

# Nutritional Efficiency and Nutrient Accumulation of Maize Cultivated in Soils With High Al-KCl Content

Gabriel Octávio de Mello Cunha<sup>1</sup>, Jaime Antonio de Almeida<sup>1</sup>, Clovis Arruda Souza<sup>1</sup> & Paulo Roberto Ernani<sup>1</sup>

<sup>1</sup> Santa Catrina State University, Lages, Santa Catarina, Brazil

Correspondence: Gabriel Octávio de Mello Cunha, Santa Catarina State University, Lages, Santa Catarina, Brazil. Tel: 55-499-9820-5999. E-mail: gabriel.cunha4@gmail.com

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## Abstract

Most Brazilian soils are weathered and acidic, generally with exchangeable aluminum levels toxic to plants. Aluminum content can exceed  $10 \text{ cmol}_c \text{ kg}^{-1}$  in certain soils, but does not interfere in plant nutrient absorption, transport and accumulation. This study aimed to assess whether the high aluminum levels extracted with  $1 \text{ mol L}^{-1}$  KCl solution affect the nutritional efficiency of maize plants grown in acidic soils in areas of Brazilian states (AC: profile 9, PE, SC and RS) never before cultivated. To that end, two greenhouse experiments were performed (soybean: 45 days and maize: 60 days) with increasing levels of lime (0; 25; 50 and 100% H+Al content). After the experiments and collection, chemical analyses were conducted to characterize the soils and determine the chemical composition of the maize plants. The Al levels did not interfere in maize plants, nutrient absorption, transport, use or accumulation in AC9 and Rosario do Sul (RS) soils, but did affect those cultivated in PE, BR and CB soils in treatments without lime. The absence of Al toxicity is related to the increased concentration and activity of basic cations and P in the soil solution.

**Keywords:** acidic soils, aluminum toxicity, soil aluminum, *Zea mays*

## 1. Introduction

The acidity of most Brazilian soils, especially in subsurface horizons (B), limits establishing and developing production systems for a substantial number of crops (Caires et al., 2008). This may be due to toxic Al and Mn concentrations (Bojórquez-Quintal et al., 2017; Tandzi et al., 2018), low exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  levels, and low sum of bases (S), base saturation (V%), and P, unfavorable soil properties for growing most crops (Yang et al., 2013; Maluf et al., 2018). However, some soils contain aluminum levels extracted with  $1 \text{ mol L}^{-1}$  KCl (Al-KCl) solution exceeding  $10 \text{ cmol}_c \text{ kg}^{-1}$ , where plants exhibit no signs of  $\text{Al}^{3+}$  toxicity and obtain satisfactory yields. Even when low doses of soil amendments are used, plant yield is satisfactory, demonstrating that not all the Al deemed exchangeable in soil chemical analysis is in fact toxic to plants (Wadt, 2002; Cunha et al., 2018a, 2018b). On the other hand, most acidic Brazilian soils respond to liming, which is widely used to raise soil pH, sum of bases, base saturation and nutrient availability in the soil solution, thereby enhancing plant nutritional efficiency, providing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , neutralizing  $\text{Al}^{3+}$  and decreasing  $\text{Al}^{3+}$  saturation (Joris et al., 2013; Rutkowska et al., 2015; Cunha et al., 2018a, 2018b).

As soil pH declines,  $\text{Al}^{3+}$  activity rises in the soil solution, exacerbating the harmful effects on crops (Rutkowska et al., 2015). The most apparent symptoms of Al toxicity are thickened and shortened roots, thereby reducing water and nutrient absorption, leading to poor plant development (Horst et al., 2010; De souza et al., 2016). Al toxicity and low basic cation levels can be resolved by plant breeding and/or soil management techniques (Joris et al., 2013). Liming is the most commonly used management practice and involves neutralizing  $\text{H}^+$  and  $\text{Al}^{3+}$  ions, thereby promoting an increase in pH, S and V%. This makes nutrients more readily available, providing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , promoting aluminum precipitation and reducing soil aluminum saturation (Rastija et al., 2014; Adisu et al., 2019). Nutrient availability is the rate at which nutrients are carried to the root surface and the ability of the plant to absorb them (Horn et al., 2006). In other words, it is the release of nutrients from the solid phase to the soil solution, and their transport to the root surface until they are absorbed by the plant (Fageria & Moreira, 2011; Sathiyavani et al., 2017). Other important mechanisms for plants are related to nutritional efficiency, which directly affects the yield of major crops and is linked to plant nutritional status (Amaral et al., 2011; Carvalho et al., 2012). Nutritional efficiency is associated with absorption efficiency (AE) indices, defined as the relation

between shoot nutrient content ( $\text{N}_{\text{Csh}}$ ) and root dry weight (RDW), demonstrating plant's ability to extract nutrients from the soil, which differs among species (Swiader et al., 1994; Fageria & Moreira, 2011; Sathiyavani et al., 2017). Some species have an extensive root system while others have high uptake per unit of root length, that is, a high nutrient uptake rate (Tomaz et al., 2009). Transport efficiency (TE) is defined as the relation between total shoot nutrient content ( $\text{TNC}_{\text{sh}}$ ) and total plant nutrient content ( $\text{TNC}_p$ ) multiplied by 100 (Li et al., 1991) and indicates the plant's ability to transport nutrients from the root to the shoot. Use efficiency (UE) is the relation between total dry weight (TDW) squared and  $\text{TNC}_p$ , and shows the plant's ability to convert the absorbed nutrient into TDW (Siddiqi & Glass, 1981; Amaral et al., 2011).

The aim of this study was to assess whether high Al levels extracted different Brazilian soils with 1 mol L<sup>-1</sup> KCl (Al-KCl) solution affect the absorption, transport, use and accumulation of N, P, K, Ca, Mg and Al by greenhouse-grown maize plants, in addition to determining why some plants exhibit Al<sup>3+</sup> toxicity and others do not.

## 2. Method

The study was conducted with subsurface horizon (B) samples of five soils. All were collected in areas never cultivated, in the same places where they had previously been described and the majority had Al-KCl levels of more than 4 cmol kg<sup>-1</sup> (Table 1). Samples of the B horizon were used because of the lower organic matter (OM) in relation to the surface horizon, since it could influence the results by forming organic complexes with Al. Based on the mineralogical and chemical differences, the soils were divided into two groups: smectites with high levels of exchangeable Al<sup>3+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, represented by AC9 (PVAal), from Acre state and Rosário do Sul (PBACal) in Rio Grande do Sul (RS) state; smectites with kaolinite containing high Al levels and low exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations, represented by PE (PVAal) from Pernambuco state and BR (CHal) from Santa Catarina (SC) state. CB (NB), another soil from Santa Catarina, was used as reference, for being more weathered, and exhibiting kaolinite mineralogy and lower exchangeable Al-KCl, Ca<sup>2+</sup> and Mg<sup>2+</sup> content. Further details of the results of these analyzes can be verified in Cunha et al. (2014) and Cunha et al. (2018a, 2018b).

