LIMING AND IONIC SPECIATION OF AN OXISOL UNDER NO-TILL SYSTEM

Fernando Cesar Bachiega Zambrosi[1]*; Luís Reynaldo Ferracciú Alleoni[2], Eduardo Fávero Caires[3]

[1]IAC - Centro de Pesquisa e Desenvolvimento de Solos e Recursos Ambientais, Av. Barão de Itapura, 1481 - 13001-970 - Campinas, SP - Brasil.
[2]USP/ESALQ - Depto. de Ciência do Solo, C.P. 09 - 13418-900 - Piracicaba, SP - Brasil.
[3]UEPG - Depto. de Ciência do Solo e Engenharia Agrícola, Av. Carlos Cavalcanti, 4748 - 84030-900 - Ponta Grossa, PR - Brasil.
*Corresponding author <zambrosi@iac.sp.gov.br>

ABSTRACT: The chemical speciation of the soil solution is an important tool for evaluating nutrient availability and aluminum phytotoxicity. The effect of liming in the composition of the soil solution under the no-till (NT) system is still not well known. We evaluated the chemical speciation of Al and nutrients in the soil solution (water extract 1:1), five years after liming at the moment of the establishment of NT in a native pasture, in Ponta Grossa, Paraná State, Brazil. Dolomitic lime was applied at a rate of 4.5 t ha^{-1} (either incorporated or surface-applied), or split in three annual rates of 1.5 t ha^{-1}. Soil samples from a dystrophic clayey Rhodic Hapludox were collected at the 0 - 0.05; 0.05 - 0.1; 0.1 - 0.2; 0.2 - 0.4; 0.4 - 0.6; and 0.6 - 0.8 m layers, in May, 2003. Aluminum was mainly complexed to dissolved organic carbon (DOC) and fluoride, while the free form Al^{3+} was present in fewer amounts even under acidic conditions. Calcium and magnesium were found as free forms (Ca^{2+}, Mg^{2+}) and complexed by organic anions. Phosphorus was found as free forms (HPO$_4^{2-}$, H$_2$PO$_4^-$) and complexed with aluminum (ionic pair Al-H$_x$PO$_4^x$) up to 0.1 m. Complexation of Al by DOC was not influenced by surface-applied or incorporated liming. Liming did not change Ca and Mg speciation in the soil solution under NT system. The presence of free forms HPO$_4^{2-}$ and H$_2$PO$_4^-$, however, was influenced by liming, because of the increase in cation associated forms.
Key words: dolomitic lime, complex, ionic pair, dissolved organic carbon

CALAGEM E ESPECIAÇÃO IÔNICA DE UM LATOSSOLO SOB SISTEMA PLANTIO DIRETO

RESUMO: A especiação química da solução do solo é uma importante ferramenta para avaliar a disponibilidade de nutrientes e o potencial fitotóxico do alumínio. As formas em que os elementos ocorrem na solução dos solos sob sistema plantio direto (SPD) ainda são pouco conhecidas, sobretudo em áreas que receberam aplicação de calcário. Avaliou-se a distribuição das espécies químicas de alumínio e nutrientes na solução do solo (extrato aquoso 1:1), cinco anos após a aplicação de calcário, na introdução do SPD em área de pastagem nativa, em Ponta Grossa -PR. Aplicaram-se 4,5 t ha^{-1} de calcário dolomítico na superfície, em dose única ou parcelada durante três anos, ou com incorporação na camada de 0 - 0,20 m, de um Latossolo Vermelho distrófico textura argilosa. As amostras de solo foram coletadas nas profundidades de 0 - 0,05; 0,05 - 0,1; 0,1 - 0,2; 0,2 - 0,4; 0,4 - 0,6 e 0,6 - 0,8 m. O alumínio (Al) ocorreu predominantemente complexado pelo carbono orgânico dissolvido (DOC) e pelo fluoreto, e em baixíssimas proporções na forma livre Al^{3+}, mesmo em condições de alta acidez. Para cálcio (Ca) e magnésio (Mg), as espécies químicas que ocorreram em maiores proporções foram as formas livres (Ca^{2+} e Mg^{2+}) e complexadas pelo DOC. O fósforo, além das formas livres (H$_2$PO$_4^-$, HPO$_4^{2-}$), interagiu com alumínio (par iônico Al-H$_x$PO$_4^x$), sobretudo até 0,1 m de profundidade. A complexação do alumínio pelo carbono orgânico dissolvido não foi influenciada pela correção da acidez do solo por meio da calagem na superfície ou com incorporação. A aplicação de calcário não alterou a especiação de cálcio e magnésio na solução do solo sob sistema plantio direto. Contudo, a ocorrência das formas livres H$_2$PO$_4^-$ e HPO$_4^{2-}$ foi influenciada pela calagem, havendo incremento das formas associadas com cátions.
Palavras-chave: calcário dolomítico, complexos, par iônico, carbono orgânico dissolvido

