https://doi.org/10.1590/1678-4499.20180183

SOIL AND PLANT NUTRITION - Article

Gypsum application, soil fertility and cotton root growth

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ABSTRACT: Since there is no consensus on phosphogypsum (PG) rates to be used in agriculture, a better understanding of its effects on the soil solution is needed. Cotton root growth was evaluated as related to Al and Ca activity in soil solution affected by PG. The experiment was carried out in rhizotrons filled with 30·dm^{-3} of soil. PG rates were estimated by multiplying the soil clay content by 0.0, 1.5, 3.0, 6.0 and 12.0, and it was mixed to the sub-soil. In the upper soil layer, limestone was applied. After 90 days, samples were taken for analysis, and cotton was planted. After 27 days, plants were harvested. PG increased soil pH and decreased Al content and activity. Without PG, dissolved organic carbon concentration was high in the soil solution, which explains the predominance of carbon Al-complexed with PG application. From 1,680 kg·ha^{-1} of PG (corresponding to 6 × clay content), sulphur and calcium had the highest concentrations, increasing the SO_4 Al-complexed. Cotton root length decreased in the upper layer and increased in the subsoil up to 2,324 kg·ha^{-1} (corresponding to 8.3 × clay content) of PG. Cotton root growth is better related with soil properties than with soil solution attributes, and the present recommendations for PG use based on soil clay content underestimate the rate to be applied.

Key words: aluminum, dissolved organic carbon, soil chemistry.

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Received: May 25, 2018 – Accepted: Sept. 18, 2018

INTRODUCTION

Aluminum (Al) is found in several primary and secondary minerals, and its constant dissociation depends on temperature, pressure and, mainly, pH (Sposito 2008). In the soil solution, it can remain as Al^{3+} or bound with OH^-, phosphate, F, silicate, organic substances, etc. (Lindsay 1979). The phytotoxic effect of Al is attributed to its free form. However, other Al species, such as the mononuclear bound to hydroxyl, may damage roots (Fageria et al. 1988; Kinraide 1991). Decreased root elongation is the first visible symptom of Al toxicity in plants (Matsumoto 2002), and it is related to reduced cell division and increased cell wall stiffness (Fageria et al. 1988). However, there are differences among species as to Al susceptibility. For example, rice tolerates Al saturation above 45% in the effective cation exchange capacity (ECEC) while cotton roots do not grow well above 10% Al saturation (Fageria et al. 1988).

Although the main tool for correcting Al toxicity in agricultural areas is liming, the application of phosphogypsum (PG, $CaSO_4 \cdot 2H_2O$) is an important strategy to reduce Al toxicity and increase Ca content, especially in systems under no-tillage. The decrease of Al^{3+} toxicity by phosphogypsum is related to several mechanisms such as the precipitation of Al by the release of OH^-, formation of insoluble complexes of Al-sulfates and ionic pairs such as $AlSO_4^+$ and AlF^{2+}, preferential adsorption of Al^{3+} to negative charges formed by specific SO_4^{2-} adsorption, and decrease of Al^{3+} activity due to an increase in the soil solution ionic strength (Carvalho and Raij 1997). In Brazil, PG rate recommendations take into account the Ca and Al concentrations and CEC Al saturation in the subsurface layer. The most used recommendation is the product of the clay content ($g \cdot kg^{-1}$) by 5 (Sousa and Lobato 2002) or 6 (Raij et al. 1996). However, several field experiments have shown yield benefits in several crops with higher rates. Caires et al. (2016) tested PG rates up to 20 times the clay content and observed an increase in maize yield. Pauletti et al. (2014) evaluated PG rates up to 70 times the clay content and observed an increase in soybean, maize and wheat yields under water deficiency. However, under adequate water availability, there was a decrease in yield at higher rates due to induced magnesium deficiency.

Therefore, the present recommendations of PG rates to deal with Al toxicity are empirical, and apparently lead to rates below the optimum in some soils. The effect may depend on soil solution characteristics rather than only the soil SO_4^{2-} adsorption capacity (as estimated by clay content). Thus, a better understanding of gypsum effect on the soil solution and ion movement in the soil profile is important to develop a better recommendation. The hypothesis of this study is that an adequate PG rate results in better cotton root growth not only because it decreases exchangeable Al^{3+} and increases exchangeable Ca^{2+}, but also because it promotes changes in Al speciation and activity in soil solution. Therefore, the aim of this study was to evaluate cotton root growth as related with Al and Ca activity and speciation in the soil solution, as affected by PG application.