Table 1. Classification, chemical (before soil incubation and greenhouse experiments) and physical properties of soils collected under natural conditions in different Brazilian regions

Soil <sup>(1)</sup>	Source	H <sup>(2)</sup>	Depth <sup>(3)</sup>	Soil classification <sup>(4)</sup>					Symbol <sup>(5)</sup>	
--- cm ---										
AC9	Embrapa (2013a) Cunha et al. (2018a)	Bt <sub>2</sub>	60-102	Argissolo Vermelho-Amarelo Alítico luvissólico (Hapludult)					PVAal	
PE	Embrapa (2011a)	Bt <sub>2</sub>	55-105	Argissolo Vermelho-Amarelo Alítico típico (Hapludult)					PVAal	
RS	Cunha et al. (2018a)	Bt <sub>3</sub>	65-80	Argissolo Bruno-Acinentado Alítico típico (Hapludult)					PBACal	
BR	Cunha et al. (2018a)	Bi	60-90	Cambissolo Húmico Alítico típico (Humudepts)					CHal	
CB	Cunha et al. (2018a)	Bw <sub>3</sub>	215-275 <sup>+</sup>	Nitossolo Bruno (Kandiudox)					NB	
Clay <sup>(6)</sup>	TOC <sup>(7)</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K	Al <sup>3+</sup>	S <sup>(9)</sup>	T <sup>(10)</sup>	V <sup>(11)</sup>	m <sup>(12)</sup>	p
----- g kg <sup>-1</sup> -----				----- cmol kg <sup>-1</sup> -----				----- % -----		mg kg <sup>-1</sup>
AC9	346	2.5	17.5	3.6	0.48	13.2	21.6	36.5	59	38
PE	382	36	1.2	3.6	0.12	19.3	5.0	25.5	20	80
RS	414	5.7	8.8	2.9	0.40	6.9	12.1	21.1	57	36
BR	590	5.1		0.38 <sup>(8)</sup>	0.51	5.4	0.9	9.9	9	85
CB	830	5.6	0.16	0.00	0.48	1.74	0.64	8.6	7	74

Note. AC9: collected in Tarauacá in Acre state, Profile 9; PE: collected in Ipojuca, Pernambuco state; RS: collected in Rosário do Sul, Rio Grande do Sul (RS) state; BR: collected in Bom Retiro, Santa Catarina (SC) state; CB: collected in Curitibanos, SC; <sup>(2)</sup> Horizons collected; <sup>(3)</sup> Soil collection layer; <sup>(4,5)</sup> Classified according to the Brazilian Soil Classification System (Embrapa, 2013b); <sup>(6)</sup> Clay fraction below 0.02 mm; <sup>(7)</sup> Total organic carbon; <sup>(8)</sup> Sum of calcium (Ca<sup>2+</sup>) and (Mg<sup>2+</sup>) levels; <sup>(9)</sup> Sum of bases; <sup>(10)</sup> Cation exchange capacity pH 7.0; <sup>(11)</sup> Base saturation and <sup>(12)</sup> Aluminum saturation.

Following collection, soil samples were air-dried in a greenhouse, broken up, ground and sieved in a 4 mm mesh sieve, and incubated separately. Chemical analyses used soil samples sieved in a 2 mm mesh sieve to obtain air-dried fine earth (ADFE). pH in water and in 1.0 mol L<sup>-1</sup> KCl (soil-solvent ratio of 1:2.5); H+Al by

neutralization volumetry, after extraction with calcium acetate buffered at pH 7 and field capacity (FC), according to (Embrapa 2011b). Chemical analyses were conducted with three repetitions and the results are presented in Table 1.

Soil incubation was performed in a greenhouse. Briefly, the treatments consisted of applying four doses of dolomite lime (PRNT = 90%, CaO = 29%, MgO = 19%, granulometry = filler), after sieving each soil in 0.25 mm mesh (Tedesco et al., 1995), corrected for 100% of total relative neutralizing power (TRNP), which is equivalent to that required to neutralize 0, 25, 50 and 100% of H<sup>+</sup>-Al content. Each treatment had four repetitions and the doses were applied and homogenized in 20 kg soil samples (dry base). Next, distilled water was applied to raise 80% moisture to FC and the samples were then added to 100 L plastic bags. The plastic bags (protected by a raffia bag) were closed after adding lime and distilled water (80% FC) to each soil. The soil + plastic bags were weighed every 15 days to determine whether they had lost moisture. Next, they were opened for sample homogenization and oxygenation and, when necessary, to replace lost moisture. This stage was performed every 15 days, and the samples were incubated for 98 days until pH was stabilized.

After soil incubation and fertilization, 8 L pots containing 5.0 kg of each soil were taken to the greenhouse. Soybean was cultivated for 60 days, followed by maize in the same soil for 45 days. The experimental design consisted of random blocks, arranged in a 4 × 5 factorial scheme, involving four doses of lime and five soils, with four repetitions. Seven seeds were sown in each pot, without pre-germination. The plants were cut 21 and 11 days after soybean and maize emergence, respectively, leaving three plants in each pot. The soils were kept at a moisture level of 80% of FC, via daily weighing of pots (subtracting the weight of the plants) and moisture replacement with deionized water.

Soybean plants were collected at the full flowering stage (R2) and maize with six fully developed leaves (V6). The plant shoots (SH) were cut at ground level, placed in paper bags and dried in a forced air oven at 65-70 °C until constant weight to obtain shoot dry weight (SDW). The roots of the two crops were separated from the soils using a 2 mm sieve. Next, they were washed in running water to remove the thickest clumps of soil, dried in a forced air oven at 65-70 °C, for 24 h and weighed to determine root dry weight (RDW). The roots were then dried again and three from each experimental unit of each crop weighed to obtain root dry weight (RDW). Shoot (SDW) and root dry weight (RDW) were summed to obtain total dry weight (TDW) produced by the plants.

The plant tissue was ground and analyzed, as described by Miller (1998). 0.1 g of each sample was weighed in digestion tubes, and 5 mL of nitric acid and 3 mL of hydrogen peroxide were added, and the solution left to settle for one night (pre-digestion). All the samples were digested in a Multiwave 3000 microwave oven (Anton Paar, Graz, Austria), at a temperature of 160 °C and pressure of around 20 Bar, for 40 minutes. The product of digestion was diluted with 30 mL of deionized water.

