0.8 m. Corn, wheat and soybean were sown between November 2011 and December 2012, and leaf samples were collected for analysis when at least 50 % of the plants showed reproductive structures. The application of PG increased Ca^{2+} concentrations in all sampled soil layers and the soil pH between 0.2 and 0.8 m, and reduced the concentrations of Al^{3+} in all layers and of Mg^{2+} to a depth of 0.6 m, without any effect of splitting the applications. The soil Ca/Mg ratio increased linearly to a depth of 0.6 m with the rates and were found to be higher in the 0.0-0.1 m layer of the P2 and P3 treatments than without splitting (P1). Sulfur concentrations increased linearly by application rates to a depth of 0.8 m, decreasing in the order P3>P2>P1 to a depth of 0.4 m and were higher in the treatments P3 and P2 than P1 between 0.4-0.6 m, whereas no differences were observed in the 0.6-0.8 m layer. No effect was recorded for K, P and potential acidity (H+Al). The leaf Ca and S concentration increased, while Mg decreased for all crops treated with PG, and there was no effect of splitting the application. The yield response of corn to PG rates was quadratic, with the maximum technical efficiency achieved at 6.38 Mg ha^{-1} of PG, while wheat yield increased linearly in a growing season with a drought period. Soybean yield was not affected by the PG rate, and splitting had no effect on the

yield of any of the crops. Phosphogypsum improved soil fertility in the profile, however, Mg^{2+} migrated downwards, regardless of application splitting. Splitting the PG application induced a higher Ca/Mg ratio in the 0.0-0.1 m layer and less S leaching, but did not affect the crop yield. The application rates had no effect on soybean yield, but were beneficial for corn and, especially, for wheat, which was affected by a drought period during growth.

Keywords: calcium sulfate, calcium/magnesium ratio, grain yield.

INTRODUCTION

Brazilian agriculture has an outstanding grain production, achieved by technologies that maximize the yield potential, such as the implementation of no-tillage (NT) systems. Since the introduction in the 1970s (Derpsch and Friedrich, 2009), NT proved to be more than a set of practices that ensure minimum soil disturbance, soil mulching with crop residues and control of soil erosion. The system improves the soil quality as a whole, favoring yield and allowing greater resource use efficiency (e.g. of soil, fertilizers and fuel), which has promoted the expansion of NT across the country. Currently, in Brazil, an acreage of nearly 32 million hectares is being managed in NT systems (FAO, 2012).

To establish well-nourished crops, the soil must retain water and nutrients in readily available forms for uptake, and no limiting factors of soil chemistry, physics and biology may stress the crop (Klein, 2011). In agriculture, short-term stresses during critical stages of the plant life cycle can greatly affect the yield of staple crops, especially due to the high precocity of current varieties. In spite of knowing NT since the 1970s, many farmers now restrict this practice to "direct seeding on crop residues" rather than applying the complete "no-tillage management system" with principles of conservation agriculture. This has affected the soil, resulting in stratified properties; satisfactory chemical conditions tend to be restricted to the topsoil, while compaction increases in the subsurface layers, intensifying the cropping problems resulting from the poor weather conditions in recent years (Denardin et al., 2008; Nunes et al., 2014).

Since in Brazil and other South American countries NT is used uninterruptedly, there is no periodic soil tillage, the accumulation of crop residues in the topsoil and the addition of lime and fertilizers to the surface intensifies soil stratification over time, leading to the accumulation of organic C and N (Ebeling et al., 2008; Venzke Filho et al., 2008), as well as P, K^+, Ca^{2+} and Mg^{2+} to depths of 0.0-0.10 m (Klein et al., 2007; Spera et al., 2011; Acqua et al., 2013; Kramer et al., 2014). Since the vertical mobility of lime is reduced in NT, the subsurface soil changes to a more acidic environment with higher concentrations of exchangeable aluminum (Al^{3+}) (Raij et al., 1998; Ernani et al., 2001), creating a chemical limitation to root growth.

Management strategies originally designed from the fundamentals of NT can minimize or mitigate the problems resulting from the vertical gradient of fertility in the soil; implementing crop diversification, reducing time between sowing and harvesting and the addition of crop residues in a manner compatible with the biological dynamics (Nunes et al., 2014) can all produce good results in the medium or long-term. Phosphogypsum (PG), on the other hand, even if applied to the soil surface, improves the chemical conditions in the soil profile for root growth, especially in deeper layers (Carvalho and Raij, 1997), after a few months (Caires et al., 2001, Rampim et al., 2011).

Due to its solubility and other specific reaction characteristics, PG ($CaSO_4.2H_2O$) moves throughout the soil profile releasing Ca^{2+} and sulfur (S) (Caires et al., 2006, 2011a; Soratto and Crusciol, 2008). Concomitantly, Mg^{2+} and K^+ – the latter only rarely – are displaced from the soil exchange sites in top layers and then move along with water to the subsurface (Caires et al., 2011b). In addition, a decrease in the Al^{3+} concentrations to levels not toxic

to plant roots can occur (Toma et al., 1999), due to the formation of ionic pairs between Al^{3+} and the sulfate (SO_4^{2-}) or fluoride (F^-) contained in PG (Zambrosi et al., 2007).

The application of PG proved effective in maximizing yields of *Poaceae* species under NT, especially those of corn (Raij et al., 1998; caires et al., 1999, 2004, 2011a; Toma et al., 1999) and wheat (Caires et al., 2002; Rashid et al., 2008). However, in most cases, no significant yield increases were observed in *Fabaceae* species, e g., in soybean (Nogueira and Melo, 2003; Caires et al., 2003, 2006, 2011a; Neis et al., 2010).

Although comprehensive information regarding the effects of gypsum on soil and plants is available, Brazil has not yet established criteria for recommending PG application rates, which can vary regionally and according to the local climate, soil order and crop. There are few available data regarding crop rotation systems, and no information about PG split-application rates, which is a common strategy for increasing the efficiency of fertilizers by reducing N and K fertilization losses (Cardoso et al., 2007).

The hypotheses of this study were that the higher availability of Ca^{2+} and S and the decrease in Al^{3+} in the soil due to PG application improve annual crop yields under long-term NT, and that PG split applications reduce the loss and, or, mobilization of S, Mg^{2+} and, or, K^+, especially at higher PG rates. The objective was to evaluate the effects of different PG rates and split applications on a Typic Hapludox chemical properties, nutrition and on yields of NT corn, wheat and soybean.

MATERIALS AND METHODS

This study was carried out between November 2011 and April 2013, as part of a long-term field trial established in 2009 at the Experimental Field of the West-Central State University, in Guarapuava, Paraná, where the climate (Köppen-Geiger System) is classified as Cfb, mesothermal humid subtropical. A meteorological station of the Agronomic Institute of Paraná (IAPAR), located 200 m away from the experimental site (25° 23' S, 51° 30' W and 1,026 m above sea level), was used to collect rainfall and temperature data throughout the experimental period, as well as long-term averages (Figure 1). In October 2009, a trench was dug for the morphological assessment of the soil and for soil sampling to determine the clay content (Claessen, 1997) and soil chemical properties (Pavan et al., 1992).

The profile (Table 1) was classified as very clayey *Latossolo Bruno Distrófico*, based on the Brazilian soil classification system (Santos et al, 2013), a Typic Hapludox (Soil Survey Staff, 2014). More information about the initial phase of the experiment was provided by Michalovicz (2012).

A randomized complete block design was used, with four replications and 16 × 6.4 m plots. The PG rates constituted the first treatment factor: 3, 6, 9, and 12 Mg ha^{-1} (dry-weight basis). The second treatment factor consisted of the split applications: P1 – without splitting, i.e., 100 % applied in November 2009; P2 – application split in two years, 50+50 % in November 2009 and 2010; and P3 – split amongst three years, 33+33+33 % in November 2009, 2010 and 2011. A control without PG was also part of the study, in a factorial arrangement (4 × 3) + 1. The Ca and S concentrations of PG were 170 and 140 g kg^{-1}, respectively, and the application rates were calculated to provide 0, 33, 66, 100, and 133 % of the required amount of Ca^{2+} in the A1 horizon (Table 1), so as to reach 60 % of Ca^{2+} saturation of the cation exchange capacity ($CEC_{pH\,7.0}$).

The factorial structure was complete when the final application of PG, the third 33 % portion in P3, was applied to the soil surface on November 15th, 2011, together with corn (P3646H®) sowing. The final plant density was 62,500 plants ha^{-1}, in a row spacing of 0.8 m, and the crop was fertilized with 300 kg ha^{-1} of 14-33-00 N-P-K fertilizer mixture, applied in the planting furrow. Side-dressing consisted of 45 kg ha^{-1} N (urea) and 54 kg ha^{-1} K_2O (KCl) at V4, plus 58 kg ha^{-1} N (urea) at V6. Wheat (OR Mirante®) was sown on July

20th, 2012, in a row spacing of 0.2 m and final plant density of 330 plants m-2. The crop was fertilized with 370 kg ha-1 of 05-20-20 N-P-K fertilizer mixture in the planting furrow and side-dressed with 40 kg ha-1 N (urea) during tillering. Soybean (Nidera 5909®) was sown on December 15th, 2012, in a row spacing of 0.4 m. Seeds were inoculated (*Bradyrhizobium* sp.) and 250 kg ha-1 of the 02-20-18 N-P-K fertilizer mixture was applied in the planting furrow. The final plant density was 325,000 plants ha-1.