MATERIAL AND METHODS

The experiment was carried out in a greenhouse in Botucatu, state of São Paulo, Brazil, using 0.6 m high semi-cylinders with glass walls (rhizotrons, diameter of 0.25 m) with 15 dm^3 of a Typic Haplortox with 280, 92 and 628 $g \cdot kg^{-1}$ clay, silt and sand, respectively.

The treatments were phosphogypsum applied in amounts of 0.0, 1.5, 3.0, 6.0 and 12.0 times the clay content, corresponding to 420, 840, 1,680 and 3,360 $kg \cdot ha^{-1}$. The experimental design was randomized blocks with four replicates. Ninety days before planting, PG was applied to the soil and mixed. It was used a commercial PG with 20% of Ca and 19% of S. The treated soil was accommodated in the lower layer of the pot (0.2 to 0.6 m). The same soil received dolomitic limestone to raise base saturation to 60% (Table 1), and was accommodated in the rizotrons as an arable layer, also 90 days before sowing. The soil in the lower layer received 50, 40 and 50 $mg \cdot dm^{-3}$ of N, P and K, respectively, and remained for 7 days with light irrigation. After this period, the soil level was marked on the glass wall and the limed soil was added in the upper layer, so the roots could be collected separately. The upper soil layer was fertilized with 150, 120 and 150 $mg \cdot dm^{-3}$ N, P and K, respectively. A hose was installed at a depth of 0.20 m to add water and avoid carrying the nutrients from the upper to the lower layer. Thus, the upper layer was irrigated by capillarity. Before sowing, samples were collected for chemical analysis of the soil and soil solution.

The cotton cultivar used was FiberMax 951LL (Bayer Seeds®), which was chosen due to its mid to late maturity

Table 1. Chemical analysis in the initial condition of the soil and after liming and fertilization in the upper layer of the pots.

Soil	pH $CaCl_2$	Organic carbon ($g \cdot dm^{-3}$)	P ($mg \cdot dm^{-3}$)	Al	H+Al	K	Ca	Mg	Cation exchange capacity (at pH 7.0)	Aluminum saturation (%)
				($mmol_c \cdot dm^{-3}$)						
Initial	4.1	9.3	2.0	14.0	75.0	0.2	1.2	0.4	76.8	89.0
Limed and fertilized	5.4	9.0	24.3	0.8	35.2	3.7	35.3	26.9	101.1	1.2

and medium-sized plants. No information about its Al^{3+} sensibility was found. Seeds were pre-germinated and transferred to rhizotrons when their radicles were approximately 5 mm long. Two plants were grown per pot and irrigated daily. The average temperature and relative air humidity during the experiment were 27.4 °C and 62.4%, respectively. At 27 days after planting (DAP), plants were sectioned in shoots and roots. The roots were separated into upper and lower layers according to PG treatments, gently washed over a 0.50 mm screen, scanned at 300 dpi resolution, and analyzed with WinRhizo (Regent Instruments Inc., Quebec, Canada) to determine root length according to Tennant (1975). Then, the samples were dried in a forced air circulation oven for 48 hours and dry matter was determined.

Soil solution was extracted by adding distilled water to the soil at a ratio of 2:1, after resting for 24 hours, and subsequent quantitative filtering (Richards 1954). In the soil, pH ($CaCl_2$), H+Al, Al, Ca, Mg, K and P were determined according to Raij et al. (2001). In the soil solution, electrical conductivity was determined with a conductivity meter, pH by potentiometry, F by fluorimetry, dissolved organic carbon (DOC) by chemical oxygen demand (APHA 1999) and Al, Ca, Mg, K, Na, Mn, Fe, $P\text{-}PO_4$ and $S\text{-}SO_4$ by ICP-OES. The ionic strength was estimated by the following equation (Eq. 1) (Griffin and Jurinak 1973):

$$I = 0{,}013EC \qquad (1)$$

In which EC is the electrical conductivity of the solution in $dS \cdot m^{-1}$, and I is the ionic strength, in $mol \cdot L^{-1}$.

The solution activity and chemical speciation of Al and Ca were estimated using Visual Minteq version 3.1 (Gustaffson 2014).

