Composition, chemical speciation and activity of ions in the solution of Brazilian acid soils

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ABSTRACT: The knowledge of the chemical composition of the soil solution through chemical speciation is important for the monitoring of nutrient availability, soil fertility management and plant nutrition. The objective of this study was to evaluate the chemical composition and activity of Al, cations and anions by chemical speciation in solution of some Brazilian acid soils (AC, PE, RS and SC) submitted to liming and cultivated with soybean and maize plants. In addition, to identify the chemical elements responsible for the reduction of Al activity in the solution and its toxicity to plants. The predominant aluminum, calcium, magnesium, potassium, sulfate, chloride and nitrate species in all soils were: Ca^{2+} and Mg^{2+}, K^+, SO_4^{2-}, Cl^- and NO_3^- in all soils. In the treatments without limestone in the soils AC9, RS and CB predominated the species of P $H_2PO_4^-$ and in the soils PE and BR was the $AlHPO_4^+$. However, with liming the P form that predominated in all soils was $H_2PO_4^-$ and, to a lesser extent, HPO_4^{2-}. The activity of the Ca^{2+} and Mg^{2+} ions was the main responsible for the neutralization of the toxic effects of Al^{3+} in the evaluated plants.

Key words: anions; dolomitic limestone; cations; complexes; plants

Composição, especiação química e atividade de íons na solução de solos ácidos brasileiros

RESUMO: O conhecimento da composição química da solução do solo, por meio da especiação química, é importante para o acompanhamento da disponibilidade de nutrientes para o manejo da fertilidade do solo e da nutrição de plantas. O estudo objetivou avaliar a composição química e a atividade do Al, dos cátions e dos ânions, por meio da especiação química, na solução de alguns solos ácidos brasileiros (AC, PE, RS e SC) submetidos à calagem e cultivados com plantas de soja e milho. Além disso, identificar os elementos químicos responsáveis pela redução da atividade do Al na solução e sua toxidez às plantas. As espécies químicas de alumínio, cálcio, magnésio, potássio, sulfato, cloreto e nitrato predominantes em maiores proporções em todos os solos foram: Al^{3+}, Ca^{2+} e Mg^{2+}, K^+, SO_4^{2-}, Cl^- e NO_3^-. Nos tratamentos sem calcário nos solos AC9, RS e CB predominou a espécie de P $H_2PO_4^-$ e nos solos PE e BR foi a $AlHPO_4^+$. Porém, com a calagem a forma de P que predominou em todos os solos foi a $H_2PO_4^-$ e, em menor proporção, a HPO_4^{2-}. A atividade dos íons Ca^{2+} e Mg^{2+} foi a principal responsável pela neutralização dos efeitos tóxicos do Al^{3+} nas plantas avaliadas.

Palavras-chave: ânions; calcário dolomítico; cátions; complexos; plantas

Introduction

Brazilian soils are mostly weathered and acidic with high Al and Mn contents, low Ca^{2+}, Mg^{2+} content, and low sum and saturation of bases. Phosphorus is the most limited nutrient, mainly in the subsurface horizon (B). There characteristics are undesirable for the good development of the main agricultural crops (Miguel et al., 2010). In this context, it is important to know the chemical composition of soil solutions through chemical speciation; this information contributes to the understanding of physical and chemical changes to aid in the monitoring of nutrient availability and for management of the environment, soil fertility, and plant nutrition, because it is in the soil that the main chemical reactions occur and nutrients are dissolved in the solution and absorbed by the plants (Souza et al., 2013; Francisco et al., 2016).

The quantification of nutrients in the soil solution through chemical speciation, especially in limestone areas, allows the understanding of the nutrient mobility and availability as well as phytotoxicity of metals (Krishnamurtiand & Naidu, 2002). Speciation includes free ions, complex ions, ion pairs and chelates in solution. The use of computer softwares such as Minteq A2 algorithm facilitates the production of these forms by rapidly providing estimates of the species and the respective ion activity in the soil solution (Rutkowska et al., 2015; De Conti et al., 2017). They simultaneously consider the various chemical equilibria involved in the reactions responsible for the formation of complexes, and solid dissolution and precipitation, calculating activity coefficients and the distribution of the free species, as well as their complexes and precipitates (Rossiello & Netto, 2006).

Although knowledge of the chemical composition of the soil solution is important, this has only been determined in scientific studies due to methodological difficulties (Cancés et al., 2003). This difficulty arises from changes in the chemical composition of ions in the solution as a function of the acid-base balance, ionic complexation, precipitation and dissolution of oxides, oxidation, reduction and exchange of cations, time of the year, soil moisture, variation between the equilibrium existing between the components of the solution and the other phases of the soil, as well as their interaction with the soil, with microfauna and microflora that alter their composition along the soil profile (Zambrosi et al., 2008; Gloaguen et al., 2009). In addition to these factors, the liming used to correct soil acidity also influences the composition of the soil solution due to the rapid equilibrium of the solid with the liquid phase, changing the dynamics of ions in solution (Spera et al., 2014). Therefore, it is necessary to choose the method of extraction from the soil solution that is close to that found under field conditions (Nolla et al., 2015). Several methods are used to simulate the soil solution but the most used are displacement, centrifugation, soil saturation paste, porous extractive capsules and aqueous extracts in different soil:water relations (Souza et al., 2013; Somavilla et al., 2017). The latter, is used to obtain a greater amount of extract for the determination of elements in the solution (Zambrosi et al., 2008).

The objective of this study was to evaluate the chemical composition and activity of Al, cations and anions, by chemical speciation and identify the chemical elements responsible for the reduction of Al activity in the solution of some Brazilian acid soils subjected to liming and used for soybean and maize cultivation in greenhouse conditions.

Material and Methods

Soil selection

The study was carried out with samples of the subsurface horizon (B) of five soils collected in areas never cultivated and most had Al-KCl contents higher than 4 $cmol_c$ kg^{-1}. Samples of the B horizon were used because of the lower organic matter (OM) in this horizon in relation to the surface horizon. This was done because OM could influence the results due to the formation of organic complexes with aluminum. Based on the mineralogical and chemical differences, we had two groups of soils: smectite with high levels of exchangeable Al^{3+}, Ca^{2+} and Mg^{2+}, whose representatives are AC9 (PVAal), from the state of Acre, and RS (PBACal), from Rio Grande do Sul (RS); smectite with kaolinite containing high aluminum content and low interchangeable Ca^{2+} and Mg^{2+} content, whose representatives are PE (PVAal), from the state of Pernambuco (PE), and BR (CHal), from Santa Catarina (SC). We also used another soil from the state of Santa Catarina: CB (NB). This was used as a reference because it is a more weathered soil, with essentially kaolinite mineralogy and lower Al-KCl, interchangeable Ca^{2+} and Mg^{2+} contents than the others.

The soil samples were collected in the same sites where the respective complete profiles had already been previously described, whose results are already published (Table 1). The mineralogical characteristics of these soils are: in AC9, there is a predominance of smectite (88%) with low amounts of kaolinite-smectite interlayer (6%) and mica-illite interlayer (6%); in PE, there is a predominance of smectite (60%) with relatively high amounts of kaolinite (40%); in RS, there is a predominance of smectite with low illite and kaolinite content; in BR, there is a predominance of kaolinite (51%), with relatively high amounts of smectite and vermiculite with interlayered hydroxy polymers (47%) (EHE and HEV, respectively) and low mica-illite interlayer content (2%); and in CB, there is a predominance of kaolinite (94%), but there is 6% of EHE. Further details on soils can be obtained from Cunha et al. (2014).

