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Ion mobility and base saturation after gypsum application in continuous soybean-wheat cropping system under no-till

Leandro Rampim, Maria do Carmo Lana

Center for Agriculture Sciences, Post-graduate Program in Agronomy, West Parana State University–UNIOESTE, Pernambuco Street No. 1777, P.O. Box 9, Zip Code 85960-000, city of Marechal Cândido Rondon, State of Paraná, Brazil

***Corresponding author: rampimleandro@yahoo.com.br.**

Abstract

Gypsum can improve the soil chemical properties; thus, affecting positively root growth and crop yield in acid soils with high aluminum (Al^{3+}) levels. However, few studies show the relationships between nutrients leached, base balance and base saturation in soils with high Ca^{2+} levels at surface and subsurface. This study aimed to evaluate the effect of surface application of gypsum on the soil chemical properties and ion mobility to increase base saturation in the subsurface of two clay Rhodic Hapludox with different exchangeable acidity levels under continuous soybean-wheat cropping in no-tillage system. The experiments were conducted in Guaíra, Paraná State, Brazil, at two different sites: Site 1 (soil with medium fertility level and with presence of exchangeable Al – 0.45 $cmol_c\ dm^{-3}$) and Site 2 (soil with high fertility and absence of exchangeable Al). Treatments consisted of surface application of six gypsum rates [0 (control), 1.0, 2.0, 3.0, 4.0, and 5.0 t ha^{-1} of $CaSO_4.2H_2O$ (17% Ca and 15% S-SO_4^{2-})] arranged in a randomized block design with six replications. Soil chemical properties (H^+ and Al, K^+, Ca^{2+}, Mg^{2+}, Al^{3+} and S-SO_4^{-2}) were evaluated 6 (October 2006) and 12 months (April 2007) after the gypsum application at depths of 0.0–0.10; 0.10–0.20 and 0.20–0.40 m. The agricultural gypsum use resulted in increase of S-SO_4^{-2} content, Ca^{2+} content, $Ca^{2+}/K^{+}+Mg^{2+}$ ratio, sum of exchangeable basic cations (SB) and effective cation exchange capacity (ECEC), as well as in reduction of $K^{+}+Mg^{2+}$ content and aluminum saturation (m%) in the soil profile. The gypsum application increased soil base saturation (V%) in the 0.20-0.40 m layer at both sites. The gypsum application improves of soil chemical properties resulting in increased grain yield of wheat crop.

Key words: base saturation, aluminum, subsurface acidity, leaching, potassium, magnesium.

Abbreviations: pH_hydrogen potential; Al_aluminum; m%_aluminum saturation; H+Al_potential acidity; Al^{3+}_exchangeable aluminum; Ca^{2+}_exchangeable calcium; Mg^{2+}_exchangeable magnesium; K^+_exchangeable potassium; Na^+_exchangeable sodium; $K^{+}+Mg^{2+}$_potassium plus magnesium; $Ca^{2+}/K^{+}+Mg^{2+}$_calcium/potassium plus magnesium ratio; SB_sum of exchangeable basic cations (Ca + Mg + K + Na); ECEC_effective cation exchange capacity; CEC_cation exchange capacity; V%_soil base saturation; C_carbon; OM_organic matter; P_phosphorus; S-SO_4^{2-}_sulfate; F_fluoride; t ha^{-1}_ton per hectare; S_South; W_West; CD_Coodetec; m_meter; ZCP_zero charge point; N-NO_3^-_nitrate; OH^-_hydroxyl; N_2_atmospheric nitrogen; ECCE_effective calcium carbonate equivalent; F_Fischer-Snedecor.

Introduction

The gypsum or calcium sulfate dehydrate ($CaSO_4.2H_2O$) is a by-product of the phosphoric acid industry, which is necessary for the production of triple superphosphate and ammonium phosphate [monoammonium phosphate (MAP) and diammonium phosphate (DAP)]. The gypsum contains mainly calcium sulfate and small amounts of P (phosphorus) and F (fluoride), and is largely available in many parts of the world (Dias et al., 2010). Gypsum has been used in tropical and subtropical agriculture when soil acidity is an important limiting factor for crop yield (Caires et al., 2011b; Blum et al., 2011). The agricultural gypsum may reduce the soil exchangeable acidity (Raij, 2011), improve the soil chemical properties (Souza et al., 2010), act as conditioner for acid and clayed soils (Bilibio el al., 2010; Souza et al., 2012b), or as soil uncompressing agent (Raij, 2011), increase the water and nutrient uptake of the plants due to improved distribution of roots in the soil (Sousa et al., 1996), increase the soil carbon accumulation (Ferreira et al., 2013), improve the structural quality and aggregate stability of the soils (Souza et al., 2011; Souza et al., 2012a; Müller et al., 2012), improve the plant growth and therefore increase the crop yield (Sousa et al., 1996; Caires et al., 2002; Soratto et al., 2010; Caires et al., 2011a). Thus, the use of agricultural gypsum avoids interruption of no-till, since after its deployment there is no soil disturbance, improving subsoil fertility in no-till system (Dias et al., 2010). The recommendation of gypsum application to mitigate the effects of subsoil acidity should be performed based on soil analysis in the layer of 0.20 to 0.40 m, and used when the soil Al saturation is greater than 20% and/or when soil Ca saturation is less than 60% of the cation exchange capacity (Sousa et al., 1996). In general, the agricultural gypsum rates are of 0.7, 1.2, 2.2 and 3.2 t ha^{-1} for sandy, medium, clayey and very clayey soils, respectively, with residual effect for five years. Studies indicate that the gypsum use resulted in increase of Ca^{2+} content and pH of the soil profile, as well as in reduction of potential acidity (H^+ +