Soil analysis data, shoot and root dry matter and root length were submitted to analysis of variance and means were compared using LSD ($p < 0.05$). Where appropriate, regressions were fit to results. Root length and dry matter of the subsoil were correlated with soil attributes (Pearson's parametric test) and soil solution (Spearman's non-parametric test). The non-parametric correlation was used because the soil solution characteristics showed no normality, except for Ca/Σ cation. Some of this soil and solution attributes were submitted to regression analysis. The tested models were: Weibull, modified by Taylor et al. (1991), exponential ($y = ae^{-bx}$), proposed by Pavan and Binghan (1982) and polynomial linear. The models were chosen based on the significance ($p < 0.05$) and the coefficient of determination. For Weibull model the toxicity threshold (TT) was defined as the concentration resulting in a reduction of 5% (of potential reduction) of each variable (Taylor et al. 1991). For the exponential model the TT was defined as the concentration associated with a reduction of 10% in each variable (Pavan and Binghan 1982). The y intercept was not considered as the maximum y value, but the maximum y calculated within the range of x values.

RESULTS

PG application improved most soil attributes (Table 2) increasing soil pH, although it is not recommended as a corrective. The Al concentration was decreased, reaching 10.8 $mmol_c \cdot dm^{-3}$ and saturation of 32%.

The soil solution ionic strength and Ca and S concentrations increased with PG rates (Table 3), while there was a decrease in Al concentration and activity. However, Al activity was highly variable, significant only at $p < 0.10$. The pH, DOC, Na and P did not change significantly with PG application. DOC was the component with the highest concentration in the soil solution with PG rates up to 1,680 $kg \cdot ha^{-1}$ (6.0 × clay content). Above this rate, S and Ca had higher concentrations than the other ions.

Aluminum complexed with DOC was the predominant species at all gypsum rates (Fig. 1a), while Al-F and Al-DOC were higher up to 840 $kg \cdot ha^{-1}$ (3.0 × clay content). From 1,680 $kg \cdot ha^{-1}$ (6.0 × clay content), $Al\text{-}SO_4$ was higher, with values similar to Al-DOC with 3,360 $kg \cdot ha^{-1}$ (12 × clay content) of PG. Although the solution pH was

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Table 2. Soil chemical analysis of the lower layer after the application of phosphogypsum (PG) rates.

PG rates¹	pH $CaCl_2$	P ($mg·dm^{-3}$)	Al	H+Al	K	Ca	Mg	Cation exchange capacity (at pH 7.0)	Base saturation (%)	Aluminum saturation (%)
			($mmol_c·dm^{-3}$)							
0.0	4.09	9.3	13.2	74.1	1.30	1.1	0.29	77	3	83
1.5	4.14	9.2	12.4	75.3	1.26	5.6	0.36	83	9	64
3.0	4.15	8.5	12.5	75.6	1.29	6.6	0.29	84	10	61
6.0	4.21	9.6	11.3	73.1	1.25	12.7	0.37	87	16	44
12.0	4.29	11.1	10.8	71.6	1.11	21.1	0.26	94	24	32
CV (%)	1.5	17.1	8.0	3.7	8.3	13.3	33.8	4.0	11.6	8.4
Effect										
Linear	**	ns	**	*	*	**	ns	**	**	**
Quadratic	ns	ns	ns	ns	ns	ns	ns	ns	*	**

[1] nº x clay content.

Table 3. pH values, ionic strength ($mmol·L^{-1}$), Al^{+3} activity ($\mu mol·L^{-1}$) and total concentration ($mmol·L^{-1}$) of some anions and cations in the soil solution used in the estimation of chemical species of aluminum and calcium as a function of phosphogypsum rates.

Parameters	Phosphogypsum rates (nº x clay content)					CV (%)	Effect	
	0	1.5	3	6	12		Linear	Quadratic
pH	4.78	4.36	4.50	4.44	4.50	7.9	not significant	not significant
Ionic strength	3.34	3.98	4.29	5.50	10.08	18.7	significant at 1%	significant at 10%
Al activity	5.71	1.56	1.06	0.59	1.39	153.3	not significant	significant at 10%
Aluminum	0.141	0.042	0.046	0.021	0.033	83.7	significant at 5%	significant at 5%
DOC	3.181	3.930	2.994	3.462	3.369	23.6	not significant	not significant
S ($St-SO_4^{-2}$)	0.882	1.061	1.061	1.874	3.740	20.4	significant at 1%	significant at 5%
Calcium	0.214	0.308	0.323	0.938	2.621	31.1	significant at 1%	significant at 1%
Potassium	0.174	0.179	0.191	0.223	0.259	21.1	significant at 1%	not significant
Magnesium	0.053	0.043	0.050	0.075	0.102	41.0	significant at 1%	not significant
Manganese	0.004	0.004	0.005	0.007	0.011	59.5	significant at 1%	not significant
Sodium	0.032	0.060	0.046	0.031	0.058	55.6	not significant	not significant
$Pt-H_xPO_4^x$	0.0010	0.0014	0.0010	0.0010	0.0011	46.9	not significant	not significant
Fluorine	0.0100	0.0100	0.0142	0.0013	0.0001	58.6	significant at 1%	not significant
Iron	0.067	0.018	0.017	0.003	0.004	143.0	significant at 5%	significant at 10%