Leaf tissue samples were collected from the central areas of each plot, when at least 50 % of the plants showed reproductive structures, i.e.: stage R1 for corn and soybean and 10.5 on the Feekes-Large scale for wheat. For each crop, specific leaves were sampled: for corn, the leaf opposite and under the ear, for soybean the third trefoil from the apex to the base and for wheat the flag leaf (CQFSRS/SC, 2004). The samples were rinsed in deionized water, dried in a forced-air oven at 60 °C to constant weight, ground in a Willey mill and sieved to pass through 0.75 mm mesh. The concentrations of P, K, Ca, Mg and S were determined by nitric digestion, and N by sulfuric digestion (Santos et al., 2009).
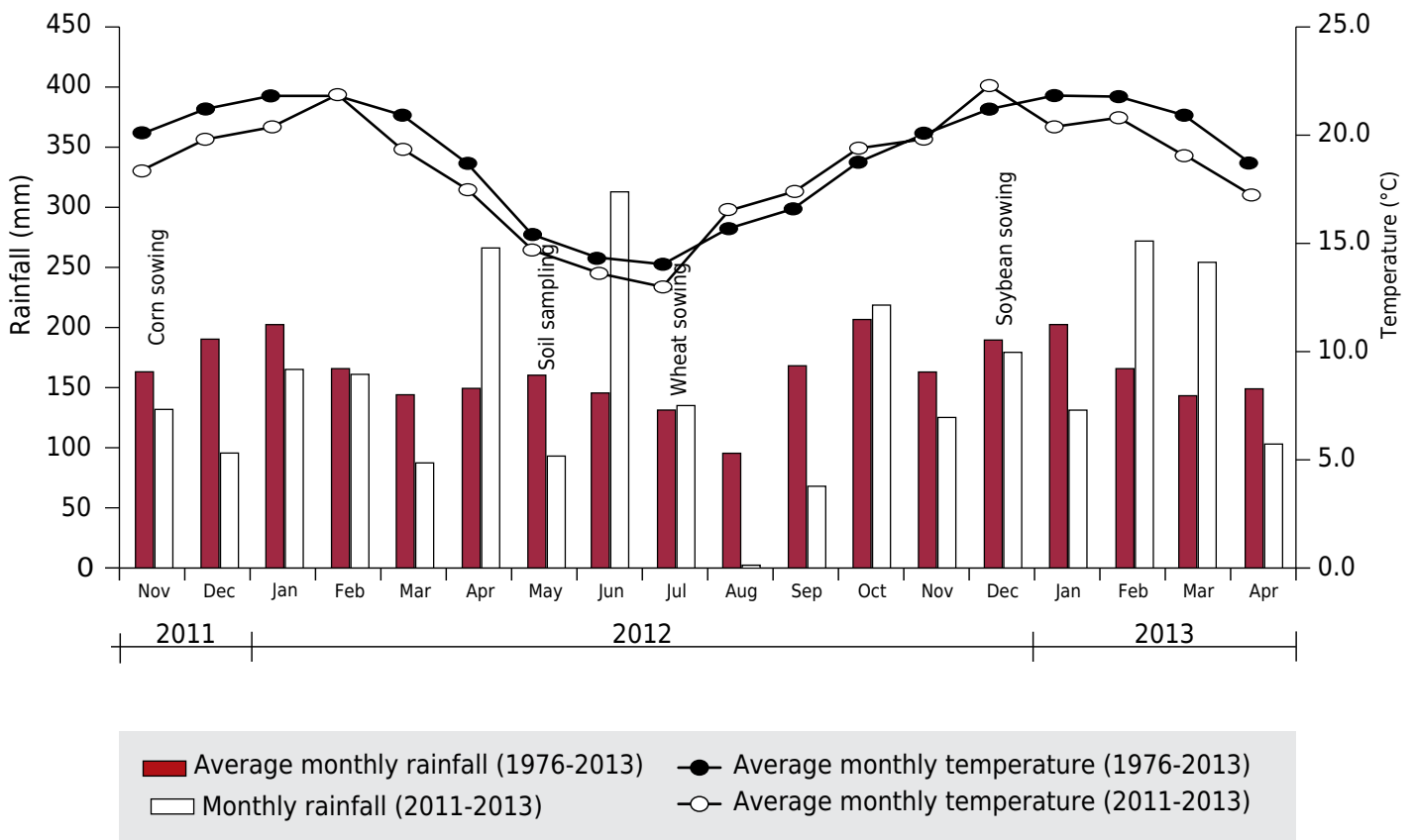
Figure 1. Monthly rainfall and temperature for the periods of 1976-2013 (long-term averages), and November 2011 to April 2013 (experimental period) in Guarapuava, Paraná state, Brazil.

Table 1. Chemical characterization and clay content of a Typic Hapludox profile before the experiment in October, 2009

Horiz.[1]	Depth	C	P	S	pH(CaCl$_2$)	Al^{3+}	H+Al	Ca^{2+}	Mg^{2+}	K$^+$	V	Clay
	m	g dm^{-3}	— mg dm^{-3} —			— cmol$_c$ dm^{-3} —					%	g kg^{-1}
A	0.0-0.3	21	1.1	4.7	5.4	0.20	4.96	5.01	2.66	0.26	61	720
AB	0.3-0.5	21	0.3	10.5	4.5	0.40	7.66	1.10	1.07	0.08	22	780
BA	0.5-0.8	11	0.5	13.3	4.7	0.40	6.18	0.85	1.14	0.04	25	810
Bw1	0.8-1.1	10	0.3	4.4	4.7	0.00	5.74	0.65	0.76	0.04	20	830
Bw2	1.1-1.4+	6	0.2	3.8	5.3	0.00	3.68	0.29	0.22	0.04	13	820

[1] Pedological horizons, data extracted from Michalovicz (2012). C: determined by dichromate-oxidation method; P and K: extracted by Mehlich-1; S (SO$_4^{2-}$): extracted by CaHPO$_3$ 0.01 mol L^{-1}; pH in CaCl$_2$ 0.01 mol L^{-1} solution; Al, Ca, Mg: extracted by KCl 1 mol L^{-1}; clay: pipette method.

Soil samples were collected in May 2012, after the corn harvest (six months after the last PG application). A composite sample, consisting of 12 subsamples per plot (four from the planting rows and eight from in-between the rows), was collected with an auger probe from the layers 0.0-0.1 and 0.1-0.2 m. At six of these points (two in and four in-between the rows), the soil was also sampled at depths of 0.2-0.4, 0.4-0.6 and 0.6-0.8 m with a Dutch auger. Samples were dried in a forced-air oven at 65 °C, and then ground in a knife-type mill and sieved through a 2 mm mesh. The analysis was done according to Pavan et al. (1992) and P extracted by Mehlich-1. The inorganic form of S (SO_4^{2-}) was extracted by calcium phosphate 0.01 mol L^{-1} as described by Cantarella and Prochnow (2001), and then determined through turbidimetry. The soil delta pH (ΔpH) was also calculated, as described by Kiehl (1979).

The yield of the crops harvested manually at physiological maturation was evaluated by collecting four sub-samples of 4 m (16 linear meters) per plot for corn and 3 m (12 linear meters) per plot for wheat and soybeans. Yields were reported at a moisture of 130 g kg^{-1} and maximum technical efficiency (MTE) rates of PG were obtained by setting the first derivative of the yield response models of each crop (regression analysis) equal to zero. All results were subjected to analysis of variance and in the case of significant ($p<0.05$) interactions between factors regression analyses were conducted separately (partitioning) for each split treatment. When no interaction was observed, split treatment means were tested by Tukey's test (α=0.05) and regression analyses were conducted using the means of each rate for all split treatments. The models with the highest level of significance were adopted.

RESULTS AND DISCUSSION

Chemical properties of soil fertility

The PG rates did not influence soil pH in the 0.0-0.1 and 0.1-0.2 m layers, with or without split applications (Table 2). However, soil pH increased in the 0.2-0.4 and 0.4-0.6 m layers when compared with the control treatment, regardless of total or split application rates, while a linear increase in soil pH was observed in the 0.6-0.8 m layer as a function of PG rate, without effect of splitting or interaction. Phosphogypsum is a neutral salt without corrective properties for soil acidity, so no change in soil pH was expected from its use. Notwithstanding, there can be a small magnitude pH increase in subsurface soil due to SO_4^{2-}-S increase, which at high concentrations can displace the OH^- that is adsorbed to Fe and Al hydrated oxides to the soil solution, a process known as "self-liming" (Reeve and Sumner, 1972), which is rather unstable and reversible (Raij, 2008). Similar results were obtained by Caires et al. (1999) for the 0.2-0.4, 0.4-0.6 and 0.6-0.8 m layers, and in another study for the 0.2-0.4 and 0.4-0.6 m layers (Caires et al., 2003).

