

# Production of soybean and maize plants cultivated in acid soils with high contents of exchangeable aluminum

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**ABSTRACT:** In several Brazilian acid soils, the extractable aluminum with the solution of 1.0 mol L<sup>-1</sup> KCI (AI-KCI) may exceed 10 cmol<sub>c</sub> kg<sup>-1</sup>, but in some soils the presence of this element seems to exert little or no interference in the productivity of the plants. The study aimed to evaluate in which conditions the high levels of AI-KCI are related to the toxicity in soybean and maize plants cultivated in greenhouse, and their possible interference in the dry matter production of the same. Also, it aimed at assessing the soil chemical attributes that best identified a probable AI toxicity and the responses of the cultivated plants to liming. AI-KCI is not related to the manifestation of toxicity by the plants, nor did it interfere in the productivity of the plants cultivated in the AC9 and RS soils. On the other hand, the high levels of AI-KCI interfered in the productivity of these plants cultivated in the PE, BR and CB soils, manly in the treatments without limestone. Aluminum saturation, sum and base saturation were the best soil chemical attributes for the identification of AI toxicity and plant response to liming.

Key words: aluminum toxicity; liming; plant response; soil chemical attributes

# Produção de plantas de soja e milho cultivadas em solos ácidos com elevados teores de alumínio trocável

**RESUMO:** Em vários solos ácidos brasileiros o alumínio extraível com a solução de KCI 1 mol L<sup>-1</sup> (AI-KCI) pode exceder a 10 cmol<sub>c</sub> kg<sup>-1</sup>, porém em alguns solos a presença desse elemento parece exercer pouca ou nenhuma interferência na produtividade das plantas. O estudo objetivou avaliar em que condições os elevados teores de AI-KCI estão relacionados com a toxidez nas plantas de soja e milho cultivadas em casa de vegetação e sua interferência na produção de matéria seca das mesmas. Também, buscou-se avaliar os atributos químicos dos solos que melhor identificou uma provável toxidez do AI e a resposta das plantas cultivadas à calagem. O AI-KCI não está relacionado com a manifestação de toxidez nas plantas cultivadas nos solos AC9 e RS e, tampouco, interferiu na produtividade das plantas cultivadas nos solos AC9 e RS. Por outro lado, os elevados teores de AI-KCI interferiram na produtividade dessas plantas cultivadas nos solos PE, BR e CB, principalmente nos tratamentos sem calcário. A saturação por alumínio, a soma e a saturação por bases foram os melhores atributos químicos dos solos para a identificação da toxidez do AI e da resposta das plantas à calagem.

Palavras-chave: toxidez de alumínio; calagem; resposta de plantas; atributos químicos do solo

### Introduction

Most of Brazilian soils has limitations to the establishment and development of the majority of crop production systems, because of acidity (Bojórquez-Quintal et al., 2017; Tandzi et al., 2018). This is generally associated with the presence of Al<sup>3+</sup> and Mn in toxic concentrations (Miguel et al., 2010; Tandzi et al., 2018), low levels of exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup>, molybdenum (Mo), low sum and base saturation, (Biscaro et al., 2011; Da Costa et al., 2016; Pauletti et al., 2014) and a limited amount of P (Miguel et al., 2010; Yang et al., 2013; Maluf et al., 2018), characteristics of soils with unfavorable conditions for the development of most crops (Fageria & Nascente, 2014; Sade et al., 2016). However, in some soils, it has been found amounts of aluminum, extracted with KCl 1 mol L<sup>-1</sup> (Al-KCl) solution, above 10 cmol kg<sup>-1</sup> although the plants do not show Al<sup>3+</sup> toxicity symptoms, but rather a satisfactory level of productivity. Even when using low limestone rates, the plants produce satisfactorily, highlighting that not all the Al indicated in the chemical analysis of the soil as exchangeable is in equilibrium with the Al that is considered toxic to plants.

A study assessing the Red-Yellow Podzolic from Sena Madureira, in the State of Acre, Brazil, Gama & Kiehl (1999) found high Al levels in the soil solution, nonetheless, the presence of this element was not toxic to rice (Oryza sativa), maize (Zea mays) and common bean (Phaseolus vulgaris L.). These authors associated a high Ca/Al ratio, above 14 in A horizon and 0.48 in B horizon, with the lack of toxicity toward these crops. For Wadt (2002), the mechanism that explains the low Al<sup>3+</sup> phytotoxicity observed in the soils of the State of Acre is related to the retention strength of the interstratified Al<sup>3+</sup> and the amorphous Al next to cation exchange surfaces: as the attractive force of Al<sup>3+</sup> ions of the solution is greater than that of other cations, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, the latter would be more free in the solution than Al<sup>3+</sup>, decreasing their activity in the soil solution. According to the same authors, the method of exchangeable Al should not be used as an acidity index in

the soils from the State of Acre, since it does not represent the appropriate quantity of limestone indicated to correct the acidity levels and to improve plant productivity. Therefore, if the other nutrients are not limiting, maybe it is not necessary to correct them. Caires et al. (2008) also concluded that in soils with medium and high levels of certain nutrients, mainly Ca<sup>2+</sup>and Mg<sup>2+</sup>, maintaining high Ca/Al or Ca+Mg/Al ratios, the Al<sup>3+</sup> exerts little or no toxicity to plants. Auxtero et al. (2012), Tandzi et al. (2018) and Zandoná et al. (2015) concluded that low amounts of limestone can prevent the harmful effects of Al on plant growth.