INTRODUCTION

The no-till (NT) system is an efficient soil con-servation practice, nevertheless, there is a lack of in-formation on soil fertility and crop management for this system (Rheinheimer et al., 2000). The better ero-

sion control as compared to the conventional tillage system leads to smaller losses of organic carbon and nutrients, mainly Ca and Mg (Bertol et al., 2005). Consequently, the area under NT in Brazil has grown in the last few years. Regarding soil fertility management, there has been an increase in studies about liming in NT, focusing on forms and rates of application and correction of soil acidity (Alleoni et al., 2003, 2005; Amaral & Anghinoni, 2001; Caires et al., 1998, 1999, 2000, 2004; Kaminski et al., 2005). Assessments on the effects of liming on soil chemical attributes should be made in a long term basis in order to obtain the residual effects of liming (Caires et al., 2005, 2006b). Nevertheless, studies that also focus on the soil solution under NT, especially through chemical speciation, are scarce. In a recent study with samples of an Oxisol collected in areas of distinct acidity conditions, and later placed in columns with several rates of phosphorus, Nolla & Anghinoni (2006) pointed out the importance of chemical speciation in the evaluation of the phytotoxic potential of aluminum in soils cultivated under the NT system.

The main soil chemical reactions happen in soil solution. Therefore, knowledge of its composition is very important, both for environmental management studies and for soil fertility and plant nutrition studies. The soil-solution interface is very dynamic, and the dissolved elements are affected by several reactions, such as acid-base equilibrium, ionic complexation, precipitation and dissolution of solids, oxidation, reduction and ionic exchange (Chaves et al., 1991; Fontes & Alleoni, 2006). The concentration of most dissolved cations in the solution is determined by the equilibrium with their exchangeable forms (Nemeth et al., 1970). Liming in acid soils is, most likely, the agricultural practice with the greatest potential for changing the composition of the exchange complex and the liquid phase, due to the quick equilibrium between phases. Thus, liming affects the dynamics of dissolved ions (Amaral et al., 1998; Zambrosi et al., 2007).

A detailed study of the soil solution thorough chemical speciation contributes to a better understanding of the mobility and availability of nutrients or phytotoxic metals (Krishnamurtiand & Naidu, 2002), despite the variability in the methods of obtaining and the dependence on edafoclimatic conditions (Wolt, 1994). In the soil solution, most of the ions are present either as free ions or interacting with other ions or molecules, forming soluble complexes (Sposito, 1994). In areas under the NT system, the presence of relatively high concentrations of organic ligands in the soil solution, due to the increment in organic matter, can reduce aluminum toxicity (Hue et al., 1986) and help mobilize cations (Tack & Verloo, 1995). When com-

pared to the soil total organic matter, the more readily available fraction, such as the dissolved organic carbon (DOC), is more sensitive to changes caused by soil management in the short and medium terms, being, therefore, used as a fundamental indicator of soil quality or of changes in native conditions (Silveira, 2005).

Chemical speciation provides a clear view of the interactions of elements in soil solution. Such interaction interferes in nutrient mobility and availability, and can help elucidate the mechanisms involved in acidity amelioration by liming in soils under NT. In the present study, the percentage of aluminum and nutrient chemical species in the soil solution of an Oxisol under NT was quantified, five years after liming, surface applied or incorporated, with single and split applications.

MATERIAL AND METHODS

Samples from a dystrophic clayey Rhodic Hapludox were collected in a field experiment set up in 1998, in a native pasture area located in Ponta Grossa, Paraná State, Brazil ($25^{o}10'$ S, $50^{o}05'$ W). The soil chemical analyses performed before the beginning of the experiment, following the methodology described by Pavan et al. (1992), indicated the following results, for the 0 - 0.2 and 0.2 - 0.4 m soil layers, respectively: pH $CaCl_2$ of 4.6 and 4.2; organic matter (OM) content of 31 and 21 g dm^{-3}; P (Mehlich-1) of 0.3 and 0.1 mg dm^{-3}; K^+ of 3.6 and 2.2; Ca^{2+} of 25 and 7; Mg^{2+} of 20 and 8; Al^{3+} of 3 and 8; H + Al of 77.6 and 97.0 $mmol_c$ dm^{-3}; base saturation (V) of 38 and 15%; aluminum saturation (m) of 6 and 32%. The soil textural composition, determined according to Embrapa (1997) methodology for these same soil layers, was 290 and 300 g kg^{-1} sand; 130 and 100 g kg^{-1} silt; 580 and 600 g kg^{-1} clay, respectively.

