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Chemical Species and Aluminum Concentration in the Solution of Acid Soils Cultivated with Soybean and Corn under Liming

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ABSTRACT: Chemical speciation of the soil solution is an important tool to identify Al species related to phytotoxicity. In some Brazilian acid soils, the Al extractable by the KCl 1.0 mol L^{-1} solution (Al-KCl) exceeds 10 $cmol_c\ kg^{-1}$ and even then, in some situations, it does not cause toxicity to the plants. This study aimed to evaluate the relationship between these high concentrations of Al-KCl found in some Brazilian acid soils and the activity of the different Al chemical species in the soil solution, as well as the response of soybean and corn plants to lime application. Subsurface horizon (B) samples of five soils were collected in four states of Brazil (AC, PE, RS, and SC) from areas that had never been cultivated. The samples were then given increasing rates of limestone, equivalent to that required to neutralize 0, 0.25, 0.5, and 1.00 times the contents of H+Al and were incubated for 98 days. After that period, the soils were fertilized and planted to soybean and corn in the greenhouse for 60 and 45 days, respectively, in 2015. The experimental units consisted of 8 L pots, filled with 5 kg of soil (dry basis). After each crop, the plants and soil samples were collected to determine the leaf, stem, and root dry matter, and chemical composition. In the soil solution, cations and anions, pH, electrical conductivity, and dissolved organic carbon were quantified. The distribution of the Al species was evaluated using the program Minteq. Free Al (Al^{3+}) was the species found in highest proportion in treatments without limestone, in all soils. Application at the lowest limestone rate, equivalent to 25 % of that required for H+Al neutralization, was sufficient to decrease Al activity in the soil solution to levels considered non-toxic to plants in four of the five soils. High levels of Al-KCl are not related to manifestation of toxicity and to Al^{3+} activity in the solution of Hapludult (Acre profile 9; AC9) and Hapludult (Rosario do Sul; RS) since dry matter (DM) production in these soils was little influenced by liming, unlike what occurred in the Hapludult (Pernambuco; PE), Humudepts (Bom Retiro; BR), and Kandiudox (Curitibanos; CB) soils, in which Al-KCl contents were related to Al activity in the solution and to DM production of the plants grown in them.

Keywords: chemical speciation, phytotoxicity, production of plants, aluminum activity.

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INTRODUCTION

In some Brazilian acid soils, the aluminum extractable by the KCl 1.0 mol L^{-1} solution (Al-KCl) may exceed 10 $cmol_c$ kg^{-1} (Almeida et al., 2010; Bernini et al., 2013; Cunha et al., 2014, 2015). However, in some of these situations, no symptoms of Al^{3+} toxicity were found in the plants, which had satisfactory yields, even when, after liming, the amounts of Al-KCl still remain high. The limestone application rates recommended for pH correction of these soils by the traditional methods are very high. However, when low rates of correctives are used, the plants produce satisfactorily, showing that not all Al indicated in the chemical analysis of the soil as exchangeable is in equilibrium with the Al toxic to the plants. This lack of response of the plants to the application of limestone in some soils is related to the presence of medium or high levels of basic cations and of complexing organic anions in the soil solution that are responsible for decreased activity of the toxic species of Al (Auxtero et al., 2012; Rutkowska et al., 2015).

The toxicity of Al in acid soils depends on the activity of the toxic forms of Al in the soil solution (Álvarez et al., 2012; Spera et al., 2014; Rutkowska et al., 2015), on the Al complexation (Nolla et al., 2015; Rutkowska et al., 2015), on the control of the solubility of Al in the soil solid phase (Siepak et al., 1999), and on the soil environment (Kinraide, 1997). The species understood as most toxic are Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ (Ryan et al., 2009; Cristancho et al., 2014; Rutkowska et al., 2015). The sum of Al in these forms represents the total concentration in the soil solution, while the sum of their chemical potential represents the total activity of the Al (Cristancho et al., 2014; Spera et al., 2014). In addition to Al activity in the solution, the effects of acidity on plants are also related to the activities of Ca^{2+}, Mg^{2+}, K^+, and the anions $H_2PO_4^-$ and SO_4^{2-} (Yang et al., 2006; Zambrosi et al., 2008; Alleoni et al., 2010; Hashimoto et al., 2010) and to the total organic carbon (TOC) content (Vieira et al., 2009; Ferro-Vásquez et al., 2014; Hagvall et al., 2015).

Quantification of the active forms of Al in the solution (especially in areas that received limestone) through chemical speciation allows understanding the mobility and availability of nutrients, as well as the phytotoxicity of metals (Krishnamurtiand and Naidu, 2002). Speciation includes free ions, complexes, ion pairs, and chelates in solution. Computational programs, such as Minteq A2, facilitate estimation of the amounts of these forms, quickly providing species estimation and the respective activities of the ions in the soil solution (Meurer and Anghinoni, 2012; Rutkowska et al., 2015; De Conti et al., 2017). These programs simultaneously consider the various chemical equilibria involved in the reactions responsible for the formation of complexes and of dissolution and solid precipitation by calculating the activity coefficients and the distribution of the free species, as well as their complexes and precipitates (Rossiello and Jacob Netto, 2006).

Simple determination of the exchangeable Al contents in the soil or the total Al in the soil solution is not a sufficient indicator to evaluate the toxicity of this element to plants. To make this evaluation, quantification of the chemical species considered toxic becomes necessary, mainly the labile species of Al, such as Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$, as well as non-toxic species, especially the complexes of Al with organic and inorganic molecules that alter the proportion and activity of the toxic forms of Al (Ferro-Vásquez et al., 2014; Hagvall et al., 2015; Nolla et al., 2015) and, furthermore, the elements that can reduce Al toxicity, such as Ca^{2+} and Mg^{2+} (Silva et al., 2008; Hashimoto et al., 2010; Auxtero et al., 2012). In general, Al^{3+} activity, rather than measurements of the soluble or exchangeable forms, is the best indicator of toxicity potential in acid soils (Ferrufino et al., 2000; Spera et al., 2014).

However, particularly in Brazil, where alitic and aluminic soil character (dystrophic soils with high aluminum contents, higher than 4 $cmol_c$ kg^{-1}) predominate, sometimes the symptoms of Al toxicity are poorly manifested, even when there are high levels of Al-KCl in the analyses. In these cases, it is believed that part of this Al does not represent the toxic forms of Al, because often in these same cases the response of plants to liming is low or nonexistent. Within this context and considering soils with very high levels of Al-KCl associated with high levels of Ca^{2+} and Mg^{2+}, the high application rates of limestone recommended by traditional methods may be inactivating Al species that are not toxic to plants, for example, the $Al(OH)_3$ and $Al(OH)_4^-$, as well as the organic and inorganic complexes bound to Al (Hernández-Soriano, 2012; Cristancho et al., 2014; Rutkowska et al., 2015).

