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PHOSPHOGYPSUM AND VINASSE APPLICATION: SOIL CHEMICAL PROPERTIES AND ALFALFA PRODUCTIVITY AND NUTRITIONAL CHARACTERISTICS[1]

RONALDO DO NASCIMENTO[2]*, JULIANA APARECIDA DE SOUZA[2], ADÔNIS MOREIRA[3], LARISSA ALEXANDRA CARDOSO MORAES[3]

ABSTRACT - The objective of this work was to evaluate the effects of the application of phosphogypsum and vinasse on soil chemical properties and productivity and nutritional characteristics of alfalfa (*Medicago sativa*). The experiment was conducted in a randomized block design, using a 3×5 factorial arrangement, with three vinasse rates (0, 150 and 300 m^3 ha^{-1}) and five phosphogypsum rates (0, 3, 6, 9 and 12 Mg ha^{-1}). The alfalfa chemical composition and shoot dry matter (SDW) and soil chemical properties (in the layers 0.0-0.2 and 0.21-0.4 m) were evaluated. The vinasse rates increased the soil potassium contents, while the phosphogypsum rates promoted linear increases in soil calcium and sulfur contents. The base saturation was increased and the magnesium content showed a quadratic response on the layer 0.21-0.4 m with the increase in phosphogypsum rates. The calcium, magnesium and phosphorus contents in the alfalfa leaves were lower with vinasse application. The phosphogypsum rates promoted linear increases in alfalfa SDW. Vinasse rated 150 m^3 ha^{-1} was been enough to SDW increase. Calcium and magnesium contents in the leaves fitted a quadratic model, with maximum calcium content in the phosphogypsum rate of 9.5 Mg ha^{-1} and the minimum magnesium content in the phosphogypsum rate of 8.7 Mg ha^{-1}. The leaf sulfur contents in all vinasse rates and leaf potassium contents in the highest vinasse rate showed maximum accumulation at near 9 Mg ha^{-1} of phosphogypsum.

Keywords: *Medicago sativa*. Calcium. Magnesium. Potassium. Sulfur.

APLICAÇÃO DE GESSO E VINHAÇA: ATRIBUTOS QUÍMICOS DO SOLO, PRODUTIVIDADE E ESTADO NUTRICIONAL DA ALFAFA

RESUMO - O objetivo do trabalho foi avaliar os efeitos da aplicação de gesso e vinhaça na produção de matéria seca, nutrição e atributos químicos do solo cultivado com alfafa. O experimento foi realizado em delineamento experimental de blocos ao acaso, em esquema fatorial 3 × 5, com três doses de vinhaça, 0, 150 e 300 m^3 ha^{-1} e cinco doses de gesso agrícola (0, 3, 6, 9 e 12 Mg ha^{-1}). Foram avaliados a composição química e matéria seca da parte aérea (MSPA) e os atributos químicos do solo (0-0,2 e 0,21-0,4 m). As doses de vinhaça aumentaram os teores de potássio, enquanto as doses de gesso promoveram acréscimos lineares nos teores de cálcio e enxofre no solo. A saturação de bases foi crescente e o magnésio teve efeito quadrático na camada de 0,21-0,4 m em função das doses de gesso. Os teores de cálcio, magnésio e fósforo na folha da alfafa foram menores com a aplicação de vinhaça. As doses de gesso promoveram acréscimos lineares na MSPA da alfafa. A dose de 150 m^3 ha^{-1} já foi suficiente para aumentar a MSPA. Os teores de cálcio e magnésio na folha tiveram ajuste quadrático, com máximo acúmulo de cálcio em 9,5 Mg ha^{-1} e o magnésio com ponto de mínimo na dose de 8,7 Mg ha^{-1} de gesso. Os teores foliares de enxofre sob doses de vinhaça e os de potássio na maior dose obtiveram máximo acumulo na presença de 9 Mg ha^{-1} de gesso.

Palavras-chave: *Medicago sativa*. Cálcio. Magnésio. Potassio. Enxofre.

*Corresponding author
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[2]Department of Agronomy, Universidade Estadual de Londrina. Londrina, PR, Brazil; ronaldonasc@yahoo.com.br, julianasouzaagro@yahoo.com.br.
[3]Embrapa Soja, Empresa Brasileira de Pesquisa Agropecuária, Londrina, PR, Brazil; adonismoreira66@gmail.com, larissa.moraes@embrapa.br.

