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EFFECT OF APPLICATION METHODS AND RATES OF CALCIUM SOURCES ON SOIL ALUMINUM FORMS

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Resumo

Efeito dos métodos de aplicação e doses de fontes de cálcio nas formas de alumínio do solo. A presença de alumínio (Al) em formas disponíveis no solo pode prejudicar as plantas cultivadas. No estudo, avaliaram-se as formas desse elemento em Cambissolo Húmico, cultivado com eucalipto e tratado com doses de calcário (CALC), gesso (GESS) e lama de cal (LAMA), em aplicações superficiais em área total (Artot), na faixa de plantio (FAIXA) e no sulco de plantio (SULCO). Os tratamentos foram: Controle; CALC-3,5 t ha^{-1} em AT; CALC-1,75 t ha^{-1} na Faixa; CALC-3,5 t ha^{-1} na Faixa; LAMA-3,5 t ha^{-1} na Faixa; CALC-3,5 t ha^{-1}+ GESS-1,75 t ha^{-1} na Faixa; CALC-1,75 t ha^{-1} no Sulco; CALC-1,75 t ha^{-1}+GESS-1,38 t ha^{-1} no Sulco; e, GESS-1,38 t ha^{-1} no Sulco. Após 31 e 56 meses da aplicação dos tratamentos, foram determinados os teores de Al trocável (Al^{3+}), Al ligado à matéria orgânica (Al-MO) e Al ligado a óxidos de baixa cristalinidade e amorfos (Al – OX), em camadas de até 0,40 m. O Al^{3+} diminuiu na camada 0-0,05 m, quando CALC e LAMA foram aplicados em AT e na FAIXA e, nas camadas inferiores, quando o primeiro foi incorporado no SULCO. Al - MO e Al - OX apresentaram teores entre 2,6 e 5,8 vezes maiores em relação ao Al^{3+}. O CALC em superfície diminui os teores de Al^{3+}, Al-MO e Al - OX na camada de 0 a 0,05 m. O gesso não afetou os teores de Al no solo.

Palavras-chave: Calagem, Gesso Agrícola, Lama de Cal, Alumínio e Eucalipto

Abstract

Effect of application methods and rates of calcium sources on soil aluminum forms. The presence of aluminum (Al) in available forms in the soil can harm cultivated plants. Aluminum forms were evaluated in a Humic Cambisol soil grown with eucalyptus and treated with dolomitic limestone (DL), gypsum (GYP), and lime mud (LM), using surface applications over the total area (TA), to the planting strip (STRIP), and to the planting furrow with incorporation (FRW). The treatments were: Control; DL 3.5 Mg ha^{-1} TA; DL 1.75 Mg ha^{-1} STRIP; DL 3.5 Mg ha^{-1} STRIP; LM 3.5 Mg ha^{-1} STRIP; DL 3.5 Mg ha^{-1} + GYP 1.75 Mg ha^{-1} STRIP; DL 1.75 Mg ha^{-1} FRW; DL 1.75 Mg ha^{-1} + GYP 1.38 Mg ha^{-1} FRW; and GYP 1.38 Mg ha^{-1} FRW. After 31 and 56 months of applying the treatments, the levels of exchangeable Al (Al^{3+}), Al bound to organic matter (Al-MO) and Al bound to low crystallinity and amorphous oxides (Al-OX) were determined in layers of up to 0.40 m. Al^{3+} contents decreased in the 0-0.05 m layer when DL and LM were applied in TA and STRIP and, in the lower layers when the first was incorporated in the FRW. Al-OM and Al-OX contents were 2.6 to 5.8-fold higher than Al^{3+}. DL on TA decreases Al^{3+}, Al-OM, and Al-OX contents in the 0-0.05 m layer. GYP application did not affect soil Al contents.

Keywords: Liming, Agricultural gypsum, Lime mud, Aluminum, Eucalyptus.

INTRODUCTION

Acidic soils occupy more than 40% of the terrestrial surface. The main factors that interfere in soil acidification are: leaching of alkaline cations, weathering of clay minerals, organic matter decomposition, carbon dioxide (CO_2) production, nitrification, acid-reaction fertilizers, and cation absorption by plants (ERNANI, 2016). Soil acidity is one of the main factors of low fertility and agricultural soil degradation. The presence of Al in it's free form (Al^{3+}) in the soil is one of the major challenges under this condition, as they occupy part of the soil cation exchange capacity (CEC) and result in serious losses to the development of plant root systems (YANG *et al.*, 2015).

Exchangeable Al (Al^{3+}) contents are obtained through extraction with a KCl solution used worldwide and it's quantified is generally done by titration, using a standardized alkaline solution (Tedesco *et al.*, 1995). However, Al^{3+} is overestimated by the KCl solution (1 mol L^{-1}) due to dissolution of amorphous inorganic forms or low crystallinity of Al compounds, which may result in inappropriate estimation of Al saturation and their potential phytotoxicity effects (CUNHA *et al.*, 2015). The most toxic chemical species are Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^{+}$, whereas non-toxic forms are those complexed with organic and inorganic bound in the soil solution (CUNHA *et al.*, 2018 a, b). Therefore, studying forest species with high soil Al levels is essential for increasing the production potential of these soils and improving yield of agricultural crops and forestry crops (YANG *et al.*, 2015).