Sample preparation and analysis prior to incubation of soils with limestone

The soil samples were air-dried in greenhouse conditions, buffered, milled and sifted through a 4-mm mesh sieve and then separately incubated. Soil samples sifted through a 2-mm mesh sieve were used for the chemical analyses. The following data were evaluated: pH values in water and in KCl 1.0 mol L^{-1} in a soil-solvent ratio of 1:2.5; H+Al through

Table 1. Classification, and chemical and physical attributes of the profiles of acid soils collected in different Brazilian regions.

Soil[1]	Source	H[2]	Depth[3] (cm)	Classification	Symb.[4]	pH Water	pH KCl	H + Al (cmol$_c$ kg^{-1})
						1:1		
AC9	Anjos et al. (2013) Cunha (2017)	Bt$_2$	60-102	Argissolo Vermelho-Amarelo Alítico luvissólico (Hapludult)	PVAal	5.42	3.60	14.73
PE	Embrapa (2011a)	Bt$_2$	55-105	Argissolo Vermelho-Amarelo Alítico típico (Hapludult)	PVAal	5.03	3.80	18.43
RS	Cunha et al. (2015)	Bt$_3$	65-80	Argissolo Bruno-Acinzentado Alítico típico (Hapludult)	PBACal	5.24	3.77	8.80
BR	Almeida et al. (2013)	Bi	60-90	Cambissolo Húmico Alítico típico (Humudepts)	CHal	4.73	3.76	9.87
CB	Almeida et al. (2003)	Bw$_3$	215-275$^+$	Nitossolo Bruno Distroférrico típico (Kandiudox)	NB	4.89	4.11	6.53

[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, Santa Catarina; CB; collected in Curitibanos, Santa Catarina; [2]Horizons collected; [3]Soil collection layer; [4]Classification according to the Brazilian System of Soil Classification (Embrapa, 2013b).

titration of neutralization, after extraction with calcium acetate buffer (pH 7) and the field capacity (Embrapa, 2011b), determined in a tension table after using a voltage equivalent to a water column of 100 cm (1 kPa) on the saturated sample. Chemical analyses were performed with three replicates and the results are presented in Table 1.

Soil incubation

The treatments consisted of the application of four doses of dolomitic limestone in each soil, corrected to 100% Relative Total Neutralizing Power (RTNP) that were equivalent to the necessary to neutralize the H+Al contents by 0; 0.25; 0.50 and 1.00-fold. Each treatment had four replicates and the doses were applied and homogenized in 20 kg soil samples (dry basis). Then, distilled water was applied to raise the FC of the soils up to 80%. Subsequently, the samples were placed in 100 L plastic bags, revolved every 15 days, and incubated for 98 days until the pH values were stabilized.

Soybean and maize crops

After incubation, the soil samples were again sifted through 4-mm mesh sieves again and 20 kg of each treatment that constituted the four replicates were fertilized with N, P and K from, respectively, urea, triple superphosphate (TSF) and potassium chloride (KCl). In soybean cultivation, 1.08 g kg^{-1} of N, 2.48 g kg^{-1} of P$_2$O$_5$ and 0,99 g kg^{-1} of K$_2$O were applied; in maize cultivation, 0.99 g kg^{-1} of N, 2.48 g kg^{-1} of P$_2$O$_5$ and 1.98 g kg^{-1} of K$_2$O were applied.

NPK fertilization was recommended by the Soil Chemistry and Fertility Committee of the states of Rio Grande do Sul and Santa Catarina (CQFS-RS/SC, 2004) in the case of soybean and maize crops, based on the results of published works (Table 1) whose goal was a productivity of, respectively, 3 and 8 t ha^{-1} of grains. After the incubation period the fertilizers were mixed in the soils.

Cultures were conducted in greenhouse conditions in 2015 in 8 L pots containing 5.0 kg of soil (dry basis). Soybean was grown for 60 days. Then, in the same soil, maize was cultivated for 45 days. This study will present the results obtained in maize cultivation because they were similar to those observed in soybean cultivation. The experiment used a randomized block design organized in a "4 x 5" factorial scheme, with four limestone doses and five soils, with four replications. Seven seeds were seeded in each vessel, without pre-germination. Plants were cut 21 days after emergence of soybean and 11 of maize, leaving three plants per pot. The soils were maintained with humidity close to 80% of the FC, through daily weighing of the vessels and replacement of moisture with deionized water. The masses corresponding to the growth of the plants of each culture were discounted for replacement of water.

At the end of the cultivation, the shoot of the plants were cut close to the soil surface. The roots were manually separated from the soil and then washed with distilled water. The samples were dried in a forced air oven until constant weight. The total dry matter yield was calculated. Approximately 140 g of soil were collected and packed in a styrofoam container containing ice. Then, they were stored in a ultra-freezer at -80°C where they remained frozen until analysis. This procedure was used to avoid biological degradation of the organic compounds. Subsequently, soil samples were air dried and sifted through a 2-mm mesh sieve to obtain the air-dried fine earth (ADFE).

Soil solution extraction

To extract the soil solution, an extract of soil:solution was obtained at a ration of 1:1 by weighing 20 g of ADFE and adding 20 mL of ultrapure water in 50 mL Falcon tubes. The samples were shaken on a horizontal shaker for 15 min at 150 rpm, followed by one hour at rest. Thereafter, they were agitated for another five minutes and centrifuged at 2000 rpm for 30 min. Immediately after that, the pH and electrical conductivity (EC) were measured in approximately 10 mL of the extracts from each sample. The extracts used for the determination of cations and dissolved organic carbon (DOC) were previously passed in 0.45 micron cellulose acetate syringe filters, and extracts used for the determination of anions were previously passed in 0.20 micron cellulose acetate filters. The final product of filtration of the extracts was stored in 15 mL Falcon tubes and cooled to 4°C for further analysis of the Ca^{2+}, Mg^{2+}, K$^+$, Al^{3+}, SO$_4^{2-}$, Cl$^-$, NO$_3^-$, PO$_4^{3-}$ and DOC concentration.

For the determination of Ca^{2+}, Mg^{2+}, K$^+$, Al^{3+} and DOC concentrations, 3 mL of the extracts were placed in 15

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mL Falcon tubes and then acidified with one drop of concentrated nitric acid (maintaining the same viscosity of the curve, prepared with 3% nitric acid) before quantification, with ions by ICP-OES and organic carbon (DOC) dissolved by colorimetry. DOC was determined using the chemical oxygen demand (COD) method (Clesceri et al., 1999) with some adaptations. In short: a 1 mL aliquot of the sample extracts was added in 10 mL COD tubes, adding to it a 0.6 mL aliquot of the digest solution (1.0216 g of potassium dichromate + 167 mL of concentrated sulfuric acid + 33.3 g of mercury sulfate II in 1 L of distilled water) and 1.4 mL of the catalyst solution (5.5 g of silver sulphate diluted in 1 L of concentrated sulfuric acid). The samples were agitated in vortex and digested in a digester block (TR 420 Merck, Germany) at 148°C for two hours, and cooled to room temperature. A spectrophotometer (Spectroquant Nova 60 Merck, Germany) was used to measure the wavelength of 605 nm in a 3 mm cuvette. The COD value was converted to DOC using a mean multiplication factor of 0.35 (Aquino et al., 2006). The calibration curve was constructed from standard solutions containing acetic acid P.A.