Ca, Mg, P, K and Al in these samples were quantified in an inductively coupled plasma-atomic emission spectrometer (ICP-OES) (Optima® 8300, Perkin Elmer, USA) and N concentration was determined using steam distillation in a semimicro Kjeldahl unit.

SDW, RDW, TDW and N, P, K, Ca and Mg levels were used to calculate accumulated content (Laviola & Dias, 2008) and the following indices: absorption efficiency (AE) (Swiader et al., 1994); transport efficiency (TE) (Li et al., 1991) and use efficiency (UE) (Siddiqi et al., 1981) of each nutrient in the shoots and roots, in line with the following formulas:

$$N_{macro \text{ and } Al} (\text{mg}) = TDW (\text{mg}) \times \text{Nutrient concentration (\%)} / 100 \quad (1)$$

$$AE (\text{mg nutrient/g RDW}) = N_{ASH} (\text{mg}) + N_{AR} (\text{mg}) / DW_{root} \quad (2)$$

$$TE (\%) = TNC_{ASH} (\text{mg}) \times 100 / TNC_{AP} (\text{mg}) \quad (3)$$

$$UE = (\text{g}^2/\text{mg of accumulated nutrient}) = (TDW)^2 (\text{g}^2) / TNC_{AP} (\text{mg}) \quad (4)$$

where,  $N_{macro \text{ and } Al}$  is the amount of macronutrients and Al accumulated in the plant tissue,  $N_{ASH}$  nutrients accumulated in the shoots,  $N_{AR}$  nutrients accumulated in the roots:  $TNC_{ASH}$  total nutrient content accumulated in the shoots,  $TNC_{AP}$  total nutrient content accumulated in the plants, and  $TDW$  total dry weight. It is important to underscore that these indices were calculated from the data presented in Table 2.

After the roots were separated from each crop, the soils were homogenized and samples weighing approximately 140 g were collected and packed in Styrofoam containers containing ice. Next, they were stored in an ultrafreezer at -80 °C, where they remained until analysis. Subsequently, the same procedures were performed to obtain the ADFE reported previously.

The following chemical attributes were determined in the ADFE: pH in water, pH in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> (1:2.5 soil-solution ratio) and pH in 1 mol L<sup>-1</sup> KCl (1:10 soil-solution ratio) and, according to Tedesco et al. (1995), exchangeable soil Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Al<sup>3+</sup> levels. P, K<sup>+</sup> and Na<sup>+</sup> were extracted using the Melich-1 solution, the first determined by colorimetry (Murphy & Riley, 1962) and the last two by flame photometry.

The soil solution was extracted by weighing 20 g of ADFE in 50 mL polyethylene (Falcon) tubes and then 20 mL of ultrapure water. The samples were agitated in a horizontal device for 15 minutes at 150 rpm, and allowed to rest for 1 hour. Next, they were agitated for five more minutes and centrifuged at 2000 rpm for 30 minutes. pH and electrical conductivity (EC) were measured and Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Al<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and DOC determined. Chemical speciation of the soil solution was estimated using the Visual Minteq program, version 3.1, based on the Minteq A2 program, version 4.0 (Gustafsson, 2016). Further details can be checked in Cunha et al. (2018a, 2018b).

Table 2. Root (RDW) and total dry weight (TDW) and macronutrient and aluminum content in the shoots and roots of maize plants grown in acidic soils

Soil <sup>(1)</sup>	Lime doses <sup>(2)</sup>	RDW	TDW	Nutrient Content							
				Shoot						Root	
				Ca	Mg	N	P	K	Al	Ca	Mg
	t ha <sup>-1</sup> × H+Al	----- g -----							% -----		
AC9	0	4.76	18.04	0.55	0.47	6.68	0.40	13.7	0.04	0.19	0.11
	0.25	3.75	13.97	0.47	0.52	8.34	0.40	15.5	0.04	0.21	0.13
	0.5	4.09	15.63	0.50	0.62	8.40	0.41	20.1	0.05	0.22	0.12
	1.00	5.42	18.15	0.60	0.86	8.79	0.37	22.3	0.05	0.34	0.17
PE	0	0.56	1.59	0.29	0.38	3.79	0.28	2.76	0.07	0.19	0.18
	0.25	1.66	4.03	0.28	0.40	3.81	0.23	3.16	0.05	0.18	0.14
	0.5	2.67	7.13	0.34	0.93	7.45	0.24	8.68	0.74	0.20	0.15
	1.00	3.29	8.65	0.50	0.95	7.69	0.26	11.50	0.07	0.27	0.21
RS	0	4.60	16.61	0.42	0.63	7.32	0.37	10.17	0.05	0.19	0.12
	0.25	5.14	20.52	0.50	0.68	8.01	0.39	10.84	0.09	0.20	0.14
	0.5	4.96	21.84	0.50	0.79	7.36	0.31	12.03	0.03	0.22	0.15
	1.00	5.24	17.75	0.78	1.06	7.44	0.33	13.41	0.04	0.39	0.28
BR	0	0.30	0.94	0.21	0.08	4.03	0.26	2.37	0.03	0.11	0.03
	0.25	3.28	10.94	0.35	0.56	8.21	0.32	11.73	0.08	0.20	0.11
	0.5	3.97	14.32	0.54	0.97	8.74	0.34	12.46	0.06	0.22	0.13
	1.00	4.76	15.51	0.86	1.26	7.34	0.29	11.83	0.06	0.31	0.22
CB	0	1.83	5.13	0.25	0.45	3.51	0.32	3.08	0.02	0.18	0.04
	0.25	4.34	11.89	0.51	0.58	7.33	0.38	12.78	0.10	0.19	0.07
	0.5	4.79	14.03	0.47	0.80	6.82	0.32	14.07	0.05	0.24	0.11
	1.00	4.02	10.17	0.59	0.96	5.47	0.26	14.49	0.07	0.39	0.22

Note. <sup>(1)</sup>AC9: collected in Tarauacá, Acre state; Profile 9; PE: collected in Ipojuca, Pernambuco state; RS: collected in Rosário do Sul, Rio Grande do Sul state; BR: collected in Bom Retiro, Santa Catarina (SC) state; CB: collected in Curitibanos, SC; <sup>(2)</sup>Lime doses applied to the soils.

## 2.1 Soybean and Maize Plant Properties

Soybean (BRS 232): 88% seed germination, semi-premature, moderately sensitive to the presence of aluminum in the soil, determinate growth and high yield potential, indicated for South and Southeastern Brazil.

Maize (30F53YHR hybrid): 100% seed germination, premature, moderately sensitive to the presence of aluminum in the soil, high yield potential, highly adaptable and good response to crop management, recommended for several Brazilian regions.