Considering the expressive occurrence of alitic and aluminic soils in Brazil, the aim of this study was to evaluate the relationship between the high concentrations of Al-KCl found in these soils and the activity of the different Al chemical species in the soil solution, and the response of soybean and corn to liming.

MATERIALS AND METHODS

Selection of soils

The study was carried out with samples from the subsurface horizon (B) of five soils. They were collected in areas never cultivated and most had contents of Al-KCl higher than 4 $cmol_c$ kg^{-1}. We used samples of the B horizon mainly due to less organic matter (OM) in this horizon than in the surface horizon, since organic matter could influence the results by formation of organic complexes with Al. Based on mineralogical and chemical differences, we had two groups of soils: smectites with high levels of exchangeable Al^{3+}, Ca^{2+}, and Mg^{2+}, whose representatives are *Argissolo Vermelho-Amarelo Alítico luvissólico* (Hapludult), from the state of Acre (profile 9; AC9), and *Argissolo Bruno-Acinzentado Alítico típico* (Hapludult), from Rio Grande do Sul (Rosario do Sul; RS); and smectites with high levels of Al and low levels of exchangeable Ca^{2+} and Mg^{2+}, whose representatives are *Argissolo Vermelho-Amarelo Alítico típico*, from the state of Pernambuco (PE), and *Cambissolo Húmico Alítico típico* (Humudepts), from Santa Catarina (Bom Retiro; BR). We also used another soil from the state of Santa Catarina (Curitibanos; CB), *Nitossolo Bruno Distroférrico típico* (Kandludox) which was used as a reference because it is more weathered, with essentially kaolinitic mineralogy, and with lower contents of exchangeable Al-KCl, Ca^{2+}, and Mg^{2+} than the others.

The soil samples were collected in the same places where the complete profiles had previously been described, the results of which one have already been published (Table 1). The mineralogical properties of these soils are as follows: in AC9, smectite predominates (88 %), with low amounts of interstratified kaolinite-smectite (6 %) and interstratified mica-illite (6 %); in PE, smectite predominates (60 %), with relatively high amounts of kaolinite (40 %); in RS, smectite predominates with low quantities of illite and kaolinite; in BR, kaolinite predominates (51 %), with relatively high amounts of smectite and vermiculite with hydroxy interlayered polymers (47 %) (HIS and HIV, respectively) and a low amount of interstratified mica-illite (2 %); and in CB, kaolinite predominates (94 %), but it has 6 % HIS. Further details on these soils can be found in Cunha et al. (2014).

Sample preparation and analysis prior to incubation with limestone

Soil samples were air dried in a greenhouse, broken up, ground, and sieved through a 4 mm mesh and then incubated separately. For chemical analyses, samples sieved through a 2 mm mesh were used.

After the samples were processed, the following determinations were made: pH in water and in KCl 1.0 mol L^{-1} by potentiometry at the soil:solvent ratio of 1:2.5; H+Al by neutralization titrations after extraction with calcium acetate buffered to pH 7.0 (Donagema et al., 2011); and field capacity (FC), according to the method described in Donagema et al. (2011), determined on a tension table after using a tension equivalent to a water column of 100 cm (1 kPa) on the saturated sample. The chemical analyses were performed with three replicates, and the results are shown in table 2.

Table 1. Classification of soil profiles collected under natural conditions in different Brazilian regions

Soil(1)	Source	H(2)	Layer	Classification(3)	Symb.(4)
			m		
AC9	Anjos et al. (2013) Cunha (2017)	Bt_2	0.60-1.02	*Argissolo Vermelho-Amarelo Alítico luvissólico* (Hapludult)	PVAal
PE	Jacomine and Amaral (2011)	Bt_2	0.55-1.05	*Argissolo Vermelho-Amarelo Alítico típico* (Hapludult)	PVAal
RS	Cunha et al. (2015)	Bt_3	0.65-0.80	*Argissolo Bruno-Acinzentado Alítico típico* (Hapludult)	PBACal
BR	Almeida et al. (2013)	Bi	0.60-0.90	*Cambissolo Húmico Alítico típico* (Humudepts)	CHal
CB	Almeida et al. (2003)	Bw_3	2.15-2.75^{+}	*Nitossolo Bruno Distroférrico típico* (Kandiudox)	NB

(1) AC9 = collected in Tarauacá, Acre, profile 9; PE = collected in Ipojuca, Pernambuco; RS = collected in Rosário do Sul, Rio Grande do Sul; BR = collected in Bom Retiro, SC; CB = collected in Curitibanos, SC. (2) Horizons collected. (3) Classification according to the Brazilian Soil Classification System (Santos et al., 2013) and to Soil Taxonomy (Soil Survey Staff, 2014).

Table 2. Chemical properties (before soil incubation and setting up the experiments in a greenhouse), and physical properties of soil profiles collected under natural conditions in different Brazilian regions

Soil(1)	pH(2)		H+Al(3)	Clay(4)	Silt(5)	Sand(6)	FC(7)
	H_2O	KCl	$cmol_c\ kg^{-1}$				
					$g\ kg^{-1}$		%
AC9	5.42	3.60	14.73	346	170	490	45
PE	5.03	3.80	18.43	382	170	180	40
RS	5.24	3.77	8.80	480	230	290	37
BR	4.73	3.76	9.87	540	270	190	42
CB	4.89	4.11	6.53	830	90	80	42

(1) AC9 = collected in Tarauacá, Acre, profile 9; PE = collected in Ipojuca, Pernambuco; RS = collected in Rosário do Sul, Rio Grande do Sul; BR = collected in Bom Retiro, SC; CB = collected in Curitibanos, SC. (2) pH in H_2O and pH KCl 1.0 mol L^{-1} at a ratio of 1:2.5 v/v. (3) Extracted with calcium acetate pH 7.0 solution. (4), (5), and (6) were determined by the densimeter method (Boyoucus, 1962). (7) Field capacity was determined according to the method described in Donagema et al. (2011).

Incubation of the soils

The treatments consisted of the application of four rates of dolomitic limestone in each soil, corrected to 100 % Relative Power of Total Neutralization, which were equivalent to those necessary to neutralize 0, 0.25, 0.50, and 1.00 times the contents of H+Al. Each treatment had four replicates, and the application rates were applied and homogenized in samples with 20 kg of soil (dry basis). Distilled water was then applied to raise soil moisture to 80 % of FC. Subsequently, the samples were placed in 100 L plastic bags, turned over every 15 days, and incubated for 98 days until the pH values were stabilized.