On the other hand, most Brazilian acid soils respond to liming, a practice commonly used to increase soil pH, sum and base saturation, and nutrient availability in the soil solution, improving plant nutritional efficiency by providing  $Ca^{2+}$  and  $Mg^{2+}$ , promoting the neutralization of  $Al^{3+}$  and decreasing Al saturation (Joris et al., 2013; Rutkowska et al., 2015; Goulding, 2016).

Given the existence of acid soils with very variable chemical and mineralogical properties in Brazil, many of which displaying very high levels of Al-KCl, but with little or no response rates to liming, the present study aimed to evaluate in which conditions the high levels of exchangeable Al are related to the toxicity in soybean and maize plants, and its interference in the dry matter production of these plants. In addition, the chemical attributes of the soils that best identified a probable toxicity caused by Al<sup>3+</sup> and the response of plants to liming were also assessed.

## **Materials and Methods**

### **Selection of soils**

The study was carried out using samples of the subsurface B horizon of five soils, collected in previously uncultivated areas. Of the five soils, four displayed Al-KCl levels higher than  $4 \text{ cmol}_{c} \text{ kg}^{-1}$  (Table 1). Samples of the B horizon were used due to its lower organic matter (OM) content in relation to the

Table 1. Classification and physical and soil chemical attributes collected in different Brazilian regions.

Soil <sup>(1)</sup>	Source	Н	<sup>2)</sup> Dej (c	oth <sup>(3)</sup> m)		Symbol. <sup>(5)</sup>					
AC9	Embrapa (2013a) Cunha et al. (2018a) Bt <sub>2</sub>			60-102 Argissolo Vermelho-Amarelo Alítico Iuvissólico (Hapludult)						udult)	PVAal
PE	Embrapa (2011a) Bt <sub>2</sub>		2 55	55-105 Argissolo Vermelho-Amarelo Alítico típico (Hapludult)					lult)	PVAal	
RSRS	Cunha et al. (	3 65	-80	Argissol	o Bruno-A	cinzentado	o Alítico típi	co (Hapluc	lult)	PBACal	
SCBR	Cunha et al. (	2018a) E	i 60	-90	Cambissolo Húmico Alítico típico (Humudepts)						CHal
SCCB	Cunha et al. (	2018a) Bv	v <sub>3</sub> 215	215-275 <sup>+</sup> Nitossolo Bruno (Kandiudox)							NB
	Clay <sup>(6)</sup>	<b>TOC</b> <sup>(7)</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	К	Al <sup>3+</sup>	<b>S</b> <sup>(9)</sup>	CEC <sup>(10)</sup>	<b>V</b> <sup>(11)</sup>	m <sup>(12)</sup>	Р
	(g k									(mg kg1)	
		·6 /			(cmo	<sub>c</sub> kg <sup>-1</sup> )				(%)	(mg kg +)
AC9	346	2.5	17.5	3.6	0.48	<mark>₅ kg-1)</mark> 13.2	21.6	36.5	59	. <b>%)</b> 38	(mg kg *) 2
AC9 PE	346 382	2.5 36	17.5 1.2	3.6 3.6	0.48 0.12	c <b>kg<sup>-1</sup>)</b> 13.2 19.3	21.6 5.0	36.5 25.5	59 20	%) 38 80	2 <1
AC9 PE RSRS	346 382 414	2.5 36 5.7	17.5 1.2 8.8	3.6 <u>3.6</u> 2.9	0.48 0.12 0.40	<b>, kg<sup>-1</sup>)</b> 13.2 19.3 6.9	21.6 5.0 12.1	36.5 25.5 21.1	59 20 57	%) 38 80 36	2 <1 -
AC9 PE RSRS SCBR	346 382 414 590	2.5 36 5.7 5.1	17.5 1.2 8.8 0.	3.6 3.6 2.9 38 <sup>(8)</sup>	0.48 0.12 0.40 0.51	c kg <sup>-1</sup> ) 13.2 19.3 6.9 5.4	21.6 5.0 12.1 0.9	36.5 25.5 21.1 9.9	59 20 57 9	%) 38 80 36 85	2 <1 - <1