## 2.2 Statistical Analysis

Data related to TDW, efficiencies (AE, TE and UE) and nutrient accumulation in maize plants with lime doses applied to soils were submitted to analysis of variance (F-test) using SISVAR 5.6 software (Ferreira, 2014). When there was a significant effect, Tukey's test was applied to the "soil types" factor. The regression test was applied to the "lime doses" factor, both at 5% error probability. For each evaluated factor was included the unfolding of limestone doses in each of the soil types.

It is important to underscore that due to the similar results for soil chemical analysis and curve behavior in terms of absorption efficiency, transport, use and accumulation after the soybean and maize cultivation, only results of the second crop will be presented.

## 3. Results and Discussion

### 3.1 Soil Chemical Properties

As expected, liming increased soil pH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , S and V% levels and reduced  $\text{Al}^{3+}$  and H+Al and  $\text{Al}^{3+}$  saturation in all the soils (Table 3). However,  $\text{Al}^{3+}$  was not completely neutralized in AC9 and PE soil samples with the dose used (100% of H+Al content). The incomplete  $\text{Al}^{3+}$  neutralization in these two soils may have occurred due to underestimation of potential acidity by calcium acetate, since other Al fractions may not have been computed in H+Al, resulting in incorrect estimation of lime requirements (Kaminski et al., 2002; Júnior et al., 2015). It could also be related to the lime not neutralizing other forms of Al, which may have been extracted by the KCl solution and computed as exchangeable after base titration.

Table 3. Soil chemical properties after lime application in samples collected after maize cultivation in a greenhouse

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

Note. <sup>(1)</sup>AC9: collected in Tarauacá, Acre state; Profile 9; PE: collected in Ipojuca, Pernambuco state; RS: collected in Rosário do Sul, Rio Grande do Sul state; BR: collected in Bom Retiro, Santa Catarina (SC) state; CB: collected in Curitibanos, SC; <sup>(2)</sup> Lime doses applied to the soils; <sup>(3)</sup> Delta pH (pH KCl-pH water); <sup>(4)</sup> Sum of the bases; <sup>(5)</sup> Cation exchange capacity pH7; <sup>(6)</sup> Effective cation exchange capacity; <sup>(7)</sup> Base saturation; <sup>(8)</sup> Aluminum saturation.

The 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 soils AC9 (3.1 cmol<sub>c</sub> kg<sup>-1</sup>) and PE (1.4 cmol<sub>c</sub> kg<sup>-1</sup>) even at the highest dose. Al saturation decreased in all soils with increasing limestone doses (Table 3). In an earlier study, using the same soils as the present investigation, Cunha et al. (2014, 2015) suggest that part of the Al-KCl does not represent the

exchangeable forms of Al, since the high concentration of KCl (1.0 mol L<sup>-1</sup>) may hydrolyze some of the non-exchangeable forms of Al, possibly originating in the amorphous compounds of these soils, overestimating its exchangeable content and, in turn, Al saturation (Table 3). Overestimating Al-KCl may mask Al toxicity to plants, since the amount of Al extracted and quantified may be greater than the actual aluminum toxicity in roots (Ebeling et al., 2008; Bernini et al., 2013; Cunha et al., 2018a, 2018b). The P levels in AC9, PE, RS and BR soils after cultivation were very high (Table 3), which may partially decrease plant response to lime application (Ernani et al., 2000).

All the soils exhibited a net negative charge, indicated by the ΔpH values. The pH values in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> and 1 mol L<sup>-1</sup> KCl were always lower than those obtained by pH in water, even with the increase in lime doses. There were no changes in K<sup>+</sup> and Na<sup>+</sup> content with the application of lime doses or significant alterations in CEC at pH 7, which was expected because the increase in Ca<sup>2+</sup> and Mg<sup>2+</sup> should be stoichiometrically similar to the decline in H+Al. The P levels in AC9, PE, RS and BR soils in samples collected after the maize harvest were very high. An exception occurred in CB soil, in which the exchangeable levels of this element were low (Table 3).

Although exchangeable Al (Al-KCl) in AC9 and RS soils was high, base saturation was above 50%. Al saturation in these soils was greater than 30% (Table 3), which would normally be toxic to plants (Smyth and Cravo, 1992; Hashimoto et al., 2010), but fell below 30% after the first lime dose, suggesting that plants may no longer exhibit Al toxicity (Wadt, 2002). In the other soils (PE, BR and CB) liming increased base saturation, reaching values above 50% with the second dose (50% of H+Al), and Al saturation declined to less than 30%, except in PE soil (Table 3). This seems to indicate that after this dose, even high levels of Al-KCl may no longer have a toxic effect.

### *3.2 Efficiency in Nutrient and Al Absorption, Transport, Use and Accumulation in Plants*

The order of absorption (Figure 1), transport (data not shown), use (Figure 2) and subsequent accumulation (Figure 3) of N, P, K, Ca, Mg changed according to their availability and increased levels in the soil solution with the application of lime and, primarily, plants' need of these nutrients to produce SDW, RDW and TDW (Table 2).

The macronutrient content in leaves, stems and roots obtained from maize plants cultivated in AC9, PE, RS, BR and CB soils was also influenced by liming and always remained at normal levels for these crops, according to Tedesco et al. (1995) and Silva et al. (2009).

Similar behavior occurred with Al, but, as expected, the highest concentrations of this element were found in the roots compared to the shoots. However, applying lime doses reduced levels of this element in the shoots and particularly the roots (Table 2).

The AE, TE, UE indices and nutrient accumulation in maize plant tissues (NA<sub>MP</sub>) exhibited quadratic adjustment and high correlation with lime doses in most soils, regardless of the doses applied. In general, the following decreasing order was found for the indices (efficiencies): AE: K > N > Ca > Mg > P > Al; TE: K > N > Mg > Ca > P > Al and UE: Mg > Al > P > Ca > N > K and for accumulated nutrients: K > N > P > Ca > Mg < Al.

K was the nutrient most absorbed (Figure 1), transported (data not shown) and accumulated (Figure 2) by maize plants, followed by N, but both were influenced by liming, as observed by Castro et al. (2015). Liming increased plant N and K absorption and accumulation in all the soils, and was more pronounced in the second dose, similar to that of the first and declining with the maximum dose used. Concomitantly, the first two doses showed a decline in transport and use of these nutrients for DW production. This decrease may have occurred due to the accumulation of these nutrients in maize plant tissues (NA<sub>MP</sub>) (Figure 2), which was higher in CB soil (Figure 2e). This interpretation is supported by Riedell (2010), Zoca et al. (2014), and Liu et al. (2017).