Al) (Chaves et al., 1988; Ferreira et al., 2013). Moreover, promoted the gradual percolation of sulfate (S-SO_4^{2-}) and basic cations (Raij, 2011) and subsequent development of deep roots in annual crops (Sousa and Ritchey, 1986). Significant increases on maize yield has been obtained with agricultural gypsum use (Caires et al., 2011a), as well as reduction of salinity and sodicity of saline-sodic soils, coupled with increased of Ca^{2+} contents and sodium (Na^+) reduction (Tavares-Filho et al., 2012), improving the soil chemical properties (Wadt and Wadt 1999; Caires et al., 2003; Souza et al., 2010). In this context, Nava et al. (2012) found increased in Ca^{2+} contents in the depth of 0.80 m in soil with Ca^{2+}/Mg^{2+} ratio of 2:1; however, it was not effective to increase the Ca concentration in the foliar tissues and fruits of apple sensitive to Ca deficiency. Caires et al. (2011b) reported mobility of Mg^{2+} and K^+ at depths up to 0-0.10 and 0-0.20 m, respectively, and economic return of annual crops with gypsum application in soil with sufficient levels of exchangeable cations (2.5 $cmol_c$ dm^{-3} of Ca^{2+} and 2.0 $cmol_c$ dm^{-3} of Mg^{2+} in the 0-0.20 m layer). Blum et al. (2011) found that gypsum application decreased the subsoil exchangeable Al level, increased the Ca^{2+} and SO_4^{2-}contents in the soil profile, and caused leaching of Mg^{2+} from the topsoil and decreases of leaf Mg concentration and fruit production. These authors estimated a critical level of Ca/Mg ratio in soil as well as in leaves of 1.9 for vine.

Some studies showed the relationships between ion mobility, base balance and soil base saturation with contents of Ca^{2+}, Mg^{2+} and K^+ in surface and subsurface soil layers have no such limitations in deep layers. This situation could harm the soil base balances and enhance the uptake of some basic cations, therefore, can change the plant nutritional balances, mainly with gypsum use resulting in increases of Ca^{2+} supply in the subsoil layer (Caires et al., 2011b; Blum et al., 2011; Raij, 2011; Nava et al., 2012; Souza et al., 2012b; Ferreira et al., 2013; Blum et al., 2013; Santos et al., 2013; Michalovicz et al., 2014). This study aimed to evaluate the effect of surface application of gypsum on the soil chemical properties and ion mobility to increase base saturation in the subsurface of two clayey Rhodic Hapludox with different exchangeable acidity levels, under continuous soybean-wheat cropping in no-tillage system.

Results and Discussion

Sulfate mobility in the soil

The application of gypsum rates increased the S-SO_4^{2-} content in the three soil depths (Table 1). The increase of S-SO_4^{2-} level in the soil profile was expected due to the high solubility of gypsum, as reported by Soratto and Crusciol (2008a), Gelain et al. (2011), Souza et al. (2012b) and Tavares-Filho et al. (2012). Michalovicz et al. (2014) also found that the application of gypsum rates increased S-SO_4^{-2} content in the soil profile, as well as increased leaf S and grain yield of barley and maize. Gypsum has higher solubility than lime (Raij, 2011); gypsum application in an tropical soil had a long residual effect on the S-SO_4^{2-} levels, and high sulfate concentrations in the subsoil being found eight years after the application (Caires et al., 2011c).

The increased S-SO_4^{2-} content in the subsurface layer can reduce zero charge point (ZCP), since there is less organic matter content in this layer (Table 1), the PCZ reduction was due to the S-SO_4^{2-} adsorption as reported by Caires et al. (2011b) and Serafim et al. (2012). When occurs the S-SO_4^{-2} adsorption in iron and aluminum oxides (Wadt and Wadt, 1999), it counteracts positive charges of the adsorbent surface and generates new sites for adsorption of cations, and thereby reduces the PCZ, enabling take cations mobilized from the upper layers. In the subsurface layer has PCZ lower than in the top layer, which is explained by the higher ECEC coupled to liming effect and a higher OM content, which facilitates the cations mobility, detected at high gypsum rates (Figure 1), as well as their accumulation on subsurface layers. Thus, when using gypsum is necessary to consider the charge balances, as it may result in intense ion mobility in profile (Caires et al., 2003; Caires et al., 2011b). Wadt and Wadt (1999) observed K^+ mobility in soils with higher OM content and lower pH value due to the low affinity of this cation where there is greater encouragement to protonation of colloids surface.

Grain yield of crops

Despite the increased S-SO_4^{2-} levels with the gypsum application, there was no response in the soybean grain yield, achieving mean yield of 3.62 t ha^{-1} for the Site 1 (with Al^{3+}) and 2.93 t ha^{-1} for Site 2 (Al^{3+}-free). Similar results were also obtained by Caires et al. (2003) and Caires et al. (2011a) for this crop. Gelain et al. (2011) observed that soil with S-SO_4^{2-} content above 7.6 and 5.3 mg dm^{-3} in the 0-0.20 and 0.20-0.40 m layers, respectively, did not increased leaf N concentration and soybean yield. On the other hand, Souza et al. (2010) found increased plant height while Raij et al. (2011) and Sousa et al. (1996) found increased grain yield of soybean crop in tropical soils.

For wheat crop there was linear increase in grain yield at Site 1, with quadratic effect for Al saturation (m%) (Table 1), and m% values of 7.4% for the 0.20-0.40 m layer (Table 2). These data report the interference of gypsum use in soils with toxic Al levels. The yield response observed in wheat crop for Site 1 (with Al^{3+}) is explained by the linear equation ($Yield_{wheat}$ = 1.368 + 0.070Gypsum in t ha^{-1}). Similar results were also observed by Caires et al. (2002) and Sousa et al. (1996) for wheat crop, as well as in maize crop as reported by Caires et al. (2011a). On the other hand, the Site 2 (Al^{3+}-free) showed no effect of gypsum use on wheat crop, with mean grain yield of 2.12 t ha^{-1}. Caires et al. (2011b) found the following response decreasing order of crops the gypsum application: wheat > maize > soybean, and demand for Ca^{2+} and S-SO_4^{2-} followed the reverse order: soybean > maize > wheat. These authors explained that wheat and maize crops require less Ca and S-SO_4^{2-} than the soybean crop, but the response to the increase in Ca^{2+} and S-SO_4^{2-} availability is greater. Cereal crops are less efficient in Ca^{2+} uptake due to lower cation exchange capacity of roots, as well as has a lower efficiency in S-SO_4^{2-} translocation (Caires et al., 2011b; Caires et al., 2011c). However, Blum et al. (2014) observed increase Mg concentration in the maize and wheat leaves in study with gypsum application, and attributed this fact to greater basic cation uptake of cereal crops in response to gypsum application. Indeed, Blum et al. (2011) showed positivity correlation between leaf Mg concentration and crop yield.