Another possible explanation for these increases in soil pH could be a higher absorption of nitrate (NO_3^-) in deeper layers, since NO_3^- is highly mobile in the soil profile and one of the plant effects described for PG is a greater root distribution in deeper soil layers (Caires et al., 2001). The OH^- is released by plants when NO_3^- is absorbed, alkalizing the soil (Bloom et al., 2003).

The application of PG resulted in a decrease in the Al^{3+} concentration in all studied soil layers, however, there was no effect of application splitting or rate increase (Table 2). The effects of PG on Al^{3+} have been associated with the formation of Al hydroxylated structures in the soil, as a result of ligand exchange between OH^- from the surfaces of hydrated Fe or Al oxides and SO_4^{2-} provided by PG (Reeve and Sumner, 1972), as well as the formation of an ionic pair between Al^{3+} and SO_4^{2-} or fluoride (F^-) (Zambrosi et al., 2007). Phosphogypsum contains approximately 15 % S and 0.6-3.2 % F, and even when considering the role of SO_4^{2-} in Al^{3+} complexation, F^- may be even more effective in this reaction (Carvalho and Raij, 1997; Zambrosi et al., 2007), which may explain why PG is more efficient than natural gypsum (gypsite) in complexing Al^{3+}. In clayey Oxisols, Rampim et al. (2011) and Caires et al. (1999) also reported a reduction in Al^{3+} concentrations due to PG application, to a depth of 0.8 m in the latter case.

Table 2. Variance and regression analyses, and averages of soil pH, exchangeable aluminum (Al^{3+}) and potential acidity (H+Al) under different total and split phosphogypsum (PG) application rates at a Typic Hapludox

Depth	PG	pH(CaCl₂)			Al^{3+}			H+Al		
		P1[1]	P2	P3	P1	P2	P3	P1	P2	P3
m	Mg ha⁻¹						cmol$_c$ dm⁻³			
0.0-0.1	0 (control)	4.48	4.48	4.48	0.27	0.27	0.27	10.62	10.62	10.62
	3	4.57	4.50	4.49	0.19	0.20	0.13	8.82	10.49	9.35
	6	4.53	4.57	4.40	0.18	0.20	0.22	9.34	9.71	8.81
	9	4.51	4.50	4.47	0.20	0.14	0.19	9.97	10.28	9.77
	12	4.47	4.43	4.47	0.15	0.20	0.17	9.42	11.73	10.37
	Split (x̄)	4.52ⁿˢ	4.48ⁿˢ	4.46ⁿˢ	0.18ⁿˢ	0.19ⁿˢ	0.18ⁿˢ	9.39ⁿˢ	10.55ⁿˢ	9.82ⁿˢ
	Rate	ns			ns			ns		
	Rate × Split	ns			ns			ns		
	Factorial × control	ns			*			ns		
	CV (%)	2.19			44.31			18.03		
0.1-0.2	0	4.51	4.51	4.51	0.25	0.25	0.25	9.86	9.86	9.86
	3	4.65	4.57	4.61	0.10	0.16	0.06	9.16	10.02	8.87
	6	4.57	4.60	4.40	0.15	0.13	0.20	9.77	10.37	10.97
	9	4.62	4.70	4.70	0.14	0.11	0.11	9.35	8.32	9.03
	12	4.72	4.47	4.52	0.13	0.19	0.13	8.74	9.64	10.31
	Split (x̄)	4.64ⁿˢ	4.59ⁿˢ	4.56ⁿˢ	0.13ⁿˢ	0.15ⁿˢ	0.13ⁿˢ	9.26ⁿˢ	9.59ⁿˢ	9.79ⁿˢ
	Rate	ns			ns			ns		
	Rate × Split	ns			ns			ns		
	Factorial × control	ns			**			ns		
	CV (%)	3.89			43.25			9.85		
0.2-0.4	0	4.43	4.43	4.43	0.42	0.42	0.42	11.12	11.12	11.12
	3	4.60	4.57	4.70	0.25	0.26	0.27	10.24	10.46	8.41
	6	4.67	4.70	4.42	0.23	0.21	0.36	10.18	10.49	11.32
	9	4.65	4.67	4.60	0.26	0.18	0.20	10.67	10.07	10.10
	12	4.64	4.48	4.55	0.23	0.30	0.26	9.93	11.28	10.67
	Split (x̄)	4.64ⁿˢ	4.61ⁿˢ	4.57ⁿˢ	0.24ⁿˢ	0.24ⁿˢ	0.27ⁿˢ	10.25ⁿˢ	10.58ⁿˢ	10.12ⁿˢ
	Rate	ns			ns			ns		
	Rate × Split	ns			ns			ns		
	Factorial × control	*			*			ns		
	CV (%)	3.39			49.87			14.51		
0.4-0.6	0	4.42	4.42	4.42	0.35	0.35	0.35	10.87	10.87	10.87
	3	4.62	4.50	4.62	0.24	0.27	0.25	10.46	10.88	9.89
	6	4.54	4.62	4.50	0.23	0.24	0.23	10.09	10.10	10.74
	9	4.62	4.62	4.60	0.20	0.21	0.20	10.07	9.90	10.14
	12	4.74	4.45	4.57	0.19	0.26	0.26	9.90	10.65	10.26
	Split (x̄)	4.63ⁿˢ	4.55ⁿˢ	4.57ⁿˢ	0.22ⁿˢ	0.25ⁿˢ	0.24ⁿˢ	10.13ⁿˢ	10.39ⁿˢ	10.27ⁿˢ
	Rate	ns			ns			ns		
	Rate × Split	ns			ns			ns		
	Factorial × control	*			*			ns		
	CV (%)	2.62			38.29			6.90		
0.6-0.8	0	4.40	4.40	4.40	0.27	0.27	0.27	10.87	10.87	10.87
	3	4.43	4.42	4.54	0.22	0.23	0.20	11.63	10.58	9.95
	6	4.55	4.62	4.45	0.23	0.15	0.26	9.92	10.20	11.03
	9	4.65	4.60	4.60	0.19	0.13	0.18	9.95	9.77	10.38
	12	4.70	4.62	4.57	0.15	0.21	0.20	9.95	10.51	10.54
	Split (x̄)	4.58ⁿˢ	4.57ⁿˢ	4.54ⁿˢ	0.20ⁿˢ	0.18ⁿˢ	0.21ⁿˢ	10.36ⁿˢ	10.27ⁿˢ	10.48ⁿˢ
	Rate	L[2]**/0.94			ns			ns		
	Rate × Split	ns			ns			ns		
	Factorial × control	**			*			ns		
	CV (%)	2.22			31.89			8.07		

[1] P1 = 100 % in 2009, P2 = 50+50 % in 2009 and 2010, P3 = 33+33+33 % in 2009, 2010 and 2011; [2] Linear adjust and R^2 value after the bar; * and **: significant at p<0.05 and p<0.01, respectively; ns: not significant.

Neither PG application rates nor splitting had an effect on H+Al concentrations in any of the soil layers (Table 2), in agreement with the observations of Caires et al. (2004) under similar soil conditions. Although there were changes in Al^{3+} and pH concentrations in this study, these were minor and not intense enough to affect the H+Al values, which is consistent with PG being a neutral salt.

The Ca^{2+} concentrations increased linearly in response to the PG application rates in all soil layers, but no splitting effect was found (Table 3). Phosphogypsum consists of 17 % Ca, and given that the Ca^{2+} concentrations were found to have increased in all soil layers, this demonstrates that PG is a Ca^{2+} source that migrates downwards through the soil profile. An increase in Ca^{2+} concentration throughout the soil profile was also observed by Caires et al. (1999, 2003, 2011b), Soratto and Crusciol (2008) and Rampim et al. (2011) during their studies, noting that PG is a complementary soil amendment tool to lime for increasing Ca^{2+} concentrations in NT soils, especially in the subsurface, due to the higher PG solubility and vertical mobility in the soil profile compared with lime (Caires et al., 1998).

Magnesium concentrations decreased linearly with increasing PG application rates in the 0.0-0.1 and 0.1-0.2 m layers, as reported in other studies (Toma et al., 1999; Soratto and Crusciol, 2008; Caires et al., 2011a), and again no effect of splitting was observed. Competing for the same adsorption sites, the Ca^{2+} added by PG displaces soil Mg^{2+} ions to the soil solution, which is further transported to deeper soil layers as the water percolates through the profile (Medeiros et al., 2008). The formation of $MgSO_4^0$, which is mobilized easily in the soil, also occurs (Zambrosi et al., 2007). At the 0.2-0.4 and 0.4-0.6 m depths, Mg^{2+} concentrations also decreased linearly, but this was different from the layers above, as no significant difference between the factorial average and the control average was observed. In these layers, incoming Mg^{2+} from surface layers leached down due to PG application, compensating in part for the Mg^{2+} that migrates downward, especially at the rates of 3 and 6 Mg ha^{-1}. In the 0.6-0.8 m layer, no effects of rate increase or split applications were observed, however, PG increased the Mg^{2+} concentration, since the factorial mean was higher in relation to the control mean, indicating that Mg^{2+} was accumulated in this layer (Table 3).