The experiment was carried out in a completely randomized block design with three replications. Dolomitic lime with an effective calcium carbonate equivalent (ECCE) of 89% was used at a rate calculated to raise the soil base saturation to 70% in the 0 - 0.2 m layer. The treatments were: control (no lime) (T1); surface application of 4.5 t ha^{-1} split in three annual applications of 1.5 t ha^{-1} (T2); a single surface application of 4.5 t ha^{-1} (T3); a single application of 4.5 t ha^{-1} incorporated to 0.2 m (T4). Lime was applied by hand to the soil surface in July 1998. In the incorporated lime plots, one-half of the lime was surface broadcasted by hand, and incorporated to a 0.2 m depth with a disk plow. The remainder was added by hand to the surface, and the soil was harrowed to a 0.1 m depth with a disk harrow. In the plots with

annual splitting of surface-applied lime, the second application was performed in May 1999, and the third, in May 2000.

The sequence of crops was soybean (1998-1999), barley (winter of 1999), soybean (1999-2000), wheat (winter of 2000), soybean (2000-2001), corn (2001-2002), and soybean (2002-2003). For the soybean crop, the fertilizer application at seeding was 75 kg ha^{-1} of P_2O_5 and K_2O (300 kg ha^{-1} of the 0-25-25 formula) in the first crop, and 60 kg ha^{-1} of P_2O_5 and K_2O (300 kg ha^{-1} of the 0-20-20 formula) in the three other crops. The fertilizers used for the soybeans contained 5% S, as $CaSO_4$, from the simple superphosphate. Thus, each soybean crop received 15 kg ha^{-1} of S. The barley crop received 28 kg ha^{-1} of N and 92 kg ha^{-1} of P_2O_5, as diammonium phosphate (DAP) at sowing, and 45 kg ha^{-1} of N, as top-dressed urea. The wheat crop received 33 kg ha^{-1} of N and 66 kg ha^{-1} of P_2O_5 and K_2O (330 kg ha^{-1} of the 10-20-20 formula) at sowing, and 100 kg ha^{-1} of N, as top-dressed urea. Corn crop fertilization was 413 kg ha^{-1} of the 8-30-20 formula at sowing, and top-dressing of 124 kg ha^{-1} of the 36-00-12 formula. Insect, weed and disease management was performed as needed, according to each crops' recommendations. The cropping sequence for each liming treatment was described by Caires et al. (2006a).

Soil samples were collected in May, 2003, right after the soybean harvest, five years after liming. Samples were taken with a probe, collecting 12 subsamples per plot, forming a composite sample for the 0 - 0.05, 0.05 - 0.1, and 0.1 - 0.2 m layers, and five subsamples per plot for the 0.2 - 0.4, 0.4 - 0.6, and 0.6 - 0.8 m layers. Air-dried samples were gently crushed and passed through a 2 mm sieve, stored in plastic bags and kept in the shade at room temperature until analysis. The samples were analyzed for pH, Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, and total organic carbon, according to Pavan et al. (1992).

The water-extraction method (Wolt, 1994) was employed extract the soil solution, using a soil:water ratio of 1:1. In a 50 mL centrifuge tube, 20 mL of ultrapure water were added to 20 g of soil. Then, the tubes were placed in a horizontal shaker for 15 minutes at 150 rpm, and left resting for 1 h. After this period, the solution was shaken again for five more minutes (Wolt, 1994) and centrifuged for 30 minutes at 1500 rpm. Three extractions were performed to obtain cation, anion and dissolved organic carbon (DOC) extracts. To obtain the extract for cation determination, the solution was passed through a 0.45 mm mesh cellulose membrane. Another extract was passed through a 0.22 mm mesh cellulose membrane for anion determination. The extract for DOC was obtained by passing the solution through a 0.7 mm mesh GF/F glass microfiber filter, previously calcinated at 500°C for 6h, and stored in flasks submitted to the same calcination process.

The filtering processes to obtain the extracts were performed with a 13 mm diameter filter support for the cation and anion fractions, and a 25 mm diameter filter support for the DOC. These supports were connected to 60 mL plastic syringes, where the extracts were placed after centrifugation, and were filtered by manual pressure. The pH was determined in the solutions immediately after centrifugation. The total contents of calcium, magnesium, potassium, sodium, aluminum, iron, and manganese were determined by ICP-OES, while nitrate, sulfate, phosphate, chloride, and fluoride contents were determined using a chromatographer. The DOC was determined in a Shimadzu 5000A carbon analyzer.