The decline of these nutrients (N and K) in the plant tissues assessed may also be related to increased availability of Ca<sup>2+</sup> and Mg<sup>2+</sup> in all the soils with a rise in lime doses (Salvador et al., 2011; Ertiftik & Zengin, 2017). With liming, both absorption (Figure 1) and transport (data not shown) of Ca and, to a lesser extent, Mg, increased, in addition to raising NA<sub>MP</sub> cultivated in PE, RS, BR and CB soils (Figure 3). The greater accumulation of Ca in plants is related to the non-redistribution of this nutrient after absorption by the roots and translocation to the shoots, due to its low mobility (Hepler, 2005; Horst et al., 2010; Lima et al., 2011). The lower accumulation of Mg may be related to its greater use (Figure 3) for TDW conversion in these plants (Gransee & Fürs, 2012). Moreover, it is plausible that this decline may have occurred due to the dilution of these nutrients in the plant tissues, as observed by Riedell (2010), Junio et al. (2013) and Martins et al. (2017). However, in the case of AC9, liming had no influence on the K supply to plants, as reported by Caires and Fonseca (2000).

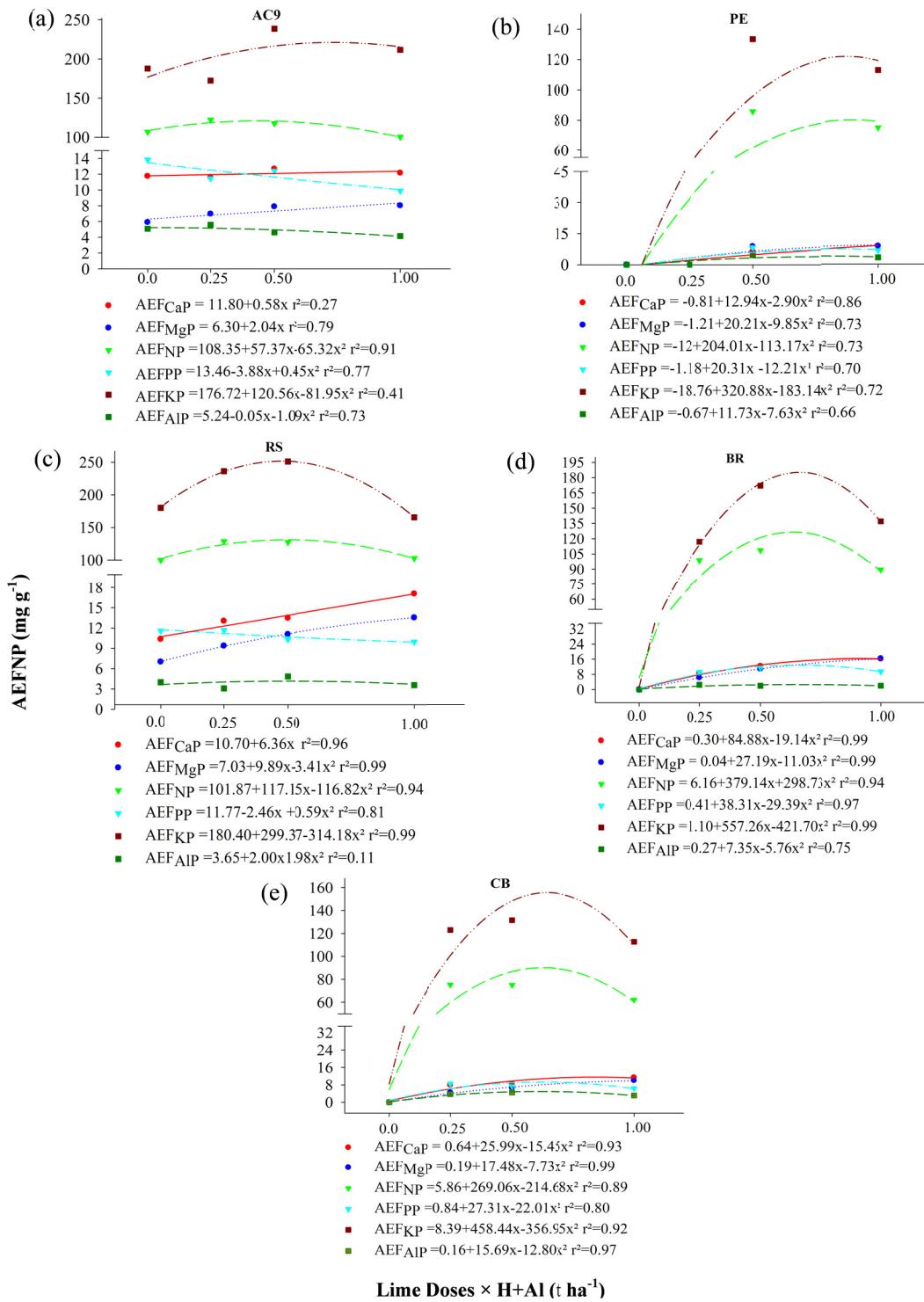


Figure 1. Relation between the nutrient absorption efficiency of maize plants (AEFNP) with soil lime doses from  
a) Acre (AC9); b) Pernambuco (PE); c) Rosário do Sul (RS); d) Bom Retiro (BR) and Curitibanos (CB)