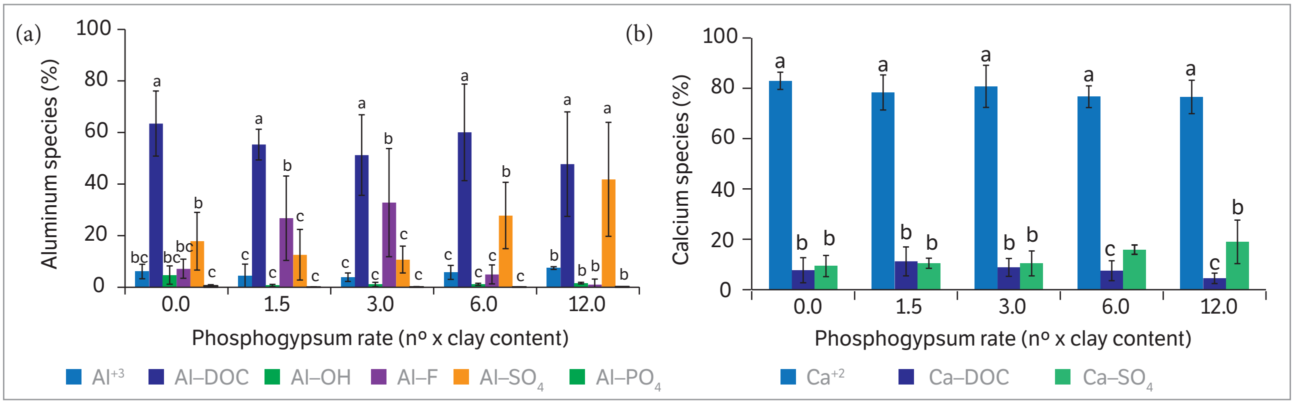

Figure 1. Chemical species of (a) Al and (b) Ca in the soil solution of a Typic Haplortox as a function of phosphogypsum rates. Al-OH = $Al(OH)^{+2} + Al(OH)^{+} + Al(OH)^0_3$; Al-F = $Al(F)^{+2} + Al(F)^{+} + Al(F)^0_3$; $Al-PO_4 = Al-H_xPO_4^x$. The inner bars represent the standard deviation of the mean. Bars with different letters at each PG rate differ at $p < 0.05$ (LSD test).

below 5.0 with all PG rates (Table 2), free Al was close to 5% (Fig. 1a). The free form Ca^{+2} was the predominant species in all PG rates, with values close to 80% (Fig. 1b). Up to the intermediate rate (3 × clay content), Ca-DOC and Ca-SO_4 presented similar values, close to 10%, but from 1,680 kg·ha^{-1} (6 × clay content), Ca-SO_4 was greater compared with Ca-DOC.

Cotton shoot dry matter was not affected by PG, with an average of 0.57 g per plant. Cotton total root length was also not affected by PG. However, there was a change in its distribution, with a decrease in root length in the upper soil layer, and a corresponding increase in the subsoil (Fig. 2a). In the lower soil layer PG had a quadratic effect on cotton root length, with a maximum at 2,324 kg.ha^{-1} (8.3 × clay content). For total root dry matter the results were similar, but there was no PG effect on the surface layer and there was a linear positive effect in the subsoil (Fig. 2b).

In general, the correlations were higher for root dry matter than root length (Table 4). The correlations of cotton root