Soil chemical properties

The application of agricultural gypsum significantly affected the Ca^{2+} and K^++Mg^{2+} content in the 0-0.10, 0.10-0.20 and 0.20-0.40 m layers, as well as influenced the levels of Al saturation (m%), sum of basic cations (SB), effective cation exchange capacity (ECEC), Ca^{2+}/K^++Mg^{2+} ratio, in addition of base saturation (V%) in the 0.20-0.40 m layer (Table 1, Figures 1, 2 and 3).

Table 1. Regression equations and determination coefficients for grain yield of wheat and soybean and some soil chemical properties after 6 and 12 months from the surface application of gypsum rates in two clayey Rhodic Hapludox with different exchangeable acidity levels, under continuous soybean-wheat cropping in no-tillage system.

Properties	Units	Period	Depth (m)	Equation	R^2
m(1)	%	6 months	0-0.10	$m = 10.58 – 3.4\ G + 5x10^{-4}\ G^2$ (2)	0.91**
			0.10-0.20	$m = 11.63 – 4.2\ G + 6x10^{-4}\ G^2$	0.90*
			0.20-0.40	$m = 16.57 – 3.4\ G + 7x10^{-4}\ G^2$	0.90*
		12 months	0-0.10	$m = 15.80 – 3.3\ G + 5x10^{-4}\ G^2$	0.85*
			0.10-0.20	$m = 19.42 – 4.3\ G + 7x10^{-4}\ G^2$	0.94*
			0.20-0.40	$m = 20.98 – 4.9\ G + 9x10^{-4}\ G^2$	0.90**
$S\text{-}SO_4^{2-}$	$mg\ dm^{-3}$	6 months	0-0.10	$S = 8.00 + 23.7\ G$	0.93**
			0.10-0.20	$S = 16.51 + 27.0\ G$	0.97**
			0.20-0.40	$S = 26.14 + 24.0\ G$	0.98**
		12 months	0-0.10	$S = 5.48 + 7.2\ G$	0.90**
			0.10-0.20	$S = 12.87 + 9.0\ G$	0.96**
			0.20-0.40	$S = 19.45 + 12.0\ G$	0.97**
Ca^{2+}	$cmol_c\ dm^{-3}$	6 months	0-0.10	$Ca = 5.06 + 0.3\ G$	0.93**
			0.10-0.20	$Ca = 4.85 + 0.3\ G$	0.95**
			0.20-0.40	$Ca = 4.36 + 0.2\ G$	0.98**
		12 months	0-0.10	$Ca = 5.13 + 0.1\ G$	0.48*
			0.10-0.20	$Ca = 4.10 + 0.4\ G – 5x10^{-5}\ G^2$	0.90**
			0.20-0.40	$Ca = 4.10 + 0.3\ G – 2x10^{-5}\ G^2$	0.97*
$K^+ + Mg^{2+}$	$cmol_c\ dm^{-3}$	6 months	0-0.10	$K+Mg = 1.79 – 0.16\ G$	0.95**
			0.10-0.20	$K+Mg = 1.57 – 0.08\ G$	0.73*
			0.20-0.40	$K+Mg = 1.43 – 0.04\ G$	0.46*
		12 months	0-0.10	$K+Mg = 2.18 – 0.12\ G$	0.99**
			0.10-0.20	$K+Mg = 2.04 – 0.09\ G$	0.90**
			0.20-0.40	$K+Mg = 1.73 – 0.02\ G$	0.60**
SB	$cmol_c\ dm^{-3}$	6 months	0-0.10	$SB = 7.24 + 0.2\ G$	0.83*
			0.10-0.20	$SB = 6.89 + 0.2\ G$	0.85**
			0.20-0.40	$SB = 6.09 + 0.2\ G$	0.96**
		12 months	0-0.10	$SB = 6.85$	ns
			0.10-0.20	$SB = 5.62 + 0.4\ G – 6\ G^2$	0.74**
			0.20-0.40	$SB = 5.36 + 0.1\ G$	0.74*
ECEC	$cmol_c\ dm^{-3}$	6 months	0-0.10	$ECEC = 7.53 + 0.2\ G$	0.76**
			0.10-0.20	$ECEC = 7.22 + 0.2\ G$	0.81**
			0.20-0.40	$ECEC = 6.54 + 0.2\ G$	0.98**
		12 months	0-0.10	$ECEC = 7.14$	ns
			0.10-0.20	$ECEC = 6.13 + 0.3\ G$	0.66*
			0.20-0.40	$ECEC = 5.58 + 0.1\ G$	0.89**
$H^+ + Al$	$cmol_c\ dm^{-3}$	6 months	0-0.10	$H+Al = 3.23$	ns
			0.10-0.20	$H+Al = 3.45$	ns
			0.20-0.40	$H+Al = 3.20$	ns
		12 months	0-0.10	$H+Al = 4.00$	ns
			0.10-0.20	$H+Al = 4.22$	ns
			0.20-0.40	$H+Al = 3.94$	ns
V	%	6 months	0-0.10	$V\% = 70.22$	ns
			0.10-0.20	$V\% = 67.39$	ns
			0.20-0.40	$V\% = 63.95 + 1.3\ G$	0.82*
		12 months	0-0.10	$V\% = 62.38$	ns
			0.10-0.20	$V\% = 58.03$	ns
			0.20-0.40	$V\% = 55.97 + 1.0\ G$	0.73*
Grain yield	Unit	Period	Site	Equation	R^2
Wheat	$kg\ ha^{-1}$	6 months	with Al	$Yield = 1,368 + 0.07\ G$	0.70*
			without Al	$Yield = 2,123$	ns
Soybean	$kg\ ha^{-1}$	12 months	with Al	$Yield = 3,624$	ns
			without Al	$Yield = 2,927$	ns