<sup>(1)</sup> AC9: collected in Tarauacá State of Acre, Profile 9; PE: collected in Ipojuca, State of Pernambuco; RS: collected in Rosário do Sul, State of Rio Grande do Sul; BR: collected in Bom Retiro, State of Santa Catarina; CB; collected in, State of Santa Catarina; <sup>(2)</sup> Collected horizons; <sup>(3)</sup> Collect soil layers; <sup>(4)</sup> Classification according to the Brazilian System of Soil Classification (Embrapa, 2013b); <sup>(5)</sup> Symbology according to the Brazilian System of Soil Classification (Embrapa, 2013b); <sup>(6)</sup> Clay fraction less than 0,02 mm; <sup>(7)</sup> Total Organic carbon; <sup>(8)</sup> Sum of calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) contents; <sup>(9)</sup> Sum of bases; <sup>(10)</sup> CEC pH7; <sup>(11)</sup> Base saturation and <sup>(12)</sup> Al saturation. surface horizon, because the OM may influence the results by the formation of Al-based complexes. Two groups of soils were used based on their mineralogical and chemical differences: smectite with high levels of exchangeable Al<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, whose representatives are AC9 (PVAal), from the State of Acre, and Rosário do Sul (RS) (PBACal), from the State of Rio Grande do Sul; smectite with kaolinite and high contents of exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup>, whose representatives are PE (PVAal), from the Pernambuco (PE) State, and BR (CHal), from the Santa Catarina (SC) State . Another soil from the State of Santa Catarina was included in this study: CB (NB), which was used as a reference, since it is more weathered, with a mineralogy essentially kaolinitic and lower levels of exchangeable Al-KCI, Ca<sup>2+</sup> and Mg<sup>2+</sup> than the others.

The soil samples were collected in the sites, where the respective complete profiles had already been previously described, and whose results were previously published (Table 1). The mineralogical characteristics of these soils are the following: smectite (88%) prevailing in AC9, with low amounts of kaolinite-smectite interlayer (6%) and mica-ilite interlayer (6%); smectite (60%) prevails in the PE, with relatively high amounts of kaolinite prevails in the RS; kaolinite (51%) prevails in the BR, with relatively high amounts of smectite and vermiculite with hydroxy polymers interlayers (47%) (EHE and VHE, respectively) and low amount of mica-ilite interlayer (2%); kaolinite prevails in the CB (94%), but it has 6% of EHE. For further details on these see Cunha et al. (2014).

# Preparation of samples and analyses before incubation with limestone

The soil samples were air-dried in a greenhouse, prepared, ground and sieved using a 4 mm mesh and then incubated separately. For the chemical analyses, the soil samples sieved with a 2 mm mesh were used. The pH values in water and in 1.0 mol L<sup>-1</sup> KCl were estimated by potentiometry in the solvent/ soil ratio of 1:2.5; as well as H+Al through neutralization titration, after extraction with calcium acetate buffered to pH 7, and field capacity (Embrapa, 2011b), determined on a tension table, after applying on the saturated sample a voltage equivalent to a column of water of 100 cm (1 kPa). The chemical analyses were performed in three replicates and the results are presented in Table 2.

### **Soil incubation**

The treatments consisted in the application of four rates of dolomitic limestone in each soil, corrected to 100% of relative power of total neutralization, which were equivalent to the necessary amount to neutralize 0; 0.25; 0.50 and 1.00 times the H+Al contents. Each treatment consisted of four replications and the rates were applied and homogenized in 20 kg soil samples (dry base). Then, distilled water was applied to increase humidity to 80% until field capacity (FC). Subsequently, the samples were placed in 100 L plastic bags, stirred every 15 days, and incubated for 98 days until the pH values were stabilized.

### Implementation and accomplishment of the experiments

After incubation, the soil samples were sieved once again using a 4 mm mesh and 20 kg of each treatment, which constituted the four repetitions, were fertilized with N, P and K from urea, triple superphosphate (TSP) and potassium chloride (KCl), respectively. For the first cultivation, soybean, 1.08 g kg<sup>-1</sup> of N, 2.48 g kg<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> and 0.99 g kg<sup>-1</sup> of K<sub>2</sub>O were applied; for the second cultivation, maize, 0.99 g kg<sup>-1</sup> of N, 2.48 g kg<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> and 1.98 g kg<sup>-1</sup> of K<sub>2</sub>O were applied.

Fertilization with N, P and K was recommended by the Commission for Soil Chemistry and Fertility of the States of Rio Grande do Sul and Santa Catarina (CQFS-RS/SC, 2004) for soybean and maize crops, based on the results of a study previously published (Table 1). The N rate was added once for soybean and parceled out in three times for maize. Fertilization calculations for soybean and maize aimed at productivity values of 3 and 8 t ha<sup>-1</sup> of grains, respectively. N, P and K sources were applied to the soils and mixed after the incubation period.

The experimental crops were conducted in a greenhouse in 2015, in 8 L pots containing 5.0 kg of soil each. Soybeans were grown for 60 days. Then, maize was cultivated for 45 days in the same soil. The experimental design was randomized block organized in a "4 x 5" factorial scheme, with four limestone rates and five soils, and four replications. In each pot, seven seeds without pre-germination were sowned. Twenty-one days after soybean emergence and 11 after maize emergence, the plants were cut, leaving three plants per pot. The soils were kept at a humidity level close to 80% of FC, by daily weighing the pots and moisture replacement with deionized water. The masses corresponding to the plant growth in each soil and treatment were discarded for water replacement.