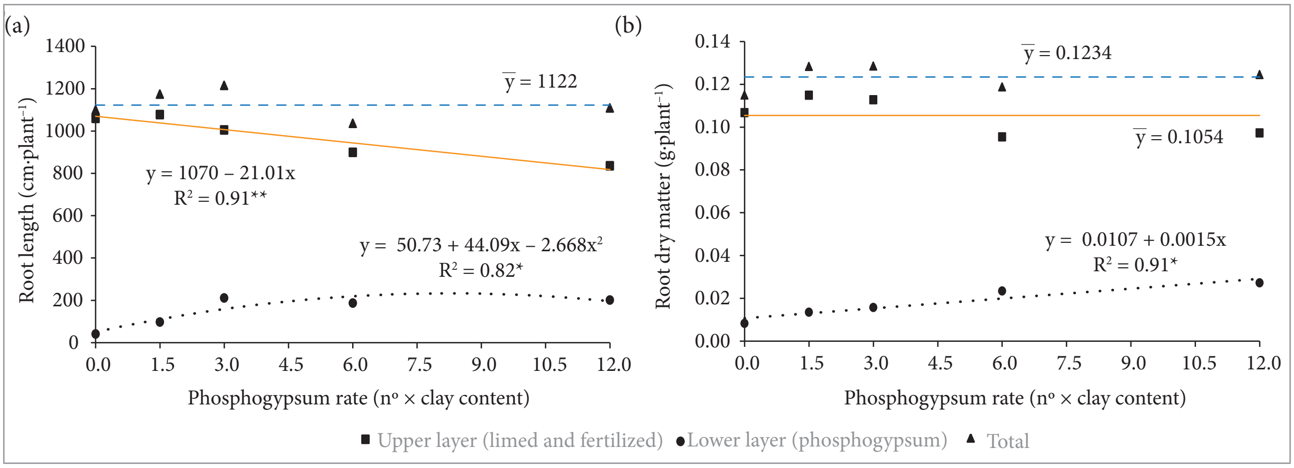

Figure 2. (a) Root length and (b) root dry matter (DM) of cotton of the upper, lower and total layers, as a function of phosphogypsum rates in the lower layer. * $p < 0.05$; ** $p < 0.01$.

Table 4. Correlations of root length and dry mass with soil acidity and soil solution attributes of the lower layer.

Local	Attribute	Length	Dry matter
Soil†	pH	0.56 (0.010)	0.65 (0.002)
	Al^{+3} ($mmol_c \cdot dm^{-3}$)	–0.49 (0.030)	–0.57 (0.009)
	Ca^{+2} ($mmol_c \cdot dm^{-3}$)	0.49 (0.028)	0.71 (0.001)
	Base saturation (%)	0.51 (0.023)	0.71 (< 0.001)
	Al saturation (%)	–0.56 (0.010)	–0.73 (< 0.001)
	Al/Ca	–0.50 (0.026)	–0.45 (0.046)
	Ca/ECEC	0.57 (0.010)	0.74 (< 0.001)
Solution – Concentration$^{\phi}$	Ionic strength (mmol·L^{-1})	0.61 (0.004)	0.73 (< 0.001)
	Al^{+3}(mmol·L^{-1})	–0.25 (0.291)	–0.49 (0.027)
	Ca^{+2} (mmol·L^{-1})	0.41 (0.077)	0.61 (0.004)
	Al^{+3} activity (μmol·L^{-1})	–0.13 (0.593)	–0.31 (0.176)
	Al/Ca	–0.44 (0.055)	–0.73 (< 0.001)
	Ca/Σcation†	0.40 (0.089)	0.56 (0.009)
Solution – Species$^{\phi}$	Al^{+3} (%)	0.15 (0.515)	0.15 (0.520)
	Al-DOC (%)	–0.09 (0.705)	–0.23 (0.332)
	Al-OH (%)	–0.11 (0.631)	–0.18 (0.444)
	Al-SO_4 (%)	0.27 (0.243)	0.38 (0.096)

†Correlations using the Pearson's parametric test. ϕ Correlations using Spearman's non-parametric test. P values are in parentheses. ECEC (effective cation exchange capacity) = Al, Ca, Mg and K; Σcation solution = Al, Fe, Mn, Ca, Mg, K and Na.

characteristics with soil attributes were all significant, with higher coefficients for dry matter. Aluminum saturation in soil showed the highest negative correlations, while the Ca/ECEC ratio showed the highest positive correlations. The solution ionic strength and the Ca^{+2} concentration showed high positive correlations, while the Al/Ca ratio showed a high negative correlation with soil solution attributes (non-parametric). There was no correlation of root attributes with Al activity and with the percentage of Al-SO_4 in the solution. The regressions had similar results to correlations, with higher significance for root dry matter than length and for soil than soil solution characteristics (Fig. 3). Root growth increased linearly with Ca concentration (Figs. 3a and 3b) and Ca saturation