The anions were determined by turbidimetry (SO_4^{2-}) in a spectrophotometer (UV/VIS Spectrometer Merck, Germany) at wavelength of 420 nm in a 5 mm cuvette. NO_3^- was quantified by colorimetry using a spectrophotometer (UV/VIS Spectrometer Merck, Germany) at the wavelength of 605 nm in a 5 mm cuvette. Chloride (Cl^-) was titrated with silver nitrate solution 0.1 mol L^{-1}, having as indicator 5% potassium chromate (Clesceri et al., 1999). Phosphate (mg L^{-1}) was obtained after conversion of phosphorus (P), which was extracted using the Melich-1 solution and determined by the methodology of Murphy & Riley (1962), in phosphate (PO_4^{3-} = P x 3.06). All determinations were done with four replicates.

Chemical speciation

Chemical speciation of the soil solution was estimated by the Visual Minteq (for Windows) software version 3.1, based on the Minteq A2 software version 4.0 (Gustafsson, 2016). For this, the average 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 the ionic strength (I), was calculated from the EC of the soil solution by the equation Log I (M) = 1.159 + 1.09 * log EC 25 (dS m^{-1}) where: EC 25 represents the electrical conductivity corrected to 25°C, according to Spera et al. (2014).

Based on the speciation, the distribution of the free and complexed ionic species of Al was estimated, obtaining the percentage distribution and the activities of each species in each treatment. Species bonded to anions were estimated based on the DOC content, and the Gaussian DOM model (Grimm et al., 1991) was used for quantification. The formation of aqueous inorganic complexes was evaluated using equilibrium constants of the standard Visual Minteq software developed by Smith et al. (2003).

Results and Discussion

Chemical attributes of soil solution

The pH values of the solution varied from 4.70 in the soil AC9 to 5.11 in RS in the treatments without limestone and they increased with liming in all soils ranging from 5.78 in the soil PE to 6.20 in CB (Table 2).

The lowest concentration of total Al in solution in the treatment without limestone was observed in the RS soil, as well as in AC9 and CB. In AC9 and RS, this behavior is explained by the high levels of basic cations, mainly Ca^{2+} and Mg^{2+}, with a high sum of bases in their solution (Table 2). This behavior may be related to the higher retention strength of Al monomers, interlayered Al amorphous polymers and amorphous Al on the cation exchange surfaces. As this force of attraction of the surface by Al ions would be superior to that exerted by the other cations, such as Ca^{2+} and Mg^{2+}, these ions of lower valence would be in the outermost double layer and the presence of these basic cations (ions) in average and/or increased concentrations in the soil solution reduces the concentration and activity of Al^{3+} (Wadt, 2002; Rutkowska et al., 2015). On the other hand, in this same treatment, the highest concentrations of Al^{3+} were verified in the PE and BR soils, because these soils are chemically poorer or because of their lower sum of bases in relation to the others. The concentration of this element in solution decreased with liming in all the soils (Table 2).

As for the fraction of Al in relation to all cations in the soil solution, in the treatments without limestone, the lowest values were verified in AC9 and RS; medium values were seen in CB; high values in PE; and much higher in BR. All values decreased with liming (Table 2). These values are directly related to the Al content and to the effective CEC of the soils. However, it is convenient to consider the relation of the basic cations (mainly Ca^{2+}) with Al that reflects more directly in the saturation values of this element. In the AC9 and RS soils, Ca^{2+} in solution was 76 and 114-fold higher than Al in solution, respectively. In the soils PE, BR and CB, the Ca^{2+} was 4-, 2.8- and 8-fold greater than Al^{3+} in solution, respectively. Although the concentration of Al^{3+} in solution in CB is similar to that of AC9 in the treatment without limestone (Table 2), the relation between the cations was much lower because the soil CB is more weathered and chemically poor.

Concentrations of Ca^{2+} and Mg^{2+} increased in the solution of all soils with liming. On the other hand, the concentrations of K^+ decreased in the solution of most soils because of the increase of the negative charges of the soils with the application of limestone, causing absorption of part of the K (Ernani et al., 2007). Na^+ concentrations remained constant and the sum of bases in the solution increased with liming (Table 2).

The DOC concentration in the soils solution in the treatments without limestone was higher in the soils RS and BR; similar in AC9 and CB; and smaller in PE. It was observed that DOC increased with liming in AC9, decreased in PE and BR, and remained constant in RS and CB (Table

Table 2. Chemical attributes of soil solution after maize cultivation under greenhouse conditions.

Soil[1]	L.D.[2]	pH S.S.[3] 1:1	Al³⁺	Ca²⁺	Mg²⁺	K⁺	Na⁺	S[4]	m[5] (%)
					(mmo L⁻¹)				
AC9	0	4.70	0.013	0.99	0.33	0.12	0	1.44	0.9
	0.25	5.42	0.011	0.90	0.36	0.13	0	1.39	0.8
	0.5	5.59	0.007	0.90	0.40	0.10	0	1.40	0.5
	1.00	5.91	0.006	0.89	0.48	0.11	0	1.48	0.4
PE	0	4.56	0.048	0.19	0.38	0.34	0.01	0.92	5.5
	0.25	4.91	0.013	1.10	1.27	0.38	0.01	2.76	0.5
	0.5	5.45	0.005	0.93	1.06	0.24	0.01	2.24	0.2
	1.00	5.78	0.001	1.75	1.84	0.20	0	3.79	0.0
RS	0	5.11	0.008	0.91	0.42	0.15	0	1.48	0.5
	0.25	5.50	0.002	1.41	0.69	0.17	0	2.27	0.1
	0.5	5.89	0.002	1.65	0.80	0.10	0	2.55	0.1
	1.00	6.17	0.000	2.84	2.07	0.21	0	5.12	0.0
BR	0	4.88	0.043	0.12	0.08	0.16	0	0.36	10.7
	0.25	5.44	0.011	0.60	0.35	0.13	0	1.08	1.5
	0.5	5.85	0.005	0.63	0.50	0.11	0	1.24	0.4
	1.00	6.15	0.003	1.71	1.60	0.10	0	3.41	0.1
CB	0	4.79	0.013	0.10	0.03	0.25	0	0.38	3.3
	0.25	5.55	0.005	1.16	0.50	0.29	0	1.95	0.8
	0.5	5.90	0.004	1.17	0.72	0.20	0	2.09	0.2
	1.00	6.20	0.002	2.52	2.26	0.28	0	5.06	0.0