The soil solution ionic strength (I) was calculated as follows:

$$I = \frac{1}{2} \sum_{i=1}^{n} Ci.(Zi)^2$$

where Ci is the concentration (mol L^{-1}), and Zi is the charge of each ion i in solution.

The ionic speciation of the soil solution was performed with the Visual MINTEQ computer program (Gustafsson, 2004), using the total concentration (mg L^{-1}) of cations, inorganic anions, and DOC, and the ionic strength (mol L^{-1}) and pH values of the solution. The distribution in percentages of each species in the soil solution was obtained as a function of the forms of limestone application and sampling depths. The percentages of each species were compared within each depth, using the mean standard error (with three replications).

RESULTS AND DISCUSSION

Lime application reduced the exchangeable aluminum content and increased the exchangeable calcium and magnesium contents and soil pH, especially at the 0 - 0.2 layer (Table 1). The composition of soil solution (water extract) are presented in Tables 2 and 3. In general, liming increased soil pH and soluble calcium and magnesium contents, especially in the surface layers. Down to the 0.1 - 0.2 m depth, there was a positive ($P < 0.05$) correlation between the exchangeable and soluble content values of calcium and magnesium (data not shown), confirming the equilibrium between these two phases, as well as the sensitivity of the water extract in reflecting changes in the exchangeable content of these nutrients in the soil. The correlation between calcium and magnesium in solu-

Table 1 - Lime treatments, contents of exchangeable of cations, organic carbon (C), and values of pH for different depths of an Oxisol under no-till system. Values between parenthesis represent the mean deviation (n = 3).

Treat*	Ca	Mg	K	Al	pH	C
	----------------------------- mmol$_c$ dm^{-3} -----------------------------					g kg^{-1}
0 - 0.05 m						
T1	37.7 ± (1.9)	24.3 ± (3.8)	6.4 ± (0.7)	1.0 ± (0.0)	4.9 ± (0.0)	33.3 ± (1.3)
T2	59.7 ± (0.9)	46.0 ± (1.5)	5.3 ± (0.7)	0.0 ± (0.0)	5.9 ± (0.0)	31.7 ± (1.5)
T3	63.0 ± (2.1)	42.7± (1.3)	5.3 ± (0.2)	0.0 ± (0.0)	5.8 ± (0.1)	35.0 ± (1.5)
T4	50.7 ± (4.8)	36.7 ± (5.2)	6.7 ± (0.7)	0.0 ± (0.0)	5.5 ± (0.1)	31.3 ± (1.5)
0.05 - 0.1 m						
T1	25.7 ± (0.9)	17.0 ± (4.0)	4.6 ± (0.7)	3.3 ± (0.9)	4.6 ± (0.0)	27.0 ± (2.1)
T2	33.7 ± (0.9)	27.0 ± (1.0)	3.1 ± (0.5)	0.0 ± (0.0)	5.1 ± (0.1)	31.3 ± (5.4)
T3	32.7 ± (3.2)	26.0 ± (0.6)	3.1 ± (0.3)	0.0 ± (0.0)	5.3 ± (0.1)	24.7 ± (1.2)
T4	40.7 ± (1.8)	34.7 ± (4.1)	5.0 ± (0.9)	0.0 ± (0.0)	5.5 ± (0.1)	26.7 ± (1.9)
0.1 - 0.2 m						
T1	15.0 ± (1.0)	15.7 ± (2.0)	2.7 ± (0.6)	4.3 ± (0.9)	4.6 ± (0.1)	21.0 ± (1.2)
T2	18.3 ± (1.5)	15.7 ± (2.0)	1.6 ± (0.3)	3.0 ± (0.0)	4.8 ± (0.0)	21.0 ± (2.0)
T3	16.3 ± (1.8)	14.3 ± (3.3)	1.7 ± (0.2)	3.0 ± (0.6)	4.8 ± (0.0)	18.7 ± (0.9)
T4	25.3 ± (2.4)	24.0 ± (1.0)	2.9 ± (0.2)	0.0 ± (0.0)	5.2 ± (0.1)	22.3 ± (2.3)
0.2 - 0.4 m						
T1	13.7 ± (1.8)	14.7 ± (2.7)	2.3± (1.1)	4.7 ± (0.9)	4.6 ± (0.1)	19.0 ± (1.0)
T2	17.3 ± (2.7)	14.3 ± (0.7)	1.8 ± (0.3)	3.0 ± (1.0)	4.5 ± (0.1)	18.7 ± (1.8)
T3	15.3 ± (2.7)	15.7 ± (3.3)	1.3 ± (0.1)	2.3 ± (0.9)	4.5 ± (0.0)	18.7 ± (1.5)
T4	15.0 ± (1.5)	18.7 ± (0.9)	1.7 ± (0.1)	0.7 ± (0.3)	4.7 ± (0.0)	18.7 ± (0.9)
0.4 - 0.6 m						
T1	8.0 ± (1.0)	10.0 ± (2.1)	1.1 ± (0.5)	4.7 ± (0.3)	4.5 ± (0.0)	14.0 ± (1.2)
T2	11.0 ± (0.6)	14.3 ± (1.9)	1.0 ± (0.3)	2.0 ± (0.0)	4.8 ± (0.0)	13.7 ± (1.8)
T3	9.0 ± (0.6)	9.3 ± (0.3)	0.6 ± (0.1)	1.7 ± (0.3)	4.8 ± (0.1)	13.7 ± (1.3)
T4	8.3 ± (1.2)	11.0 ± (1.2)	2.1 ± (1.1)	2.7 ± (0.3)	4.7 ± (0.0)	13.7 ± (1.5)
0.6 - 0.8 m						
T1	7.0 ± (1.0)	10.7 ± (2.2)	1.2 ± (0.8)	3.0 ± (0.6)	4.7 ± (0.0)	11.7 ± (0.7)
T2	8.0 ± (0.6)	10.0 ± (1.2)	0.5 ± (0.1)	2.3 ± (0.3)	4.8 ± (0.0)	11.7 ± (0.7)
T3	10.7 ± (2.3)	8.7 ± (0.3)	1.2 ± (0.7)	2.3 ± (0.7)	4.8 ± (0.1)	16.3 ± (4.5)
T4	7.0 ± (0.6)	9.7 ± (1.2)	1.9 ± (0.9)	2.7 ± (0.7)	4.7 ± (0.1)	10.3 ± (0.7)