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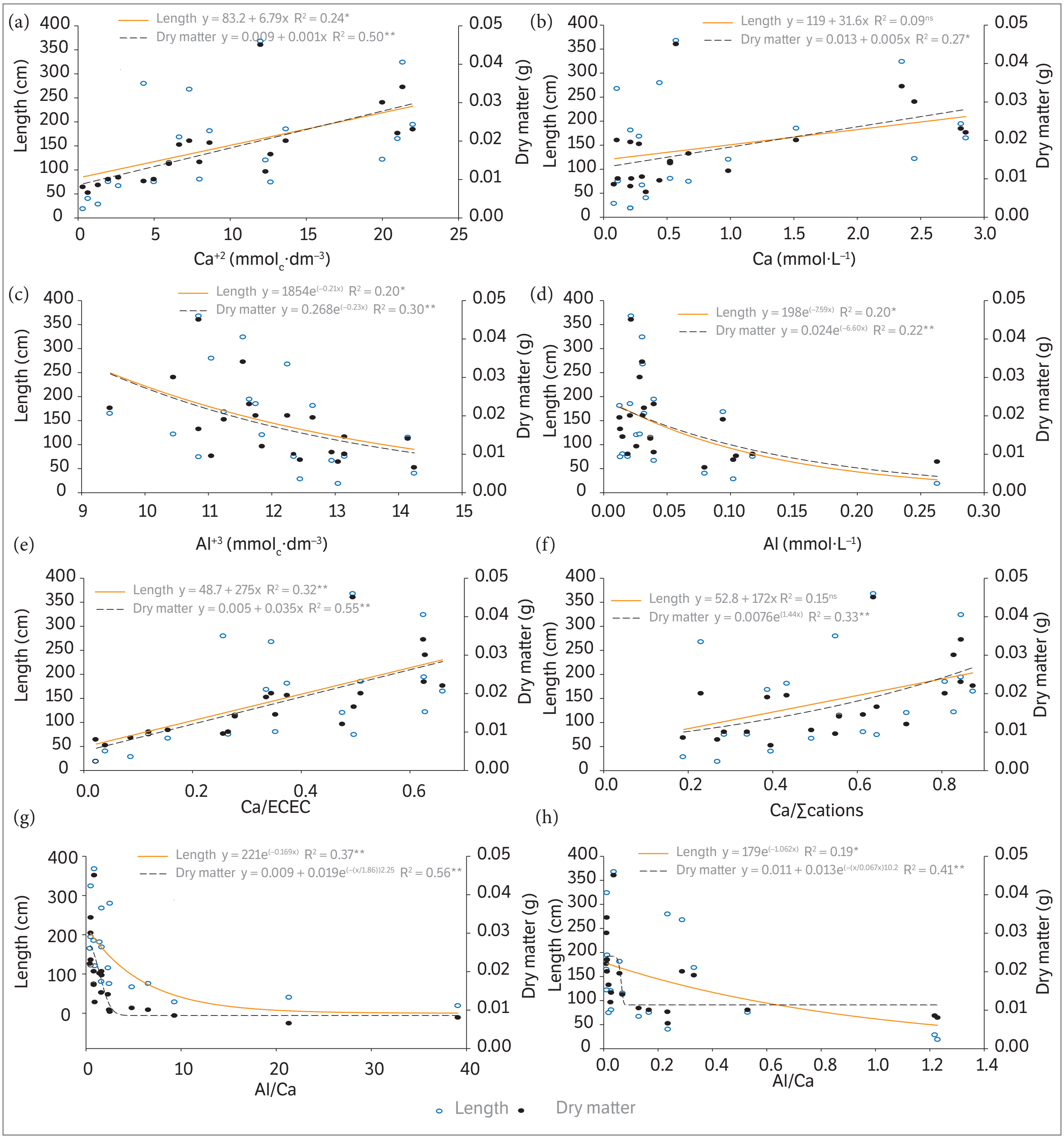

Figure 3. Effect of (a, b) calcium, (c, d) aluminum, (e, f) Ca/cations ratios, and (g, h) Al/Ca ratio on root length and root dry matter in the lower layer, in (a, c, e, g) soil and (b, d, f, h) soil solution. ** $p < 0.01$;* $p < 0.05$; ^{ns} not significant

(Figs. 3e and 3f), except for Ca/∑cations in soil solution (Fig. 3f). The root length and dry matter decreased with aluminum concentration in soil and solution, and was best described by exponential models (Figs. 3c and 3d). However, the best fit to Al/Ca ratio was the exponential model for root length and Weibull model for root dry matter (Figs. 3g and 3h).

The soil solution showed smaller toxicity thresholds (TT) than soil (Table 5). The TT was similar between root length and dry matter for Al concentration, both in soil and soil solution. For Al/Ca ratio, the TT was smaller for root dry matter than root length.

Table 5. Toxicity threshold of root length and dry matter for Al and Al/Ca ratio in soil and soil solution.