(1) Al saturation only for site 1, with the presence of exchangeable Al. (2) G- Gypsum rates in t ha^{-1}. ns, * and **: non-significant and significant at 5 and 1% by the F test, respectively. Abbreviations: m- aluminum saturation; $S\text{-}SO_4^{2-}$- sulfate; Ca^{2+}-calcium; $K^+ + Mg^{2+}$-potassium plus magnesium; SB-sum of exchangeable basic cations; ECEC-effective cation exchange capacity; $H^+ + Al$-potential acidity; V%-soil

Table 2. Soil chemical properties and particle size at 0-0.10, 0.10-0.20 and 0.20-0, 40 m depth at the beginning of the experiments (March 2006), for the two study sites

Properties	Unit	Site 1 (with Al)			Site 2 (without Al)		
		0-0.10 m	0.10-0.20 m	0.20-0.40 m	0-0.10 m	0.10-0.20 m	0.20-0.40 m
pH(1)		4.80	4.10	4.10	5.80	5.40	4.80
Al^{+3}(2)	cmol$_c$ dm^{-3}	0.20	0.35	0.45	0.00	0.00	0.00
H+Al(3)	cmol$_c$ dm^{-3}	4.61	4.28	4.96	3.40	3.60	3.90
Ca^{+2}(2)	cmol$_c$ dm^{-3}	4.77	4.04	3.77	6.20	6.03	5.89
Mg^{+2}(2)	cmol$_c$ dm^{-3}	1.98	1.85	1.60	1.64	1.50	1.40
K^{+}(4)	cmol$_c$ dm^{-3}	0.59	0.35	0.26	0.40	0.35	0.28
SB	cmol$_c$ dm^{-3}	7.34	6.24	5.63	8.24	7.88	7.57
CEC $_{\text{pH 7.0}}$	cmol$_c$ dm^{-3}	11.95	10.52	10.59	11.64	11.48	11.47
V	%	61.42	59.32	53.16	70.79	68.64	66.00
m	%	2.65	5.31	7.40	0.00	0.00	0.00
OM(5)	g kg^{-1}	20.00	15.00	11.00	26.00	22.00	19.00
P(4)	mg dm^{-3}	12.32	7.19	3.11	15.00	12.00	8.00
S-SO$_4^{-}$(6)	mg dm^{-3}	11.43	18.50	21.49	9.27	9.50	12.15
Sand(6)	g kg^{-1}	66	74	55	63	64	64
Silt6)	g kg^{-1}	204	129	145	190	132	133
Clay(6)	g kg^{-1}	730	797	800	747	804	803

(1) Measured in 0.01 mol L^{-1} CaCl$_2$ suspensions (1:2.5 soil:solution ratio); (2) Extracted by 1 mol L^{-1} KCl; (3) Extracted by calcium acetate (0.5 mol L^{-1} Ca(C$_2$H$_3$O$_2$)$_2$; pH 7.0); (4) Extracted by Mehlich-1; (5) Measured by Walkley-Black method; (5) Extracted by 500 mg L^{-1} Ca(H$_2$PO$_4$)$_2$ of P in 2 mol L^{-1} HOAc; (7) Measured by densimeter method (Embrapa, 2009). Abbreviations: pH-hydrogen potential; Al^{+3}-exchangeable aluminum; H+Al-potential acidity; Ca^{2+}-calcium; Mg^{2+}-magnesium; K^{+}-potassium; SB-sum of exchangeable basic cations (Ca^{2+} + Mg^{2+} + K^{+} + Na^{+}); CEC-cation exchange capacity; V-soil base saturation; m- aluminum saturation; OM-organic matter; P-phosphorus; S-SO$_4^{2-}$-sulfate.

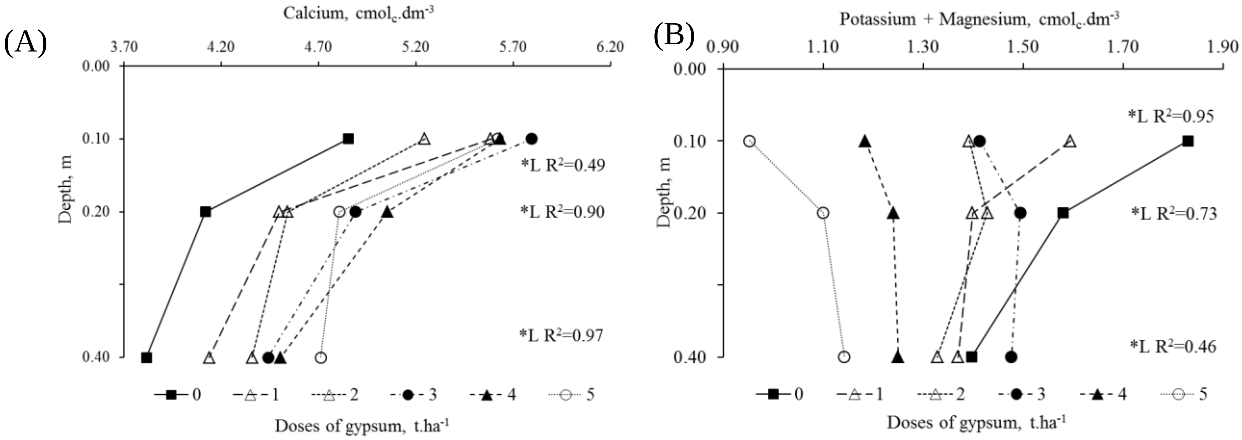

Fig 1. Calcium (A) and magnesium plus potassium contents (B) in the soil profile after 12 months from the surface application of gypsum rates in two clayey Rhodic Hapludox with different exchangeable acidity levels, under continuous soybean-wheat cropping in no-tillage system. Data refer to mean values of the two soils. *L: statistical significance at 5% by the F test, with linear regression effect.