INTRODUCTION

The Brazilian sugarcane production has been standing out, mainly due to its high yields and high energy efficiency, achieved especially on the ethanol processing. Each liter of ethanol produced generates 14 liters of vinasse waste, which is potentially polluting when not properly treated, presenting acidifying effect, high nitrate levels and can reduce the concentration of oxygen available when applied in large amounts (BLEY JUNIOR et al., 2009; FUESS; GARCIA, 2014).

Vinasse is applied usually in sugarcane crop areas, aiming to minimize the environmental impact and reintroduce the nutrients exported (SILVA; GRIEBELER; BORGES, 2007). Therefore, vinasse improves soil fertility, supplying nutrients such as potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) and organic matter (OM), which have average concentrations of 4.92, 2.08, 0.49 and 2.70 g L^{-1} in the vinasse, respectively (LEITE, 1999).

The application of vinasse has increased sugarcane production (SILVA; BONO; PEREIRA, 2014). Basso et al. (2013) used vinasse for 100% of potassium fertilization, applying 200 m^3 ha^{-1} of vinasse and found an increase of almost 10% in K^+ content in the topsoil, and increases of 7 to 15 Mg ha^{-1} in sugarcane yield. Other studies also reported increases in K^+, Ca^{2+}, Mg^{2+} and S-SO_4^{2-} contents due to vinasse application (CARVALHO et al., 2013; SILVA; BONO; PEREIRA, 2014; PAULA; CARVALHO; NOGUEIRA, 1992; ANDREOTTI et al. 2015).

Liming and vinasse application to the soil surface usually reach shallow depths, thus, alternatives to improve acidity correction of soil subsurface are needed. Caires, Feldhaus and Blum (2001) compared mechanical incorporation of lime and use phosphogypsum and found increases of nutrients in the soil subsurface layers and consequently, improvement of plant nutrition, due to nutrient mobilization in the soil profile, and recovery of the nitrogen translocated to the subsurface. Other studies also reported increases in Ca^{2+}, Mg^{2+}, K^+ and S-SO_4^{2-} contents in subsurface due to lime incorporation and use phosphogypsum (CAIRES et al., 2004; CAIRES; JORIS; CHURKA, 2011; MICHALOVICZ et al., 2014; PAULETTI et al., 2014).

The cultivation of plants that require high fertility and have deep root systems, such as alfalfa, need good soil conditions (MOREIRA et al., 2007), with good nutrient distribution in the soil profile. Silva, Bono and Pereira (2014) found significant increases in K^+ contents up to the depth of 0.4 m due to vinasse application (400 m^3 ha^{-1}). Caires, Feldhaus and Blum (2001) and Caires et al. (2004) reported increases in the Ca^{2+} and Mg^{2+} contents up to the depth of 0.6 m, and Sumner (2009) found high concentrations of alfalfa roots in layers deeper than 0.2 m, with phosphogypsum application.

In this context, the objective of this work was to assess the variations in soil chemical properties and the productivity and nutritional characteristics of alfalfa (*Medicago sativa*), depending on the application of different rates of phosphogypsum and vinasse.

MATERIAL AND METHODS

The experiment was conducted under field conditions in the experimental station of the Embrapa Southwest Livestock, located in São Carlos, São Paulo, Brazil (21°59'37"S, 47°52'38"W). The region has average altitude of 830 meters, and its climate is Cwa, characterized as tropical of altitude with dry winter and rainy and warm summer, according to the Köppen classification.

The experimental area was cultivated using a central pivot irrigation. The soil was classified as an Oxisol (dystrophic Red-Yellow Latosol – SiBCS), which had the following chemical attributes: pH in $CaCl_2$= 4.3, organic matter (OM)= 27 g kg^{-1}, phosphorus (P) (resin)= 8.0 mg kg^{-1}, potassium (K^+) (resin)= 0.18 $cmol_c$ dm^{-3}, calcium (Ca^{2+}) (resin)= 2.0 $cmol_c$ dm^{-3}, magnesium (Mg^{2+}) (resin)= 0.70 $cmol_c$ dm^{-3}, aluminum (Al^{3+}) (resin)= 0.1 $cmol_c$ dm^{-3}, H^++Al^{3+} (SMP)= 2.9 $cmol_c$ dm^{-3}, base saturation (V%)= 50 (EMBRAPA, 2009). The soil presented sand, silt and clay contents of 479, 144 and 377 g kg^{-1} in the layer 0.0-0.2 m, and 415, 102 and 483 g kg^{-1} in the layer 0.21-0.4 m, respectively.