	Length	Dry matter
Soil solution – Al^{+3} ($mmol·L^{-1}$)	0.03	0.03
Soil – Al^{+3} ($mmol_c·dm^{-3}$)	9.95	9.91
Soil solution – Al/Ca	0.11	0.05
Soil – Al/Ca	1.07	0.69

DISCUSSION

Phosphogypsum application increased Ca, soil base saturation, and decreased Al concentration and saturation, as it was expected (Rhoton and McChesney 2011; Pauletti et al. 2014). However, a larger reduction in exchangeable Al and aluminum saturation was anticipated, considering that we had PG rates above the presently recommended. In addition, PG was applied and mixed directly in the evaluated soil layer, while under field conditions it would have to percolate, or be leached through the soil profile. Although Al saturation was not reduced below 10%, considered the threshold toxic level for cotton (Fageria et al. 1988), the decrease was above 50% (83 to 32%), while the exchangeable Al was decreased by 20% only (13.1 to 10.8 $mmol_c·dm^{-3}$). This effect occurred due to the increase in the ECEC, showing the importance of PG application. Despite its high mobility, if PG was applied on the soil surface it could interact in the upper layer. Caires et al. (2016) observed a decrease of only 13% in Al saturation in the layer from 0.4 to 0.6 m in a very clayey soil after the surface application of 15,000 $kg·ha^{-1}$ of PG, which corresponded to 20 × clay content. In four no-till long term experiments, Nora et al. (2017) also observed reduction in Al saturation with higher surface applied PG rates than the standard recommendation (approximately 1.5 to 2 times the standard rate).

Dissolved Organic Carbon was the predominant solute in the soil solution up to the third PG rate and there is a high affinity of DOC with Al (Ritchie et al. 1988). Under no-till, Al-DOC species are predominant in many situations, but mainly in the upper layer of the soil (Zambrosi et al. 2007; 2008). The same authors found great participation of Al-F species, mainly in deeper soil layers. This behavior was observed in the present experiment only at rates up to 0,840 $kg·ha^{-1}$ (1.5 and 3 × clay content). Above this rate, Al-SO_4 was higher than Al-F (Fig. 1a). This can be explained, at least in part, by the higher affinity of Al with F than S, since the S concentration in the soil solution was higher than F (Table 3). Gibson et al. (1992) observed that F forms strong complexes with Al, whereas Al binding with SO_4 is weak, and is more important on the increase of Al soil sorption by the generation of negative charges.

The predominance of free Ca and low percentage of Ca-DOC species (Fig. 1b) is in disagreement with Zambrosi et al. (2007; 2008). They observed a high percentage of Ca-DOC up to the depth of 0.80 m, in spite of the predominance of free Ca up to 0.10 m depth. The authors attributed the high percentage of Ca-DOC to a high affinity of organic anions with calcium, what is important to increase calcium mobilization in soil profile. However, DOC values were higher in the present study than in those cited above. The predominance of free Ca can be attributed to the competition with other cations to bind with COD (Zambrosi et al. 2007).

Cotton shoot growth was not affected by PG because the experiment was short, there was no water shortage, and soil acidity amelioration and fertilization were sufficient to supply the nutrient demand of cotton. As the roots were not able to grow in the subsoil due to Al toxicity with low PG rates and no PG, the root system was concentrated in the soil upper layer, what would lead to fast water exhaustion in the event of drought. Alleviating Al toxicity in the subsoil allowed for a better root distribution in the soil profile, with a decrease in root length in the upper soil layer, as a consequence of a better growth in the lower layer with adequate PG rates (Fig. 2a). Although the root dry matter and root length were adjusted to different regression models, the compensatory behavior was always observed (Fig. 2b).

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Cotton is considered highly sensitive to Al, with a critical ECEC saturation of 10% (Fageria et al. 1988). Howard and Adams (1965) argue that the absolute content of Ca limiting the growth of primary cotton roots varies according to the soil type, so the value of Ca relative to the total cations would be more stable, becoming a more appropriate indicator. The authors also proposed the values from 0.10 to 0.15 of Ca/total cations ratio in nutrient solution or in the soil solution as the Ca critical value for cotton root growth. In the present work it was not possible to establish a critical value for this ratio because the Ca/Σcations ratio tested in soil solution had minimum values around 0.2 and root response was exponential with higher ratios (Fig. 3f). Howard and Adams (1965) observed no increase in cotton root growth with Ca/Σ cations ratio above 0.2, what indicates that cotton, at least the tested cultivar, needs more calcium than it was found in former studies.