**Table 2.** Chemical attributes before the incubation of soils and implantation of greenhouse experiments and physical properties of soil profiles collected in natural conditions in different Brazilian regions.

Solo <sup>(1)</sup>	H <sup>(2)</sup>	Depth <sup>(3)</sup>	pH Water	KCI	H+AI	FC <sup>(4)</sup>	Clay	Silt	Sand			
		(cm)	(1:2,5)		(cmolc Kg <sup>-+</sup> )	(%)						
AC9	Bt <sub>2</sub>	60-102	5.42	3.60	14.73	45	34	17	49			
PE	Bt <sub>2</sub>	55-105	5.03	3.80	18.43	40	38	17	18			
RS	$Bt_3$	65-80	5.24	3.77	8.80	37	48	23	29			
BR	Bi	60-90	4.73	3.76	9.87	42	54	27	19			
CB	Bw <sub>3</sub>	215-275+	4.89	4.11	6.53	42	83	9	8			

<sup>(1)</sup> AC9: collected in Tarauacá State of Acre, Profile 9; PE: collected in Ipojuca, State of Pernambuco; RS: collected in Rosário do Sul, State of Rio Grande do Sul; BR: collected in Bom Retiro, State of Santa Catarina; CB; collected in, State of Santa Catarina; <sup>(2)</sup> Collected horizons; <sup>(3)</sup> Collect soil layers; <sup>(4)</sup> Field Capacity.

# Experiment collection and plant tissues concentration of the two crops

The soybean plants were collected in the phenological stage of full bloom and the maize plants at V6, with six leaves developed. The aerial part (AP) of the plants was cut close to the soil, placed in paper bags, and dried in a forced circulation oven at 65-70°C until reach constant weight, when finally, after weighing, the shoot dry weight (SDW) was obtained. The roots of both crops were separated from the soils using a 2 mm sieve. They were subsequently washed in tap water to remove the coarser fractions of the soil and forced-dried in the oven at 65-70°C for 24 hours. After that, they were washed once again in tap water to remove fine soil particles. In each experimental unit of each crop, the roots of two plants were dried for root dry weight (RDW) determination; the third root of each plant (one of each experimental unit, totaling 4 per soil and treatment) was packed in a plastic container and kept in 70% alcohol in a refrigerator. In the next step, it was scanned using the Winrhizo Pro (2009) scanning system (Reagent Instruments Canada Inc.) and the Epson Expression 10000 XL scanner to determine root system length (RSL), root surface area (RSA), among other parameters; then it was dried, weighed and its RDW was estimated together with the others. With the addition of the SDW to the RDW, the total dry weight (TDW) produce by the plants was obtained.

### Soil chemical attributes after cultivation

After the roots were separated from each crop, the soils were homogenized and samples of approximately 140 g were collected and packed in polystyrene containers with ice. Afterwards, they were stored in an ultra-low temperature freezer at -80°C, where they were kept frozen until analysis, in order to avoid biological degradation of the organic compounds. Subsequently, the soils were air-dried, milled and sieved with a 2 mm mesh for obtaining the air-dried fine earth.

In the soil samples, pH in water, pH in CaCl<sub>2</sub> 0,01 mol L<sup>-1</sup> (soil/solution ratio 1:2.5) and pH in KCl 1 mol L<sup>-1</sup> (soil/solution ratio 1:10) were determined, and, according to Tedesco et al. (1995), exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> e Al<sup>3+</sup> levels in the soil were also estimated. P, K<sup>+</sup> and Na<sup>+</sup> were extracted using the Melich-1 solution and determined by colorimetry (Murphy & Riley, 1962) and flame photometer, respectively.

### **Statistical analysis**

Data relating the production of SDW, RDW, TDW, of RSA, of RSL in soybean and maize plants with the limestone rates applied in the soils were submitted to analysis of variance (F test) using the SISVAR 5.6 software (Ferreira, 2014). When a significant effect was found, Tukey's multiple comparisons test was applied to the "soil types" factor (including the split of soil types at each limestone dose). The regression test was applied to the "limestone dose" factor (including the split of limestone rates in each of the soil types), both at 5% of probability of error.