In view of the effect of PG on Mg^{2+} availability in the soil, it is important to consider the initial Mg^{2+} concentrations in different soil layers before recommending PG rates, because the redistribution of the Mg^{2+} concentrated superficially in NT soils may be benefic for crops. It is also necessary to maintain Mg^{2+} concentrations above the critical level of the nutrient in surface layers to ensure adequate Mg^{2+} supply. Therefore, the planning of PG application must consider other agricultural practices that interact in this context, such as the use of dolomitic lime, magnesium thermophosphate, or other of Mg^{2+} sources, depending on the situation.

The soil Ca/Mg ratio increased linearly with PG application rates in all soil layers, although in the 0.4-0.6 and 0.6-0.8 m layers, the increase was not significant in relation to the control (Table 3). In the 0.0-0.1 m layer, the application of single rates (P1) resulted in a lower Ca/Mg ratio compared with rates where the applications were distributed over two (P2) or three (P3) years. Despite not being significantly different, the Ca^{2+} concentrations were higher while those of Mg^{2+} were lower in P2 and P3, where the time between PG application and soil sampling was shorter than in P1. The combination of these variations resulted in a statistical difference for the Ca/Mg ratio among split treatments. A Ca/Mg increase in response to PG application rates was also reported by Caires et al. (2011a), attributing these results to increases in Ca^{2+} concentrations and Mg^{2+} leaching.

There was no effect of treatment on soil K^+ concentrations (Table 4). Despite K^+ competes for the same adsorption sites as Ca^{2+} and Mg^{2+}, the downward migration of K^+ was not comparable to Mg^{2+}. This movement for K^+ (low magnitude) after PG application was reported by Caires et al. (1998, 2002), but other studies did not show the same behavior

Table 3. Variance and regression analyses, and averages of soil calcium and magnesium concentrations and Ca/Mg ratio under different total and split phosphogypsum (PG) application rates of a Typic Hapludox

Depth	PG	Ca^{2+}			Mg^{2+}			Ca/Mg ratio		
		P1[1]	P2	P3	P1	P2	P3	P1	P2	P3
m	Mg ha^{-1}	cmol$_c$ dm^{-3}								
0.0-0.1	0 (control)	4.18	4.18	4.18	1.68	1.68	1.68	2.64	2.64	2.64
	3	4.70	4.91	5.41	1.48	1.13	1.49	3.40	4.97	3.71
	6	4.80	5.23	4.82	0.84	0.97	0.60	5.75	6.02	8.27
	9	5.09	5.48	6.10	0.72	0.59	0.67	7.45	10.01	9.79
	12	5.73	5.09	6.17	0.73	0.33	0.51	8.42	17.06	14.86
	Split ($\bar{x}$)	5.07^{ns}	5.18^{ns}	5.65^{ns}	0.94^{ns}	0.76^{ns}	0.82^{ns}	5.53 B	8.14 A	7.85 A
	Rate	L$^{(2)}$*/0.83			L**/0.87			L**/0.98		
	Rate × Split	ns			ns			ns		
	Factorial × control	*			**			**		
	CV (%)	15.17			40.16			36.48		
0.1-0.2	0	3.85	3.85	3.85	1.62	1.62	1.62	2.80	2.80	2.80
	3	4.38	4.29	4.68	1.63	1.15	1.90	2.90	4.41	2.74
	6	4.82	4.67	4.56	0.93	1.20	0.90	5.87	4.14	5.67
	9	4.77	4.96	4.57	0.64	0.68	1.11	7.09	8.84	4.35
	12	5.22	5.07	5.55	0.56	0.36	0.55	11.55	16.62	10.19
	Split ($\bar{x}$)	4.80^{ns}	4.75^{ns}	4.84^{ns}	0.94^{ns}	0.85^{ns}	1.11^{ns}	6.85^{ns}	8.55^{ns}	5.66^{ns}
	Rate	L*/0.91			L**/0.96			L**/0.89		
	Rate × Split	ns			ns			ns		
	Factorial × control	*			**			*		
	CV (%)	16.41			38.74			51.02		
0.2-0.4	0	2.69	2.69	2.69	1.18	1.18	1.18	2.51	2.51	2.51
	3	2.83	3.42	3.38	1.28	1.30	1.35	2.78	3.43	2.70
	6	3.70	3.88	3.40	1.04	1.14	0.93	3.91	3.43	3.66
	9	3.86	3.68	3.85	0.88	1.06	1.25	4.44	4.15	3.54
	12	3.92	3.94	4.10	0.91	0.84	0.80	4.62	4.92	5.26
	Split ($\bar{x}$)	3.58^{ns}	3.73^{ns}	3.68^{ns}	1.03^{ns}	1.09^{ns}	1.08^{ns}	3.93^{ns}	3.98^{ns}	3.79^{ns}
	Rate	L**/0.93			L**/0.85			L**/0.97		
	Rate × Split	ns			ns			ns		
	Factorial × control	**			ns			*		
	CV (%)	17.21			30.99			32.35		
0.4-0.6	0	2.30	2.30	2.30	1.16	1.16	1.16	2.09	2.09	2.09
	3	2.55	3.03	2.56	1.33	1.45	1.43	1.94	2.22	1.79
	6	2.92	2.74	2.77	1.16	1.25	1.15	2.54	2.19	2.40
	9	2.91	3.00	3.39	1.13	1.23	1.35	2.78	2.46	2.53
	12	3.05	3.23	3.40	1.05	1.05	1.15	3.08	3.14	3.27
	Split ($\bar{x}$)	2.86^{ns}	3.00^{ns}	3.03^{ns}	1.03^{ns}	1.16^{ns}	1.22^{ns}	2.58^{ns}	2.50^{ns}	2.50^{ns}
	Rate	L**/0.97			L*/0.83			L**/0.97		
	Rate × Split	ns			ns			ns		
	Factorial × control	**			ns			ns		
	CV (%)	13.88			36.75			26.35		
0.6-0.8	0	1.80	1.80	1.80	1.13	1.13	1.13	1.73	1.73	1.73
	3	2.28	2.29	2.12	1.50	1.51	1.55	1.51	1.59	1.38
	6	2.55	2.26	2.18	1.28	1.83	1.22	2.00	1.23	1.88
	9	2.47	2.27	2.23	1.42	1.61	1.71	1.88	1.40	1.32
	12	2.73	2.79	2.62	1.45	1.42	1.48	1.96	2.12	1.81
	Split ($\bar{x}$)	2.51^{ns}	2.40^{ns}	2.29^{ns}	1.41^{ns}	1.59^{ns}	1.49^{ns}	1.83^{ns}	1.58^{ns}	1.60^{ns}
	Rate	L*/0.77			ns			L*/0.56		
	Rate × Split	ns			ns			ns		
	Factorial × control	**			*			ns		
	CV (%)	18.02			18.15			28.16		

[1] P1 = 100 % in 2009, P2 = 50+50 % in 2009 and 2010, P3 = 33+33+33 % in 2009, 2010 and 2011; [2] Linear adjust and R^2 value after the bar; * and **: significant at p<0.05 and p<0.01, respectively; ns: not significant.

(Raij et al., 1998; Caires et al., 2004). It is possible that K^+, added periodically at crop planting throughout the years, compensates any effect possibly caused by PG mobilization. Nevertheless, since the K^+ concentrations in the soil were considered high, the amount of K^+ available for leaching was high, therefore, the absence of the effect of PG is evidence that mobilization would be lower for K^+ than for Mg^{2+}, and, or, that the relatively higher cycling of K^+ (kg ha^{-1}) by the crops reduces the leaching effect (Raij et al., 1998). Another hypothesis is that the KSO_4^- formed after the PG reaction can bind to positive charges in the soil, which is not the case for $MgSO_4^0$, making it more prone to leaching. Zambrosi et al. (2008) evaluated the ionic speciation of a clayey Oxisol under NT, and found that K^+ was not complexed by organic anions, and that the complexation with inorganic anions (KCl, KNO_3 and KSO_4^-) represented a maximum of 0.2 % of the total, remaining as free ions and favoring soil adsorption.