Soybean and corn crops

After incubation, the soil samples were once more passed through 4 mm mesh sieves, and the 20 kg of each treatment, which were the four replicates, were fertilized with N (urea), P (triple superphosphate), and K (potassium chloride). To the first crop (soybean), 1.08 g kg^{-1} of N, 2.48 g kg^{-1} of P_2O_5, and 0.99 g kg^{-1} of K_2O were applied; to the second crop (corn), 0.99 g kg^{-1} of N, 2.48 g kg^{-1} of P_2O_5, and 1.98 g kg^{-1} of K_2O were applied.

The fertilization with N, P, and K was that recommended by the Commission of Chemistry and Soil Fertility for the states of Rio Grande do Sul and Santa Catarina (CQFS-RS/SC, 2004) for soybean and corn crops, based on the results of the study already published (Table 2). The N was applied a single time for soybean and divided into three applications for corn. The fertilizer calculations for soybean aimed for a grain yield of 3 Mg ha^{-1} and for corn of 8 Mg ha^{-1}.

After incubation and fertilization of the soils, the experiments were conducted in the greenhouse in 2015 in 8 L pots containing 5.0 kg of soil (dry basis). Soybeans and later corn were grown, for 60 and 45 days respectively. The experimental design was randomized blocks, organized in a 4 × 5 factorial arrangement, with four application rates of limestone and five soils, with four replications. In each pot, seven plants were sown, leaving only three after thinning. The soils were maintained with moisture close to 80 % of FC, through daily weighing of the pots and replenishment of moisture with deionized water. The masses corresponding to the growth of the plants (the weight of 60 g was estimated for soybean and 75 g for corn) of each crop in each experimental unit and treatment were subtracted for water replenishment. The soybean plants were collected in the phenological stage of full bloom and those of corn after 45 days of cultivation. The aerial part (AP) of the plants was cut close to the soil, placed in paper bags, and dried in a forced air circulation oven at 65-70 °C until constant weight, at which time the shoot dry matter (SDM) was weighed. The roots of the two crops were separated from the soils using a 2 mm sieve. They were then washed in tap water to remove the coarser soil fractions and dried in the laboratory oven at 65-70 °C for 24 hours. After that, they were washed again in tap water to remove the fine soil particles. Immediately after, they were dried again, and the root dry matter (RDM) was obtained by weighing the three roots of each experimental unit of each crop. By adding the SDM to the RDM, the total dry matter (TDM) produced by the plants was obtained. In the present study, only the results obtained from the TDM of the soybean and corn plants will be presented.

Plant tissue was ground and later analyzed, as described in Miller (1998), with some adaptations. To summarize, 0.100 g of tissue was transferred to digestion tubes to which 5 mL of nitric acid and 3 mL of hydrogen peroxide were added, and the mixture remained for one night at rest (pre-digestion). All samples were digested in a Multiwave 3000 microwave oven (Anton Paar, Graz, Austria), set at 160 °C and 20 Bar of pressure for 40 min. The extract was diluted in 30 mL of deionized water. The concentrations of Ca, Mg, P, K, and Al in the plant tissue were quantified in an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima® 8300, Perkin Elmer, USA). The concentration of N was determined by means of steam distillation, in a semi-micro Kjeldahl device.

Chemical analysis of the soil

After the roots of each crop were separated, the soils were homogenized and samples of approximately 140 g were collected and packed in expanded polystyrene with ice. They were then stored in an ultra-freezer at -80 °C, where they remained frozen until analysis to avoid biological degradation of the organic compounds. Subsequently, the soils were air dried, ground, and passed through 2 mm mesh sieves to obtain air-dried fine earth (ADFE).

In the soil samples, pH in water, pH in $CaCl_2$ 0.01 mol L^{-1} (soil:solution ratio of 1:2.5), and pH in KCl 1 mol L^{-1} (soil:solution ratio of 1:10), and the contents of exchangeable Ca, Mg, K, and Al were determined after obtaining the extract in the soil:solution at a ratio of 1:10 (Donagema et al., 2011) and quantified as described in Tedesco et al. (1995). To simulate the soil solution, a soil:solution extract was obtained at a 1:1 ratio by weighing 20 g of ADFE and mixing it with 20 mL of ultrapure water in 50 mL (Falcon) polyethylene tubes. The samples were shaken in a horizontal device for 15 min at 150 rpm, followed by 1 h of rest. They were then shaken for another 5 min and centrifuged at 2000 rpm for 30 min. Subsequently, in approximately 10 mL of extracts from each sample, pH and electrical conductivity (EC) were immediately measured. The extracts used for determination of the cations and of dissolved organic carbon (DOC) had previously passed through 0.45 micrometer (μm) cellulose acetate syringe filters; the extracts of the anions, through 0.20 μm cellulose acetate filters. The final product of the extract filtration was stored in polyethylene tubes with a 15 mL capacity and cooled to 4 °C for further analysis of the concentration of Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-}, and DOC.

To determine Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, and DOC, 3 mL of the extracts obtained from the 1:1 (soil:solution) extraction were placed in 15 mL Falcon tubes and then acidified with a drop of concentrated nitric acid, the ions being quantified by ICP-OES and the DOC by colorimetry. The DOC was determined by the chemical oxygen demand (COD) method, as described in Clesceri et al. (1999), with the following modifications: a 1.0 mL aliquot of the sample extracts was added to 10 mL COD tubes, along with a 0.6 mL aliquot of the digesting solution and 1.4 mL of the catalyst solution. The samples were vortexed and digested in a digester block (TR 420 Merck, Germany) at 148 °C for 2 h, and then cooled to room temperature. Reading was carried out by means of a spectrophotometer (Spectroquant Nova 60 Merck, Germany) in the 605 nm wavelength in a 3 mm cuvette. The value obtained for the COD was converted to dissolved organic carbon (DOC), using a mean multiplication factor of 0.35 (Aquino et al., 2006). The calibration curve was constructed from standard solutions containing acetic acid analytical reagent.

Anions were determined by turbidimetry (SO_4^{2-}) in a spectrophotometer (UV/VIS Spectrometer Merck, Germany) at a wavelength of 420 nm in a 5 mm cuvette in approximately 7 mL of the extracts. Nitrate was quantified by colorimetry using a spectrophotometer (UV/VIS Spectrometer Merck, Germany) at a wavelength of 605 nm in a 5 mm cuvette. Chloride (Cl^-) was titrated with 0.1 mol L^{-1} silver nitrate solution, with a 5 % potassium chromate solution as indicator (Clesceri et al., 1999). Phosphate (mg L^{-1}) was obtained after conversion of phosphorus (P), determined by the methodology of Murphy and Riley (1962), into phosphate ($PO_4^{3-} = P \times 3.06$), which was then converted to mmol L^{-1}. All determinations were made in four replicates.