## **Results and Discussion**

### Dry weight yield in soybean and maize plants

Liming increased soil pH values, mainly Ca<sup>2+</sup> and Mg<sup>2+</sup> contents, sum and base saturation and, consequently, decreased the contents of Al3+, H++Al3+ and Al saturation in all soils of the samples collected after two cultivations. However, a complete Al<sup>3+</sup> neutralization did not occur in the samples of AC9 and PE soils with the maximum dose (100% of the  $H^++AI^{3+}$  content) (Table 3). The non-neutralization of  $AI^{3+}$  in these two soils may have occurred due to an underestimation of the potential acidity by calcium acetate, since there may be other AI fractions that were not computed in H<sup>+</sup>+AI<sup>3+</sup>, resulting in an incorrect estimate of the needed limestone (Kaminski et al., 2002; Silva et al., 2006; Almeida Júnior et al., 2015), and probably during soil incubation, they consumed the limestone. Or it may be related to the non-neutralization of other Al<sup>3+</sup> fractions by limestone, which may have been extracted by the KCl solution and computed as exchangeable after base titration. On the other hand, no change was observed in K<sup>+</sup> (Table 3) and Na<sup>+</sup> (data not shown) contents with the application of limestone and no significant change in CEC at pH 7 was noticed, and this was expected as the increase in Ca<sup>2+</sup> and Mg<sup>2+</sup> must be stoichiometrically similar to the H<sup>+</sup>+Al<sup>3+</sup> decrease. P levels in the AC9, PE and RS soil samples after soybean cultivation were very high, except in BR and CB soils, where the exchangeable contents of this element were low. Nonetheless, after maize cultivation the contents of this element were very high in the AC9, PE, RS, BR soils and remained low in the CB soil (Table 3).

Due to the benefits brought by limestone, as it increased nutrient availability for soybean and maize plants, it was observed that the production of SDW, RDW and TDW presented high correlation and quadratic behavior according to limestone rates in all soils (Figure 1). A similar behavior was observed in RSL and RSA parameters, except for the AC9 soil, where the adjustment was linear in RSA (Figure 2c).

In the smectitic AC9 soil, with very high levels of exchangeable Al<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> (Bernini et al., 2013; Cunha et al., 2014, 2015), an increase in the production of SDW, RDW and TDW in both crops with the addition of limestone (Figure 1) was detected. This occurred even though there was an increase in the RSL, of the RSA of the plants grown in this limed soil (Figure 2) and more than 13 cmol<sub>c</sub> kg<sup>-1</sup> of Al, pH 4.85-4.91 and Al saturation of 38-40% (Table 3).

The RS soil, also smectitic (Cunha et al., 2014; Santos et al., 2017) and with similar characteristics to those found in the AC9 soil (Table 3), favored, in soybean plants, in the treatments without limestone, a higher production of RDW, TDW, RSL and RSA than the PE, BR and CB soils (Figures 1 and 2). In this soil, a limited response from plants to liming was observed. The highest dry weight (DW) yield by soybean in the RS soil occurred in the treatment that received the first dose of limestone (25% of the H<sup>+</sup>+Al<sup>3+</sup> content) (Figure 1), with Al saturation at 27%, considered, according to Smyth & Cravo (1992), still acceptable for a good crop development.

Table 3.	Chemical attribu	ites of five acid	soils profiles afte	r 60 and 45	days of soybea	an and maize	e cultivation,	respectively,	, in a
greenho	ouse.								