Compared with the control treatment, the application of PG increased the soil S concentration and unlike for the other nutrients, there was an interaction between application rate and splitting for all soil layers (Table 4). The S concentration increased in the 0.0-0.1, 0.1-0.2 and 0.2-0.4 m layers in the following order: P1<P2<P3. As PG rates increased, the S concentrations also increased linearly, in all splitting treatments and soil layers, except for the 0.0-0.1 m layer where this response occurred only in P2 and P3. The effect of split applications changed in the deeper layers, so that in 0.4-0.6 m, no difference was observed between P1 and P2 and both were exceeded by P3, while in the 0.6-0.8 m layer, no splitting effect occurred. Increased S concentration in the soil was also reported in other studies, to a depth of 0.6 m (Caires et al., 2011a) and 0.8 m (Raij et al., 1998). In addition, the above results indicate that splitting the PG application could benefit the S levels in the soil, especially in the near-surface layers, improving S cycling by plants and increasing the soil stock.

The retention of SO_4^{2-} in the soil is low, especially in the topsoil where electronegativity is higher. In NT, soil net charge is even more negative in this layer due to the accumulation of organic matter and surface liming (Casagrande et al., 2003), thus repelling SO_4^{2-}. In fact, due to the absence of tillage and to the natural low mobility of phosphate anions, they accumulate in the topsoil along with fertilization in the furrow during crop planting, and phosphates are preferably retained in the anion exchange capacity (AEC). Higher concentrations of S are common in subsurface layers (Borges, 1997; Alvarez V et al., 2000), where lower organic matter content allows for a higher AEC (Lima et al., 2013). In this study, this trend was estimated by the ΔpH values, which were less negative for the 0.4-0.6 and 0.6-0.8 m layers, -0.92 and -0.80, respectively, in comparison with the values for the 0.0-0.1, 0.1-0.2 and 0.2-0.4 m layers, where the ΔpH values were -1.13, -1.04 and -1.04, respectively.

Phosphorus concentrations in the soil were not affected by treatments (Table 4), although residual concentrations of P (0.2-0.6 % P_2O_5) are present in PG, due to its origin in the phosphate fertilizer manufacturing process. In this study, the combination of the broadcast application of PG to the area and the very clayey soil texture creates a large P retention capacity, preventing increases in available P concentrations in the soil analysis.

Macronutrient plant leaf tissue concentrations

The N concentration of corn, wheat and soybean leaves (Table 5) were not affected by any of the treatments. Raij et al. (1998) and Caires et al. (2011a) found similar results regarding corn, and despite the fact that rainfall in December 2011 was about 100 mm lower than the monthly mean, there was no water stress in the corn growing season (Figure 1), with regular precipitation every 7-10 days. Wheat emerged on July 30th, 2012 and was affected by water stress in the early stages of its life cycle, with rainfall precipitation in August being only 2 mm while there was 100 mm less precipitation than the monthly mean of September. In this case, the absence of a

possible effect of PG on leaf N concentrations could be due to absorption limitations imposed by the dry period, which reduced wheat growth and the yield. No effect of PG application on wheat leaf N concentration under water stress was also reported by Caires et al. (2002). Soybean obtains most of the necessary N through symbiosis, resulting in a reduced potential effect of PG on N absorption from the soil, as was observed in this study and also reported by Nogueira and Melo (2003) and Caires et al. (2003; 2011a).

The treatments had no effect on leaf P concentrations (Table 5), corroborating findings of other studies for corn (Raij et al., 1998; Caires et al., 2004), wheat (Caires et al., 2002), and soybean (Nogueira and Melo, 2003). The same concordance between the soil and leaf tissue results occurred for K in corn, wheat and soybean (Table 5). Despite increasing Ca^{2+} concentrations in soil layers due to PG application, K plant uptake was not influenced by competitive inhibition. In this case, the high concentrations of K^+ in the soil and K^+ supply through NPK fertilization in planting furrows for each crop may explain the results. Other studies with PG also reported similar results for leaf K regarding corn (Caires et al., 2011a), wheat (Caires et al., 2002) and soybean (Caires et al., 2003, 2011a; Nogueira and Melo, 2003).

The reduction in Al^{3+} concentration combined with Ca^{2+} increase throughout the soil profile improved soil fertility, especially in the subsurface, which may have benefited root growth (Carvalho and Raij, 1997) and enhanced root interception, the second most important ion-root contact component for Ca absorption (Prado, 2008). Thus, the linear increase in leaf Ca concentration for corn, wheat and soybean (Table 5) in response to PG application rates was explained. Increases in leaf Ca concentrations were also reported in other studies for corn (Caires et al., 2004; 2011a) and wheat (Caires et al., 1999; 2002), as well as soybeans (Caires et al., 2003, 2006; Rampim et al., 2011).

The decrease in Mg^{2+} concentrations in soil layers to a depth of 0.60 m was followed by a reduction in Mg absorption by corn, wheat and soybean (Table 5). High soil concentrations of Ca^{2+} and K^+ inhibit Mg absorption by ionic competition, leading to possible nutrient deficiency (Prado, 2008). However, wheat was the only crop with Mg leaf concentration below the sufficiency range (1.5 – 4 g kg^{-1}), and only for 6, 9 and 12 Mg ha^{-1} of PG. A decrease in Mg concentration in corn leaf tissue after PG application was reported also by Raij et al. (1998) and Caires et al. (2004). For wheat, Caires et al. (2002) reported no effect of PG application on Mg leaf concentration, while Rampim et al. (2011) also observed a decline in leaf Mg, and the studies of Caires et al. (2003; 2006) and Gelain et al. (2011) found increasing PG application rates related to a decrease in Mg concentration in soybean leaves.

The S concentrations in corn, wheat and soybean leaves (Table 5) were linearly increased by PG application rates, reflecting the S increase in the soil due to PG application rates. This result was similar to those reported in other studies on corn (Caires et al., 2011a), wheat (Caires et al., 2002) and soybean (Caires et al., 2003, 2011a; Nogueira and Melo, 2003). In contrast, although application splitting also resulted in a higher soil S concentration to 0.6 m deep, this factor did not affect leaf S concentration in any of the crops; the same was true for the Ca and Mg leaf concentrations, even though splitting resulted in a higher Ca/Mg ratio in the 0.0-0.1 m soil layer. The macronutrients did not demonstrate a response in terms of leaf concentration for any of the studied crops due to the effect of splitting, demonstrating that the magnitude of the variation in soil properties due to splitting the PG application rates was not high enough to affect plant uptake.

Crop yields

Corn yield was not influenced by splitting, but the effect of PG application rate was quadratic (Figure 2), with a decrease at higher rates, especially at 12 Mg ha^{-1} of PG,

Table 4. Variance and regression analyses, and averages of soil potassium, sulfur and phosphorus concentrations under different total and split phosphogypsum (PG) application rates of a Typic Hapludox

Depth	PG	K+			S			P		
		P1[1]	P2	P3	P1	P2	P3	P1	P2	P3
m	Mg ha⁻¹	——— cmol_c dm⁻³ ———			———————————— mg dm⁻³ ————————————					
0.0-0.1	0 (control)	0.56	0.56	0.56	41.52	41.52	41.52	8.24	8.24	8.24
	3	0.47	0.54	0.50	47.95	56.02	90.79	8.37	9.52	9.75
	6	0.52	0.44	0.49	63.11	63.42	108.9	9.28	9.20	10.63
	9	0.51	0.49	0.49	52.08	67.69	105.6	10.06	7.82	10.20
	12	0.46	0.50	0.49	58.69	100.4	113.6	11.82	9.65	9.82
	Split (x̄)	0.49ⁿˢ	0.49ⁿˢ	0.50ⁿˢ	55.46 C	71.89 B	104.7 A	9.88ⁿˢ	9.05ⁿˢ	10.09ⁿˢ
	Rate	ns			**			ns		
	Rate × Split	ns			ns	L[2]**/0.82	L**/0.73	ns		
	Factorial × control	ns			**			ns		
	CV (%)	14.19			13.98			21.32		
0.1-0.2	0	0.23	0.23	0.23	51.99	51.99	51.99	2.33	2.33	2.33
	3	0.20	0.22	0.23	60.23	83.04	98.70	1.59	2.70	2.06
	6	0.20	0.17	0.23	73.91	83.27	126.3	2.09	1.60	2.51
	9	0.20	0.18	0.22	88.91	88.51	148.0	2.24	2.04	2.20
	12	0.20	0.19	0.25	81.37	132.0	153.4	2.25	1.81	2.35
	Split (x̄)	0.20ⁿˢ	0.19ⁿˢ	0.23ⁿˢ	76.11 C	96.72 B	131.6 A	2.04ⁿˢ	2.04ⁿˢ	2.28ⁿˢ
	Rate	ns			**			ns		
	Rate × Split	ns			L*/0.69	L**/0.69	L**/0.93	ns		
	Factorial × control	ns			**			ns		
	CV (%)	22.59			14.27			26.80		
0.2-0.4	0	0.16	0.16	0.16	88.24	88.24	88.24	1.00	1.00	1.00
	3	0.16	0.19	0.14	118.1	140.2	145.7	1.00	1.56	1.35
	6	0.20	0.18	0.21	132.9	135.1	164.9	1.85	1.42	1.67
	9	0.16	0.13	0.17	162.9	170.9	193.2	1.69	0.96	1.10
	12	0.14	0.12	0.18	155.7	188.0	232.1	1.14	1.13	1.82
	Split (x̄)	0.17ⁿˢ	0.16ⁿˢ	0.17ⁿˢ	142.4 C	158.6 B	184.0 A	1.41ⁿˢ	1.27ⁿˢ	1.49ⁿˢ
	Rate	ns			**			ns		
	Rate × Split	ns			L**/0.80	L**/0.84	L**/0.98	ns		
	Factorial × control	**			**			ns		
	CV (%)	33.50			9.36			42.41		
0.4-0.6	0	0.11	0.11	0.11	92.13	92.13	92.13	0.52	0.52	0.52
	3	0.13	0.09	0.09	152.1	160.5	162.6	0.61	0.57	0.65
	6	0.13	0.11	0.11	169.6	173.6	183.5	0.75	0.68	0.67
	9	0.10	0.11	0.13	180.9	204.8	214.7	0.64	0.60	0.66
	12	0.08	0.08	0.10	202.2	195.1	248.1	0.68	0.62	0.78
	Split (x̄)	0.11ⁿˢ	0.10ⁿˢ	0.11ⁿˢ	176.2 B	183.5 B	202.2 A	0.67ⁿˢ	0.62ⁿˢ	0.69ⁿˢ
	Rate	ns			**			ns		
	Rate × Split	ns			L**/0.99	L**/0.75	L**/0.99	ns		
	Factorial × control	ns			**			ns		
	CV (%)	38.24			7.52			41.09		
0.6-0.8	0	0.06	0.06	0.06	82.73	82.73	82.73	0.30	0.30	0.30
	3	0.09	0.08	0.08	162.1	132.2	127.4	0.21	0.43	0.43
	6	0.06	0.06	0.08	180.0	184.9	169.2	0.39	0.39	0.44
	9	0.08	0.07	0.07	195.0	237.0	185.1	0.65	0.25	0.35
	12	0.08	0.06	0.07	216.2	202.0	216.8	0.62	0.26	0.46
	Split (x̄)	0.08ⁿˢ	0.07ⁿˢ	0.08ⁿˢ	188.3ⁿˢ	189.0ⁿˢ	174.6ⁿˢ	0.47ⁿˢ	0.33ⁿˢ	0.42ⁿˢ
	Rate	ns			**			ns		
	Rate × Split	ns			L**/0.99	L**/0.60	L**/0.97	ns		
	Factorial × control	ns			**			ns		
	CV (%)	26.83			9.48			57.84		