*T1 = control (without lime); T2 = three annual surface liming of 1.5 t ha^{-1}; T3 = 4.5 t ha^{-1} of surface-applied lime; T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth.

tion and their exchangeable content was also observed by Ciotta et al. (2004) in an Oxisol under NT after surface and incorporated application of lime.

Aluminum was detected in free form (Al^{3+}) and, in greater proportion, forming complexes in the soil solution (Figure 1). Plant toxicity decreases in the following order: Al$_{13}$ polymers (except for phosphates and silicates), Al^{3+}, Al(OH)$^{2+}$, Al(OH)$_2^+$, Al(OH)$_4^-$, and AlSO$_4^+$, considering that the toxicity of this last species is not always accepted (Drabeck et al., 2005). The Al species bonded with fluoride and organic compounds, Al(OH)$_3$, are considered nontoxic. Although Al$_{13}$ is the most toxic species, it is not commonly present in soils (Drabeck et al., 2005). The free form Al^{3+} is, therefore, the most harmful to plant roots. Nevertheless, in the present study, there were proportionally low concentrations of Al^{3+}, regardless of the depth sampled, even in the treatment without liming. Under natural conditions, low or moderate concentrations of Al^{3+} are usually observed in the solution of acid soils, while the complexes formed between aluminum and fluoride (Al-F) and aluminum and dissolved organic carbon (Al-DOC) represent the majority of Al species (Merino et al., 1998).

Table 2 - Lime treatments, values of pH, and total concentration of dissolved organic carbon (DOC) and inorganic anions in solution for different depths of an Oxisol under no-till system. Values between parenthesis represent the mean deviation (n = 3).