		EC[6] (µS cm⁻¹)	I[7]	DOC[8]	SO₄⁻²[9]	NO₃⁻[10]	Cl⁻[11]	PO₄³⁻[12]	P (mg L⁻¹)
					(mmo L⁻¹)				
AC9	0	369.48	0.0112	0.0733	0.01194	0.0834	9.1667	0.0028	0.09
	0.25	426.23	0.0131	0.0760	0.01368	0.2263	9.0000	0.0035	0.11
	0.5	473.48	0.0146	0.1186	0.01248	0.1944	10.5000	0.0028	0.09
	1.00	511.73	0.0159	0.1025	0.01147	0.2644	9.1667	0.0079	0.24
PE	0	265.23	0.0078	0.0645	0.01066	1.0203	12.6667	0.0042	0.13
	0.25	360.98	0.0109	0.0879	0.01524	1.0773	12.0000	0.0060	0.19
	0.5	857.23	0.0279	0.1098	0.01650	1.1117	10.1667	0.0114	0.35
	1.00	1028.48	0.0328	0.0549	0.01808	1.8436	11.6667	0.0118	0.36
RS	0	269.48	0.0079	0.1167	0.00906	0.4300	10.6667	0.0044	0.14
	0.25	739.73	0.0238	0.1224	0.01154	0.5008	9.0000	0.0042	0.13
	0.5	772.23	0.0249	0.1025	0.01292	0.8383	9.3333	0.0040	0.13
	1.00	1211.98	0.0408	0.1159	0.01396	2.6256	10.1667	0.0062	0.19
BR	0	185.23	0.0053	0.1408	0.00488	0.1055	10.6667	0.0039	0.12
	0.25	554.48	0.0174	0.1155	0.01030	0.1343	9.0000	0.0032	0.10
	0.5	569.23	0.0179	0.0959	0.00971	0.3978	9.1667	0.0055	0.17
	1.00	796.73	0.0258	0.0890	0.00924	3.2742	7.3333	0.0075	0.23
CB	0	147.48	0.0041	0.0806	0.00449	1.5642	7.6667	0.0020	0.06
	0.25	580.23	0.0183	0.0741	0.00624	1.2406	10.0000	0.0081	0.25
	0.5	660.81	0.0201	0.0929	0.00884	1.2614	7.6667	0.0056	0.17
	1.00	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 Rio Grande do Sul; BR: collected in Bom Retiro, SC; CB; collected in Curitibanos, SC; [2]Limestone doses applied to soils; [3]Soil Solution; [4]Sum of bases; [5]Fraction of aluminum in relation to all cations in the soil solution; [6]Electrical conductivity; [7]Ionic strenght; [8]Dissolved organic carbon; [9]Sulfate; [10]Nitrate; [11]Chloride and [12]Phosphate.

2). These differences in DOC concentrations in the solution can be attributed to the natural total organic carbon (TOC) contents, quantified in the samples collected under natural TOC conditions, and quantified in the samples collected under natural conditions of these soils, with clay amounts and type of clay minerals in the soils. This is because the sorption of organic compounds to the solid phase of the soil, in particular Fe and Al oxides and hydroxides, can decrease DOC concentration in the soil solution (Peralta & Costa, 2013; De Conti et al., 2017).

Values of electrical conductivity (EC) and, consequently, of ionic strength (I) of all soils increased with liming (Table 2).

The increase of pH, Ca²⁺ and Mg²⁺ contents can be considered the main factors that cause the EC of the soil to increase, as a consequence of the concentration and I (Table 2) of the solution of the soils (Peralta & Costa, 2013; Carmo et al., 2016), taking into account that the other nutrients were supplied in equal amounts and had their availability increased with liming. Higher EC values observed in the soils PE, RS and CB with the use of the maximum dose may be related to their capacity to retain larger amounts of ions, especially Ca²⁺ and Mg²⁺ after addition of limestone. These soils have high TOC and clay contents that act as ion accumulators resulting in higher EC values in the soil solution. Similar behavior was

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verified by Peralta & Costa (2013) and Carmo et al. (2016). The soil AC9 was an exception, for it presented an inverse behavior, with reduction of EC after soybean cultivation (data not shown). This reduction is related to the Ca^{2+} and Mg^{2+} contents and can be explained by the buffering power of each soil presented on the increase of EC, by the content of OM, clay and CEC and by the precipitation and adsorption of other processes that remove ions from the liquid phase of the soil (Tamir et al., 2013).

The dynamics of the anions in the soil solution was influenced by liming. The direct effect of the addition of this corrective factor to the soil is the increase of the pH and its negative electrical potential, of hydroxyls (OH^-), of the decomposition of OM that releases organic acids in the soil solution and, mainly because of the decrease of the content and solubility of Al and Fe compounds (Zambrosi et al., 2008, Hernández-Soriano, 2012). It is therefore observed in Table 2 that, in general, liming increased the concentration of anions in all the soils. The most significant increases occurred for nitrate and chloride anions in practically all soils and treatments, possibly due to increased mineralization of OM by the effect of liming and KCl fertilization, respectively (Table 2).

Cations in solution

Aluminum: The chemical species of aluminum observed in greater proportion in all soils in the treatments without liming was Al^{3+} (61% in AC9, 69% in PE, 31% in RS, 47% in BR and 50% in CB), which was more abundant in absolute values than the species $AlOH^{2+}$, $Al(OH)_2^+$, Al bonded to other species (Al-OE) ($AlCl^{2+}$, $AlSO_4^+$, $AlHPO_4^+$ and $Al_2PO_4^{3+}$) and organic carbon dissolved (Al-COD) which were, on the average of all treatments and soils, 20%, 27%, 16% and 4.7% of the total in solution, respectively. However, the activity of the main toxic species of Al (Al^{3+}, $AlOH^{2+}$ and $Al(OH)_2^+$) decreased in the solution of all soils with liming, reaching, at maximum dose, the following averages of all soils and treatments: 21% in AC9, 11% in PE, 18% in BR and 17% in CB, due to the increase of pH, cations and anions concentration in the solution, as well as EC and I (Table 2), as verified by Zambrosi et al. al. (2008), Peralta & Costa (2013) and Carmo et al. (2016). Al-COD and Al-OE also decreased with liming; however, there was an increase in activity, to a lesser extent, of $Al(OH)_3$ and $Al(OH)_4^-$ (7% and 5.5%, respectively) on the average of all soils and treatments in the solution of all soils that are considered non-toxic to plants (Hernández-Soriano, 2012; Rutkowska et al., 2015; Antonangelo et al., 2017).

Calcium and magnesium: The chemical species of free Ca and Mg found in greater proportions in the treatments with and without liming were Ca^{2+} (98% in AC9, RS and CB; and 97% in PE) and Mg^{2+} (97% in AC9, RS, BR; 96% in PE; and 98% in CB), surpassing the proportion of those bonded to dissolved organic carbon (Ca-COD and Mg-COD, 0.27% and 0.02% in the average of all soils and treatments, respectively), bonded to sulfate ($CaSO_4$ and $MgSO_4$, 0.08% and 0.06% in

the average of all soils and treatments, respectively) and to the other species (Ca-OE and Mg-OE, 1.58% and 2.26% in the average of all soils and treatments, respectively) in all soils, regardless of their physical, chemical and mineralogical characteristics. The other Ca (inorganic) species were formed by: $CaCl^+$, $CaNO_3^+$, $CaHPO_4(aq)$ and $CaH_2PO_4^+$, and those of Mg by: $MgCl^+$ and $MgHPO_4(aq)$. The percentage of interaction of these ionic pairs in the average of all soils and treatments was 1.6% Ca and 2.3% Mg of the total species of these nutrients in the solution. The highest percentage of Ca^{2+} and Mg^{2+} free species occurred as a result of liming, as these nutrients are part of the chemical composition of limestone molecules and may also be related to the low complexation of these cations with organic and inorganic anions (Zambrosi et al., 2008), since only B horizon samples were used, and this horizon has relatively low total organic carbon (TOC) levels (Data not shown).

Potassium: The free species of K found in the highest proportion was K^+ (99% of the total K of the solution in all soils and treatments, separately), followed by the K-OE [(KCl aq), KNO_3 (aq)] representing 0.4% (considering all soils and treatments) of the total of this element in the solution, agreeing with the results obtained by Zambrosi et al. (2008). The highest proportion of K^+ species in the soil solution can be explained by the application of KCl in soils prior to the implantation of the experiments. Differently from Ca and Mg, K was not complexed by organic anions (data not shown), and this could also be explained by the use of B horizon samples with relatively low TOC levels.