Some *Eucalyptus* and *Pinus* species present good adaptation to acidic soil conditions, but exhibit a high demand for alkaline cations, which are linearly connected to the growth rate (ROCHA *et al.*, 2019). The photosynthetic rate of eucalyptus clones can be a reference indicator of tolerance to Al; however, different species present varied responses due to the most diverse levels of tolerance (YANG *et al.*, 2015). Neutralizing soil Al while providing sufficient levels of essential nutrients, such as Ca, is essential. Thus, the negative effects of soil acidity justify its correction, which is commonly carried out through application of limestone. Changes in soil chemical properties caused by surface application of limestone depend on the application rate and reaction time and are usually limited to the upper layer of the soil profile (RHEINHEIMER *et al.*, 2018).

The main hypothesis raised in this research is that the contents of soil all Al forms decrease in soils treated for acidity correction, which does not occur when using gypsum. In this context, the objective of this study is to verify the influence the long-term effect of application methods and rates of Ca sources (dolomitic limestone, agricultural gypsum, and lime mud) on Al forms in a Humic Cambisol with high Al^{3+} content, grown with *Eucalyptus dunnii* Maiden in the Southern Plateau of Santa Catarina, Brazil.

MATERIAL AND METHODS

Area experimental

The experiment was conducted at the Guarujá Farm, Bocaína do Sul, Santa Catarina, Brazil (69° 36'70.0' S, 59° 99'80.0"W, and altitude of 860 m), which belongs to the Klabin company. The region's climate is Cfb, subtropical, without a dry season, according to the Köppen classification (ALVARES *et al.*, 2014). The parent material of the soil in the region is alkaline volcanic rock, which occupies most of the Southern Plateau of Santa Catarina (POTTER *et al.*, 2004) and was classified as a Dystrophic Humic Cambisols of clayey texture and undulating relief.

The soil of the experimental area was analyzed before the experiment implementation. The results for the 0-0.20 m layer presented the following characteristics: clay content = 350 g kg^{-1}; organic matter = 40 g kg^{-1}; pH (water) = 4.1; Al = 10.7 $cmol_c$ kg^{-1}; Ca = 0.25 $cmol_c$ kg^{-1}; Mg = 0.30 $cmol_c$ kg^{-1}; P = 2.6 mg dm^{-3}; K = 75.5 mg dm^{-3}; S = 11 mg dm^{-3}; Zn = 0.45 mg dm^{-3}; Cu = 0.8 mg dm^{-3}; B = 0.45 mg dm^{-3}; and Mn = 5 mg dm^{-3}. The results for the 0.20-0.40 m layer presented the following characteristics: clay = 380 g kg^{-1}; organic matter = 32 g kg^{-1}; pH (water) = 4.2; Al = 10.8 $cmol_c$ kg^{-1}; Ca = 0.15 $cmol_c$ kg^{-1}; Mg = 0.15 $cmol_c$ kg^{-1}; P = 1.1 mg dm^{-3}; K = 57.5 mg dm^{-3}; S = 14 mg dm^{-3}; Zn = 0.25 mg dm^{-3}; Cu = 0.8 mg dm^{-3}; B = 0.35 mg dm^{-3}; and Mn = 3.5 mg dm^{-3}.

The need for limestone application was determined based on the Manual for Liming and Fertilizer Application for the States of Rio Grande do Sul and Santa Catarina (CQFS, 2016). However, the standard rate was defined based on the study of Almeida *et al.* (1999), focusing on raising the soil pH in water to 5.2 in the 0-10 cm layer. According Almeida *et al.* (1999), the reduction of soil acidity by increasing the soil pH to 5.2 can be sufficient to ensure an adequate plant development in buffered soils of the South region of Brazil. Additionally, low responses to liming have been observed for forest species such as eucalyptus (CQFS, 2016).

There was application of 2.0 Mg ha^{-1} of limestone on the surface of the total area; this dose was subtracted from the recommended dose of 5.5 Mg ha^{-1} of limestone. With this, the dose of 3.5 Mg ha^{-1} of limestone to be applied to achieve the desired pH was established as a reference. The dose of gypsum was calculated to provide an amount equivalent to half the amount of Ca added through limestone.

The Ca sources used in the experiment were dolomitic limestone, with total neutralizing power (TNP) of 56% (51% Ca) and 1% moisture; gypsum (33% Ca); and lime mud, with a TNP of 87% and 30.5% moisture. These materials were analyzed in an x-ray fluorescence spectrometer by energy dispersion. This analysis was caried out using 2 g of each material, which was crushed using an agate mortar and pistil until reaching granulometric sizes lower than 0.25 mm. The results of this analysis showed that the limestone, gypsum, and lime mud used had the following contents (%): CaO = 50.83, 33.47, and 93.15; MgO = 22.38, 3.16, and 1.42; Al_2O_3 = 4.55, 1.45, and 0.48, respectively (PFLEGER *et al.*, 2020).