Treat.*	pH	DOC	N-NO$_3^-$	Cl	S-SO$_4^{2-}$	P-PO$_4^{3-}$	F
				-- mmol L^{-1} --			
				0 - 0.05 m			
T1	5.0 ± (0.0)	16.8 ± (0.4)	0.27 ± (0.01)	0.16 ± (0.04)	0.057 ± (0.004)	0.0011 ± (0.0009)	0.11 ± (0.00)
T2	6.2 ± (0.1)	15.0 ± (0.3)	0.24 ± (0.00)	0.24 ± (0.07)	0.080 ± (0.006)	0.0010 ± (0.0005)	0.18 ± (0.03)
T3	5.9 ± (0.0)	17.7 ± (1.0)	0.29 ± (0.02)	0.16 ± (0.01)	0.073 ± (0.022)	0.0002 ± (0.0000)	0.14 ± (0.06)
T4	5.5 ± (0.2)	18.4 ± (1.2)	0.30 ± (0.02)	0.17 ± (0.03)	0.055 ± (0.001)	0.0001 ± (0.0001)	0.11 ± (0.05)
				0.05 - 0.1 m			
T1	4.8 ± (0.1)	16.5 ± (2.5)	0.27 ± (0.04)	0.18 ± (0.04)	0.026 ± (0.003)	0.0014 ± (0.0009)	0.08 ± (0.02)
T2	5.5 ± (0.2)	14.8 ± (0.0)	0.24 ± (0.00)	0.10 ± (0.02)	0.040 ± (0.008)	0.0001 ± (0.0000)	0.05 ± (0.02)
T3	5.1 ± (0.1)	16.2 ± (1.6)	0.26 ± (0.03)	0.13 ± (0.05)	0.048 ± (0.017)	0.0002 ± (0.0001)	0.08 ± (0.03)
T4	5.3 ± (0.1)	15.5 ± (1.5)	0.25 ± (0.02)	0.09 ± (0.02)	0.021 ± (0.006)	0.0002 ± (0.0000)	0.03 ± (0.00)
				0.1 - 0.2 m			
T1	4.8 ± (0.1)	12.1 ± (1.9)	0.20 ± (0.03)	0.15 ± (0.03)	0.015 ± (0.003)	0.0001 ± (0.0000)	0.07 ± (0.01)
T2	5.0 ± (0.1)	10.7 ± (0.5)	0.17 ± (0.01)	0.21 ± (0.06)	0.023 ± (0.002)	0.0003 ± (0.0001)	0.06 ± (0.01)
T3	4.9 ± (0.2)	11.7 ± (1.2)	0.19 ± (0.02)	0.12 ± (0.00)	0.018 ± (0.002)	0.0004 ± (0.0002)	0.06 ± (0.02)
T4	5.2 ± (0.0)	10.8 ± (0.3)	0.17 ± (0.01)	0.20 ± (0.06)	0.031 ± (0.007)	0.0001 ± (0.0000)	0.07 ± (0.01)
				0.2 - 0.4 m			
T1	4.9 ± (0.1)	6.4 ± (1.0)	0.10 ± (0.02)	0.27 ± (0.10)	0.010 ± (0.002)	0.0002 ± (0.0001)	0.04 ± (0.01)
T2	5.0 ± (0.1)	6.0 ± (0.4)	0.10 ± (0.01)	0.14 ± (0.01)	0.018 ± (0.009)	0.0001 ± (0.0001)	0.04 ± (0.00)
T3	4.8 ± (0.2)	6.9 ± (1.0)	0.11 ± (0.02)	0.17 ± (0.04)	0.010 ± (0.004)	0.0002 ± (0.0002)	0.04 ± (0.01)
T4	4.9 ± (0.1)	6.8 ± (0.2)	0.11 ± (0.00)	0.22 ± (0.11)	0.023 ± (0.004)	nd**	0.05 ± (0.01)
				0.4 - 0.6 m			
T1	4.8 ± (0.1)	4.6 ± (0.7)	0.07 ± (0.01)	0.27 ± (0.03)	0.001 ± (0.001)	0.0001 ± (0.0001)	0.03 ± (0.00)
T2	5.0 ± (0.0)	3.6 ± (0.1)	0.06 ± (0.00)	0.31 ± (0.06)	0.011 ± (0.009)	0.0003 ± (0.0002)	0.03 ± (0.00)
T3	4.7 ± (0.2)	4.0 ± (0.7)	0.06 ± (0.01)	0.30 ± (0.04)	0.001 ± (0.000)	0.0002 ± (0.0002)	0.03 ± (0.00)
T4	4.7 ± (0.2)	3.7 ± (0.4)	0.06 ± (0.01)	0.19 ± (0.05)	0.001 ± (0.000)	0.0001 ± (0.0001)	0.03 ± (0.01)
				0.6 - 0.8 m			
T1	4.8 ± (0.1)	2.6 ± (0.4)	0.04 ± (0.01)	0.30 ± (0.04)	0.011 ± (0.002)	0.0001 ± (0.0001)	0.02 ± (0.00)
T2	4.9 ± (0.2)	2.4 ± (0.1)	0.04 ± (0.00)	0.30 ± (0.02)	0.001 ± (0.001)	0.0002 ± (0.0001)	0.01 ± (0.00)
T3	4.8 ± (0.1)	2.5 ± (0.1)	0.04 ± (0.00)	0.22 ± (0.09)	0.002 ± (0.000)	0.0001 ± (0.0000)	0.02 ± (0.00)
T4	4.7 ± (0.2)	2.8 ± (0.2)	0.04 ± (0.00)	0.23 ± (0.05)	0.001 ± (0.000)	nd	0.01 ± (0.00)

*T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth.**nd: not detected.