The experiment was conducted in a randomized block design, using a 3×5 factorial arrangement, consisting of three vinasse rates (0, 150 and 300 m^3 ha^{-1}) and five phosphogypsum rates (0, 3, 6, 9 and 12 Mg ha^{-1}), with three replications. The vinasse contained 1.2 g L^{-1} of K_2O, 0.18 g L^{-1} of CaO, 0.088 g L^{-1} of MgO and its $pH_{(CaCl)}$ was 4.3. The soil fertilization was carried out with P (superphosphate; 21% of P_2O_5) and micronutrients (B, Cu, Fe, Mn e Zn), which were added to the seed furrows. The treatments were applied as topdressing. The nutrient rates used were according the recommendations of Moreira et al., (2007), except K and S. A dolomitic lime (Relative Power of Total Neutralization = 95%) application was carried out thirty days before planting, which was calculated to increase the base saturation to 80% (MOREIRA et al., 2007).

The plots consisted of 8 rows with length of 7 meters and 0.2 m between rows, considering for evaluations the central 6 m^2, discarding the borders. The alfalfa cultivar used was the *Crioula*. The alfalfa seeds were inoculated with *Rhizobium meliloti*, (strain SEMIA-116) before planting, along with a Mo, Co and Ni solution (MOREIRA et al., 2007). The plant population of 150 to 200 plants m^{-2} was achieved by planting the equivalent to 20±2 kg ha^{-1} of seeds.

Irrigation was performed in periods of low precipitation, applying a water depth of 16.3 mm every four days, adjusted with a tensiometer. Four alfalfa cuts were performed, 30 days apart. The first cut was three months after the full establishment of the alfalfa crop. The plant material was dried in a forced-air oven at 65°C to a constant weight to obtain the shoot dry weight (SDW), the samples were ground in a Wiley mill and taken to the laboratory for determination of macro and micronutrients according to Malavolta, Vitti and Oliveira (1997) and Embrapa (2009).

Phosphorus content in the shoot were determined by the metavanadate colorimetric method, using UV-VIS; K by the flame photometry method; Ca and Mg by atomic emission spectrometry (ICP-AES); and S by the $BaSO_4$ turbidimetry. (MALAVOLTA; VITTI; OLIVEIRA, 1997).

Soil samples were collected in the layers 0.0-0.2 m and 0.21-0.4 m soon after the fourth alfalfa cut. The soil samples were air dried in order to assess the pH, P and S available, as well as the contents of exchangeable K, Ca and Mg, according to the methodology described in Embrapa (2009).

The results were subjected to analysis of variance (ANOVA; F test p≤0.05) and, when significance and interaction between factors were found, each vinasse rate was subjected to regression analysis as a function of phosphogypsum rates; when no interaction were found, the vinasse rates were subjected to the Tukey's test, and the average of the three vinasse rates was subjected to regression analysis as a function of the phosphogypsum rates.

RESULTS AND DISCUSSION

The soil chemical analysis indicated that the phosphogypsum increased the $S\text{-}SO_4^{2-}$ levels (Table 1). These results confirm those found by Caires, Feldhaus and Blum (2001), Caires et al. (2004), Michalovicz et al. (2014) and Pauletti et al. (2014). Increases in leaf S are usually directly related to the nutrient supply due to phosphogypsum application (RAIJ, 2011), as observed in this study.

Increase the soil sulfate content has various implications. Zambrosi, Alleoni and Caires (2007) studied ionic speciation involving sulfate and found higher susceptibility to pair formation between SO_4^{2-} and Ca^{2+}, however representing only 1% of the Ca^{2+} in solution, with more significant pair formation with Mg^{2+}, Al^{3+} and K^+ (CAIRES et al., 2004; PAULETTI et al., 2014).

The layer 0.0-0.2 m had no decrease in K^+ contents with increasing phosphogypsum rates, however, the soil Ca^{2+} content showed an increase (Table 1).

Table 1. Regression equations fitted to K^+, Ca^{2+}, Mg^{2+} and $S\text{-}SO_4^{2-}$ contents and base saturation (V%) of soil samples, collected in the layers 0.0-0.2 and 0.21-0.4 m at the end of the experiment, depending on phosphogypsum rates.