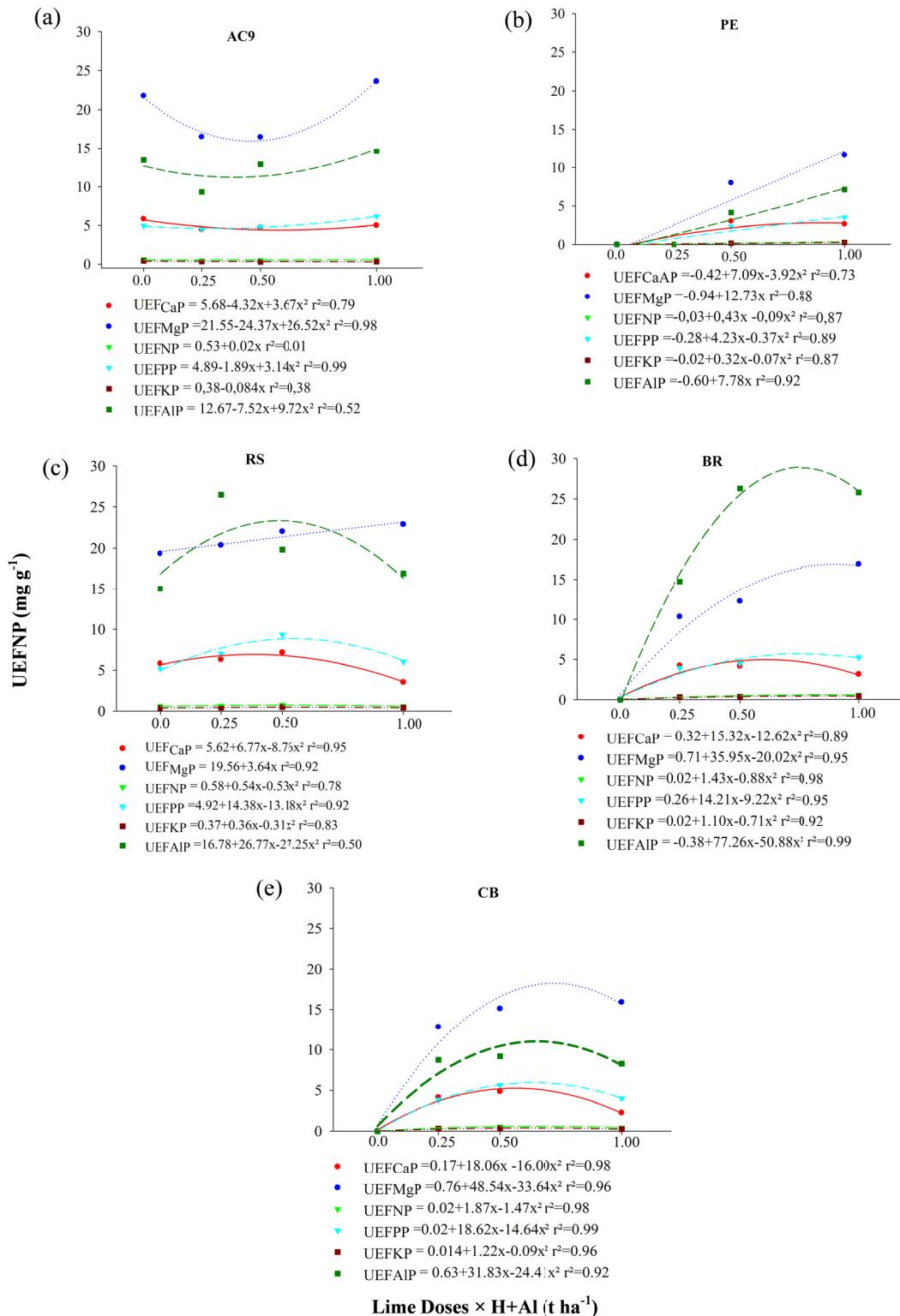


Figure 2. Relation between efficiency of nutrient use by maize plants (UEFNP) with soil lime doses from a) Acre (AC9); b) Pernambuco (PE); c) Rosário do Sul (RS); d) Bom Retiro (BR) and Curitibanos (CB)

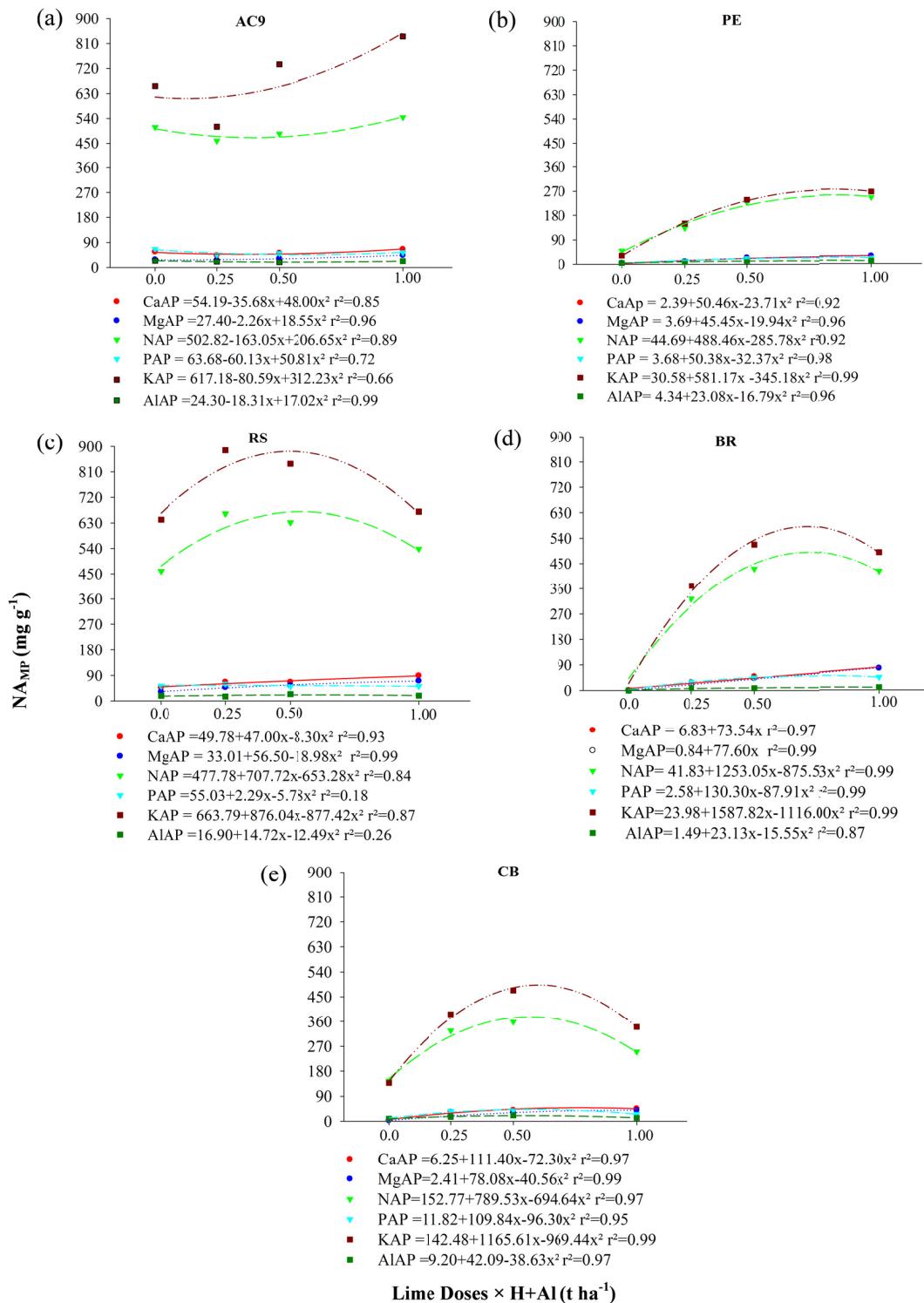


Figure 3. Relation between nutrient accumulation in maize plant tissues (NAT<sub>MP</sub>) with soil lime doses from a) Acre (AC9); b) Pernambuco (PE); c) Rosário do Sul (RS); d) Bom Retiro (BR) and Curitibanos (CB)

In general, the order of absorption (Figure 1), transport (data not shown), use (Figure 3) and subsequent accumulation (Figure 2) of Ca and Mg changes according to their increased availability in the soil (Table 3) with liming (Joris et al., 2013), primarily with plants' need for these nutrients in SDW, RDW and TDW production (Table 2). With a rise in lime doses, regardless of the soil in which the plants were grown, the levels of these absorbed (Figure 1), transported (data not shown), and accumulated nutrients also increased (Figure 3). The greater accumulation of Ca is related to the non-redistribution of this nutrient inside the plant after absorption by

the roots and translocation to the shoots, because of its low mobility (Horst et al., 2010; Szczepaniak et al., 2016).