[1] P1 = 100 % in 2009, P2 = 50+50 % in 2009 and 2010, P3 = 33+33+33 % in 2009, 2010 and 2011; [2] Linear adjust and R² value after the bar; * and **: significant at $p<0.05$ and $p<0.01$, respectively; ns: not significant.

Table 5. Variance and regression analyses, and averages of nitrogen, phosphorus, potassium, calcium, magnesium and sulfur leaf contents of corn, wheat and soybean plants under different total and split phosphogypsum (PG) application rates

PG	N	P	K	Ca	Mg	S
Mg ha^{-1}				g kg^{-1}		
			Corn			
0 (control)	38.56	3.20	19.72	4.53	3.13	3.91
3	37.51	3.25	19.73	4.71	2.94	5.04
6	37.42	3.12	20.08	4.82	2.71	4.87
9	37.90	3.21	19.94	5.09	2.63	5.08
12	37.91	3.25	20.36	5.26	2.39	5.56
Regression/R^2	ns	ns	ns	L$^{(2)}$**/0.98	L**/0.97	L*/0.64
CV (%)	7.73	7.84	4.18	5.86	14.68	12.01
Split						
P1$^{(1)}$	37.51	3.14	19.88	5.11	2.81	5.22
P2	36.86	3.17	19.83	4.92	2.56	4.94
P3	39.02	3.31	20.39	4.89	2.63	5.25
Effect	ns	ns	ns	ns	ns	ns
CV (%)	7.17	7.56	4.09	7.09	15.97	12.68
Rate × Split	ns	ns	ns	ns	ns	ns
Factorial × control	ns	ns	ns	**	*	**
			Wheat			
0	42.51	4.26	21.51	2.97	1.58	6.21
3	42.63	4.30	21.33	3.26	1.56	6.57
6	40.25	4.31	21.75	3.31	1.39	6.65
9	42.37	4.38	21.41	3.57	1.44	6.73
12	40.22	4.37	21.19	3.45	1.29	7.10
Regression/R^2	n.s.	n.s.	n.s.	L*/0.60	L**/0.77	L*/0.85
CV (%)	7.01	3.38	4.47	7.11	11.00	7.52
Split						
P1$^{(1)}$	42.09	4.34	21.18	3.45	1.48	6.71
P2	41.25	4.35	21.72	3.36	1.37	6.69
P3	40.77	4.34	21.35	3.38	1.40	6.89
Effect	ns	ns	ns	ns	ns	ns
CV (%)	7.39	3.45	4.40	7.88	12.47	7.98
Rate × Split	ns	ns	ns	ns	ns	ns
Factorial × control	ns	ns	ns	**	*	*
			Soybean			
0	51.90	3.52	21.85	8.47	4.50	3.24
3	52.95	3.48	23.40	9.24	4.46	3.42
6	53.04	3.52	23.42	9.11	4.19	3.67
9	54.62	3.47	22.21	9.57	4.08	3.71
12	55.40	3.57	22.63	9.85	4.05	3.81
Regression/R^2	ns	ns	ns	L*/0.80	L**/0.85	L*/0.89
CV (%)	9.18	9.20	9.12	8.28	6.47	10.05
Split						
P1$^{(1)}$	54.73	3.53	23.18	9.47	4.28	3.57
P2	53.31	3.51	22.28	9.40	4.16	3.62
P3	53.96	3.49	23.28	9.47	4.15	3.77
Effect	ns	ns	ns	ns	ns	ns
CV (%)	9.24	9.17	9.10	8.81	7.44	10.48
Rate × Split	ns	ns	ns	ns	ns	ns
Factorial × control	ns	ns	ns	*	**	*

$^{(1)}$ P1 = 100 % in 2009, P2 = 50+50 % in 2009 and 2010, P3 = 33+33+33 % in 2009, 2010 and 2011; $^{(2)}$ Linear adjust and R^2 value after the bar; * and **: significant at p<0.05 and p<0.01, respectively; ns: not significant.

(a)

$\hat{y} = 10.29^{**} + 0.204x^{**} - 0.016^{**}x^2 \quad R^2 = 0.93^{**}$

(b)

$\hat{y} = 2.063^{**} + 0.049x^{**} \quad R^2 = 0.94^{**}$
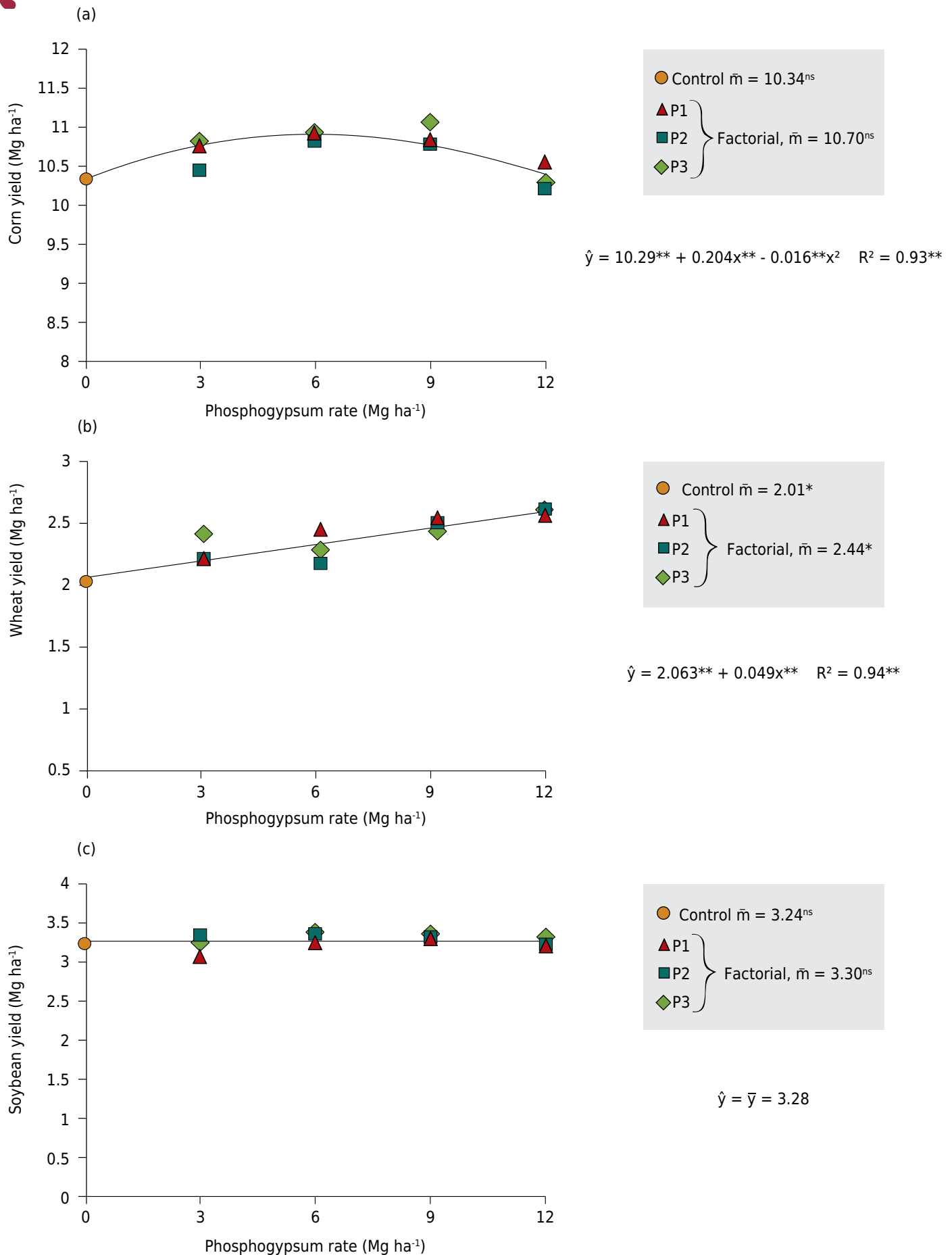
(c)