Layer	Nutrients	Equation	P	R^2	CV (%)
0.0-0.2 m	Potassium	$\bar{Y} = 0.17$	ns	-	12.0
	Calcium	$Y = 2.9 + 0.29x$	p≤0.001	0.86	7.27
	Magnesium	$\bar{Y} = 1.51$	ns	-	9.92
	Sulfate	$Y = 33.4 + 29.289x$	p≤0.001	0.97	8.00
	V (%)	$\bar{Y} = 68.20$	ns	-	8.62
0.21-0.4 m	Potassium	$\bar{Y} = 0.05$	ns	-	16.59
	Calcium	$Y = 1.5 + 0.103x$	p≤0.001	0.97	9.76
	Magnesium	$Y = 1.009 + 0.059x - 0.006x^2$	p≤0.05	0.75	8.46
	Sulfate	$Y = 12.93 + 11.589x$	p≤0.001	0.86	8.54
	V (%)	$Y = 44.8 + 1.467x$	p≤0.001	0.89	7.32

ns= not significant.

Similar effects were observed by Carvalho et al. (2013), who found increases in Ca^{2+} and sulfate contents in the soil layers 0.0-0.2 m with the phosphogypsum application, and a consequent increase in base saturation (V%), which is directly related to the displacement of hydroxyl (OH^-) and sulfate adsorption, enabling the formation of metal binders, increasing the cation exchange capacity (CEC) predominantly related to the cation Ca^{2+} (RAIJ, 2011).

Linear increases in base saturation in the layer 0.21-0.4 m was found (Table 1), showing an improvement of fertility in the soil profile. Rampim and Lana (2015) and Soratto and Crusciol (2008) evaluated the application phosphogypsum rates and also found increases in base saturation in the soil layer 0.21-0.4 m. Both studies showed the phosphogypsum as responsible for the soil conditioning. Effects similar to those found in the layer 0.0-0.2 m were found in the layer 0.21-0.4 m, as also found by Pauletti et al. (2014) with phosphogypsum application, with a reduced availability of Mg^{2+} in soil layer 0.21-0.4 m.

The base saturation increased in the layer 0.21-0.4 m, and the Ca^{2+} contents increased in the surface layer, however with small reductions in Mg^{2+} contents. Caires et al. (2004) found increases in corn gain yield due to increase in CEC by Ca^{2+} saturation. Rampim et al. (2011) found that an increase in saturation occurring due to the leaching and neutralization of Al^{3+} to subsurface layers. In the present work, the H^{+}+Al^{3+} contents presented no changes in any of the phosphogypsum rates applied, probably due to the lime application.

The application of vinasse increased the K^{+} content in the soil layers 0.0-0.2 m and 0.21-0.4 m (Table 2) and was not affected by the phosphogypsum. Carvalho et al. (2013) found different results, with reductions in K^{+} contents in a soil of sandier texture, which differ from the soil of the present study, which had around 400 g kg^{-1} of soil. This difference in texture, may explain the difference in K contents, since, according to Brito (2009), who studied the K movement in the soil surface layers, differences in K contents are related to the soil texture.

Table 2. Analysis of variance of average potassium, calcium, magnesium, sulfate contents and base saturation (V%) of the soil layers 0.0-0.2 m and 0.21-0.4 m depending on vinasse rates.

Vinasse Rates (m^3 ha^{-1})	Potassium ($cmol_c$ dm^{-3})	Calcium ($cmol_c$ dm^{-3})	Magnesium ($cmol_c$ dm^{-3})	Sulfate (mg dm^{-3})	V %
Soil layer 0.0-0.2 m					
0	0.13 a	4.63 a	1.49	208.73	68.20
150	0.20 b	4.78 a	1.27	245.07	64.47
300	0.24 c	4.13 b	1.19	204.31	63.47
F test	**	**	ns	ns	ns
CV (%)	12.76	10.72	13.87	10.16	8.69
Soil layer 0.21-0.4 m					
0	0.07 b	1.96	1.07	97.47	53.60
150	0.08 a	1.84	0.94	116.47	46.13
300	0.09 a	1.84	0.99	110.00	46.47
F test	**	ns	ns	ns	ns
CV (%)	16.71	10.96	12.57	15.32	12.29

ns = not significant, * $p \leq 0.05$; **$p \leq 0.01$.