	D.Cal. <sup>(2)</sup>	рН			A 12+	11++ 612+	<b>C</b> -2+	NA-2+	1/+	<b>c</b> (4)	CEC(5)	V(6)	<b>m</b> (7)		
Soil <sup>(1)</sup>		Water	CaCl₂	KCI	ΔpH <sup>(3)</sup>	AIST	Al <sup>3+</sup> H <sup>+</sup> +Al <sup>3+</sup>	Carr	Ca <sup>2+</sup> IVIg <sup>2+</sup>		2(-/	CEC(3)	<b>V</b> <sup>(0)</sup> <b>m</b> <sup>(1)</sup>		P (maliant)
	t na** x H*+Al3*	(1:2	2.5)	1:10				(cr	nol <sub>c</sub> kg <sup>-</sup>	<sup>1</sup> )			(%	6)	(mg kg-+)
Soybean															
	0	4.91	4.08	3.70	-1.21	13.8	15.89	16.8	3.5	0.40	20.9	36.7	57	40	17.2
100	0.25	5.26	4.34	3.83	-1.43	9.6	12.00	18.2	4.4	0.41	23.1	35.1	66	29	15.8
AC9	0.5	5.33	4.50	3.94	-1.39	5.9	8.51	19.4	5.4	0.41	25.2	33.8	75	19	15.8
	1.00	5.61	4.62	4.10	-1.51	3.6	6.51	24.6	6.2	0.42	31.4	37.9	83	10	17.2
	0	4.63	3.86	3.86	-0.77	19.8	20.37	1.7	2.3	0.22	4.4	24.8	18	82	27.2
DE	0.25	4.88	4.10	3.97	-0.91	14.6	15.93	4.9	3.7	0.21	9.1	25.0	36	62	23.5
PE	0.5	5.17	4.30	4.03	-1.14	9.8	11.64	6.8	5.3	0.21	12.5	24.1	52	44	21.7
	1.00	5.63	4.75	4.31	-1.32	1.8	4.32	13.6	5.8	0.19	19.8	24.1	82	8	16.5
	0	4.89	4.11	3.85	-1.04	6.7	9.56	8.6	2.6	0.30	11.5	21.1	55	37	16.4
DC	0.25	5.08	4.25	3.91	-1.17	4.6	7.54	8.4	3.5	0.29	12.3	19.8	62	27	16.5
1.5	0.5	5.20	4.43	4.04	-1.16	2.6	5.72	9.1	3.8	0.27	13.2	18.9	70	16	15.5
	1.00	6.02	5.29	4.46	-1.56	0.2	3.00	14.6	4.7	0.29	19.8	22.7	87	1	12.1
	0	4.62	3.85	3.73	-0.89	6.7	9.06	0.14	0.0	0.19	0.36	9.4	4	95	9.4
BR	0.25	4.91	4.04	3.80	-1.11	4.4	8.08	2.1	1.1	0.19	3.4	11.5	30	56	10.8
DI	0.5	5.21	4.33	3.98	-1.23	2.2	5.74	3.6	1.9	0.18	5.7	11.4	50	28	7.6
	1.00	5.98	5.21	4.47	-1.51	0.3	3.59	5.9	3.2	0.20	9.4	13.0	72	3	9.4
СВ	0	4.78	4.02	4.18	-0.6	2.2	7.81	0.17	0.0	0.20	0.38	8.2	5	86	3.6
	0.25	4.91	4.24	4.26	-0.65	1.2	7.50	1.3	0.74	0.18	2.3	9.8	24	33	3.4
	0.5	5.20	4.56	4.49	-0.71	0.3	5.49	2.7	1.5	0.17	4.4	9.9	45	7	2.4
	1.00	6.21	5.61	5.08	-1.13	0.02	3.53	4.4	2.2	0.17	6.8	10.3	66	0	3.3
							Maize								
	0	4.85	4.58	3.72	-1.13	13.2	14.9	17.5	3.6	0.48	21.7	36.6	59	38	16.3
AC9	0.25	5.45	5.38	3.89	-1.56	9.3	10.7	18.8	5.2	0.65	24.6	35.4	70	27	16.2
ACJ	0.5	5.58	5.52	3.99	-1.59	5.6	9.2	22.9	6.5	0.69	30.1	39.2	77	16	14.4
	1.00	5.84	5.75	4.10	-1.74	3.1	6.7	24.9	6.8	0.73	32.5	39.2	83	9	14.9
	0	4.66	4.59	3.90	-0.76	18.1	18.5	2.9	2.0	0.68	5.6	24.2	23	76	17.3
PF	0.25	4.97	4.89	4.03	-0.94	13.7	15.8	6.9	3.7	0.53	11.2	26.9	41	55	18.1
	0.5	5.59	5.52	4.15	-1.44	8.9	10.8	7.1	5.6	0.44	13.2	24.0	55	40	16.6
	1.00	5.90	5.82	4.41	-1.49	1.4	9.0	14.3	6.3	0.43	21.0	30.0	70	6	15.6
	0	5.01	4.94	3.80	-1.21	6.9	9.0	8.8	2.9	0.40	12.2	21.2	58	36	17.8
RS	0.25	5.73	5.66	3.90	-1.83	4.6	7.9	9.7	3.8	0.39	13.9	21.9	64	25	15.4
	0.5	5.82	5.75	4.02	-1.8	2.7	6.6	10.1	4.0	0.34	14.4	21.0	69	16	15.7
	1.00	6.18	6.11	4.47	-1.71	0.4	3.9	14.8	5.7	0.34	20.8	24.7	84	2	15.3
	0	4.82	4.75	3.86	-0.96	5.4	9.0	0.38	0.0	0.51	0.89	9.8	9	86	14.0
BR	0.25	5.56	5.49	3.89	-1.67	3.7	7.9	4.6	1.4	0.31	6.4	14.3	45	37	13.7
DI	0.5	5.83	5.74	4.08	-1.75	1.5	6.0	5.5	2.0	0.41	7.9	13.9	57	16	13.0
	1.00	6.09	6.02	4.45	-1.64	0.2	4.3	7.3	3.5	0.29	11.2	15.4	72	3	12.2
	0	4.74	4.69	4.10	-0.64	2.0	8.0	0.16	0.0	0.48	0.64	8.6	7	76	4.3
CB	0.25	5.63	5.56	4.28	-1.35	0.8	6.7	3.7	0.7	0.34	4.8	11.5	42	15	3.3
00	0.5	5.81	5.74	4.54	-1.27	0.3	5.7	4.7	1.4	0.43	6.6	12.3	54	5	3.1
	1.00	6.19	6.10	5.22	-0.97	0.0	4.3	6.2	2.5	0.40	9.2	13.4	68	0	3.2

(1) AC9: collected in Tarauacá, State of Acre, Profile 9; PE: collected in, State of Pernambuco; RS: collected in Rosário do Sul, State of RS; BR: collected in Bom Retiro, State of SC; CB; collected in Curitibanos, State of SC; <sup>(2)</sup> Limestone rates applied in the soils; <sup>(3)</sup> Delta pH (pH KCl – pH Water); <sup>(4)</sup> Sum of bases; <sup>(5)</sup> CEC pH7; <sup>(6)</sup> Base saturation; <sup>(7)</sup> Aluminum saturation.