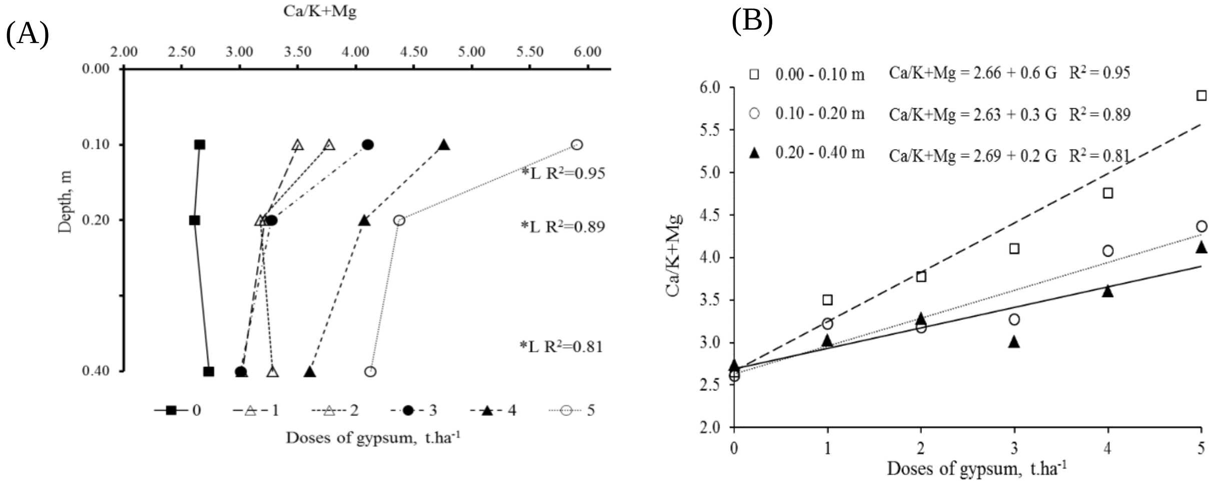

Fig 2. Calcium/potassium plus magnesium ratio (Ca^{2+}/K^{+} + Mg^{2+}) in the soil profile after 12 months from the application of gypsum (A) and as result of the surface application of gypsum rates in the different soil layers (B). Data refer to mean values of the two clayey Rhodic Hapludox with different exchangeable acidity levels, under continuous soybean-wheat cropping in no-tillage system. *L: statistical significance at 5% by the F test, with linear regression effect.

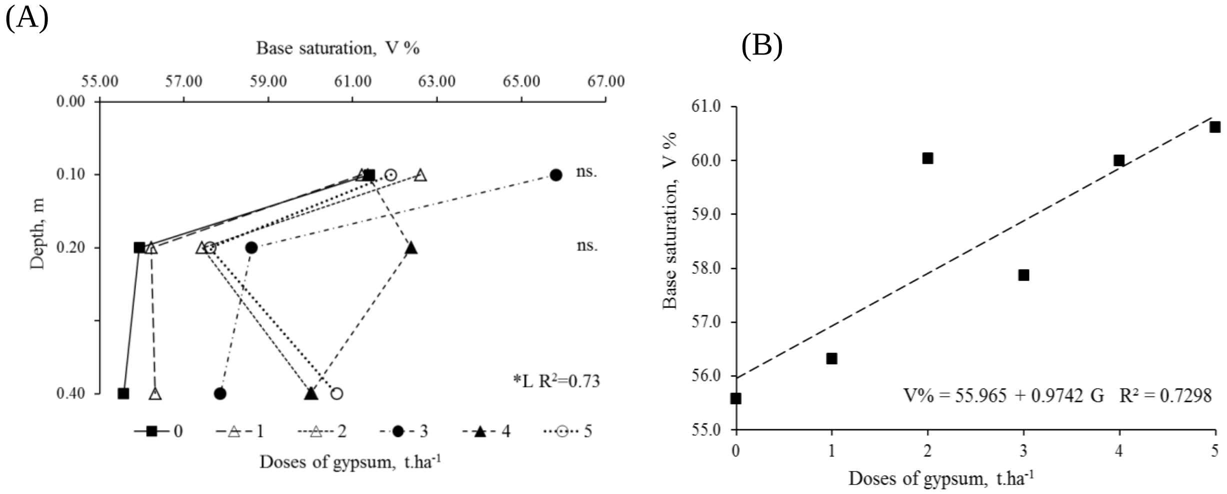

Fig 3. Soil base saturation (V%) in the soil profile after 12 months from the application of gypsum (A) and as result of the surface application of gypsum rates in the 0.0-0.40 m layer (B). Data refer to mean values of the two clayey Rhodic Hapludox with different exchangeable acidity levels, under continuous soybean-wheat cropping in no-tillage system. ^{ns}: non-significant. *L: statistical significance at 5% by the F test, with linear regression effect.

The value of m%, SB and ECEC and V% are higher after 6 months from the surface application of gypsum rates (after growing wheat). However, the H^++Al values are higher at 12 months in all layers of soil (Table 1). This result may be related to the differences in the nutrient uptake of each crop, changing the cations availability in the rhizosphere. Soybean has the ability to fix atmospheric nitrogen (N_2), and hence taken up less N-NO_3^- of rhizosphere region with lower pH value (Maschner, 2012). Moreover, according to Haynes (1990) the wheat crop has preferential uptake of anions, providing greater release of OH^- in the rhizosphere, fact that increases the availability of cations. The Al saturation at 6 months, in the absence of gypsum, was around 16.57% in the 0.20-0.40 m layer, while that the m% was around 20.98% at 12 months for Site 1 (with Al^{3+}) (Table 1), but higher than the initial chemical analysis (Table 2). The decrease of m% levels at Site 1 (with Al^{3+}) is consistent with Nava et al. (2012), who found lowest m% value with the application of 3.0 t ha^{-1}. Furthermore, Maria et al. (1993) observed Al^{3+} reduction in the surface layer. Moreover, Nava et al. (2012) found no effect on Al^{3+} content, even with annual applications of 3 t ha^{-1} of gypsum in the soil surface for eight years in apple orchards.