Anions in solution

Phosphate: Free species of phosphate- ($H_2PO_4^-$ and HPO_4^{2-}) depend on the pH of the soil solution. At pH 7.2 the amounts of these two species are nearly the same (Lindsay, 1979). Thus, as the pH of the solution of all soils was lower than 7.2 (Table 2), it was expected that the predominant species would be $H_2PO_4^-$, as observed in AC9 (74%), RS (69%) and CB (65%) in treatments without limestone. However, in PE and BR, in the same treatments, the species found in the highest proportion was formed by the bond between phosphate ions and aluminum ($Al-HPO_4^+$), corresponding to 55% in the soil PE and 59% in BR of the total of P species in the solution. This may have occurred because these soils have a high concentration of Al in the solution and the addition of P increases the concentration of phosphate ions (Table 2), favoring the formation of $Al-HPO_4^+$, (55% in PE and 59% in BR of the total phosphate ions in the solution). The strong interaction of these ions with Al, Fe and Mn is well known and results in decreased availability of P in the solution and also reduced risk of Al toxicity to plants (Rutkowska et al., 2015; De Conti et al., 2017). In a lower proportion, HPO_4^{2-} was found in the same treatments, 0.33% in AC9, 0.12% in PE, 0.75% in RS, 0.2 in BR and 0.3% in CB.

The application of limestone doses increased the percentage of $H_2PO_4^-$ and HPO_4^{2-} species, reaching the

maximum dose (100% of H+Al content) at 79% in AC9, 91% in PE, 78% in RS, and 76% in CB of $H_2PO_4^-$, and 6% in AC9, 3.9% in PE and 13% in soil RS and CB of HPO_4^{2-}, in a lower proportion of organic and inorganic species, as a consequence, decreased $Al-HPO_4^+$ (19% in the average of all soils and treatments), mainly in the soils PE (3.4%) and BR (3.0%) in the solution. It is therefore possible to assume that P was available to the plants, since there were no ionic pairs of the phosphate ions with the cations in the solution of the soils, mainly in the treatments with the use of limestone.

In field conditions, Nolla et al. (2013) also observed the formation of Al phosphate by the release of organic acids by soybean plants that are able to complex the Al in the soil solution under conditions of higher acidity. De Conti et al. (2017) applied increasing doses of swine manure and also verified the increase of the formation of Al complexed with P due to the increase of the concentration of this element in solution, mainly in the upper layers of the soil evaluated in this study. Zambrosi et al. (2008) evaluated the distribution of Al and nutrient species in the solution in a dystrophic Red Latosol after five years of limestone application and also identified the presence of the complex formed between Al and phosphate in the upper layers and concluded that the phosphate ions in the solution are prone to strong interactions with Al, Fe, Ca and Mg.

Sulphate, chloride and nitrate: In all soils and treatments the free SO_4^{2-} and Cl^- species were found in greater amounts, regardless of the soils and the limestone rates applied to them. A proportion of 90% of SO_4^{2-} and 99% of Cl^- were found in the average of all soils and treatments. However, ionic pairs were found to a lesser extent with sulfate $CaSO_4$, $MgSO_4$ and those bonded to other species (HSO_4^-, $AlSO_4^+$ and KSO_4^-),

representing 0.92% of total sulfate solution in the average of all soils and treatments. However, the pairs formed with the chloride were $KCl(aq)$, $CaCl^+$, $MgCl^+$, corresponding to 0.31% of the total chloride in the soil solution in the average of all soils and treatments (Table 2). The free chemical species of N found in higher percentage (99% in the average of all soils and treatments) in the solution of all soils was NO_3^-.

The higher proportion of the free species SO_4^{2-}, most notably Cl^- and NO_3^- found in the solution of all soils (Table 2) can be explained by the low interaction of these anions with cations, and also by the addition of dolomitic limestone that increases the pH of the solution and the number of negative electrical charges of the soil. As a consequence, these anions are not adsorbed to the solid phase by any mechanism other than the electrostatic. The low adsorption of these chemical species by the inorganic solids of the soil causes them to be present in greater quantity and in field conditions, they can be leached (Francisco et al., 2016). For Zambrosi et al. (2008) and De Conti et al. (2017), the increase of sulfate ions in the solution of the studied soils resulted from the application of limestone and swine manure, respectively.

Relationship between cations and anions activity with aluminum in the solution and its toxicity to plants

The concentration and activity of cations, anions and Al in the solution of all soils were influenced by liming (Tables 2 and 3). In general, the free ions that had the highest activity, regardless of soils and treatments, in descending order, were: $Cl^->Ca^{2+}>Mg^{2+}>K^+>NO_3^->Al^{3+}>SO_4^{2-}>H_2PO_4^->HPO_4^{2-}$ (Table 3), followed to a lesser extent by the ionic pairs formed by organic and inorganic complexes (data not shown), evidencing that the concentration of the majority of the ions is related to their activity in the solution of these soils.

Table 3. Activity of the chemical species in the soil solution after maize cultivation.

Soil[1]	L.D.[2]	Ca²⁺	Mg²⁺	K⁺	SO₄²⁻	NO₃⁻	Cl⁻	H₂PO₄⁻	HPO₄²⁻	Al³⁺	Al-DOC[3]
							(µmol L⁻¹)				
AC9	0	973.1	322.1	119.5	10.6	83.2	9144.1	2.1	0.0	7.93	1.17
	0.25	884.3	351.7	129.5	12.3	225.9	8979.1	2.1	0.1	2.31	0.44
	0.5	881.5	389.6	99.6	11.3	194.1	10475.3	2.0	0.1	0.91	0.35
	1.00	873.8	469.2	109.6	10.4	263.9	9143.9	6.3	0.5	0.24	0.06
PE	0	185.2	366.9	338.0	9.4	1019.7	12648.0	1.6	0.0	33.4	2.4
	0.25	1073.6	1230.5	377.9	12.6	1074.7	11939.2	3.9	0.0	6.0	1.0
	0.5	912.5	1036.7	239.0	14.8	1109.9	10131.3	9.4	0.3	0.8	0.18
	1.00	1718.6	1800.3	199.3	16.5	1841.6	11639.3	10.7	0.5	0.0	0.01
RS	0	893.8	407.7	149.3	8.4	428.1	10637.8	3.1	0.0	2.48	0.96
	0.25	1387.1	676.1	169.4	10.9	499.6	8968.9	3.7	0.1	0.44	0.09
	0.5	1622.6	783.5	99.6	12.1	835.9	9296.4	3.4	0.3	0.10	0.02
	1.00	2789.3	2029.4	209.0	12.5	2614.3	10092.8	4.8	0.8	0.00	0.00
BR	0	117.6	77.6	159.3	4.5	105.5	10661.3	1.3	0.0	20.21	5.16
	0.25	582.0	343.0	129.5	9.6	134.1	8984.4	2.2	0.1	3.57	1.19
	0.5	617.4	490.0	109.6	8.9	397.3	9147.4	4.6	0.3	0.25	0.1
	1.00	1675.8	1568.0	99.6	7.8	3264.7	7291.6	5.9	0.8	0.03	0.006
CB	0	98.0	29.4	248.9	4.3	1563.6	7663.8	1.3	0.0	6.50	2.08
	0.25	1136.8	490.0	288.7	5.6	1237.8	9970.8	6.8	0.2	1.95	0.3
	0.5	1146.6	705.6	199.3	7.8	1258.7	7641.1	4.6	0.4	0.16	0.04
	1.00	2469.6	2214.8	278.8	8.5	1743.2	9925.9	4.8	0.8	0.02	0.002

[1]AC9: collected in Tarauacá, Acre, Profile 9; PE: collected in Ipojuca, Pernambuco; RS: collected in Rio Grande do Sul; BR: collected in Bom Retiro, SC; CB: collected in Curitibanos, SC; [2]Limestone doses applied to soils; [3]Aluminum bound to dissolved organic carbon.