The use of the second dose (50% H<sup>+</sup>+Al<sup>3+</sup>content) and the maximum dose (100% of the H<sup>+</sup>+Al<sup>3+</sup>content) did not trigger any response from the plants in terms of DW productivity in the RSL and RSA (Figures 2a and 2c). For maize, the highest production of DW, RSL and RSA occurred with the second dose of limestone, similar to the first dose; in the treatment that used the maximum dose a decrease in the DW yield was observed in these plants (Figure 1), although an increase in the pH and a reduction in Al<sup>3+</sup> and Al saturation was also found (Table 3).

In AC9 and RS soils, despite the high Al-KCl levels and increased Al saturation, its presence does not seem to have

exerted toxicity in the plants, since the sum of bases of these soils exceeded the Al<sup>3+</sup> contents and the base saturation exceeded the Al saturation in treatments without limestone (Table 3). When this occurred, Al<sup>3+</sup> in these treatments and soils did not exert toxicity in the plants, even though the pH was below 5.5 and Al saturation above 27% (Table 3), indicating a probable toxicity to the plants. For these two soils (AC9 and RS), due to the limited or the lack of response to liming, high Al-KCl contents may not represent properly the exchangeable forms of the element, once the high salt concentration of the KCl not only dissolves the monomeric forms of the Al compounds, but also the Al inorganic polymers of discrete



**Figure 1.** Relation between the production of shoot dry matter (SDW), the roots (RDW) and total (TDW) of soybean (A) (B) and (C) and maize plants (D) (E) and (F), cultivated in a greenhouse, in the soils of Acre (AC9), Pernambuco (PE), Rosário do Sul (RS), Bom Retiro (BR) and Curitibanos (CB), according to the limestone rates applied.



**Figure 2.** Relation between the root system length (RSL) and the root surface area (RSA) of soybean (A and C) and maize (B and D) plants grown in a greenhouse, in the soils from Acre (AC9), Pernambuco (PE), Rosário do Sul (RS), Bom Retiro (BR) and Curitibanos (CB) according to the limestone rates applied.

phases, hydroxy-Al polymers intercalated into the interlayers of 2:1 clay minerals and probably also the Al portion bound to organic compounds, forms which may not be in equilibrium with the Al<sup>3+</sup> present in the soil solution (Cunha et al., 2014; Caballero et al., 2015), overestimating the exchangeable Al and, consequently, the Al saturation and the need for limestone, without affecting plant productivity. In this context, the analytical determination of the exchangeable contents of Al<sup>3+</sup> and the other elements can overestimate the values that are in real equilibrium with those of the soil solution, since for its production no chemical extractors are used, providing a rough estimation of the concentration of the elements that are in equilibrium with the solid phase (Silva & Bohnen, 2006; Spera et al., 2014; Cunha et al., 2018a, b). Therefore, the interaction between the ions in the solution, which in most cases may exist at a lower effective concentration than the analytical concentration, may determine a lower chemical

potential of the element, reflecting the lower toxicity of  $AI^{3+}$  to the plants (Silva & Bohnen, 2006).

A response and/or lack of response of plants to liming may also be related to soil P contents (Table 3). When the negative effect of  $AI^{3+}$  only impairs root system development (morphological effect), the increase of P levels in the soil may decrease the response of plants to liming, as higher P levels in the soil decrease the need for a developed root system to absorb this nutrient (Nolla et al., 2013).

Under field conditions, Ernani et al. (2000) evaluated limestone and P rates ratios and observed that, at higher P rates, liming did not affect the productivity of maize grown in a clayed Oxisol (Hapludox). Nolla & Anghinoni (2006) observed that in a Oxisol (Rhodic Hapludox) (pH=4.0 and Al=3.22 cmol<sub>c</sub> kg<sup>-1</sup>), high phosphate rates displaced organic anions of the exchange by mass action, reducing Al in solution through the formation of organic Al. Zambrosi et al. (2008) surveyed the

chemical speciation of the solution of a dystrophic clayey Rhodic Hapludox after five years of limestone application and also found formation of Al complexed with P (AlHPO $_{4}^{+}$ ) in the surface layers of this soil. The formation of this complex in the upper layers of the evaluated soil, according to the same authors, may have occurred due to the increase of Ca<sup>2+</sup> and Mg<sup>2+</sup> in solution that displaced the Al, favoring the formation of ionic pairs with phosphate and decreasing the activity of Al<sup>3+</sup> in the solution of the soil assessed. Nolla et al. (2013) also found a decrease in the toxicity of Al with the P application, resulting in an improved development of soybean roots. The authors concluded that the formation of Al phosphate occurred through the release of organic acids capable of complexing the Al<sup>3+</sup> present in the soil solution under conditions of higher acidity. De Conti et al. (2017), when applying higher pig slurry rates, also verified a decrease in the toxic potential of Al<sup>3+</sup> with the increase of the formation of AlHPO<sup>+</sup> due to a runup in the concentration of P in the solution, especially in the upper layers of a Typic Hapludalf. For these reasons, the available levels of this element in soils will be used in conjunction as a criterion to estimate the need for limestone (CQFSRS/SC, 2016).