The presence of Al^{3+} at Site 1 (with Al) coupled to calcium deficiency are among the main factors inhibiting the root growth, especially in tropical soils (Oliveira et al., 2009). In no-till, the gypsum affects the nutrient cycling when dragging S-SO_4^{2-} and basic cations to the deeper layers (Soratto and Crusciol 2008b; Caires et al., 2011a; Raij, 2011; Serafim et al., 2012). Thus, the gypsum use may mobilize elements of the surface layers and deposit them into the deeper layers, improving the chemical conditions of subsoil (Souza et al. 1996; Souza et al., 2010). This provides favorable conditions for root growing in depth, where, besides obtaining of nutrients also increases the root surface area for water absorption during the crop cycle, particularly under water stress, as reported by Chaves et al. (1988).

Potential acidity and cation exchange capacity

The potential acidity (H^++Al) was lower in the three depths relative to the baselines (Table 1); however, there was no significant effect of the gypsum application. Soratto and Crusciol (2008a) also found no effect on the values of H^++Al below the surface layer after 18 months from the application 2.1 t ha^{-1} of gypsum. The evaluation of potential acidity at depths reveals that there was higher values of H^++Al in the 0.10-0.20 m layer at 6 and 12 months after gypsum application (Table 1). The use of agricultural gypsum resulted in increased Ca^{2+} level in the soil (Figure 1), confirming the results reported by Soratto and Crusciol (2008a), Bilibio et al. (2010), Souza et al. (2012b) and Nava et al. (2012). This increase in the Ca^{2+} level resulted in increase of the SB and ECEC to the 6 months at all depths analyzed (Table 1). However, Chaves et al. (1988) reported increase in ECEC only in the 0.20-0.40 m layer. After 12 months of gypsum application was not detected significant change in the SB up to 0.10 m depth; however, the amount of SB in the 0.10-0.20 m layer was affected with maximum value of 6.3 $cmol_c$ dm^{-3} with application of 3.3 t ha^{-1} of gypsum, as well as linear increase to the depth of 0.20-0.40 m. The absence of change in ECEC in the 0-0.10 m layer after 12 months of gypsum application (Table 1) was also reported by Wadt and Wadt (1999), who verified that gypsum reduced the Al^{3+} in the surface layer without resulting in change in CEC. However, the gypsum application showed linear ECEC increase in the 0.10-0.20 and 0.20-0.40 m, indicating being first necessary the CEC increase in the subsurface for soil chemical reactions be favorable to the Al^{3+} reduction. Santos et al. (2013) found that gypsum application resulted in increased of the CEC (27%) in a saline-sodic Inceptisol with high exchangeable Ca^{2+} level. The CEC increase is related by Ca^{2+} solubilized by gypsum remain in the soil solution, acting as C pool, consequently reduce H^++Al. Although, the increase of organic matter content may increase CEC and microbial activity of surface layer in no-till (Caires et al., 2011b), less in subsoil layer. Ferreira et al. (2013) observed increase of CEC when had high exchangeable Ca^{2+} by the gypsum application, and detected positivity correlation between Ca^{2+} and C in an tropical soil; therefore, the C accumulation resulted in increased CEC. Müller et al. (2012) verified that gypsum application increased of soil porosity and reduction of soil bulk density due to the increase of the carbon content and aggregation forces enhanced by the increase of Ca^{2+} availability in surface layer.

Soil base saturation

Part of gypsum may be mobilized to the subsoil layer where dissociation occurs, since there is lower pH at the depth (Table 1), and lower values of SB and ECEC (Table 1 and 2). This chemical conditions are favorable for dissociation, whereas increased the SB, CEC and V%, even with the mobility of K^{+}+Mg^{2+} it the 0.20-0.40 m layer (Figure 3). Thus, the addition of Ca^{2+} detected to the depth could reverse the interference of mobility of K^{+}+Mg^{2+} with gypsum surface application on the SB and ECEC. The SB and ECEC remained unchanged in the 0-0.10 m and after 12 months of gypsum surface application. In this study, the improvement of subsoil chemical properties with gypsum use was evidenced by the increase in the base saturation (V%) in soil profile (Table 1). The application of gypsum rates resulted in increased linearly the V% value in the 0.20-0.40 m layer. This results was due to increased Ca^{2+} content in the soil profile (Figure 1a), resulting in higher SB value and, consequently, in an increase of the V% (Figure 3), even with reduction of K^{+}+Mg^{2+} content in the subsoil (Figure 1b). The increase of soil base saturation after 12 months of gypsum application was due to increased Ca^{2+} content of soil from the dissociation of calcium sulfate. Soratto and Crusciol (2008a) observed increased of V% up to depth of 0.60 m, as result of movement of Ca^{2+} and Mg^{2+} in the soil profile after 12 months of application of 2.1 t ha^{-1} of gypsum. However, Soratto and Crusciol (2008b) detected increased of V% in the 0-0.20 m layer after 6 and 18 months gypsum application. In this study, the gypsum use was not enough to increase the V% in the surface layers (i.e., 0-0.10 and 0.10-0.20 m), since that there was mobility of K^{+}+Mg^{2+} (Figure 1b), as verified by the higher Ca^{2+}/K^{+}+Mg^{2+} ratio in the surface layers (Figure 2). Caires et al. (2011b) verified that exchangeable K losses by leaching were low; however, larger mobility of exchangeable Mg in soil profile was reported with the gypsum application in a subtropical no-till cropping system. Blum et al. (2013) showed that the Mg ion was most susceptible to leaching compared to K^{+} and Ca^{2+}, resulting in increased of Mg^{2+} content in the 0.80-1.20 m depth.