The planting of the tree seedlings took place in October 2015. The area received a second rotation with planting of clonal seedlings of Eucalyptus dunnii Maiden (CL7003) of Australian origin. The plant material was obtained by first-generation vegetative propagation, coming from the nursery of the company Rigesa S.A. The seedlings were transplanted in the spacing of 3.5 m between rows and 2.0 m between plants in a second rotation area that received initial soil preparation by a crawler tractor and subsoiler, with negative-angle shanks and 4 pairs of ploughing discs, to a depth of 0.5 m.

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Treatments applied

The treatments were established as described in Table 1. In treatments in which Ca sources were not applied throughout the area, the same pre-established doses per hectare were applied in a concentrated manner in smaller areas, in the planting strip or furrow.

Table 1. Description of treatments with the Ca sources, rates, application method, and application site in the soil.
Tabela 1. Descrição dos tratamentos e respectivas doses, materiais, forma e local de aplicação no solo.

Identification	Sources	Rates (Mg ha^{-1})	Application method	Application site
T1	Control			
T2	DL	3.5	Surface	TA
T3	DL	1.75	Surface	STRIP
T4	DL	3.5	Surface	STRIP
T5	LM	3.5	Surface	STRIP
T6	DL + GYP	3.5 + 2.75	Surface	STRIP
T7	DL	1.75	Incorporation	FRW
T8	DL + GYP	1.75 + 1.38	Incorporation	FRW
T9	GYP	1.38	Incorporation	FRW

Legend: DL = dolomitic limestone; LM = lime mud; GYP = agricultural gypsum; TA = total area; STRIP = planting strip; FRW = planting furrow. Legenda: CALC = calcário dolomítico; LAMA= lama de cal; GESS= gesso agrícola; AT = área total; FAIXA = faixa de plantio; SULCO = sulco de plantio.

The treatments were applied in April 2016 with manual surface distribution or application to the planting furrow, which was opened with a hoe (0.20 m depth), with manual distribution of the products and closing the same it by covering it with the soil that had been removed. The application in the seedling preparation strip was superficial, corresponding to a one-meter strip, in the planting line. The application in the furrow was carried out after opening with a hoe up to 0.20 m depth, with manual distribution of the products and closing of the furrow, covering it with the soil that had been removed.

Soil the mineral fertilizing were applied using N (ammonium nitrate), P_2O_5 (triple superphosphate), and K_2O, (potassium chloride) in three applications with equal rates for all treatments: the first application at 10 days after planting, using 8, 52, and 12 g $plant^{-1}$ of N, P_2O_5, and K_2O, respectively; the second application at 90 days after planting, using 30, 0, and 60 g $plant^{-1}$ of N, P_2O_5, and K_2O, respectively; and the third application at 365 days after planting, using 15, 7.5, and 45 g $plant^{-1}$ of N, P_2O_5, and K_2O, respectively.

Experimental design and soil sampling

Each experimental unit consisted of 4 six-plant rows, with 2 two-plant rows as border. Thus, the evaluation area of the experimental units corresponded to 8 plants (56 m^2), 4 plants in each of the two central rows. The experiment was conducted in a randomized complete block design with 4 replications, totaling 36 experimental units.

The first of two soil samplings was carried out 31 months after the application of treatments, in November 2018, soil samples were composed of 6 subsample points of soil in the planting line in all treatments with the aid of a cutting shovel in the layers of 0 - 0.05; 0.05 - 0.10 m and Dutch auger in the layers of 0.10 - 0.20; 0.20 - 0.40 m in depth. The second soil sampling was carried out at 56 months after the application of treatments, in November 2020, within the space between plants in the planting row; 7 subsamples were collected (3 exactly on the planting row and 4 approximately 5 cm away from the row center, two on each side) for composite soil samples from the 0-0.05 m, 0.05-0.10 m, 0.10-0.20 m, and 0.20-0.40 m layers, using Dutch auger.

Extraction of soil aluminum forms

Al extractions were carried out after processing the soil samples. A potassium chloride (KCl) solution (1 mol L^{-1}) was used for extracting Al^{3+} as follows: 2.5 g of soil with 50 mL of KCl solution (1 mol L^{-1}) were shaken in a horizontal shaker at 120 rpm for 30 minutes and then left to rest until the following day (15-18 hours) to favor decantation; the supernatant was then separated for later analysis of Al^{3+} content by acid-base titration; the extract was titrated with NaOH 0.0125 M, and three phenolphthalein drops were added until the solution presented a pink color persistent for more than 10 seconds (TEDESCO *et al.*, 1995).