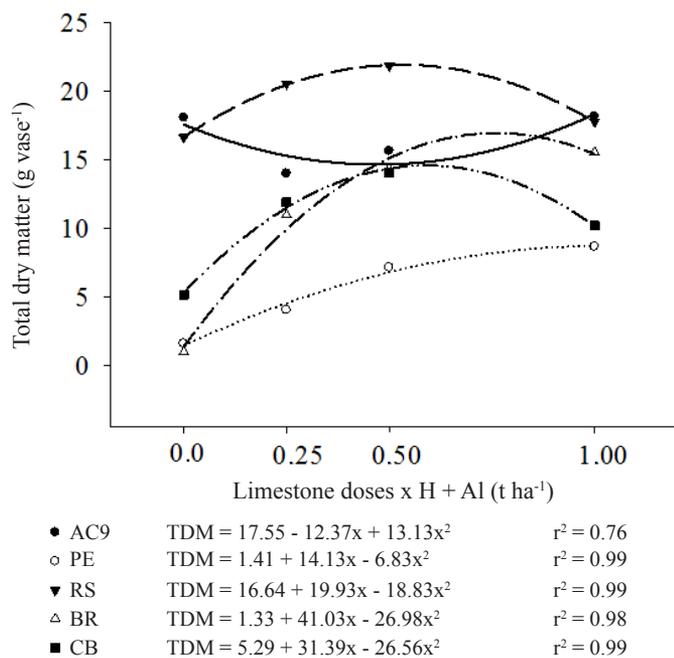|		
● AC9	TDM = 17.55 - 12.37x + 13.13x^2	r^2 = 0.76
○ PE	TDM = 1.41 + 14.13x - 6.83x^2	r^2 = 0.99
▼ RS	TDM = 16.64 + 19.93x - 18.83x^2	r^2 = 0.99
△ BR	TDM = 1.33 + 41.03x - 26.98x^2	r^2 = 0.98
■ CB	TDM = 5.29 + 31.39x - 26.56x^2	r^2 = 0.99

Figure 1. Total dry matter (TDM) yield of maize plants grown in Acre (AC9), Pernambuco (PE), Rosário do Sul (RS), Bom Retiro (BR) and Curitibanos (CB) soils as a function of application of limestone.

Although the anions NO_3^- and Cl^- had the highest activities in absolute values when compared to the anions SO_4^{2-} and PO_4^{3-} and even to the chemical species of Al, they had little or no influence on the inactivation of Al^{3+} in the solution, because there was little contribution of them to the formation of inorganic complexes with Al. The same occurred with the organic complexes (DOC), whose activity in the solution was lower (Table 3). This can be explained by the use of the subsurface horizon (B) of the soils, where the total organic carbon contents are relatively low (data not shown). Thus, the activity of the ions Ca^{2+} and Mg^{2+} (Table 3), besides the EC, I and pH of the solution of the studied soils were responsible for the inactivation of the main chemical species of Al^{3+}, $AlOH^{2+}$ and $Al(OH)_2^+$, considered to be toxic to plants (Nolla et al., 2015; Rutkowska et al., 2015).

The soils AC9 and RS, which were both smectite soils (Cunha et al., 2014), presented the highest activities of Ca^{2+} and Mg^{2+} (except in PE, where Mg activity was higher) in the solution in treatments without limestone, overcoming the activity of Al^{3+} and the activity of the sum of the toxic species of Al (AΣFTAl) in the solution (data not shown). In the soil AC9, in this same treatment, the activity of Ca^{2+} was found to be 91-fold and of Mg^{2+}, 29-fold higher than the AΣFTAl in the soil solution and it was observed the highest total dry matter (TDM) production of maize plants in relation to the other soils (Figure 1), indicating that Al^{3+} in the solution may have exerted little or no toxicity to the plants. With liming, the activity of these ions in relation to Al^{3+} in the solution increased even more (Table 3); however, there was no increase in the yield of the plants (Figure 1).

On the other hand, in the soil RS, the highest TDM production occurred in the second limestone dose (50% H+Al content), where the activity of Ca was 1622.6 and of Mg was 783.5 µmol L^{-1} and AΣFTAl in the soil solution was 1.5 µmol L^{-1}. However, being very similar to the first dose (25% H+Al content); in the treatment with the highest dose (100% of H+Al) there was a decrease in TDM production, indicating that even with the notable increase of activity of these ions in the solution (2789.3 µmol L^{-1}) in relation to AΣFTAl (Table 1) and to Al^{3+} (Table 3), promoted by liming, this did not reflect the dry matter yield of the plants (Figure 1). In these two soils (AC9 and RS), in the treatment without liming, Al^{3+} did not present toxicity to the plants, because in addition to the high activity of the ions Ca^{2+} and Mg^{2+}, the AΣFTAl (data not shown) in the solution was already well below the critical threshold of 24-27 µmol L^{-1} (Diatloff et al., 1998) for maize. It should be noted that these soils have very high (AC9) and high (RS) levels of Al^{3+}, Ca^{2+} and Mg^{2+}, maintaining equilibrium with the liquid phase, but these two ions controlled the activity of Al^{3+} in the solution, thus reducing its activity and its harmful effects on plants.

In the PE (smectite), BR and CB (kaolinites with or without presence of smectite and vermiculite with hydroxy-Al interlayers) (Cunha et al., 2014), it was also verified that in limestone treatments the concentration and activity of the chemical species Ca^{2+} and Mg^{2+} was much higher than that of Al^{3+} (Table 3) and AΣFTAl in their solution (data not shown). The concentration ratio between Ca^{2+} and Al^{3+} (Ca^{2+}/Al^{3+}) in this same treatment and soils was approximately 4; 3 and 8-fold higher than the concentration of Al^{3+} in solution, respectively. In contrast, the ratio of the total concentration of Mg^{2+} in the solution in relation to Al^{3+} (Ca^{2+}/Al^{3+}) was 8-fold higher in the soil PE and 2-fold higher in BR and CB than the concentration of Al^{3+} in the solution. Under these conditions, when Ca^{2+} and Mg^{2+} exceed Al^{3+} in the solution, Al^{3+} was expected to exert no toxicity to plants. However, it is observed that the TDM production of the plants grown in these soils was much lower than those grown in AC9 and RS (Figure 1), indicating that Al^{3+} influenced the yield of the plants.

The behavior of Al^{3+} in these soils (PE, BR and CB) can be explained by clay fraction mineralogy: in the PE soil, there was a predominance of smectite (E) with smectite with hydroxy-Al interlayers (EHE) and a relatively high proportion of kaolinite; in BR, there was kaolinite with similar amounts of smectite and vermiculite with hydroxy-Al interlayers (EHE and HEV); and in CB, there was kaolinite, with low amounts of EHE (Cunha et al., 2014). Therefore, for this group of soils, it is plausible to assume that the activity of Al^{3+} in the solution was controlled by the amorphous polymers from EHE and HEV that maintained the equilibrium of this species in the solution, restraining its toxic potential, as also verified by Dahlgren & Walker (1993) despite the high activity of the basic cations in the solution of these soils (Table 3). Furthermore, the intense agitation of the samples for soil solution simulation (soil:solution extraction in a

1:1 ratio) may have destroyed the natural arrangement of the soil:solution porous system (Gloaguen et al., 2009), favoring the dissolution of amorphous species of Al, what may have contributed to the solubilization and increase of the concentration of Al^{3+} and also of the cationic and anionic species in their solution.