The correlations indicated that the attributes related to soil analysis were more important for root growth than those evaluated in soil solution, highlighting Ca content, base saturation, Al saturation and Ca/ECEC. In addition, none of the Al species in the solution showed significant correlation with root growth, showing that the use of simple attribute, which do not require chemical speciation as indicators of root growth, would be better. The absence of significant correlation with Al activity was not expected, since this parameter has been associated with reduced root growth in coffee and cotton (Pavan and Bingham 1982; Adams and Lund 1966). This may have happened due to high variability of aluminum activity (CV = 153%, Table 3). In an indirect way, the effect of Al activity was demonstrated by the Al/Ca ratio because it is intrinsically related to aluminum activity. The only advantage of the Al/Ca ratio would be its lower variability compared to aluminum activity.

Differently from other variables, the Al/Ca ratio was best fit by the Weibull model both in soil and soil solution for root dry matter response (Figs. 3g and 3h). The toxicity thresholds (TT) were 0.69 and 0.05 for Al/Ca in soil and soil solution, respectively (Table 5). Lund (1970) suggested 0.02 as a critical point of Al/Ca activities ratio in subsurface nutrient solution, above which the soybean root growth rate would be decreased. This result shows that root growth has a fine adjustment as a function of Al/Ca ratio and that Al in soil solution is more deleterious to roots than the Al in soil, once the TT of Al/Ca ratio in soil solution was 13 times lower than in soil.

Considering that the correlations (Table 4) and regressions (Fig. 3) were higher for root dry matter than for root length and that the dry matter showed a linear increase with PG rates (Fig. 2b), it seems that the adequate PG rate is higher than the one estimated according to the current recommendation based on clay content. The highest rate was 12 times the clay content, which would correspond to 3.36 $t \cdot ha^{-1}$ gypsum. The results of this study do not allow suggesting a new method to estimate PG recommendation, however it is clear that the current recommendation should be reviewed. In addition, PG was applied directly to the subsurface layer, and if it were applied on the soil surface, as it is the usual practice, the effect on subsurface might be reduced, which would probably result in a greater PG requirement.

The high correlations of root length and dry matter with Ca/ECEC ratio in the soil and Ca/Σ cation in the soil solution (Table 4 and Figs. 3e and 3f) and the critical values of Al/Ca ratios (Table 5) are indicative that these characteristics must be taken into account along with the well-known Ca and Al concentration.

In an extensive review of gypsum use in agriculture, Zoca and Penn (2017) reported that there is still not a single method for determining suitable gypsum rates for different soil environments and crop systems, thus corroborating our findings. However, recently Caires and Guimarães (2018) proposed a novel PG rate recommendation based on increasing Ca^{2+} saturation to 60% in the ECEC at the 0.2 to 0.4 m soil layer. The PG rates of the new method showed better adjustments to the PG rates associated with maximum economic yield than the PG rates based on subsoil clay content. According to this new method, the PG rate for the present soil would be 5,600 $kg \cdot ha^{-1}$, corresponding to 20 × clay content. However, it is well known that excessive rates of PG can decrease grain yields, since they induces K and Mg deficiency (Tiecher et al. 2018). Therefore, results of the present experiment show that the proposed method (Caires and Guimarães 2018) would not be adequate for this plant/soil system, which reinforces the need for better adjustments of PG rate recommendations.

CONCLUSION

Most of the Al in soil solution is bound to DOC, with the Al-SO_4 fraction increasing only with high phosphogypsum rates, higher than 3 × clay content. In contrast, Al activity

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is drastically reduced with low PG rates, at least 1.5 × clay content. Nevertheless, the speciation and the activity of Al in the soil solution are not good indicators of cotton root growth, which is more related to soil properties, such as Ca content, base saturation, Al saturation, Ca/ECEC and Al/Ca ratios, than to the soil solution characteristics.

Phosphogypsum recommendation methods must be reviewed, since presently done they lead to rate underestimation.

AUTHORS' CONTRIBUTION

Conceptualization, Pivetta L. A., Castoldi G., Pivetta L. G., Maia S. C. M. and Rosolem C. A.; Methodology, Pivetta L. A., Castoldi G., Pivetta L. G., Maia S. C. M. and Rosolem C. A.; Investigation, Pivetta L. A., Castoldi G., Pivetta L. G., Maia S. C. M. and Rosolem C. A.; Writing – Original Draft, Pivetta L. A.; Writing – Review and Editing, Pivetta L. A., Castoldi G., Pivetta L. G., Maia S. C. M. and Rosolem C. A.; Resources, Rosolem C. A.; Supervision, Rosolem C. A.

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