For the form of Al bound to organic matter in low to medium stability complexes (URRUTIA et al., 1995), the copper chloride ($CuCl_2$) extracting solution 0.5 mol L^{-1} was used, according to Juo and Kamprath

(1979). Two grams of soil were placed in 50-mL Falcon tubes, and 20 mL of the extractant was added (keeping the proportion). The samples were then shaken at 120 rpm for 30 minutes in a horizontal shaker and left to rest until the following day (15-18 hours) to favor decantation (adaptation). Al was quantified in this extract by atomic absorption spectrophotometry. The $CuCl_2$ extractant proved to be effective for extracting both exchangeable and non-exchangeable Al forms, mainly organic matter-bound Al complexes, although it can equally extract inorganic hydroxy-Al (JUO; KAMPRATH, 1979). Therefore, Al extracted by $CuCl_2$ is considered both exchangeable + non-exchangeable Al. Additionally, subtracting the Al^{+3} extracted with KCl solution (1 mol L^{-1}) from the exchangeable + non-exchangeable Al extracted with copper chloride ($CuCl_2$; 0.5 mol L^{-1}) results in the non-exchangeable Al content (FIGUEIREDO; ALMEIDA, 1991).

Low-crystallinity and amorphous Al oxides were extracted using an ammonium oxalate solution ($(NH_4)_2C_2O_4$) 0.2 mol L^{-1} buffered at pH 3.0, as described by McKeague and Day (1966). The ammonium oxalate solution was prepared using 81 g of monohydrated ammonium oxalate and 54 g of oxalic acid $(COOH)_2.2H_2O$ dissolved in 5 L of distilled water. Two individual 500-mL solutions were prepared with ammonium oxalate (28 g L^{-1}) and 500 mL of acid oxalic (25 g L^{-1}) for pH correction. The solutions were stocked in a polyethylene flask after reaching a pH of 3, keeping them in a dark place. Then, 0.4 g of soil were placed in 50-mL Falcon tubes, and 20 mL of the extractant (keeping the proportion) were added; the samples were shaken at 120 rpm for 4 hours in the darkness to avoid photochemical reaction, centrifuged at 2000 rpm for 10 minutes, and measured for pH level. The Al extracted by this method was quantified by atomic absorption spectrophotometry.

Total soil Al was determined according to the Brazilian Agricultural Research Corporation (EMBRAPA, 2017) by adding 1 g of soil to a 250-mL Erlenmeyer flask, followed by 20-mL of acid sulfuric and of water solution (1:1), which was heated on a hot plate and left to boil for 30 minutes with funnels. After cooling, 50 mL of distilled water was added, and the solution was filtered and brought to a final volume of 250 mL. Al was quantified by atomic absorption spectrophotometry. Total Al (g kg^{-1}) was assessed only for the control treatment (T1) in the 0-0.40 m layer at 56 months after the application of treatments. The means of the 4 blocks were calculate.

Statistical analysis

Data were subjected to analysis of variance (ANOVA) and, when significant, the means were compared using the Scott-Knott test at a 5% significance level. The statistical analyses were conducted using software RStudio (RStudio Team, 2021) and software Sisvar version 5.8 (FERREIRA, 2014).

RESULTS

Total aluminum contents

The total Al contents found in the evaluation at 56 months after the application of treatments, in the control treatment (T1) showed means of 34.4 g kg^{-1} for the 0-0.05 m soil layer, 45.5 g kg^{-1} for the 0.05-0.10 m layer, 45.6 g kg^{-1} for the 0.10-0.20 m layer, and 47.0 g kg^{-1} for the 0.20-0.40 m soil layer.

Al in the extractor potassium chloride 1.0 mol L^{-1}

Exchangeable aluminum (Al^{+3}) contents, extracted with 1.0 mol L^{-1} KCl, in the evaluation at 31 months after the application of treatments (A) decreased in all treatments, except for the treatment with application of agricultural gypsum (GYP) to the planting furrow (FRW) (T9), reaching 0.24 $cmol_c$ dm^{-3} in the 0-0.05 m surface soil layer for the treatment consisted of application of the highest dolomitic limestone (DL)+GYP rate to the planting strip (STRIP) (T6), and of 0.06 and 0.07 $cmol_c$ dm^{-3} in the 0.05-0.10 and 0.10-0.20 m soil layers, respectively, for the application of the lowest DL rate to FRW (T7). The means in the control treatment (T1) were 9.44, 10.61, and 10.72 $cmol_c$ dm^{-3} for the 0-0.5, 0.05-0.10, and 0.10-0.20 m layers, respectively (Figure 1A).

In the evaluation at 56 months after the application of treatments, Al^{3+} contents decreased, reaching 2.18 $cmol_c$ dm^{-3} in the 0-0.05 m surface layer for the application of the highest DL+GYP rate to STRIP (T6), and 3.98 $cmol_c$ dm^{-3} in the 0.20-0.40 m layer for the application of DL+GYP to FRW (T8). The means in the control (T1) were 10.50 and 11.47 $cmol_c$ dm^{-3} for the 0-0.5 and 0.20-0.40 m soil layers, respectively (Figure 1B).