Chemical speciation

Chemical speciation of the soil solution was estimated by Visual Minteq (for Windows) 3.1 software, based on the Minteq A2 4.0 program (Gustaffson, 2016). For that purpose, the mean of four replicates of the total concentrations of Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, SO_4^{2-}, Cl^-, NO_3^-, and PO_4^{3-}, of the pH measured in the solution, and of ionic strength (I) were used. Ionic strength was calculated from the EC of the soil solution, according to the equation $\log I (M) = 1.159 + 1.09 \times \log EC\ 25\ (dS\ m^{-1})$, in which EC 25 represents electrical conductivity corrected to 25 °C, according to Spera et al. (2014).

Based on speciation, distribution of the free ionic species and the complexed species of Al were estimated, obtaining the percentage distribution and the activities of each species in each treatment. The species bound to the anions were estimated based on DOC content, and the “Gaussian DOM” (DOM - Dissolved Organic Matter) model was used for quantification, according to Grimm et al. (1991). Formation of aqueous inorganic complexes was evaluated using equilibrium constants of the standard database of the Visual Minteq program developed by Smith et al. (2003).

Statistical analysis

Data relating the total dry matter yield (SDM + RDM) to the limestone rates applied to the soils were subjected to analysis of variance (F test) using the Sisvar 5.6 software (Ferreira, 2014). When there was a significant effect, the Tukey multiple comparison test was applied to the “soil type” factor (including decomposition of the soil types for each one of the limestone rates), while the regression test was applied to the “limestone application rates” factor (including decomposition of the limestone rates in each one of the soil types), both with a 5 % probability of error.

RESULTS AND DISCUSSION

As results of the soil analysis performed after each of the two crops (soybean and corn) were similar, only the results referring to the second crop, corn, will be presented.

Liming and general chemical properties of the soils

In the treatments without limestone, the pH(H_2O) ranged from 4.66 in the PE soil to 5.01 in the RS soil after the corn crop. With increasing lime application rates, the pH values increased in all soils (Table 3). The pH(KCl) were lower than those determined in water, ranging from 0.64 to 1.21 in treatments without limestone, the difference of which increased with increasing limestone application rates (Table 3). This occurred because the soils exhibited negative net electric charge, consistent with the mineralogy of the clay fraction, composed of kaolinite and 2:1 clay minerals, with little or no gibbsite (Inda et al., 2010; Bernini et al., 2013; Heckman et al., 2013; Cunha et al., 2014; Santos et al., 2017). The pH values determined with the 0.01 mol L^{-1} $CaCl_2$ solution in the limestone treatments ranged from 4.58 in the AC9 soil to 4.94 in the RS soil. With liming, they ranged from 5.77 in the AC9 soil to 6.12 in the CB soil. In general, the pH values determined in this solution were lower than those determined in water, even though they increased with liming and were higher than those measured in KCl 1 mol L^{-1} (Table 3).

Liming decreased the Al content in the RS, BR, and CB soils, but did not promote its complete neutralization. The values were still high in the AC9 soil (3.1 $cmol_c$ kg^{-1}) and PE soil (1.4 $cmol_c$ kg^{-1}), even at the highest application rate. Aluminum saturation decreased in all soils with increasing limestone application rates (Table 3). In a previous study, using the same soils of the present study, Cunha et al. (2015) suggest that part of the Al-KCl does not represent the exchangeable forms of Al. The high concentration of KCl (1.0 mol L^{-1}) may be causing hydrolysis of part of the Al of non-exchangeable forms, possibly coming from amorphous compounds present in these soils, overestimating “exchangeable” Al contents and, consequently, saturation by Al (Table 3). Overestimation of Al-KCl may be masking toxicity of Al to plants without this toxicity occurring (Ebeling et al., 2008; Coelho et al., 2011; Bernini et al., 2013; Cunha et al., 2015). It must be considered that the levels of P in the AC9, PE, RS, and BR soils after cropping were very high (Table 3), which can partially decrease the response of the plants to limestone application (Ernani et al., 2000).

In the AC9 and RS soils, although “exchangeable” Al (Al-KCl) was high, base saturation is greater than 50 %. In these soils, Al saturation was higher than 30 % (Table 3), which would normally be toxic to plants (Smyth and Cravo, 1992; Hashimoto et al., 2010). However, as of the first application rate of limestone, it diminished to values below 30 %, suggesting that the plants might no longer show toxicity from the presence of Al (Wadt, 2002). Liming in the AC9 soil did not completely eliminate the Al-KCl, even at the highest application rate (Table 3). In the other soils (PE, BR, and CB), whose values of sum of bases and base saturation were originally low, and those of saturation by Al were very high, liming increased base saturation, reaching values generally higher than 50 % already at the second application rate (50 % of H+Al), with reduction in saturation by Al to less than 30 %, except in the PE soil (Table 3). This seems to indicate that, from this rate on, Al-KCl, though still present in high amounts, may no longer have a toxic effect.

Aluminum chemical speciation in the soil solution

Chemical speciation showed that in the treatments with no limestone in the AC9, PE, BR, CB, and RS soils, Al^{3+} was the free species in largest quantity, both in percentage and in absolute values of activity; Al^{3+} surpassed the species $AlOH^{2+}$, $Al(OH)_2^+$, Al bound to other species (Al-OS) ($AlCl^{2+}$, $AlSO_4^+$, $AlHPO_4^+$, and $Al_2PO_4^{3+}$), and Al bound to dissolved organic carbon (Al-DOC) (Table 4).

In the treatment without limestone, the highest percentages (69 %) and activities of Al^{3+} in the solution (33.4 µmol L^{-1}) occurred in the PE soil (Table 4). Although the BR soil showed a lower percentage (47 %) of Al^{3+} in the solution than the soils PE, AC9 (61 %), and CB (50 %), the activity of this species in the solution was high (20.21 µmol L^{-1}) (Table 4). In the AC9 and CB soils, the activity in the solution was relatively high (7.93 and 6.50 µmol L^{-1}, respectively), while the RS soil exhibited the lowest percentage (31 %) and the lowest Al^{3+} activity (2.48 µmol L^{-1}) in the solution (Table 4). The lower Al^{3+} activity in the RS soil occurred due to the lower concentration of Al^{3+}, high sum of cations, and high concentration of anions (Cl^-, NO_3^-, and especially PO_4^{3-}) in solution (Table 5), which can form inorganic complexes with Al and, to a lesser extent, by the Al-DOC (Table 4) that form organic complex with Al. The high level of cations and anions in the solution of this

Table 3. Chemical properties of the soils after application of limestone treatments in samples collected after corn cultivation under greenhouse conditions