Relationship between ions

Gypsum application resulted in reduction in K^{+}+Mg^{2+} content in the 0-0.10 and 0.10-0.20 m layers (Figure 1b), similar results were also reported by Caires et al. (2011a). These results indicated that the K^{+} and Mg^{2+} ions were mobilized to layers beyond 0.40 m, above all, with greater intensity in the higher gypsum rates (Figure 1b). The reduction of K^{+} in the surface layer was also observed by Maria et al. (1993) and Bilibio et al. (2010), while Caires et al. (2011a) observed decrease of Mg^{+}ion in a tropical soil. Moreover, Serafim et al. (2012) found no change in the K content, and Nava et al. (2012) identified no K^{+} reduction even with applications up to 3 t ha^{-1} during 8 years in soil with 450 g dm^{-3} of clay, but found reduction of Mg^{2+} content in the surface layer of 0-0.20 m. Similarly, Serafim et al. (2012) found reduction in Mg^{2+} content in the surface layer and increase of this ion in the subsoil layer. Gypsum may reduce the exchangeable sodium (Na^{+}) and K^{+} in saline-sodic soil, because increased at Ca^{2+} level and provide imbalance of cations (Santos et al., 2013). The cation imbalance in the soils is one of the most important problem for crop development and yield (Holanda et al., 1998).

The Ca^{2+}/K^{+}+Mg^{2+} ratio increased progressively with increasing of gypsum rates in all soil layers (Figure 2). In the absence of gypsum application the Ca^{2+}/K^{+}+Mg^{2+} ratio was similar in the three soil layers. Table 2 show values of 3.77:1.60:0.26 $cmol_c$ dm^{-3} and 5.89:1.40:0.28 $cmol_c$ dm^{-3} for the contents of Ca^{2+}:Mg^{2+}: K^{+} in site 1 (with Al^{3+}) and site 2 (Al^{3+}-free), respectively, in the 0.20-0.40 m layer, similarly to surface layers. Caires et al. (2011b) detected increase of Mg^{2+} and K^{+} mobility to the topsoil layer in tropical soil with Ca^{2+}:Mg^{2+}:K^{+} values of 0.70:0.80:0.22 $cmol_c$ dm^{-3} in the subsurface (0.20-0.40 m) and 2.5:2:0.36 $cmol_c$ dm^{-3} in the soil surface (0-0.20 m). These authors verified that this condition result in increased grain yield of the annual crops. In this study, the chemical conditions of subsoil were different by show highest Ca^{2+} levels in this layer; however, Caires et al. (2011b) also observed low availability of others exchangeable cations. In fact, the gypsum recommendation necessary investigate various relationship of basic cations in soil profile. Further, the Ca^{2+}/K^{+}+Mg^{2+} ratio showed that the mobility of K^{+}+Mg^{2+} (Figure 1b) occurs more intensively in the surface layer (0-0.10 m) linked to the Ca^{2+} addition (Figure 1a), being evident at 5 t ha^{-1} of gypsum. Similarly, Caires et al. (2011a) observed that the Ca^{2+}/Mg^{2+} ratio was higher in the soil profile (0-0.60 m) with rates up to 12 t ha^{-1} of gypsum. Although, exchangeable K leaching from gypsum use varies according to the rates, soil type and rainfall (Raij, 2011). Even in soils with low exchangeable Ca^{2+} levels, Caires et al. (2011b) showed that gypsum application reduced Mg concentration of soybean leaves and did not interfere in Mg concentration in the wheat crop, although increased concentrations of S-SO_4, Ca and K in the wheat leaves.

No-till system

Results of this study indicated the possibility of improving of subsoil chemical properties and subsequent plant root growing in subsurface through of gypsum use. According to Raij (2011), the gypsum rates should be twice larger than those recommended by Souza et al. (1996), to achieve maximum yields. Previous research shows that gypsum increased plant tissue concentrations of Ca and S in maize, wheat, and soybean (Caires et al., 2011b; Blum et al., 2013). Moreover, Elrashidi et al. (2010) observed that the physiological effects of large amount additions of Ca^{2+} and S-SO_4^{2-} in the region of nutrient uptake by the roots may reduce crop yields after gypsum application. Is added to the increased Ca^{+2}/K^{+}+Mg $^{+2}$ ratio (Figure 2), the excessive Ca^{+2} uptake damage the uptake of K^{+} and Mg^{+2} due to an antagonistic effect, while also being constrained by the cations mobility in the soil profile (Figure 1b). Other side, Raij (2011) related increase K uptake by plants due to gypsum application because increased available Ca^{2+} in soils with low Ca^{+2} availability, similarly results were observed in wheat by Caires et al. (2011b). Souza et al. (2012b) observed that gypsum application resulted in low Mg concentration in the soybean leaves under cropping system with low fertility soil. These results suggest the interference of Ca^{2+} ion in the competitive inhibition by gypsum and Mg^{2+} in the cation absorption process at soil solution, damaging Mg uptake. Reducing in content of available Mg was detected in maize and barley with negative impact on uptake of this cation by Ca^{2+} uptake increase after gypsum application; therefore, gypsum elevate Ca^{2+}/Mg^{2+} ratio, mainly by the Ca^{+2} increase, Mg^{2+} leaching, but did not affect the K^{+} leaching in the soil profile (Michalovicz et al. (2014), even in soil high exchangeable K (Table 2).