It is worth mentioning that there was a balance between Al of the solid and liquid phase, because a high correlation between these two phases was observed in all soils (AC9 r^2 = 0.97, PE r^2 = 0.71, RS r^2 = 0.82, BR r^2 = 0.77 and CB r^2 = 0.97), indicating that the solid phase of the soil controlled the activity of Al^{3+} in the liquid phase of the studied soils.

With liming, TDM production in PE, BR and CB increased in the first two doses, in which the activities of the ions, mainly of Ca^{2+} and Mg^{2+}, were much higher than those of Al^{3+} (Table 3) and AΣFTAl in their solution (data not shown). Therefore, in this condition, Al^{3+} no longer exerted toxicity on the plants. With the use of the maximum limestone dose, the TDM yield decreased, indicating that despite the increase of availability of nutrients to a greater extent than the requirement by the plants, there is no need to increase its concentration in the solution because the addition will not increase the yield of the plants (Fontes et al., 2014).

The results of this study indicate that the chemical composition of the solution of the soils AC9 and RS provided a good chemical environment for the development of plants. However, in the case of the soils PE, BR and CB, the application of ¼ and ½ of the dose of limestone was enough to increase the nutrient supply in solution, allowing the plants to express their maximum production potential.

Conclusions

The predominant aluminum, calcium, magnesium, potassium, sulfate, nitrate, chloride and nitrate species in all soils were: Al^{3+}, Ca^{2+} and Mg^{2+}, K^+, SO_4^{2-}, Cl^- and NO_3^-. The chemical species $H_2PO_4^-$ predominated in the soils AC9, RS and CB and $AlHPO_4^+$ in the soils PE and BR. With liming, the form $H_2PO_4^-$ predominated in all soils.

The activity of Ca^{2+} and Mg^{2+} were the main responsible for the neutralization of the toxic effects of Al^{3+} in the evaluated plants.

Literature Cited

Almeida, J. A.; Santos, P.G.; Shimizu, S.H.; Dortzbach, D.; Neto, A.L.; Heberle, D.A. Guia de excursão pedológica. In: Congresso Brasileiro de Ciência do Solo [Guia de campo], 34., 2013, Florianópolis. Anais. Florianópolis. Sociedade Brasileira de Ciência do Solo, 2013. 56p.

Almeida, J.A.; Torrent, J.; Barrón, V. Cor de solo, formas do fósforo e adsorção de fosfato em Latossolos desenvolvidos de Basalto do extremo-sul do Brasil. Revista Brasileira de Ciência do Solo, v.27, n.6, p.985-1002, 2003. https://doi.org/10.1590/S0100-06832003000600003.

Anjos, L. H. C.; Silva, L. M.; Wadt, P. G. S.; Lumbreras, J. F.; Pereira, M. G. (Eds.). Guia de campo da IX Reunião Brasileira de Classificação e Correção de Solos. Solos sedimentares em sistemas amazônicos: potencialidades e demandas de pesquisas. Brasília: Embrapa, 2013a. 204p. http://ainfo.cnptia.embrapa.br/digital/bitstream/item/97587/1/246682.pdf. 07 Jan. 2017.

Antonangelo, J.A.; Ferrari Neto, J.; Crusciol, C.A.C.; Alleoni, L.R.F. Lime and calcium-magnesium silicate in the ionic speciation of on Oxisol. Scientia Agricola, v.74, n.4, p.317-333, 2017. https://doi.org/10.1590/1678-992X-2016-0372.

Aquino, S.F.; Silva, S.Q.; Chechicharo, C.A.L. Considerações práticas sobre o teste de demanda química de oxigênio (DQO) aplicado a análise de efluentes anaeróbios. Engenharia Sanitária e Ambiental. 2006:11:295-304. https://doi.org/10.1590/S1413-41522006000400001.

Cancés, B.; Ponthieu, M.; Castrec-Rouelle, M.; Aubry E.; Benedetti, M. Metal ions speciation and its solution: experimental data and model results. Geoderma, v.113, n.3-4, p. 341-355, 2003. https://doi.org/10.1016/S0016-7061(02)00369-5.

Carmo, D.L.; Silva, C.A. Condutividade elétrica e Crescimento do milho em solos contrastantes sob aplicação de diversos níveis de calagem. Pesquisa Agropecuária Brasileira, v.51, n.10, p.1762-1772, 2016. https://doi.org/10.1590/S0100-204X2016001000008.

Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D. Standard Methods for the examination of water and wastewater. 20.ed. Washington: American Public Health Association; American Water Works Association; Water Environment Federation, 1999. 2671p.

Comissão de Química e Fertilidade do Solo – CQFS RS/SC. Manual de adubação e de calagem para os Estados do Rio Grande do Sul e de Santa Catarina. 10.ed. Porto Alegre: Sociedade Brasileira de Ciência do Solo, 2004. 400p. http://www.sbcs-nrs.org.br/docs/manual_de_adubacao_2004_versao_internet.pdf. 10 Jan. 2017.

Cunha, G.O.M. Formas de alumínio em solos com altos teores trocáveis e toxidez na soja e no milho. Lages: Universidade do Estado de Santa Catarina, 2017. 162p. Tese Doutorado. http://repositorio.ufsm.br/bitstream/handle/1/5570/WENDLING%2C%20GRAZIELE%20FELTRIN%20DIAS.pdf?sequence=1&isAllowed=y. 10 Jan. 2017.

Cunha, G.O.M.; Almeida, J.A.; Barboza, B.B. Relação entre o alumínio extraível com KCl e oxalato de amônio e a mineralogia da fração argila, em solos ácidos brasileiros. Revista Brasileira de Ciência do Solo, v.38, n.5, p.1387-1401, 2014. https://doi.org/10.1590/S0100-06832014000500004.

Cunha, G.O.M.; Almeida, J.A.; Testoni, S.; Barboza, B.B. Formas de alumínio em solos ácidos brasileiros com teores excepcionalmente altos de Al^{3+} extraível com KCl. Revista Brasileira de Ciência do Solo, v.39, n.5, p.1362-1377, 2015. https://doi.org/10.1590/01000683rbcs20150017.

Dahlgren, R.A.; Walker, W.J. Aluminum release rates from selected Spodosol Bs horizons: effect of pH and solid-phase aluminum pools. Geochim Cosmochim Acta, v.57, n.1, p. 57-66, 1993. https://doi.org/10.1016/0016-7037(93)90468-C.

Rev. Bras. Cienc. Agrar., Recife, v.13, n.3, e5542, 2018

9/10

De Conti, L.; Ceretta, C.A.; Couto, R.R.; Ferreira, P.A.A.; Silva, L.O.S.; Piccin, R.; Lourenzi, C.R.; Girotto E, Brunetto G. Aluminum species and activity in sand soil solution with pig slurry addition. Pesquisa Agropecuária Brasileira, v.52, n.10, p.914-922, 2017. https://doi.org/10.1590/S0100-2042017001000011.

Diatloff, E.; Harper, S.M; Asher, C.; Smith, F.W. Effects of humic and fulvic acids on the rhizotoxicity of lanthanum and aluminum to corn. Australian Journal of Soil Research. v. 36, n,6, p.913-919, 1998. https://doi.org/10.1071/S98018.