Soil[1]	Lime Appl.[2]	pH			ΔpH[5]	Al^{3+}[6]	H+Al[7]	Ca^{2+}[8]	Mg^{2+}[9]	Na^{+}[10]	K^{+}[11]	S[12]	CEC_{pH7}[13]	CECe[14]	V[15]	m[16]	P[17]
		H_2O[3]	$CaCl_2$[3]	KCl[4]													
						cmol$_c$ kg^{-1}									%		mg kg^{-1}
AC9	0	4.85	4.58	3.72	-1.13	13.2	14.9	17.5	3.6	0.00	0.48	21.6	36.5	34.8	59	38	16.3
	0.25	5.45	5.38	3.89	-1.56	9.3	10.7	18.8	5.2	0.00	0.65	24.7	35.4	33.9	70	27	16.2
	0.5	5.58	5.52	3.99	-1.59	5.6	9.2	22.9	6.5	0.00	0.69	30.1	39.3	35.7	77	16	14.4
	1.00	5.84	5.75	4.10	-1.74	3.1	6.7	24.9	6.8	0.00	0.73	32.4	39.1	35.5	83	9	14.9
PE	0	4.66	4.59	3.90	-0.76	18.1	18.5	2.9	2.0	0.00	0.68	5.6	24.1	23.7	23	76	17.3
	0.25	4.97	4.89	4.03	-0.94	13.7	15.8	6.9	3.7	0.00	0.53	11.1	26.9	24.9	41	55	18.1
	0.5	5.59	5.52	4.15	-1.44	8.9	10.8	7.1	5.6	0.00	0.44	13.1	24.0	22.1	55	40	16.6
	1.00	5.90	5.82	4.41	-1.49	1.4	9.0	14.3	6.3	0.00	0.43	21.0	30.1	22.5	70	6	15.6
RS	0	5.01	4.94	3.80	-1.21	6.9	9.0	8.8	2.9	0.00	0.40	12.1	21.1	19.0	57	36	17.8
	0.25	5.73	5.66	3.90	-1.83	4.6	7.9	9.7	3.8	0.00	0.39	13.9	21.8	18.6	64	25	15.4
	0.5	5.82	5.75	4.02	-1.8	2.7	6.6	10.1	4.0	0.00	0.34	14.4	21.0	17.1	69	16	15.7
	1.00	6.18	6.11	4.47	-1.71	0.4	3.9	14.8	5.7	0.00	0.34	20.8	24.7	21.2	84	2	15.3
BR	0	4.82	4.75	3.86	-0.96	5.4	9.0	0.38	0.0	0.00	0.51	0.9	9.9	6.4	9	85	14.0
	0.25	5.56	5.49	3.89	-1.67	3.7	7.9	4.6	1.4	0.00	0.31	6.3	14.2	10.1	44	37	13.7
	0.5	5.83	5.74	4.08	-1.75	1.5	6.0	5.5	2.0	0.00	0.41	7.9	13.9	9.4	57	16	13.0
	1.00	6.09	6.02	4.45	-1.64	0.2	4.3	7.3	3.5	0.00	0.29	11.1	15.3	11.4	72	2	12.2
CB	0	4.74	4.69	4.10	-0.64	2.0	8.0	0.16	0.0	0.00	0.48	0.6	8.6	2.7	7	74	4.3
	0.25	5.63	5.56	4.28	-1.35	0.8	6.7	3.7	0.7	0.00	0.34	4.7	11.5	5.6	41	14	3.3
	0.5	5.81	5.74	4.54	-1.27	0.3	5.7	4.7	1.4	0.00	0.43	6.5	12.2	6.8	54	4	3.1
	1.00	6.19	6.10	5.22	-0.97	0.0	4.3	6.2	2.5	0.00	0.40	9.1	13.4	9.1	68	0	3.2

(1) AC9 = collected in Tarauacá in Acre, profile 9; PE = collected in Ipojuca, Pernambuco; RS = collected in Rosário do Sul, Rio Grande do Sul; BR = collected in Bom Retiro, SC; CB = collected in Curitibanos, SC. (2) Limestone rates applied to neutralize 0, 0.25, 0.50, and 1.00 times the soil contents of H+Al. (3) pH(H_2O) and pH in calcium chloride 0.01 mol L^{-1}, both at a ratio of 1:2.5 v/v. (4) pH in KCl 1 mol L^{-1} at a ratio of 1:10 v/v. (5) ΔpH (pH KCl - pH in water). (6) Extracted with the KCl 1 mol L^{-1} solution. (7) Extracted with calcium acetate pH 7.0 solution. (8) and (9) extracted with KCl 1 mol L^{-1} solution. (10) and (11) extracted with Melich-1 solution. (12) Sum of bases. (13) Cation exchange capacity pH 7 (S + H+Al) (14) Effective cation exchange capacity (S + Al^{3+}). (15) Base saturation (100 × S)/$CEC_{pH\ 7}$. (16) Saturation by aluminum (100 × Al^{3+})/CEC_e. (17) Extracted with the Melich-1 solution

soil was responsible for reduction in the toxic potential of this element to the plants, even in the treatments without limestone. The complexation of Al by organic and inorganic binders in the soil solution was also verified by Zambrosi et al. (2008), Crusciol et al. (2011), Hernández-Soriano (2012), Hagvall et al. (2015), and Rutkowska et al. (2015).

The Al-DOC, in treatments without limestone, exhibited lower percentages and activities compared to the toxic species of Al (Al^{3+} and $AlOH^{2+}$) and was not responsible for reduction in the activity of this element in the soil solution (Table 4). This occurred because, in this study, only the subsurface horizon (B) of the soils was evaluated, in which the amount of TOC is low, thus not favoring the formation of the organometallic complex with Al and, consequently, its inactivation (Table 4). Formation of the organometallic complex with Al was verified by Álvarez et al. (2012), Castro and Crusciol (2015), Drábek et al. (2015), Hagvall et al. (2015), Nolla et al. (2015), and De Conti et al. (2017).

The application of limestone rates decreased the activity of the main toxic species of Al [Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^{+}$] (Zambrosi et al., 2008; Ryan et al., 2009; Rutkowska et al., 2015) in the soil solution, as liming increased the pH, the concentration of the basic cations and anions, and the EC and the ionic strength of the solution (Table 5). The Al-DOC and the Al-OS also decreased with liming; however, to a lesser extent, there was an increase in the activity of the species $Al(OH)_3$ and $Al(OH)_4^{-}$ in the soil solution, which are considered non-toxic to the plants (Table 4).