P was the fifth most absorbed nutrient (Figure 1) and transported (data not shown), the third most used (Figure 2) and accumulated (Figure 3) in the PA of maize plants. The liming associated to the fertilization provided the supply of P to the evaluated plants due to the increase of the pH of the soils (Table 3), making it more available in the solution of the soils facilitating the absorption of the same by the plants (Opala, 2017; Cunha et al., 2018a, b). The absorption of this nutrient, according to Tomaz et al. (2009), depends on the morphological and physiological characteristics of the roots, however, their importance in the absorption process depends on the root access to the nutrient. When there is no limitation on the arrival of the ion at the root surface, the physiological factors are more important than the morphological ones regarding nutrient absorption (Delhaize et al., 2007; Balemi & Negisho, 2012).

Al was the least absorbed (Figure 1), transported (data not shown) and accumulated (Figure 3) by maize plants. However, this element was the most used (Figure 2) for TDW production (Table 2). For this reason, the use efficiency index is not suitable/indicated for Al, since TDW production is considered to calculate it (Table 2) and this rises with liming in relation to total Al content in the plant (low levels found mainly in the shoot), meaning this index may not accurately reflect reality. The lower UE of N, K, Ca and P (Figure 2), primarily by maize plants, may be related to their higher absorption (Fernandes & Soratto, 2013; Zoca et al., 2014) by these crops, since, according to Silva et al. (2002), as plant nutrient concentration rises, the EU index declines due to the growing nutrient accumulation, which is proportionally higher than the plant DW.

### 3.3 Aluminum × Absorption, Transport, Use and Nutrient Accumulation in Maize Plants

The absorption, transport, use and subsequent nutrient accumulation by maize plants was not influenced directly by the aluminum present in both the solid (Table 3) and liquid phase (Table 4) in two of the five soils. This behavior was observed in AC9 and RS soils, where in treatments without lime, plants exhibited good nutrient use (Figures 1, 2 and 3). This occurred even at low pH values and high  $\text{Al}^{3+}$  content in the solid phase (Table 3), with the exception of PE, BR and CB soils, where the presence of  $\text{Al}^{3+}$  in the solution had a direct influence on nutrient dynamics, evidenced by the low amounts absorbed, transported (data not shown), used and accumulated by plants cultivated in these soils compared to those grown in AC9 and RS. However, the application of lime doses, particularly the first two (25 and 50% of H+Al), enhanced the use of all the nutrients available in the solution by the plants cultivated in all the soils (Figures 1, 2 and 3).

The non-influence of Al on the dynamics of the nutrients available in the present study may be directly related to the rise in basic cations (primarily  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and the sum of bases in both the liquid and solid phase, as well as the other nutrients with an increase in lime doses in all the soils (Tables 3 and 4). When the cation and sum of bases concentrations are higher than those of Al and the sum of toxic aluminum species in the soil solution ( $\Delta\text{SFTAI}$ ), the presence of this element may cause little or no harm to plants. This interpretation is corroborated by the results obtained in plants grown in AC9 and RS soils (Figures 1, 2 and 3) and by studies conducted by Caires et al. (2013), Rutkowska et al. (2015) and Cunha et al. (2018a, 2018b). In PE, BR and CB soils,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  concentration and sum of bases exceeded that of  $\text{Al}^{3+}$  in the soil solution, primarily in treatments without lime (Table 4). In these conditions,  $\text{Al}^{3+}$  is not expected to be toxic to plants or interfere in the dynamics of nutrients in plants grown in these soils. However,  $\text{Al}^{3+}$  compromised root growth in the plants assessed (data not shown), as well as nutrient absorption (Figures 1b, 1d and 1e, respectively), transport (data not shown), use (Figures 2b, 2d and 2e, respectively) and subsequent accumulation (Figures 3b, 3d and 3e, respectively) of nutrients in the tissues of plants cultivated in these soils, particularly in treatments without lime. This interference may be explained by the high concentration of toxic  $\text{Al}^{3+}$  species and  $\Delta\text{SFTAI}$  in the solution of these soils, far above (except in the CB soil) the critical values ( $24-27 \mu\text{mol L}^{-1}$ ) that Diatloff et al. (1998) consider toxic. In the CB soil, although the  $\Delta\text{SFTAI}$  was lower than the aforementioned critical threshold, the presence of Al and its toxic species compromised plant development and nutrient use (Figures 1, 2 and 3).