Empresa Brasileira de Pesquisa Agropecuária - Embrapa. Centro Nacional de Pesquisa de Solos. Sistema brasileiro de classificação de solo. 3.ed. Brasília: Embrapa, 2013b. 353p.

Empresa Brasileira de Pesquisa Agropecuária - Embrapa. Centro Nacional de Pesquisa de Solos. Sistema brasileiro de classificação de solo. Projeto – Solos Alíticos. Pernambuco. Recife: Embrapa Solos, 2011a. 63p.

Empresa Brasileira de Pesquisa Agropecuária - Embrapa. Centro Nacional de Pesquisas de Solos. Manual de métodos de análises de solos. 2.ed. Rio de Janeiro: Embrapa Solos, 2011b. 230p.

Ernani, P.R.; Bayer, C.; Almeida, J.A.; Cassol, P.C. Mobilidade vertical de cátions influenciada pelo método de aplicação de cloreto de potássio em solos com carga variável. Revista Brasileira de Ciência do Solo, v.21, n.2, p.393-402, 2007. https://doi.org/10.1590/S0100-06832007000200022.

Fontes, P.C.R. Nutrição mineral de hortaliças: horizontes e desafios para um agrônomo. Horticultura Brasileira, v.32, n.3, p.247-253, 2014. https://doi.org/10.1590/S0102-05362014000300002.

Francisco, J.P; Folegatti, M.V.; Silva, L.B.D.; Silva, J.B.G.; Diotto, A.V. Variations in the chemical composition of the solution extracted from a Latosol under fertigation with vinasse. Revista Ciência Agronômica, v.47, n.2, p.229-239, 2016. https://doi.org/10.5935/1806-6690.20160027.

Gloaguen, T.V.; Pereira, F.A.C.; Gonçalves, R.A.B.; Paz, V.S. Composição química da solução do solo nas diferentes classes de poro do solo. Revista Brasileira de Ciência do Solo, v.33, n.5, p.1105-1113, 2009. https://doi.org/10.1590/S0100-06832009000500004.

Grimm, D.M.; Azarraga, V.L.; Carreira, L.A.; Sustyo, W. Continuous multiligand distribution model used to predict the stability constant of copper (II) metal complexation with humic material from fluorescence quenching data. Environmental Science and Technology, v.25, n.8, p.1427-1431, 1991. https://doi.org/10.1021/es00020a010.

Gustafsson, J.P. Visual Minteq, 3.1. Stockholm: KTH; Departamento of Land and Water Resources Engineering; 2016. https://vminteq.lwr.kth.se/download. 12 Dez. 2016.

Hernández-Soriano, M. C. The role of aluminum-organo complexes in soil organic matter dynamics. In: Hernández-Soriano, M. C. (Ed.). Soil health and land use management, 2012. Chap. 2, p.17-32. http://dx.doi.org/10.5772/39117.

Krishnamurtiand, G.R.S.; Naidu, R. Solid solution speciation and phytoavailability of cooper and zinc in soil. Environmental Science and Technology, v. 36, n.12, p.2645-2651, 2002. https://doi.org/10.1021/es001601t.

Lindsay, W.L. Chemical equilibria in soils. New York: John Wiley, 1979. 450p.

Miguel, P.S.B.; Gomes, F.T.; Rocha, W.S.D.; Martins, C.E.; Carvalho, C.A.; Oliveira, A.V. Efeitos tóxicos do alumínio no crescimento das plantas: mecanismos de tolerância, sintomas, efeitos fisiológicos, bioquímicos e controles genéticos. CES Revista, v.24, n. 1, p.13-29, 2010. https://seer.cesjf.br/index.php/cesRevista/article/viewFile/661/519. 10 Jan. 2017.

Murphy, J.; Riley, J.P. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, v.27, p.31-36, 1962. https://doi.org/10.1016/S0003-2670(00)88444-5.

Nolla, A.; Anghinoni, I.; Castaldo, J.H.; Alves, E.O.S.; Neto L.V.M.N.; Silva, M.A.G.; Muniz, A.S. Disponibilidade de nutrientes e fitotoxidez de alumínio; influência da complexação por ligantes orgânicos na solução do solo. Journal of Agronomic Science, v.4, n. especial, p.1-16, 2015. http://www.dca.uem.br/V4NE/01.pdf. 22 Jan. 2017.

Nolla, A.; Anghinoni, I.; Silva, T.R.B.; Silva, M.A.G. Lime-phosphate relation and soybean growth in an Oxisol from no-tillage system. Journal of Food Agriculture and Environment, v.11, n.1, p.294-298, 2013. https://www.wflpublisher.com/Abstract/3850. 10 Jan. 2017.

Peralta, N.R.; Costa, J.L.; Balzarini, M.; Franco, M.C.; Córdoba, M.; Bullock, D. Delineation of management zones with soil apparent electrical conductivity to improve nutrient managment. Computers and Electtonics in Agriculture, v.99, p.218-226, 2013. https://doi.org/10.1016/j.compag.2013.09.014.

Rossiello, R.O.P.; Netto, J.J. Toxidez de alumínio em plantas: novos enfoques para um velho problema. In: Fernandes, M.S. (Ed.). Nutrição mineral de plantas. 2.ed. Viçosa: Sociedade Brasileira de Ciência do Solo; 2006. p.375-418.

Rutkowska, B.; Szulc, W.; Hoch, M.; Spychaj-Fabisiak, E. Forms of Al in soil and soil solution in a long-term fertilizer application experiment. Soil and Use Management, v.31, p.114-120, 2015. https://doi.org/10.1111/sum.12150.

Smith, R.M.; Martell, A.E.; Motekaitis, R.J. NIST critically selected stability constants of metal complexes database. NIST Standard Reference Database 46, version 7.0. Gaithersburg: National Institute of Standar and Technology, 2003. p.1-30.

Somavilla, A.; Dessbesell, A.; Santos, D.R. Centrifugation methogology to extract soil solution. Scientia Agraria, v.18, n.3, p.44-47, 2017. https://doi.org/10.5380/rsav18i3.52805.

Souza, E.R.; Melo, H.F.; Almeida, B.G.; Melo, D.V.M. Comparação de métodos de extração da solução do solo. Revista Brasileira de Engenharia Agrícola e Ambiental, v.17, n.5, p.210-517, 2013. https://doi.org/10.1590/S1415-43662013000500007.

Spera, S.T.; Varella, P.A.; Escosteguy, P.A.V.; Santos, H.P.; Klein, V.A. A solução de um Latossolo Vermelho distrófico submetido a três tipos de manejo de solo e de culturas. Nativa, v.2, n.2, p.58-64, 2014. https://doi.org/10.14583/2318-7670.v02n02a01.

Tamir, G.; Shenker, M.; Heller, H.; Bloom, P.R.; Fine, P.; Bar-Tal, A. Organic N mieralization and transfromations in soils treated with animal waste in relation to carbonate dissolution and precipitation. Geoderma, v.209-210, p.50-59, 2013. https://doi.org/10.1016/j.geoderma.2013.05.028.

Wadt, P.G.S. Manejo de solos ácidos do Estado do Acre. Rio Branco: Embrapa Acre, 2002. 29p. (Embrapa Acre. Documentos, 79).

Zambrosi, F.C.B.; Alleoni, L.R.F.; Caires, E.F. Liming and ionic speciation of an Oxisol under no-till system. Scientia Agricola, v.65, n. 2, p.190-203, 2008. https://doi.org/10.1590/S0103-90162008000200013.