With the application of the lowest limestone rate, which corresponds to 25 % of the soil H+Al content, the Al^{3+} decreased 21 % in the AC9, 46 % in the PE, 19 % in the RS, 21 % in the BR, and 13 % in the CB soil, representing the following percentages in terms of Al activity in the soil solution after corn cultivation: 2.31, 6.0, 0.44, 3.57, and 1.95 µmol L^{-1}, respectively (Table 4). These values are lower than the critical values envisioned as toxic by some authors: 4.6 µmol L^{-1} for soybean (Silva et al., 2001) and 18-19 µmol L^{-1} (Harper et al., 1995) or 24-27 µmol L^{-1} (Diatloff et al., 1998) for corn. Except in the PE soil after soybean cultivation, in which Al^{3+} activity in the soil solution was above the critical level (6.16 µmol L^{-1}) established in the literature, through the use of the second application rate of limestone (50 % of H+Al), Al^{3+} activity was below 4.6 µmol L^{-1}. Similar behavior occurred in the activity of the sum of the toxic forms of Al (A∑FTAl), which corresponds to the sum of the activity of the toxic species of Al in the solution $[Al^{3+}+AlOH^{2+}+Al(OH)_2^+]$. After soybean cultivation, the values of the sum of these elements in solution were above the critical level in the soils AC9, PE, BR, and CB in the treatments without limestone, except in RS. After corn cultivation, the A∑FTAl in solution, in the same treatment, was above the critical limit only in the PE and BR soils. However, beginning with the lowest rate of limestone applied (25 % of H+Al), the A∑FTAl in the solution of these soils (AC9, PE, BR, and CB) were below the critical level mentioned in the literature for the corn crop (Table 4), and for the soybean crop, only in the RS and CB soils (data not shown).

Table 4. Values of the ionic strength and activity of different Al toxic species extracted from the soil solution after corn cultivation

Soil[1]	Lim. Appl.[2]	I[3]	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	A∑FTAl[4]	$Al(OH)_3$ (aq)	$Al(OH)_4^-$	Al-DOC[5]	Al-OS[6]
		mmol L^{-1}				µmol L^{-1}				
AC9	0	0.0112	7.93	2.3	0.4	10.63	0.013	-	1.17	1.09
	0.25	0.0131	2.31	3.4	3.2	8.91	0.330	0.044	0.44	1.43
	0.5	0.0146	0.91	2.0	2.7	5.61	0.350	0.07	0.35	0.70
	1	0.0159	0.24	1.0	2.6	3.84	0.780	0.36	0.06	1.02
PE	0	0.0078	33.4	7.7	1.0	42.1	0.015	-	2.4	3.87
	0.25	0.0109	6.0	2.9	0.9	9.8	0.026	-	1.0	2.36
	0.5	0.0279	0.8	1.0	0.9	2.7	0.090	0.01	0.18	1.49
	1	0.0328	0.0	0.1	0.2	0.3	0.026	0.01	0.01	0.54
RS	0	0.0079	2.48	2.1	1.0	5.66	0.080	0.003	0.96	1.36
	0.25	0.0238	0.44	0.7	0.7	1.84	0.070	0.023	0.09	0.37
	0.5	0.0249	0.10	0.4	1.0	1.5	0.263	0.12	0.02	0.20
	1	0.0408	0.00	0.0	0.1	0.1	0.026	0.02	0.00	0.01
BR	0	0.0053	20.21	10.3	3.0	33.51	0.086	-	5.16	3.44
	0.25	0.0174	3.57	5.1	4.8	13.47	0.510	0.068	1.19	1.87
	0.5	0.0179	0.25	1.0	2.3	3.55	0.550	0.2	0.1	0.70
	1	0.0258	0.03	0.3	1.3	1.63	0.630	0.51	0.006	0.24
CB	0	0.0041	6.50	2.9	0.7	10.1	0.013	-	2.08	0.91
	0.25	0.0183	1.95	3.6	4.4	9.95	0.600	0.15	0.3	3.90
	0.5	0.0201	0.16	0.7	1.8	2.66	0.520	0.24	0.04	0.52
	1	0.0380	0.02	0.2	0.8	1.02	0.440	0.42	0.002	0.12

[1] AC9 = collected in Tarauacá in Acre, profile 9; PE = collected in Ipojuca, Pernambuco; RS = collected in Rosário do Sul, Rio Grande do Sul; BR = collected in Bom Retiro, SC; CB = collected in Curitibanos, SC. [2] Limestone rates applied to neutralize 0, 0.25, 0.50, and 1.00 times the soil contents of H+Al. [3] Ionic strength, calculated by equation log I (M) = 1.159 + 1.09 × log EC 25 (dS m^{-1}). [4] Activity of the sum of the toxic forms of aluminum. [5] Aluminum bound to dissolved organic carbon and. [6] Aluminum bound to other species. All Al chemical species were calculated by Minteq A2 (version 3.1) program after extraction of the soil solution in the ration soil:water 1:1.

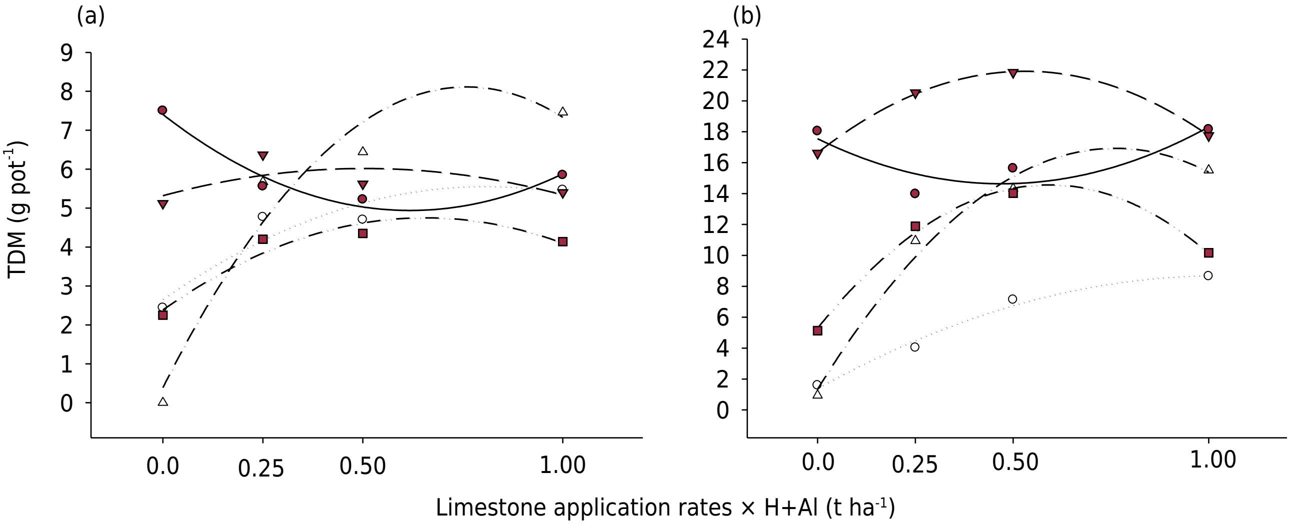
Relation between liming and total dry matter (TDM) of plants