Table 4. Chemical composition and toxic Al species activity in the soil solution

Soil <sup>(1)</sup>	H <sup>(2)</sup>	D. C. <sup>(3)</sup>	Composition of the Soil Solution							AETAI <sup>(6)</sup> in the Soil Solution				
			Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	S <sup>(4)</sup>	Al <sup>3+</sup>	P	m × cations <sup>(5)</sup>	Al <sup>3+</sup>	AlOH <sup>2+</sup>	Al(OH) <sub>2</sub> <sup>+</sup>	AΣFTAI <sup>(7)</sup>
AC9	Bt <sub>2</sub>	0	0.99	0.33	0.12	0	1.4	0.013	0.09	1.0	7.93	2.3	0.4	10.63
		0.25	0.90	0.36	0.13	0	1.3	0.011	0.11	0.8	2.31	3.4	3.2	8.91
		0.5	0.90	0.40	0.10	0	0.9	0.007	0.09	0.4	0.91	2.0	2.7	5.61
		1	0.89	0.48	0.11	0	0.8	0.006	0.24	0.2	0.24	1.0	2.6	3.84
PE	Bt <sub>2</sub>	0	0.19	0.38	0.34	0.01	0.8	0.048	0.13	6.6	33.4	7.7	1.0	42.1
		0.25	1.10	1.27	0.38	0.01	0.8	0.013	0.19	1.7	6.0	2.9	0.9	9.8
		0.5	0.93	1.06	0.24	0.01	0.9	0.005	0.35	0.8	0.8	1.0	0.9	2.7
		1	1.75	1.84	0.20	0	1.1	0.001	0.36	0.2	0.0	0.1	0.2	0.3
RS	Bt <sub>3</sub>	0	0.91	0.42	0.15	0	0.8	0.008	0.14	0.9	2.48	2.1	1.0	5.66
		0.25	1.41	0.69	0.17	0	0.7	0.002	0.13	0.4	0.44	0.7	0.7	1.84
		0.5	1.65	0.80	0.10	0	0.8	0.002	0.13	0.4	0.10	0.4	1.0	1.5
		1	2.84	2.07	0.21	0	1.4	0.000	0.19	0.1	0.00	0.0	0.1	0.1
BR	B <sub>i</sub>	0	0.12	0.08	0.16	0	0.3	0.043	0.12	13.9	20.21	10.3	3.0	33.51
		0.25	0.60	0.35	0.13	0	0.6	0.011	0.10	1.4	3.57	5.1	4.8	13.47
		0.5	0.63	0.50	0.11	0	0.6	0.005	0.17	0.5	0.25	1.0	2.3	3.55
		1	1.71	1.60	0.10	0	1.0	0.003	0.23	0.1	0.03	0.3	1.3	1.63
CB	Bw <sub>3</sub>	0	0.10	0.03	0.25	0	0.3	0.013	0.06	4.0	6.50	2.9	0.7	10.1
		0.25	1.16	0.50	0.29	0	0.6	0.005	0.25	0.8	1.95	3.6	4.4	9.95
		0.5	1.17	0.72	0.20	0	0.7	0.004	0.17	0.3	0.16	0.7	1.8	2.66
		1	2.52	2.26	0.28	0	1.2	0.002	0.19	0.1	0.02	0.2	0.8	1.02

Note. <sup>(1)</sup> AC9: collected in Tarauacá, Acre state; Profile 9; PE: collected in Ipojuca, Pernambuco state; RS: collected in Rosário do Sul, Rio Grande do Sul state; BR: collected in Bom Retiro, Santa Catarina (SC) state; CB: collected in Curitibanos, SC; <sup>(2)</sup> Soil collection layer; <sup>(3)</sup> lime doses applied to the soils; <sup>(4)</sup> Sum of the bases; <sup>(5)</sup> Aluminum fraction in relation to all the cations in the soil solution; <sup>(6)</sup> Activity of toxic Al species in the soil solution; <sup>(7)</sup> Sum of toxic Al species in the soil solution.

Cunha et al. (2018b) assessed chemical species activity of all the cations and anions present in the soil solutions and crops. The authors reported that for these soils (PE, BR and CB) the high AΣFTAI in the solution was controlled by the amorphous polymers from hydroxy-interlayered vermiculite (HIV) and hydroxy-interlayered smectite (HIS), which maintained the balance of this chemical species of Al<sup>3+</sup> in the solution and its toxic potential to plants, as reported by Dahlgren and Walker (1993), even with high basic cation activity in the soil solutions (Table 3).

The use of these nutrients by plants with a rise in lime doses is directly related to the increased sum of bases in the solid and liquid phase with a decline in the chemical species of Al and AΣFTAI in the soil solutions (Tables 2 and 3). This use is particularly evident in the first two lime doses (Figures 1, 2 and 3), possibly because of the rise in basic cation concentration and their activity (Cunha et al., 2018b) in the solution that exceeds the concentration of Al species and activity of this element in the solution (Table 3).

It is important to underscore that Al inactivation in the soil solution may also be related to the levels available and P concentration in the soil solution studied. In field conditions, Nolla and Anghinoni (2006) observed that high phosphate levels displaced organic exchange anions via the mass action mechanism in typical dystrophic Red Latosol (pH = 4.0 and Al = 3.22 cmol<sub>c</sub> kg<sup>-1</sup>), thereby reducing the Al in solution by forming organic complexes with Al. Nolla et al. (2013) also observed a decline in Al toxicity with P application, which provided better soybean root development. The authors concluded that Al phosphate formed from the release of organic acids capable of complexing the Al present in the soil solution under high acidity conditions. Ernani et al. (2000) assessed the lime/phosphate ratio and found that the highest P doses in liming did not affect maize yield. For these reasons, levels of this element available in soils are jointly indicated as the criterion for calculating lime requirements (CQFSRS/SC, 2016). These results are supported by the studies developed by Rutkowska et al. (2015), De Conti et al. (2017), and Cunha et al. (2018a, 2018b).

Another important point to consider regarding the manifestation or not of Al toxicity to plants is the exchangeable Ca/Al ratio of soils, in addition to chemical composition assessment, chemical spetiation and the activity of toxic aluminum species in solution. In AC9 and RS soils in which little or no response to liming occurred, the ratio between these two exchangeable cations after cultivation was 1.32 and 1.28, respectively. In

other words, in this condition, Al would not be toxic to plants, because they were below the critical limit (0.42 and 0.48) reported by Smyth and Cravo (1992) and Gama and Kiehl (1999). For PE, BR and CB soils, the lowest lime dose (25% of H+Al) was enough to make the Ca/Al ratio greater than or equal to the critical level proposed by the aforementioned authors. Given the results of this study, lime application increases nutrient availability in the soil solution, in addition to reducing exchangeable Al levels, concentration and activity, favoring its absorption, transport, use and accumulation, providing good nutrition to the plants under study. However, it is important to underscore that the efficiency indices and nutrient accumulation were higher, primarily with the use of the first two lime doses (25 and 50% of H+Al). This occurred even though the exchangeable Al levels in most of the soils were above  $4 \text{ cmol}_c \text{ kg}^{-1}$  and saturation was more than 30%, indicative of aluminum toxicity. This seems to suggest that at these and higher doses, Al-KCl may no longer exert a toxic effect. Thus, the exchangeable Al method should be viewed with caution and in conjunction with the other nutrients, since their levels are used to calculate the degree of Al saturation and liming, thereby overestimating lime doses and the cost of implementing crops, with no return on plant yield.

#### 4. Conclusions

The Al-KCl did not affect nutrient absorption, transport, use and accumulation in the tissues of maize plants cultivated in AC9 and RS soils. However, it did interfere in plants grown in PE, BR and CB soils. The plants made good use of the nutrients dissolved in solution with the first two doses (25 and 50% of H+Al).

The absence of Al toxicity is related to an increase in concentration, basic cation activity and P availability in the soil solution, which, taken together, decreased Al activity in the solution, inactivating it and making the element non-toxic to the maize plants.

In soils with a high Ca/Al or Ca+Mg/Al ratio (AC9 and RS, respectively), Al activity in the solution is low, even when absolute Al-KCl levels are high, and may not be toxic to maize plants. On the other hand, in soils (PE, BR and CB) where this ratio is lower than that of Al in solution, Al activity is high and toxic to maize plants.

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