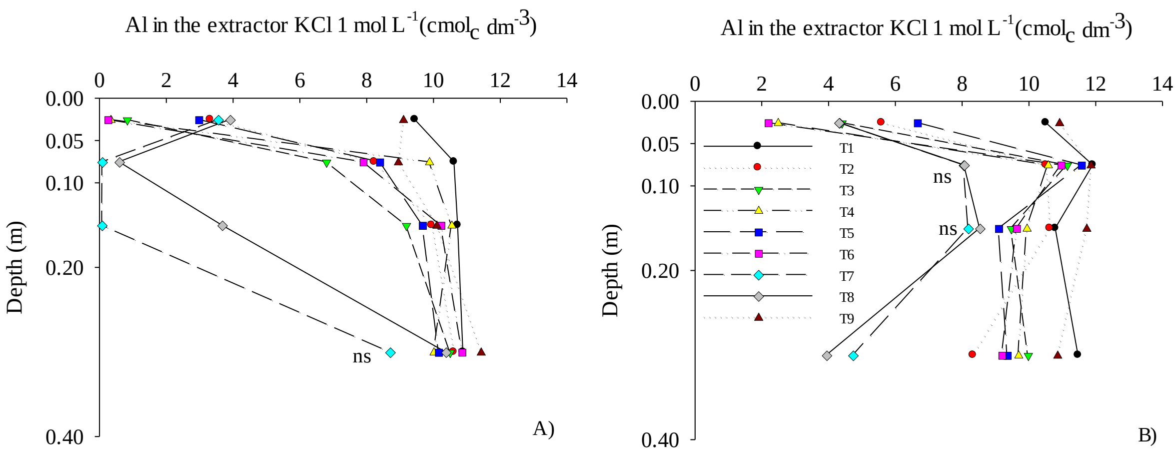

Figure 1. Aluminum contents (cmol$_c$ dm^3; extracted with 1 mol L^{-1} KCl) in soil layers (up to 0.40 m) of a Humic Cambisols in a plantation area with *Eucalyptus dunnii* Maiden, based on nine treatments with different rates and methods of limestone, gypsum, and lime mud application, assessed 31 (A) and 56 (B) months after the applications of treatments.

Figura 1. Teores de alumínio (cmol$_c$ dm^3; extraído com 1 mol L^{-1} de KCl) em camadas de solo (até 0,40 m) de um Cambissolo Húmico em uma área de plantio de *Eucalyptus dunnii* Maiden, com base em nove tratamentos com diferentes doses e métodos de aplicação de calcário, gesso e lama de cal, avaliados aos 31 meses (A) e 56 meses (B) após as aplicações dos tratamentos.

The application of dolomitic limestone, with addition gypsum, and with lime mud decreased Al^{3+} contents by up to 91.4% in the evaluation at 31 months after the application of treatments, with reductions from approximately 9.4 to less than 1 cmol$_c$ dm^{-3} in the 0-0.5 m surface layer compared to the control (T1). The application of the lowest DL rate to FRW (T7) and the lowest DL+GYP rate to FRW (T8) decreased Al^{3+} contents by approximately 99.4% and 80.2% in the 0.05-0.10 and 0.10-0.20 m layers, respectively, compared to the control (T1), according to Figure 1, (A).

All treatments showed decreases of up to 79.2% in Al^{3+} contents in the evaluation at 56 months after the application of treatments, with reductions from approximately 10.5 cmol$_c$ dm^{-3} to less than 2.2 cmol$_c$ dm^{-3} in the 0-0.5 m surface layer, compared to the control (T1), except for the treatment with application of GYP to FRW (T9). The lowest DL rate applied to FRW (T7) and the lowest DL+GYP rate applied to FRW (T8) decreased Al^{3+} contents by approximately 58.9% and 65.8% in the 0.10-0.20 and 0.20-0.40 m soil layers, respectively, compared to the control (T1), according to Figure 1, (B).

Applying the lowest DL rate to FRW (T7) and the lowest DL+GYP rate to FRW (T8) resulted in higher soil acidity correction at depth due to the incorporation of the products into the soil, reaching deeper layers. Thus, lower Al^{3+} contents were found at depth, benefiting root growth.

Al in the extractor copper chloride 0.5 mol L^{-1}

The results for copper chloride-extractable Al (Al-$CuCl_2$**)**, which extracts both exchangeable and non-exchangeable Al forms, are shown in Figure 2, (A). Subtracting Al^{+3} extracted with KCl solution (1 mol L^{-1}) from exchangeable + non-exchangeable Al extracted with copper chloride (0.5 mol L^{-1}) resulted in the non-exchangeable Al content, according to Figure 2, (B).