In the NT system, organic anions have an important role in Al chemistry, being the main responsible for reduction of the activity of this element in solution, and thus, reducing its phytoxicity (Vance et al., 1996). The complexation of Al by DOC, in general, was not affected by the liming treatments. Cambri et al. (2004) observed that the proportion of Al-DOC in the soil solution under NT was approximately 85% in the 0 - 0.2 m layer, and that this proportion was little affected by surface application of lime. Adams et al. (1999) verified that the Al bonded to DOC was strongly correlated to the concentration of dissolved humic acid substances in acid soils of New Zealand.

Fluoride (F), which competed intensely with DOC, was another ligand responsible for the strong complexation of Al in the soil solution (Figure 1). While DOC and fluoride complexed aluminum in a large scale, other anions such as sulfate (S-SO$_4^{2-}$) and phosphate (P-H$_x$PO$_4^x$) formed ionic pairs in a much smaller proportion, representing, at the most, 0.3% of the total Al species (other species). Sulfate and

Table 3 - Lime treatments, total concentration of cations, and ionic strength (I) of solution for different depths of an Oxisol under no-till system. Values between parenthesis represent the mean deviation (n = 3).

Treat.*	Al	Ca	Mg	K	Na	Fe	Mn	I
	-- mmol L^{-1} --							
				0 - 0.05 m				
T1	0.25 ± (0.01)	0.32 ± (0.02)	0.36 ± (0.03)	0.82 ± (0.13)	0.06 ± (0.01)	0.084 ± (0.062)	0.003 ± (0.000)	4.6 ± (1.0)
T2	0.29 ± (0.08)	0.55 ± (0.02)	0.80 ± (0.02)	0.66 ± (0.11)	0.06 ± (0.02)	0.031 ± (0.008)	0.001 ± (0.000)	5.6 ± (0.3)
T3	0.25 ± (0.06)	0.55 ± (0.05)	0.78 ± (0.06)	0.68 ± (0.04)	0.06 ± (0.02)	0.029 ± (0.011)	0.001 ± (0.000)	5.2 ± (0.6)
T4	0.98 ± (0.44)	0.38 ± (0.02)	0.54 ± (0.04)	0.68 ± (0.08)	0.06 ± (0.01)	0.090 ± (0.066)	0.001 ± (0.000)	7.9 ± (2.2)
				0.05 - 0.1 m				
T1	0.40 ± (0.14)	0.19 ± (0.00)	0.18 ± (0.01)	0.43 ± (0.06)	0.06 ± (0.02)	0.032 ± (0.011)	0.001 ± (0.000)	3.4 ± (0.7)
T2	0.38 ± (0.03)	0.23 ± (0.03)	0.37 ± (0.04)	0.28 ± (0.06)	0.05 ± (0.02)	0.025 ± (0.003)	0.001 ± (0.000)	3.7 ± (0.4)
T3	0.42 ± (0.09)	0.23 ± (0.02)	0.37 ± (0.02)	0.34 ± (0.02)	0.05 ± (0.03)	0.037 ± (0.01)	0.001 ± (0.000)	4.1 ± (0.6)
T4	0.65 ± (0.24)	0.31 ± (0.01)	0.45 ± (0.02)	0.36 ± (0.04)	0.04 ± (0.01)	0.048 ± (0.020)	0.001 ± (0.000)	5.7 ± (1.6)
				0.1 - 0.2 m				
T1	0.09 ± (0.05)	0.13 ± (0.02)	0.16 ± (0.01)	0.29 ± (0.03)	0.05 ± (0.02)	0.010 ± (0.006)	0.001 ± (0.000)	1.6 ± (0.2)
T2	0.10 ± (0.04)	0.16 ± (0.01)	0.26 ± (0.01)	0.21 ± (0.03)	0.05 ± (0.02)	0.013 ± (0.006)	0.001 ± (0.000)	1.9 ± (0.2)
T3	0.07 ± (0.02)	0.14 ± (0.00)	0.22 ± (0.01)	0.20 ± (0.02)	0.05 ± (0.02)	0.009 ± (0.003)	0.001 ± (0.000)	1.6 ± (0.1)
T4	0.53 ± (0.31)	0.21 ± (0.02)	0.36 ± (0.01)	0.22 ± (0.03)	0.04 ± (0.01)	0.025 ± (0.004)	0.001 ± (0.000)	4.2 ± (1.4)
				0.2 - 0.4 m				
T1	0.05 ± (0.05)	0.12 ± (0.00)	0.15 ± (0.01)	0.22 ± (0.06)	0.06 ± (0.03)	0.007 ± (0.007)	0.001 ± (0.000)	1.4 ± (0.3)
T2	0.01 ± (0.00)	0.14 ± (0.01)	0.21 ± (0.02)	0.15 ± (0.02)	0.05 ± (0.01)	0.001 ± (0.000)	0.001 ± (0.000)	1.2 ± (0.1)
T3	0.01 ± (0.00)	0.14 ± (0.02)	0.22 ± (0.01)	0.11 ± (0.01)	0.03 ± (0.01)	nd**	0.001 ± (0.000)	1.2 ± (0.1)
T4	0.10 ± (0.09)	0.14 ± (0.02)	0.27 ± (0.04)	0.12 ± (0.03)	0.03 ± (0.01)	0.001 ± (0.000)	0.001 ± (0.000)	1.8 ± (0.5)
				0.4 - 0.6 m				
T1	0.01 ± (0.00)	0.08 ± (0.01)	0.12 ± (0.02)	0.10 ± (0.04)	0.04 ± (0.02)	nd	0.003 ± (0.000)	0.8 ± (0.1)
T2	0.02 ± (0.01)	0.10 ± (0.02)	0.14 ± (0.03)	0.06 ± (0.00)	0.03 ± (0.01)	0.007 ± (0.006)	0.008 ± (0.006)	1.0 ± (0.2)
T3	0.01 ± (0.00)	0.09 ± (0.00)	0.12 ± (0.01)	0.05 ± (0.02)	0.03 ± (0.01)	nd	0.002 ± (0.000)	0.8 ± (0.0)
T4	0.01 ± (0.00)	0.08 ± (0.02)	0.13 ± (0.02)	0.05 ± (0.02)	0.03 ± (0.01)	nd	0.003 ± (0.000)	0.7 ± (0.2)
				0.6 - 0.8 m				
T1	0.01 ± (0.00)	0.09 ± (0.01)	0.10 ± (0.01)	0.07 ± (0.03)	0.05 ± (0.02)	nd	0.004 ± (0.000)	0.8 ± (0.1)
T2	0.01 ± (0.00)	0.08 ± (0.02)	0.12 ± (0.02)	0.04 ± (0.01)	0.07 ± (0.03)	0.001 ± (0.000)	0.004 ± (0.001)	0.8 ± (0.1)
T3	0.07 ± (0.07)	0.09 ± (0.02)	0.14 ± (0.05)	0.04 ± (0.01)	0.05 ± (0.03)	0.028 ± (0.028)	0.027 ± (0.023)	1.2 ± (0.7)
T4	0.01 ± (0.01)	0.06 ± (0.01)	0.11 ± (0.00)	0.03 ± (0.02)	0.02 ± (0.00)	0.001 ± (0.000)	0.005 ± (0.000)	0.6 ± (0.0)