In the soils of PE (smectitic), BR and CB (kaolinitic with or without smectite and/or vermiculite with hydroxy-Al interlayers) (Almeida et al., 2003; Teske et al., 2013; Cunha et al., 2014; Da Costa et al., 2018), in which were found, respectively, very high, high and low levels of Al-KCI, associated with low levels of Ca<sup>2+</sup> and Mg<sup>2+</sup> (Table 3) the two crops responded to liming in both DW production as in RSL and RSA (Figures 1 and 2). This response occurred due to an increase in the pH, basic cations, mainly Ca<sup>2+</sup> and Mg<sup>2+</sup>, the sum and base saturation, and a decrease in the Al-KCI levels and Al saturation (Table 3).

The highest DW, RSL and RSA yield of the two crops in these soils (PE, BR and CB) occurred particularly in the second dose of limestone, similarly to that observed in the first one (Figures 1 and 2), which corresponded, respectively, to 50 and 25% of the H<sup>+</sup>+Al<sup>3+</sup>content. The highest yield of the plants occurred with the second dose, because the Ca<sup>2+</sup> and Mg<sup>2+</sup> levels and the sum of bases exceeded the AI-KCI contents, and the base saturation exceeded AI saturation, thus, under these conditions, Al<sup>3+</sup> exerted little or no toxicity in the plants. However, it should be considered that, with the first dose, the plants also had satisfactory yields even with Al-KCl levels exceeding the sum of bases (except in the CB soil) and the base saturation lower than the Al saturation, the latter above 30% (Table 3), indicating a probable toxicity caused by Al<sup>3+</sup> to the plants (Smyth & Cravo, 1992; Hashimoto et al., 2010). This behavior reinforces the hypothesis that Al<sup>3+</sup> at these rates may have exerted little or no toxicity, indicating that the plants tolerated the high acidity of these soils, especially in the treatments that received the first dose of limestone. It is therefore plausible to assume that the sum of bases, base saturation and Al saturation should be considered in the evaluation of a probable presence or absence of Al on the toxicity to the plants. At the same rates, it was observed that the production of TDW in BR and CB soils were similar and

higher than in the PE soil, respectively (Figure 1). When using the maximum dose, the plants continued to respond to liming, however, the slight little difference in the DW yield of RSL and RSA at the maximum dose does not justify the application of higher limestone rates of as there is no response effect in their productivity (Figures 1 and 2). For this soil group, the KCl 1.0 mol L<sup>-1</sup> solution adequately determined the toxic forms and a probable toxicity of Al<sup>3+</sup> to the plants.

Another important point that should be highlighted about the toxicity of Al<sup>3+</sup> to plants is the exchangeable Ca/Al ratio of soils. In AC9 and RS soils, where a limited or the lack of response to liming was observed, the ratio between these two exchangeable cations after soybean cultivation in limestone treatments was 1.32 and 1.28 (calculated from the results found in Table 3) respectively. In other words, under these conditions, Al<sup>3+</sup> is not toxic to plants, because, according to Gama & Kiehl (1999) and Smyth & Cravo (1992), the critical level for plants to have maximum productivity without being affected by the presence of exchangeable AI is 0.42 and 0.48, respectively. For PE, BR and CB soils, the lowest limestone dose (25% of H<sup>+</sup>+Al<sup>3+</sup> content) was enough to achieve an exchangeable Ca/Al ratio equal to or above the critical level proposed by the aforementioned authors. The same behavior was observed in soils after maize cultivation (Table 3).

It is worth mentioning that in soils with a high level of natural fertility, such as AC9 and RS, in which Al<sup>3+</sup> exerted little or no toxicity to the plants, one must consider the amount of nutrients required by the plants as well as the amount of nutrients available in the soil. Insofar as this availability is greater than the amount needed by plants, there is no need to apply the nutrient to the soil, since the addition will not increase the plants productivity (Fontes, 2014; Lacerda et al., 2015).

In view of the results, it can be concluded that, although liming decreased the AI exchangeability of the soils, there was little reflection on the productivity of the studied plants. Hence, the AI exchangeable method must be approached with caution and in conjunction with other nutrients, as its contents are used to estimate the degree of AI saturation and then the liming value, increasing therefore the limestone rates and the costs of implementing the crops, without productivity gains.

### Conclusions

In soils, under natural conditions, with high levels of exchangeable Al<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, increased sum of bases, base saturation and Ca/Al and Ca+Mg/Al ratios, such as AC9 and RS, the high Al-KCl contents did not affect the productivity of the plants. In highly weathered and acid soils (PE, BR and CB) also showing increased Al-KCl contents, but low levels of basic cations, sum and base saturation, the high Al-KCl levels interfered in the plant productivity. Nonetheless, the plants responded satisfactorily when low amounts of limestone were applied.

Al saturation, sum and base saturation were the most important soil chemical attributes to identify a possible aluminum toxicity and the presence or absence of response to liming of plants.

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