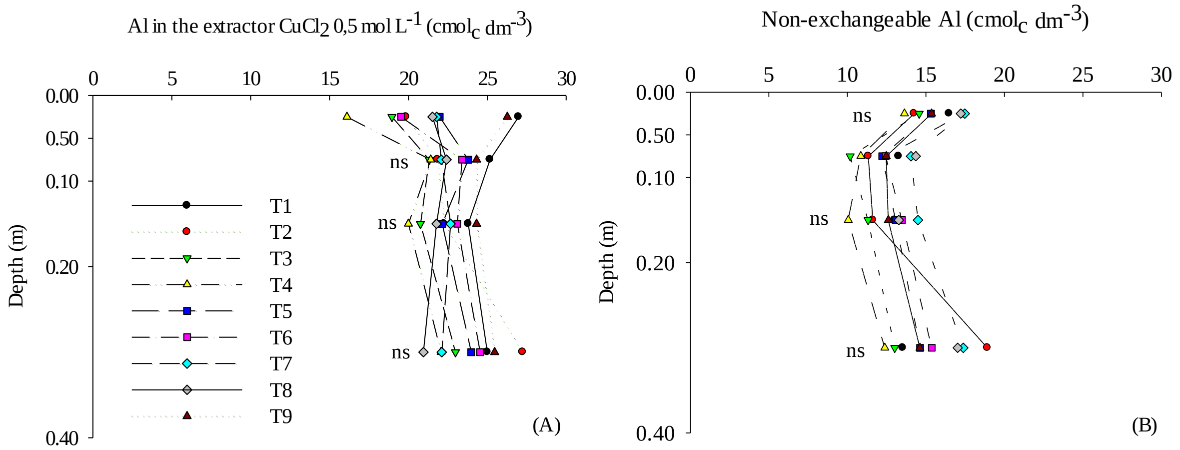

Figure 2. Aluminum contents (cmol$_c$ dm^3) extracted with 0.5 mol L^{-1} $CuCl_2$ (A) and non-exchangeable aluminum contents (B) in soil layers (up to 0,40 m) of a Humic Cambisols in a plantation area with *Eucalyptus dunnii* Maiden, based on nine treatments with different rates and methods of limestone, gypsum, and lime mud application, assessed 56 months after the applications of treatments.

Figura 2. Teores (cmol$_c$ dm^3) de alumínio extraído com 0,5 mol L^{-1} de $CuCl_2$ (A) e alumínio não trocável (B) em camadas de solo (até 0,40 m) de um Cambissolo Húmico em uma área de plantio de *Eucalyptus dunnii* Maiden, com base em nove tratamentos com diferentes doses e métodos de aplicação de calcário, gesso e lama de cal, avaliados aos 56 meses após as aplicações dos tratamentos.

In the evaluation at 56 months after the applications of treatments, Al-$CuCl_2$ contents in the form exchangeable + non-exchangeable Al decreased by to 40.3% in the 0-0.5 m surface layer when applying the highest DL rate to STRIP (T4) compared to the control (T1), according to Figure 2, (A). However, no significant response was found for the other evaluated soil layers. The mean content of KCl-extractable Al in the evaluation at 56 months after the application of treatments and in the 0-0.10 m surface layer was 8.1 cmolc dm-^{3}, whereas the mean Al - $CuCl_2$ content was 22.1 cmolc dm^{-3}, denoting a mean 2.7-fold higher for the latter. In the subsurface layer (0.10-0.40 m), the mean content of KCl-extractable Al was 9.2 cmolc dm-^{3}, whereas the mean Al-$CuCl_2$ was approximately 2.5-fold higher (23.1 cmolc dm^{-3}).

In the evaluation at 56 months after the application of treatments, the following treatments were the most effective in decreasing non-exchangeable Al in the 0.5-0.10 m soil layer: application of the highest DL rate applied over the total area (TA) (T2), with 11.3 cmol$_c$ dm^{-3}; and DL at rate the lowest and highest rates to ROW (T3 and T4), with 10.1 and 10.8 cmol$_c$ dm^{-3}, respectively (Figure 2B). The mean of the other treatments was 13.1 cmol$_c$ dm^{-3}.

Al in the extractor ammonium oxalate 0.2 mol L^{-1} buffered at pH 3.0

In the evaluation at 56 months after the applications of treatments, contents of Al in the extractor ammonium oxalate 0.2 mol L^{-1} buffered at pH 3.0 **(**Al–OX) decreased by up to 24.7% in the 0-0.05 m surface layer when applying the highest DL rate to STRIP (T4) compared to the control (T1). In the 0.05-0.10 m surface layer, the means Al - OX decreased by up to 16% when applying the highest DL rate to STRIP (T4) and lime mud (LM) to STRIP (T5) compared to the control (T1). The contents of ammonium oxalate-extractable Al in the 0.10-0.20 and 0.20-0.40 m soil layers were not significantly affected by the treatments, according to Figure 3.

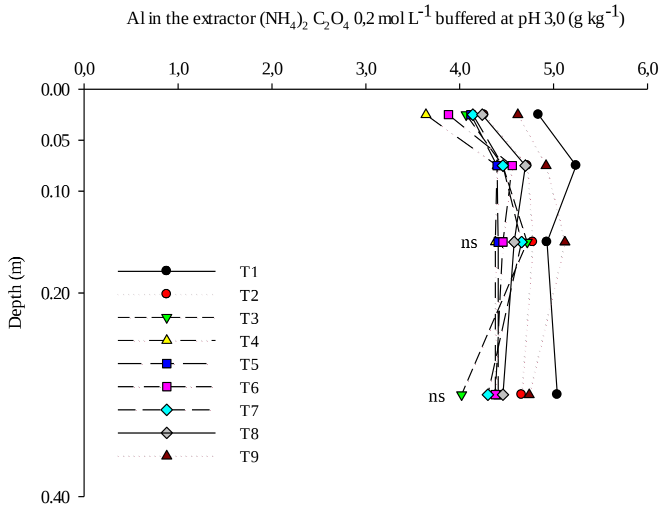

Figure 3. Aluminum contents (g kg^{-1}); extracted with 0.2 mol L^{-1} ammonium oxalate buffered at pH 3.0 in soil layers (up to 0,40 m) of a Humic Cambisols in a plantation area with *Eucalyptus dunnii* Maiden, based on nine treatments with different rates and methods of limestone, gypsum, and lime mud application, assessed 56 months after the applications of treatments.