$\hat{y} = \bar{y} = 3.28$

Figure 2. (a) Corn yield (growing season 2011/12), (b) Wheat yield (growing season 2012) and (c) Soybean yield (growing season 2012/13), as a function of different total and split phosphogypsum application rates (P1 = 100 % in 2009; P2 = 50+50 % in 2009 and 2010; P3 = 33+33+33 % in 2009, 2010 and 2011) to the soil surface of a Typic Hapludox, under no-tillage.* and **: significant at p<0.05 and p<0.01, respectively; ns: not significant.

which produced 0.3 % less than the control. The maximum technical efficiency (MTE) rate of PG was 6.38 Mg ha^{-1}, corresponding to 10.94 Mg ha^{-1} of corn, which is about 5.5 % higher than the control yield. Similar results in another study with PG application rates in Guarapuava, with a quadratic effect and a MTE of 7.8 Mg ha^{-1} of PG was reported by Caires et al. (2011a), concluding that the yield decrease at higher rates was due to Mg^{2+} and K$^+$ leaching from the topsoil.

Leaf P, K, Ca and Mg concentrations were within the sufficiency ranges, whereas N and S concentrations were above the sufficiency range for corn (Santos et al., 2009). Although the Mg concentrations were higher than the critical level for the crop, the average with 12 Mg ha^{-1} of PG was 23 % lower compared with the control, consistent with the lower yield. Unlike corn, wheat yield increased linearly with PG rates, without any effect of split applications (Figure 2), and the significance in the contrast between control and factorial treatments showed that by the average of the rates and splitting the application of PG improved wheat yield.

Soybean showed no yield response to treatments and no significant difference between the control and the factorial treatments (Figure 2). Leaf concentrations of macronutrients were within the sufficiency ranges for all treatments, except for 12 Mg ha^{-1} of PG in the case of N and for all rates in the case of S, where concentrations exceeded the sufficiency range for the crop (santos et al., 2009). No effect of PG application on soybean yield was reported by Caires et al. (2003; 2006; 2011b), Neis et al. (2010) and Rampim et al. (2011). The roots of this crop, compared with corn for example, have a higher root cation exchange capacity (Fernandes and Souza, 2006), leading to a higher efficiency in the accumulation of soil divalent cations, such as Ca^{2+} and Mg^{2+}, in the rhizosphere, which favors absorption even under low concentrations of these cations in the soil. Soybean roots are influenced slightly by low Al^{3+} concentrations in the soil when rainfall is regular (Caires et al., 2001), as was the case in this study.

CONCLUSIONS

The use of phosphogypsum increased grain yield of poaceous crops, with a quadratic response to the rates for corn under a normal growing season, and a linear response for wheat in a growing season with water restriction. Soybean yield was not significantly influenced.

The splitting of phosphogypsum rates decreased downward migration of SO_4^{2-} through the soil profile, but did not reduce Mg^{2+} mobilization and had no influence on the yield of the studied crops. No K$^+$ mobilization was observed as a function of phosphogypsum application.

REFERENCES

Acqua NHD, Silva GP, Benites VM, Assis RL, Simon GA. Métodos de amostragem de solos em áreas sob plantio direto no Sudoeste Goiano. Rev Bras Eng Agric Amb. 2013;17:117-22. doi:10.1590/S1415-43662013000200001

Alvarez V VH, Novais RF, Dias LE, Oliveira JA. Determinação e uso do fósforo remanescente. Bol Inf SBCS. 2000;25:27-32.

Bloom AJ, Meyerhoff PA, Taylor AR, Rost TL. Root development and absorption of ammonium and nitrate from the rhizosphere. J Plant Growth Regul. 2003;21:416-31. doi:10.1007/s00344-003-0009-8

Borges EN. Efeito de calcário e gesso nos teores de cálcio e alumínio da camada compactada em Latossolo Vermelho-Escuro. Pesq Agropec Bras. 1997;32:107-14.

Caires EF, Blum J, Barth G, Garbuio FJ, Kusman MT. Alterações químicas do solo e resposta da soja ao calcário e gesso aplicados na implantação do sistema de plantio direto. Rev Bras Cienc Solo. 2003;27:275-86. doi:10.1590/S0100-06832003000200008

Caires EF, Chueiri WA, Madruga EF, Figueiredo A. Alterações de características químicas do solo e resposta da soja ao calcário e gesso aplicados na superfície em sistema de cultivo sem preparo do solo. Rev Bras Cienc Solo. 1998;22:27-34. doi:10.1590/S0100-06831998000100004

Caires EF, Churka S, Garbuio FJ, Ferrari RA, Morgano MA. Soybean yield and quality a function of lime and gypsum applications. Sci Agric. 2006;63:370-9. doi:10.1590/S0103-90162006000400008

Caires EF, Feldhaus IC, Barth G, Garbuio FJ. Lime and gypsum application on the wheat crop. Sci Agric. 2002;59:357-64. doi:10.1590/S0103-90162002000200023

Caires EF, Feldhaus IC, Blum J. Crescimento radicular e nutrição da cevada em função da calagem e aplicação de gesso. Bragantia. 2001;60:213-23. doi:10.1590/S0006-87052001000300009

Caires EF, Fonseca AF, Mendes J, Chueiri WA, Madruga EF. Produção de milho, trigo e soja em função das alterações das características químicas do solo pela aplicação de calcário e gesso na superfície, em sistema de plantio direto. Rev Bras Cienc Solo. 1999;23:315-27. doi:10.1590/S0100-06831999000200016

Caires EF, Joris HAW, Churka S. Long-term effects of lime and gypsum additions on no-till corn and soybean yield and soil chemical properties in southern Brazil. Soil Use Manage. 2011b;27:45-53. doi:10.1111/j.1475-2743.2010.00310.x

Caires EF, Kusman MT, Barth G, Garbuio FJ, Padilha JM. Alterações químicas do solo e resposta do milho à calagem e aplicação de gesso. Rev Bras Cienc Solo. 2004; 28:125-36. doi:10.1590/S0100-06832004000100013

Caires EF, Maschietto EHG, Garbuio FJ, Churka S, Joris HAW. Surface application of gypsum in low acidic Oxisol under no-till cropping system. Sci Agric. 2011a;68:209-16. doi:10.1590/S0103-90162011000200011

Cantarella H, Prochnow LI. Determinação de sulfato em solos. In: Raij Bvan, Andrade JC, Cantarella H, Quaggio JA, editores. Análise química para avaliação da fertilidade de solos tropicais. Campinas: Instituto Agronômico de Campinas; 2001. p.225-30.

Cardoso AD, Alvarenga MAR, Melo TL, Viana AES. Produtividade e qualidade de tubérculos de batata em função de doses e parcelamentos de nitrogênio e potássio. Cienc Agrotec. 2007;31:1729-36. doi:10.1590/S1413-70542007000600019

Carvalho MCS, Raij Bvan. Calcium sulphate, phosphogypsum and calcium carbonate in the amelioration of acid subsoils for root growth. Plant Soil. 1997;192:37-48. doi:10.1023/A:1004285113189

Casagrande JC, Alleoni LRF, Camargo OA, Borges M. Adsorção de fosfato e sulfato em solos com cargas variáveis. Rev Bras Cienc Solo. 2003;27:51-9. doi:10.1590/S0100-06832003000100006

Claessen MEC, organizador. Manual de métodos de análise de solo. 2ª ed. Rio de Janeiro: Centro Nacional de Pesquisa de Solos; 1997.