The K^{+} results differ from those found by Rampim et al. (2011) who studied the effects of phosphogypsum rates in an Oxisol (eutropherric Red Latosol - SiBCS) and reported a K displacement from the soil surface layers to depths below 0.2 m, resulting in an increase in the subsurface layers. The K contents in the present work was similar to those found by Carvalho et al. (2013), who evaluated vinasse rates in a sugarcane crop. The vinasse rates application did not affected the contents of nutrients, except calcium in the soil layer 0.0-0.2 m and potassium in both layers. Andreotti et al. (2015) assessed the changes in the soil under vinasse applications of up to 200 m^3 and found similar results, with the main effects related to the large amount of potassium present in the vinasse.

The SDW presented linear increases depending on the phosphogypsum rates, and did not differ with vinasse rates of 150 and 300 m^3 ha^{-1}, both surpassing the control (Table 3). Similar results of yield increases were observed in sugarcane by Silva, Bono and Pereira, (2014) and in maize by Caires et al. (2004), with vinasse and phosphogypsum application, respectively. According to Carvalho et al. (2013), these increases are due to the improvement of soil fertility with Ca^{2+} and S-SO_4^{2-} (Table 1) by the phosphogypsum and the large quantities of potassium present in the vinasse (Table 2), both improving the soil conditions.

Leaf nutrient contents are usually correlated to increased yield, as reported by Paula, Carvalho and Nogueira (1992), who studied increasing rates of vinasse on onion crops and found for a maximum yield the rate of 160 m^3 per ha^{-1}, which increased the leaf K^{+}, differing from the control which showed nutrient deficiency symptoms and low yield.

The K and S contents presented significant interaction for the phosphogypsum and vinasse applications. The S contents increased with the increasing vinasse rates, and showed a quadratic fit to the phosphogypsum rates (Figure 1B). These results confirm those found by Moreira, Carvalho and Evangelista (1997), who reported increases in S content followed by a similar increase in dry weight, however, the results of K^{+} were similar only to the vinasse rate of 300 m^3 ha^{-1}, with no significant interaction to the other vinasse rates depending on the phosphogypsum rates (Figure 1A).

Table 3. Analysis of variance of alfalfa shoot dry weight (SDW) and leaf nutritional content depending on vinasse (m^3 ha^{-1}) and phosphogypsum (Mg ha^{-1}) rates, using average values from four cuts.

Rates	SDW (g kg^{-1})	Calcium (g kg^{-1})	Magnesium (g kg^{-1})	Phosphorus (g kg^{-1})	Potassium (g mg^{-1})	Sulfur (g kg^{-1})
	--- Vinasse ---					
0	1467.36 b	13.90 a	3.07 a	3.06 a	27.11	4.76
150	1574.93 a	11.86 b	2.47 b	2.92 ab	30.12	4.28
300	1606.50 a	12.06 b	2.46 b	2.89 b	32.19	4.33
F test	**	**	**	*	-	-
CV (%)	7.65	6.08	5.31	5.36	5.97	6.17
	--- Phosphogypsum ---					
0	1436	10.98	3.06	2.87	29.4	3.43
3	1494	12.47	2.69	2.92	29.85	4.45
6	1533	13.32	2.61	2.98	30.17	4.83
9	1654	12.84	2.41	2.94	30.56	4.68
12	1631	13.43	2.57	3.06	29.05	4.9
Effect	L/0.89**	Q/0.89*	Q/0.95**	ns	-	-
Interaction	ns	ns	ns	ns	*	*
CV (%)	7.65	6.08	5.31	5.36	5.97	6.17

ns= not significant. *$p \leq 0.05$; **$p \leq 0.01$. Means followed by the same letter in the column do not differ from each other by the Tukey test. SDW= 18.37x +1439.4, Ca= $-0.025x^2+0.47x+11.11$, Mg= $0.0074x^2-0.13x+3.05$.