The use of gypsum and lime in no-till system with the use of green manure and pasture, improve the soil physical properties in depths of 0 to 0.40 m (Bonini and Alves 2012), since they provide increased soil organic matter – SOM (Nicoloso 2008; Blainski et al. 2,012; Cavalcante et al. 2012). This fact result in root growth in the subsoil because improves the soil properties and, also allows initiating a sequence of events that improve the subsurface layer conditions over time, as observed in study conducted by 17 years by Bonini and Alves (2012) using green manure/gypsum/pasture/lime in the production system. Thus, green manure/brachiaria linked to lime and gypsum favor the development of annual crops, since that there was increased V% with the gypsum application in the layer 0.20-0.40 m (Figure 3). This situation favors the root growth of plants in depth such as soybean and wheat, to the point that the gypsum can help this union the tolerance of crops to drought periods in locations that available Ca^{2+} was equilibrate with the others cations (i.e., Mg^{+2} and K^+). Other side, necessity soil conditions when have high available Ca^{+2} levels in surface and subsurface. Tropical soils with low basic cation levels, especially Ca^{2+} and Mg^{2+}, and with the presence of exchangeable acidity (Al^{3+}) show low levels of crop yields, as verified at the site 1 (Table 1), even after four decades of soil agricultural use with annual crops and 15 years under no-till. In this conditions, the low available Ca^{2+} content, the acidity and excess Al^{3+} in plants result in reduced root growth and, consequently, exploiting low soil volume. This fact reflect in low uptake of water and nutrients and promotes water deficits to the crops and mineral deficiencies. Therefore, gypsum rates enables improved conditions for the development of roots in the subsoil layers, providing increased $S\text{-}SO_4^{2-}$ content, decrease Al^{3+} saturation and increased SB, ECEC and V%.

Materials and Methods

Description of study sites

The experiments were conducted in Guairá, Paraná, Brazil at two different sites: Site 1 (24° 09' 12" S and 54° 12' 23" W) and Site 2 (24° 18' 38" S and 54° 12' 12" W). In both sites, the soils were classified as clayey Rhodic Hapludox (Eutroferric Red Latosol in the Brazilian classification; EMBRAPA, 2013), but fertility levels were different: one was of medium fertility and with the presence of exchangeable Al (Site 1 with Al) and the other was of high fertility and absence of exchangeable Al (Site 2 Al-free). Two areas have been grown under no-till for 15 years, with soybean in the summer and wheat or maize in the fall/winter. The regional climate is relatively warm and wet. The 30-year mean annual temperature is 21.4 °C with a July minimum of 14.7 °C and a January maximum of 28.6 °C, and mean annual precipitation of 1,500 mm. Soil particle size and chemical properties before of the treatment application are shown in Table 2. In October 2005, six months before starting the experiment, the two areas received the surface application of 1.65 t ha^{-1} of lime (36% CaO, 12% MgO and 70% ECCE), followed by chiseling with a maximum operating depth of 0.30 m and subsequent soybean cultivation.

Experimental design and treatments

The experiments were arranged in a randomized block design with six treatments and six replications. Treatments consisted of six gypsum rates [0 (control), 1.0, 2.0, 3.0, 4.0, and 5.0 t ha^{-1} of $CaSO_4.2H_2O$ (17% Ca and 15% $S\text{-}SO_4^{2-}$)] applied in April 2006. A total of 36 plots, 3.0 m wide × 4.0 m long, comprised the entire study area of each experiment.

Field management and measurements

Wheat (*Triticum aestivum* L., cultivar CD 104) was sown on May 8, 2006 at 0.17-m row spacing and 68 seeds-m^{-1} rate. This medium maturation-cycle genotype is highly demanding for soil fertility and moderately sensitive to aluminum toxicity. Base fertilization was carried out by applying 200 kg ha^{-1} 04-20-20 formulation at sowing, and 80 kg ha^{-1} N topdressing in the form of urea at the beginning of plant's tillering. Plants were harvested on September 15, 2006 and grain yield (13% moisture content) were evaluated. Soybean [*Glycine max* L. (Merrill), cultivar CD 214-RR] was sown on October 2, 2006 at 0.45-m row spacing and 18 seeds-m^{-1} rate. This intermediate maturation-cycled genotype has medium-high demand for soil fertility and is tolerant to soil exchangeable aluminum. Seeds were treated with fungicide (vitavax+thiram - 50+50 g of the active ingredient every 100 kg of seeds) and inoculant (*Bradyrhizobium japonicum*). Base fertilization was carried out by applying of 250 kg ha^{-1} 04-20-20 formulation at sowing. Soybean plants were harvested on March 3, 2006 and grain yield (14% moisture content) were evaluated. The rainfall between April 2006 and March 2007, during the experiment was 1,535 mm. Soil samples were collected at 6 (October 2006) and 12 months (April 2007) after the application of gypsum at depths of 0.0-0.10; 0.10–0.20 and 0.20–0.40 m using a hole auger in three different points per plot. These samples were air-dried, ground to pass through a 2.0 mm mesh screen and analyzed for contents of calcium (Ca^{+2}), magnesium (Mg^{+2}), exchangeable potassium (K^+), sulfate ($S\text{-}SO_4^{2-}$), potential acidity (H^+ + Al) according to Embrapa (2009). Subsequently, were calculated the values of soil base saturation (V%), aluminum saturation (m%), sum of exchangeable basic cations (SB), effective cation exchange capacity (ECEC), potassium plus magnesium (K^++Mg^{2+}) and calcium/potassium plus magnesium ratio ($Ca^{2+}/K^+ + Mg^{2+}$).

Statistical analysis

Original data underwent the analysis of variance for each site separately and the mean square values of the residues of two sites for all variables were evaluated. The data then from both locations were analyzed in combination due to that the ratio of the waste mean squares of sites were lower than 7. However, from the F test evaluation for location (with or without Al^{3+}) in the analysis of variance was significant for yield of both crops, fact that directed the analysis of variance of that variable for each location. For the gypsum rates were used regression analysis and significant equations with the higher value of the coefficients of determination were adjusted ($p \leq 0.05$). All analyses were performed using Saeg 8.0 software for Windows (Saeg, 1999).

Conclusions

The agricultural gypsum use resulted in increase of $S\text{-}SO_4^{2-}$ content, Ca^{2+} content, $Ca^{2+}/K^+ + Mg^{2+}$ ratio, sum of exchangeable basic cations (SB) and effective cation exchange capacity (ECEC), as well as in reduction of $K^+ + Mg^{2+}$ content and aluminum saturation (m%) in the soil profile. The gypsum application increased soil base saturation (V%) in the 0.20-0.40 m layer at both sites. The gypsum use increased grain yield of wheat due the improved of soil chemical properties and reduction of the soil exchangeable acidity.

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