Figura 3. Teores de alumínio (g kg^{-1}); extraído com 0,2 mol L^{-1} de oxalato de amônio tamponado a pH 3,0 em camadas de solo de um Cambissolo Húmico em área de plantio de *Eucalyptus dunnii* Maiden, com base em nove tratamentos com diferentes doses e métodos de aplicação de calcário, gesso e lama de cal, avaliados aos 56 meses após as aplicações dos tratamentos.

DISCUSSION

Al contents is usually determined in routine analyses such as Al^{3+} through extraction with 1 mol L^{-1} KCl solution (CQFS – RS/SC, 2016). Decreases in Al^{3+} contents are connected to increases in soil pH. The main strategy for neutralizing toxic Al forms is correcting the soil acidity with acidity correctors, how limestone application. Agricultural gypsum, despite not altering the pH, can contribute to reducing the concentration of this element in the soil and aluminum saturation (m%).

Soils of the Southern Plateau of Santa Catarina, Brazil, are acidic, and the studied soil (Humic Cambisol) had approximately 10 cmolc dm^{-3} of Al^{3+}. However, all treatments were effective in reducing soil Al forms, including Al^{3+}, exchangeable + non-exchangeable Al, and low-crystallinity and amorphous Al, regardless of the application rates and methods used, even after a long period, except for gypsum application to the planting furrow (FRW), even if this involves the application of 2 Mg ha^{-1} of dolomitic limestone on the surface in the total area.

Dalla Nora *et al.* (2014) evaluated the efficiency of gypsum combined with limestone in improving soil chemical attributes, maize yield in a Ferralsols in Rio Grande do Sul, Brazil, and found higher decreases in Al contents in the 0.25-0.40 m layer; this is due to the high solubility of gypsum (approximately 10-fold higher than limestone), showing positive results in the first six months, as confirmed in the present study.

Zandoná *et al.* (2015) evaluated the effect of agricultural gypsum application, with and without limestone, on soil chemical attributes and maize and soybean grain yields in no-tillage system and found low soil Al^{3+} contents in the 0-10 and 10-20 cm layers, as well as aluminum saturation lower than 10%. However, Al^{3+} contents were, overall, higher in the 20-40 cm layer than in the surface layer, as confirmed in the present study.

In the experiment that originated the present work, Pfleger *et al.* (2020) conducted evaluations 9 months after the applications of treatments, in January 2017, and found that the dolomitic limestone application to FRW (T7) and dolomitic limestone + gypsum to FRW (T8) decreased Al^{3+} by 89% and 80% in the 0-0.20 m layer, and by 69% and 47% in the 0.20-0.40 m layer, respectively. Similarly, in the present study, these treatments were also effective in decreasing Al^{3+} in the 0.05-0.20 m layer at 31 months after the applications of treatments (December 2018) and in the 0.20-0.40 m layer at 56 months after the applications of treatments (November 2020), which are reductions often greater than those reported by Pfleger *et al.* (2020). This indicates that Al^{3+} decreases, due to the concentration of these Ca sources in smaller areas and their incorporation into the soil, contributing to their effect at all depths evaluated.

The $CuCl_2$ extractor (JUO; KAMPRATH, 1979) proved effective in extracting both exchangeable and non-exchangeable Al forms, mainly organic matter-bound Al, although it can also extract inorganic hydroxy-Al polymers. Non-exchangeable Al forms, although have no direct phytotoxic effects, act to buffer soil pH and affect the activity of Al^{3+} in the soil solution (JUO; KAMPRATH, 1979) and, influencing, thus, your need for limestone.

Figueiredo and Almeida (1991) evaluated the presence of exchangeable and non-exchangeable Al forms in acidic soils in Santa Catarina by assessing their correlations with soils properties and their results as a function of application of increasing limestone rates. They reported that Al contents extracted with $CuCl_2$ solution were, overall, higher than those extracted with 1 mol L^{-1} KCl solution; therefore, $CuCl_2$ is more effective in extracting non-exchangeable Al forms. They also found that liming rapidly neutralized Al^{3+}, but that non-exchangeable Al forms decreased more slowly and were not fully eliminated, even when using high liming levels, as confirmed in the present study.