Comissão de Química e Fertilidade do Solo – CQFSRS/SC. Manual de adubação e de calagem para os estados do Rio Grande do Sul e de Santa Catarina. 10ª. ed. Porto Alegre: Sociedade Brasileira de Ciência do Solo/Núcleo Regional Sul; 2004.

Denardin JE, Kochhann RA, Bacaltchuk B, Sattler A, Denardin ND'A, Faganello A, Wiethölter S. Sistema plantio direto: fator de potencialidade da agricultura tropical brasileira. In: Albuquerque ACS, Silva AG, editores. Agricultura tropical: quatro décadas de inovações tecnológicas, institucionais e políticas. Brasília, DF: Embrapa Informação Tecnológica; 2008. p.1251-73.

Derpsch R, Friedrich T. Global overview of conservation agriculture adoption. In: Proceedings of the 4th World Congress on Conservation Agriculture; 2009; New Delhi. p.429-38.

Ebeling AG, Anjos LHC, Perez DV, Pereira MG, Valladares GS. Relação entre acidez e outros atributos químicos em solos com teores elevados de matéria orgânica. Bragantia. 2008;67:429-39. doi:10.1590/S0006-87052008000200019

Ernani PR, Ribeiro MS, Bayer C. Modificações químicas em solos ácidos ocasionadas pelo método de aplicação de corretivos da acidez e de gesso agrícola. Sci Agric. 2001;58:825-31. doi:10.1590/S0103-90162001000400026

Fernandes MS, Souza SR. Absorção de nutrientes. In: Fernandes MS, editor. Nutrição mineral de plantas. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 2006. p.115-52.

Food and Agriculture Organization of the United Nations – FAO. Adoption worldwide [internet]. Comissioned for the exclusive use of FAO, 2012 [Accessed on: 23 Feb 2015]. Available at: http://www.fao.org/ag/ca/6c.html.

Gelain E, Rosa Junior EJ, Mercante FM, Fortes DG, Souza FR, Rosa YBCJ. Fixação biológica de nitrogênio e teores foliares de nutrientes na soja em função de doses de molibdênio e gesso agrícola. Cienc Agrotec. 2011;35:259-69. doi:10.1590/S1413-70542011000200005

Kiehl EJ. Manual de edafologia. São Paulo: Agronômica Ceres; 1979.

Klein VA, Dallmeyer AU, Escosteguy PAV, Boller W, Fioreze I, Vieira ML, Durigon FF, Fávero F. Adaptação de um equipamento para incorporação de calcário em solos sob plantio direto. Rev Cienc Agrovet. 2007;6:95-103.

Klein VA. Gradiente químico de solos sob plantio direto: uma condição que limita a produtividade das plantas. Rev Plantio Dir. 2011;126:23-26.

Kramer LFM, Müller MML, Tormena CA, Genú AM, Michalovicz L, Vicensi M. Atributos químicos do solo associados à produtividade do trigo em um talhão com diferentes potenciais produtivos. Rev Bras Cienc Solo. 2014;38:1190-9. doi:10.1590/S0100-06832014000400015

Lima JSS, Silva SA, Silva JM. Variabilidade espacial de atributos químicos de um Latossolo Vermelho-Amarelo cultivado em plantio direto. Rev Cienc Agron. 2013;44:16-23.

Medeiros JC, Albuquerque JA, Mafra AL, Rosa JD, Gatiboni LC. Calcium: magnesium ratio in amendments of soil acidity: nutrition and initial development of corn plants in a Humic Alic Cambisol. Semina: Cienc Agron. 2008;29:799-806. doi:10.5433/1679-0359.2008v29n4p799

Michalovicz L. Atributos químicos do solo e resposta da sucessão milho-cevada-feijão-trigo influenciados por doses e parcelamento de gesso em plantio direto [dissertação]. Guarapuava: Universidade Estadual do Centro-Oeste; 2012.

Neis L, Paulino HB, Souza ED, Reis EF, Pinto FA. Gesso agrícola e rendimento de grãos de soja na região do sudoeste de Goiás. Rev Bras Cienc Solo. 2010;34:409-16. doi:10.1590/S0100-06832010000200014

Nogueira MA, Melo WJ. Enxofre disponível para a soja e atividade de arilsulfatase em solo tratado com gesso agrícola. Rev Bras Cienc Solo. 2003;27:655-63. doi:10.1590/S0100-06832003000400010

Nunes MR, Denardin JE, Faganello A, Pauletto EA, Pinto LFS. Efeito de semeadora com haste sulcadora para ação profunda em solo manejado com plantio direto. Rev Bras Cienc Solo. 2014;38:627-38. doi:10.1590/S0100-06832014000200027

Pavan MA, Bloch MF, Zempulski HC, Miyazawa M, Zocoler DC. Manual de análise química de solo e controle de qualidade. Londrina: Instituto Agronômico do Paraná; 1992. (Boletim técnico).

Prado RM. Nutrição de plantas. São Paulo: Universidade Estadual de São Paulo; 2008.

Raij Bvan, Furlani PR, Quaggio JA, Pettinelli Jr A. Gesso na produção de cultivares de milho com tolerância diferencial a alumínio em três níveis de calagem. Rev Bras Cienc Solo. 1998;22:101-8. doi:10.1590/S0100-06831998000100014

Raij Bvan. Gesso na agricultura. Campinas: Instituto Agronômico; 2008. doi:10.1590/S0100-06831998000100014

Rampim L, Lana MC, Frandoloso JF, Fontaniva S. Atributos químicos de solo e resposta do trigo e da soja ao gesso em sistema de semeadura direta. Rev Bras Cienc Solo. 2011;35:1687-98. doi:10.1590/S0100-06832011000500023

Rashid M, Iqbal MN, Akram M, Ansar M, Hussain R. Role of gypsum in wheat production in rainfed areas. Soil Environ. 2008;27:166-70.

Reeve NG, Sumner ME. Amelioration of subsoil acidity in Natal Oxisols by leaching of surface-applied amedments. Agrochemophysica. 1972;4:1-6.

Santos AD, Coscione AR, Vitti AC, Boaretto AE, Coelho AM, Raij Bvan, Silva CA, Abreu Júnior CH, Carmo CAFS, Silva CR, Abreu CA, Gianello C, Andrade CA, Perez DV, Casarini DCP, Silva FC, Prata F, Carvalho FC, Santos GCG, Cantarella H, Fernandes HMG, Andrade JC, Quaggio JA, Chitolina JC, Cunha LMS, Pavan MA, Rosias MFGG, Tedesco MJ, Miyazawa M, Abreu MF, Eira PA, Higa RH, Massrubá SMFS, Gomes TF, Muraoka T, Vieira W, Melo WJ, Barreto WO. Manual de análises químicas de solos, plantas e fertilizantes. 2ª. ed. Brasília, DF: Embrapa Informação Tecnológica; Rio de Janeiro: Embrapa Solos; 2009.

Santos HG, Jacomine PKT, Anjos LHC, Oliveira VA, Oliveira JB, Coelho MR, Lumbreras JF, Cunha TJF. Sistema brasileiro de classificação de solos. 3ª. ed. Rio de Janeiro: Embrapa Solos; 2013.

Soil Survey Staff. Keys to soil taxonomy. 12th.ed. Washington, DC: United States Department of Agriculture, Natural Resources Conservation Service; 2014.

Soratto RP, Crusciol CAC. Nutrição e produtividade de grãos de aveia-preta em função da aplicação de calcário e gesso em superfície na implantação do sistema de plantio direto. Rev Bras Cienc Solo. 2008;32:715-25. doi:10.1590/S0100-06832008000200026

Spera ST, Escosteguy PAV, Denardin JE, Klein VA, Santos HP. Atributos químicos restritivos de Latossolo Vermelho distrófico e tipos de manejo de solo e rotação de culturas. Agrarian. 2011;4:324-34.

Tang C, Rengel Z, Diatloff E, Gazey C. Responses of wheat and barley to liming on a sandy soil with subsoil acidity. Field Crop Res. 2003;80:235-44. doi:10.1016/S0378-4290(02)00192-2

Toma M, Sumner M, Weeks G, Saigusa M. Long-term effects of Gypsum on crop yield and subsoil chemical properties. Soil Sci Soc Am J. 1999;63:891-5. doi:10.2136/sssaj1999.634891x

Venzke Filho SP, Feigl BJ, Piccolo MC, Siqueira Neto M, Cerri CC. Biomassa microbiana do solo em sistema de plantio direto na região de Campos Gerais – Tibagi, PR. Rev Bras Cienc Solo. 2008;32:599-610. doi:10.1590/S0100-06832008000200015

Zambrosi FCB, Alleoni LRF, Caires EF. Aplicação de gesso agrícola e especiação iônica da solução de um Latossolo sob sistema de plantio direto. Cienc Rural. 2007;37:110-7. doi:10.1590/S0103-84782007000100018

Zambrosi FCB, Alleoni LRF, Caires EF. Liming and ionic speciation of an Oxisol under no-till system. Sci Agric. 2008;65:190-203. doi:10.1590/S0103-90162008000200013