The TDM production of soybean and corn showed quadratic behavior as a function of limestone rates in all soils (Figure 1). The AC9 soil was the only one in which there was no increase in the DM yield from the addition of limestone, even though it had more than 13 $\text{cmol}_c\ \text{kg}^{-1}$ of Al, pH 4.85, and Al^{3+} saturation of 38 %. This shows that the Al^{3+} quantified through the KCl solution is overestimating the exchangeable Al^{3+}. Although the RS soil had high Al-KCl content, high sum of bases, and low Al-saturation, it provided higher TDM production than the PE, BR, and CB soils (Figure 1) in the treatment without limestone (Table 3). In this soil (RS), there was little response of the plants to liming, but the production of TDM, in general, was higher compared to the other soils. The highest TDM production in the RS soil occurred in the treatment that received the second application rate of limestone (50 % of H+Al), where Al^{3+} saturation was 25 % (Table 3), similar to the first application rate (25 % of H+Al) of limestone. In the treatment with the highest application rate (100 % of the H+Al content), there was a decrease in the TDM production of the plants (Figure 1). For these soils (AC9 and RS), due to little or no response to liming, the high levels of Al-KCl may not be adequately representing only the exchangeable Al. This lack of response may be related to the interaction among the ions in the soil solution, which can most often exist at an effective concentration lower than the analytical concentration (data not shown), which determines a lower chemical potential of the element, and is reflected in lower toxicity of the Al^{3+} to the plants (Matúš, 2007; Nolla et al., 2015; Rutkowska et al., 2015). Therefore, the use of the activity level of this element, instead of the concentration, is more closely related to plant response (Cristancho et al., 2014; Spera et al., 2014).

Table 5. Chemical properties of the soil solution after corn cultivation under greenhouse conditions

Soil[1]	Lim. Appl.[2]	pH[3]	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	Na^+	S[4]	m × cations[5]	EC[6]	I[7]	DOC[8]	SO_4^{-2}[9]	NO_3^-[10]	Cl^-[11]	PO_4^{3-}[12]	P
			mmol L^{-1}						%	µS cm^{-1}	mmol L^{-1}						mg L^{-1}
AC9	0	4.70	0.013	0.99	0.33	0.12	0	1.44	0.9	369.48	0.0112	0.0733	0.01194	0.0834	9.1667	0.0028	0.09
	0.25	5.42	0.011	0.90	0.36	0.13	0	1.39	0.8	426.23	0.0131	0.0760	0.01368	0.2263	9.0000	0.0035	0.11
	0.5	5.59	0.007	0.90	0.40	0.10	0	1.40	0.5	473.48	0.0146	0.1186	0.01248	0.1944	10.5000	0.0028	0.09
	1.00	5.91	0.006	0.89	0.48	0.11	0	1.48	0.4	511.73	0.0159	0.1025	0.01147	0.2644	9.1667	0.0079	0.24
PE	0	4.56	0.048	0.19	0.38	0.34	0.01	0.92	5.5	265.23	0.0078	0.0645	0.01066	1.0203	12.6667	0.0042	0.13
	0.25	4.91	0.013	1.10	1.27	0.38	0.01	2.76	0.5	360.98	0.0109	0.0879	0.01524	1.0773	12.0000	0.0060	0.19
	0.5	5.45	0.005	0.93	1.06	0.24	0.01	2.24	0.2	857.23	0.0279	0.1098	0.01650	1.1117	10.1667	0.0114	0.35
	1.00	5.78	0.001	1.75	1.84	0.20	0	3.79	0.0	1028.48	0.0328	0.0549	0.01808	1.8436	11.6667	0.0118	0.36
RS	0	5.11	0.008	0.91	0.42	0.15	0	1.48	0.5	269.48	0.0079	0.1167	0.00906	0.4300	10.6667	0.0044	0.14
	0.25	5.50	0.002	1.41	0.69	0.17	0	2.27	0.1	739.73	0.0238	0.1224	0.01154	0.5008	9.0000	0.0042	0.13
	0.5	5.89	0.002	1.65	0.80	0.10	0	2.55	0.1	772.23	0.0249	0.1025	0.01292	0.8383	9.3333	0.0040	0.13
	1.00	6.17	0.000	2.84	2.07	0.21	0	5.12	0.0	1211.98	0.0408	0.1159	0.01396	2.6256	10.1667	0.0062	0.19
BR	0	4.88	0.043	0.12	0.08	0.16	0	0.36	10.7	185.23	0.0053	0.1408	0.00488	0.1055	10.6667	0.0039	0.12
	0.25	5.44	0.011	0.60	0.35	0.13	0	1.08	1.5	554.48	0.0174	0.1155	0.01030	0.1343	9.0000	0.0032	0.10
	0.5	5.85	0.005	0.63	0.50	0.11	0	1.24	0.4	569.23	0.0179	0.0959	0.00971	0.3978	9.1667	0.0055	0.17
	1.00	6.15	0.003	1.71	1.60	0.10	0	3.41	0.1	796.73	0.0258	0.0890	0.00924	3.2742	7.3333	0.0075	0.23
CB	0	4.79	0.013	0.10	0.03	0.25	0	0.38	3.3	147.48	0.0041	0.0806	0.00449	1.5642	7.6667	0.0020	0.06
	0.25	5.55	0.005	1.16	0.50	0.29	0	1.95	0.8	580.23	0.0183	0.0741	0.00624	1.2406	10.0000	0.0081	0.25
	0.5	5.90	0.004	1.17	0.72	0.20	0	2.09	0.2	660.81	0.0201	0.0929	0.00884	1.2614	7.6667	0.0056	0.17
	1.00	6.20	0.002	2.52	2.26	0.28	0	5.06	0.0	1137.73	0.0380	0.0802	0.01055	1.7501	10.0000	0.0063	0.19

(1) AC9 = collected in Tarauacá in Acre, Profile 9; PE = collected in Ipojuca, Pernambuco; RS = collected in Rosário do Sul, Rio Grande do Sul; BR = collected in Bom Retiro, SC; CB = collected in Curitibanos, SC. (2) Limestone rates applied to neutralize 0, 0.25, 0.50, and 1.00 times the soil contents of H+Al. (3) pH measured in the soil solution by potentiometry in the soil:water ration 1:1 . (4) Sum of bases ($Ca^{2+} + Mg^{2+} + K^+ + Na$). (5) Fraction of aluminum in relation to all cations in the soil solution (Al^{3+}/S) × 100. (6) Electrical conductivity, obtained by conductivity meter after shaking and centrifugation of the samples in the soil:water of 1:1 ration. (7) Ionic strength, calculated by equation $\log I\ (M) = 1.159 + 1.09 \times \log EC\ 25\ (dS\ m^{-1})$. (8) Dissolved organic carbon. (9) Sulfate. (10) Nitrate. (11) Chloride. (12) Phosphate. The cations (Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, Na) and the anions (SO_4^{2-}, NO_3^-, Cl^- and PO_4^{3-}), as well as the DOC and the P were obtained after shaking and centrifugation of the samples in the ration soil solution of 1:1. After obtaining the extracts, the cations were quantified by ICP-OES, the $SO4^{2-}$ by turbidimetry, the NO_3^- by colorimetry, the Cl^- by titration, $PO4^{3-}$ by equation (P x 3.06).