Cunha *et al.* (2015) evaluated acidic soils across several regions of Brazil, including Santa Catarina, and found that contents of $CuCl_2$-extractable Al were, on average, 1.9-fold higher than KCl-extractable Al and, in some cases, well higher. Similar results were found for the treatments evaluated in the present study. The highest contents of $CuCl_2$-extractable Al in surface horizons can be attributed to the greater affinity of Cu ions to organic compounds, which displaces Al to organic matter (JUO; KAMPRATH, 1979). Furthermore, the buffered solution must have high acidity, which allows the release of reactive environmental forms of Al, originating from complexes with organic matter, as well as from part of discrete inorganic polymers of Al-OH, amorphous or low crystallinity Al and hydroxy-Al polymers located in the interlayer spaces of 2:1 phyllosilicate. (URRUTIA *et al.*, 1995). Cunha *et al.* (2015) also quantified Al forms associated with organic compounds and found very high Al contents, inconsistent with the low organic matter content of most soils, indicating that the extractor may have also dissolved inorganic forms of low-crystallinity Al.

Extraction of Al contents from low-crystallinity or amorphous oxides using a 0.2 mol L^{-1} ammonium oxalate solution buffered at pH 3.0 was performed by Cunha *et al.* (2014) for acidic soils from several regions of Brazil. The results indicated that Al contents were higher than those extracted using an unbuffered 1 mol L^{-1} KCl solution, as confirmed in the present study. The ammonium oxalate solution may have dissolved not only Al from amorphous inorganic compounds but also a significant part of organic compounds, probably due to more complex and stable associations of Al with organic matter. They also found that the extraction of Al^{3+} using a 1 mol L^{-1} KCl solution overestimated contents of soil Al^{3+} forms in the soil. This effect was due to the high saline concentration of the salt used, which, by increasing hydrolysis, dissolved part of the Al from amorphous inorganic compounds and Al from organic compounds.

According to Cunha *et al.* (2015), the high contents of ammonium oxalate-extractable Al in acidic soils in several regions of Brazil were significantly influenced by amorphous inorganic forms and low-crystallinity Al compounds in most soils, indicating that these compounds can be dissolved and quantified as Al^{3+} when using this methodology, which consequently overestimates Al contents. They found a mean Al content of 2.8 $cmol_c$ kg^{-1} in surface soil horizons when using the KCl (1 mol L^{-1}) extraction method and 89 cmolc kg^{-1} when using the ammonium-oxalate extraction method, corresponding to a mean 31-fold higher for the latter. The mean Al content in subsurface horizons was 10.8 $cmol_c$ kg^{-1} when extracted with 1 mol L^{-1} KCl solution, whereas the extraction with ammonium oxalate yielded a mean 11-fold higher (110 $cmol_c$ kg^{-1}). In the present study, the Al content in the surface layer (0-0.10 m) was 49.2 $cmol_c$ dm^{-3} when extracted with ammonium oxalate, a mean 6-fold higher than that found with KCl solution: 8.1 $cmol_c$ dm^{-3}. The mean Al contents in the subsurface layer (0.10-0.40 m) were 9.2 and 50.9 $cmol_c$ dm^{-3} for extractions with KCl and ammonium oxalate solutions, respectively, the latter yielding a mean 5.5-fold higher. This emphasizes the importance of understanding soil Al forms in the soil and the dynamics of these forms after applying Ca sources that primarily increase soil pH.

Supplying Ca may be more important than completely neutralizing soil acidity, and two other factors should be considered: first, plant tolerance to Al^{3+} and the potential accessibility to less available forms of soil nutrients. Forest plants, such as eucalyptus, have higher tolerance to Al^{3+}, with a lower risk of this element causing toxicity to the root system (RAHMAN; UPADHYAYA, 2021). Another factor to be discussed is the possible utilization of some nutrients, such as Ca, Mg, K, and P, in less available forms, since access to stocks of these nutrients in less labile forms can ensure the adequate development of forest plants (GATIBONI *et al.*, 2020).

CONCLUSIONS

- The application of Ca sources, even in addition to the application of 2 Mg ha^{-1} of limestone on the surface in the total area, in doses and applied on the surface either in the total area, in the planting strip or incorporated in the planting furrow, with or without the addition of gypsum, as well as the application of lime mud, reduces Al contents extracted with KCl (1 mol L^{-1}), Al contents extracted with $CuCl_2$ (0.5 mol L^{-1}), Al contents extracted with $CuCl_2$ minus Al contents extracted with KCl (non-exchangeable), and Al

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contents extracted with ammonium oxalate (0.2 mol L^{-1}) buffered at pH 3.0. However, this effect is restricted to the soil surface layer in the long-term.

- The application of agricultural gypsum to the planting furrow with incorporation has no effect on Al^{3+} contents, Al contents extracted with 0.5 mol L^{-1} $CuCl_2$ or 0.2 mol L^{-1} ammonium oxalate buffered at pH 3.0, even when using surface application of 2 Mg ha^{-1} of limestone over the total area.
- For all these reasons, doses higher than 2 Mg ha^{-1} of dolomitic limestone, as well as the use of lime mud and the combination of limestone and agricultural gypsum, regardless of the form of application, and even after a long period of application, are important for the reduction of Al in its exchangeable form.

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