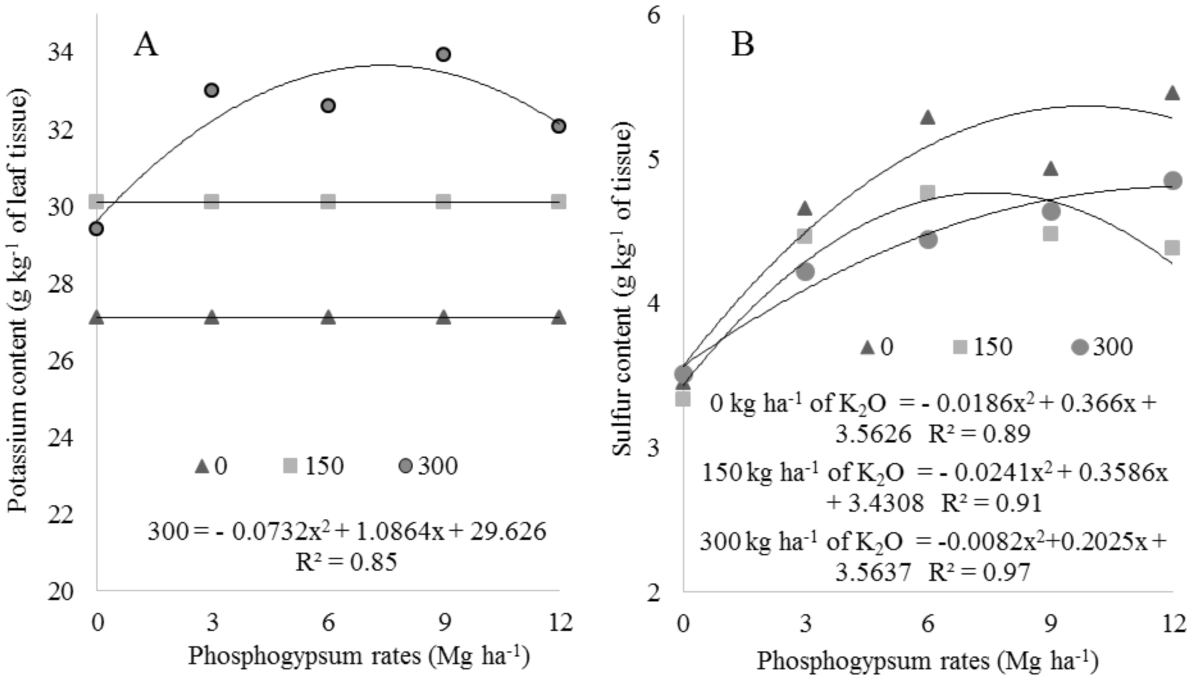

Figure 1. Potassium (A) and sulfur (B) contents in alfalfa leaves depending on three vinasse rates (0, 150 and 300 m^3 ha^{-1}) and five phosphogypsum rates (0, 3, 6, 9 and 12 Mg ha^{-1}), using average values from four cuts.

The vinasse application, especially at a rate of 300 m^3 ha^{-1}, increased the K content, which is related to the phosphogypsum application, with linear increases in Ca and a quadratic response in Mg in the layer 0.21-0.4 m, probably promoting competitive inhibition between Ca and K (MALAVOLTA, 2006). The most marked inhibition was observed in the K with Mg, as reported by Carvalho et al. (2013) and Ferreira Neto et al. (2014) and between Ca and Mg (SOUZA et al., 2012), showing that, from

7.42 Mg ha^{-1}, due to the large amount of Ca, the K uptake decreases.

The increase in K contents with the lower phosphogypsum rates, according to Caires, Feldhaus and Blum (2001), who studied barley (*Hordeum vulgare*), is due the increase in Ca in the soil, which displace the K to the soil solution, making it available to absorption. According to Michalovicz et al. (2014), the leaf K content is related to its availability in the soil, and the phosphogypsum application can change this nutrient dynamic in the soil.

The leaf P showed no changes as a function of phosphogypsum rates, however, the Ca showed a quadratic response and maximum accumulation with an estimated phosphogypsum rate of 4.5 mg ha^{-1}. These results differ from those reported by Vicensi et al (2016), who studied a soil with lower Ca contents and found a linear fit up to 12 mg ha^{-1}.

CONCLUSIONS

The phosphogypsum rates promoted linear increases of soil calcium and sulfate contents, however, did not change the potassium contents in the layer 0.0-0.4 m. The base saturation increased linearly and the magnesium contents showed a quadratic response in the layer 0.21-0.4 m.

The vinasse rates increased only the soil potassium contents, up to the depth of 0.4 m. The increase in phosphogypsum rates promoted linear increases of alfalfa shoot dry weight (SDW), and its maximum production was reached with the vinasse rate of 150 m^3 ha^{-1}.

The calcium, magnesium and phosphorus contents were lower with vinasse application. Calcium contents showed a quadratic fit, with maximum accumulation at 9.5 Mg ha^{-1}, and magnesium showed minimal accumulation at 8.7 Mg ha^{-1} of phosphogypsum. The contents of sulfur in all vinasse rates and potassium at rate of 300 m^3 ha^{-1} had maximum accumulation at near 9 Mg ha^{-1} of phosphogypsum.

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