●	AC9	TDM=7.40-7.98x+6.45x²	r²=0.96	●	AC9	TDM=17.55-12.37x+13.13x²	r²=0.76
○	PE	TDM=2.66+7.19x-4.45x²	r²=0.88	○	PE	TDM=1.41+14.13x-6.83x²	r²=0.99
▼	RS	TDM=5.32+2.78x-2.76x²	r²=0.44	▼	RS	TDM=16.64+19.93x-18.83x²	r²=0.99
△	BR	TDM=0.39+20.36x-13.42x²	r²=0.94	△	BR	TDM=1.33+41.03x-26.98x²	r²=0.98
■	CB	TDM=2.38+7.22x-5.51x²	r²=0.93	■	CB	TDM=5.29+31.39x-26.56x²	r²=0.99

Figure 1. Total dry matter (TDM) yield of soybean (a) and corn (b) plants grown in soils of Acre (AC9), Pernambuco (PE), Rosário do Sul (RS), Bom Retiro (BR), and Curitibanos (CB), resulting from the application of different limestone rates.

The soils PE, BR, and CB had low production of TDM in treatments without limestone (Figure 1). In the absence of limestone in these soils, there was high Al^{3+} activity in the solution (Table 4), high Al fraction in relation to all cations (Table 5), and very high (PE), high (BR), and low (CB) levels of Al-KCl and of saturation by Al (Table 3). Therefore, for this group of soils, the Al-KCl levels adequately indicated probable Al toxicity to plants. However, with liming, due to the decrease in Al-KCl contents and Al saturation (Table 3), the TDM production of the plants increased already in the first two rates of limestone applied, corresponding to 25 and 50 % of the H+Al content of the soils (Figure 1). The pH values were 4.97 (25 %) and 5.59 (50 %) in the PE soil, 5.56 and 5.83 in the BR soil, and 5.63 and 5.81 in the CB soil (Table 3). At these rates, the TDM production in the BR and CB soils were similar and larger than in the PE soil. However, in the treatment that received the highest rate applied, TDM production was higher in the BR soil than in the PE and CB soils.

It should be noted that the absence or small response of the plants to liming in these soils may also be related to the high levels of P applied. When the negative effect of the Al^{3+} only impairs root growth (morphological effect), the increase in P contents in the soil can decrease plant response to liming since higher levels of P in the soil decrease dependence on the existence of an ample root system to take up this nutrient. (Ernani et al., 2004; Nolla et al., 2013a,b; Rutkowska et al., 2015).

In an Oxisol (Rhodic Hapludox) (pH = 4.0 and Al^{3+} = 3.22 $cmol_c$ kg^{-1}), Nolla and Anghinoni (2006) observed that under field conditions, high application rates of phosphate displaced organic anions of exchange by mass action, reducing the Al^{3+} in solution by the formation of organic Al^{3+}. According to Nolla et al. (2013b), the better development of soybean roots occurred due to the decrease in Al^{3+} toxicity with the application of P. The authors concluded that the formation of Al phosphate occurred by the release of organic acids capable of complexing Al^{3+} present in the soil solution under conditions of higher acidity. Evaluating the relation of rates of limestone application and P, Ernani et al. (2000) observed that with higher P rates, liming did not affect corn yield. For that reason, the contents of this element available in the soils will be used as a joint criterion for calculating the need for limestone (CQFS-RS/SC, 2016).

In addition to chemical speciation, another important point to be addressed about whether or not Al^{3+} is toxic to plants is the exchangeable Ca/Al ratio of the soils. In the

AC9 and RS soils, in which there was little or no response to liming, the ratio of these two exchangeable cations after cultivation was 1.32 in AC9 and 1.28 in RS. In other words, under those conditions, Al^{3+} is not toxic to plants because, according to Smyth and Cravo (1992) and Gama and Kiehl (1999), the critical level for plants achieve maximum yield without being affected by the presence of exchangeable Al is 0.42 and 0.48, respectively. For the PE, BR, and CB soils, the lowest limestone application rate (25 % of H+Al) was already enough for the exchangeable Ca/Al ratio to be equal to or above the critical level proposed by the authors mentioned above. Under these conditions, Al^{3+} is not toxic to plants (Wadt, 2002; Araújo et al., 2004; Caires, 2013).

Results show that the toxic Al species (Al^{3+}) in the AC9 and RS soils, regardless of the treatment, were little or not at all toxic to the corn and soybean plants since they produced satisfactorily and there was no increase in their yield with the use of liming (Figure 1a). In contrast, in the PE and BR soils, where the highest Al^{3+} activities were found in the treatments without limestone (Table 4), the plants showed toxicity from this element, with a reduction in TDM. However, with the application of the first two limestone rates, the Al^{3+} activity was below 4.6 μmol L^{-1} for soybean and 18 to 27 μmol L^{-1} for corn (Table 4), and the plants did not show Al^{3+} toxicity or the toxicity effect was small, since there was an increase in TDM production (Figure 1). In the CB soil, Al^{3+} activity in the soil solution was already below the critical limit previously mentioned in the treatments without limestone, and the TDM production of the corn plants grown in it was higher than the TDM production of plants grown in the PE and BR soils (Figure 1b). However, in the soil solution after soybean cultivation, in the same treatment and soil, Al^{3+} activity was above the critical limit, and the plants produced less than those cultivated in the PE soil, indicating that these plants were affected by Al^{3+} toxicity. With liming, there was a decrease in Al^{3+} activity in the solution of that soil and, as a consequence, the TDM production of soybean and corn plants increased.

CONCLUSIONS

The high levels of Al extracted by KCl 1.0 mol L^{-1} solution in the AC9 and RS soils are not related only to the exchangeable forms of the element and to the manifestation of toxicity by the soybean and corn plants. In the more weathered and acidic soils (PE, BR, and CB), the contents of Al extracted by this solution are effective in estimating the “exchangeable” Al and also its potential toxic effect.

In the solution of all soils, Al^{3+} was the chemical species that occurred in highest proportion, and the lowest limestone application rate (25 % of H+Al) was enough to decrease the activity of this species to levels considered non-toxic to plants.

When the Ca^{2+}/Al^{3+} or $Ca^{2+}+Mg^{2+}/Al^{3+}$ ratio is high, even if the absolute levels of Al-KCl of the soils are high, the Al^{3+} activity in the solution is low and might not be toxic to soybean and corn plants.

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