*T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth. **nd: not detected.

phosphate have similar values of ligand constant to Al, both much smaller than the values of ligand constant of fluoride and Al (Lindsay & Walthall, 1996). In many instances, the chemical species $Al-H_xPO_4^x$ ($AlHPO_4^+ + Al_2PO_4^{3+}$) was practically not detected, due to the very low concentration of phosphate in the soil solution (Table 2). For the conditions of the present study, both sulfate and phosphate had little influence on Al behavior. Álvarez et al. (2002) reported that the $AlSO_4^+$ species rarely occurred in Spanish soils with different parent materials. Nolla & Anghinoni (2006) verified that aluminum phosphate was not present in the soil solution of an Oxisol under NT, even after the application of high rates of P.

Regardless of the treatment or the sampling depth, calcium speciation was basically divided into the free form (Ca^{2+}) and the complexation of Ca with the dissolved OM fraction in the soil solution (Ca-DOC) (Figure 2). The Ca-DOC was predominant in the soil solution, except for the 0 - 0.05 and 0.05 - 0.1 m-layers, which reflects the marked influence of DOC in the speciation of Ca in soil solution. Sulfate was the inorganic anion which formed more ionic pairs with Ca ($CaSO_4^0$), but always with values under 1%. There were also associations of calcium with fluoride (CaF^+), phosphate ($CaHPO_{4(aq)}$; $CaH_2PO_4^+$), chloride ($CaCl^+$), and nitrate ($CaNO_3^+$), designated as "other species" in Figure 2, representing, when added up, less than 1% of the total Ca species. The levels of association of Ca
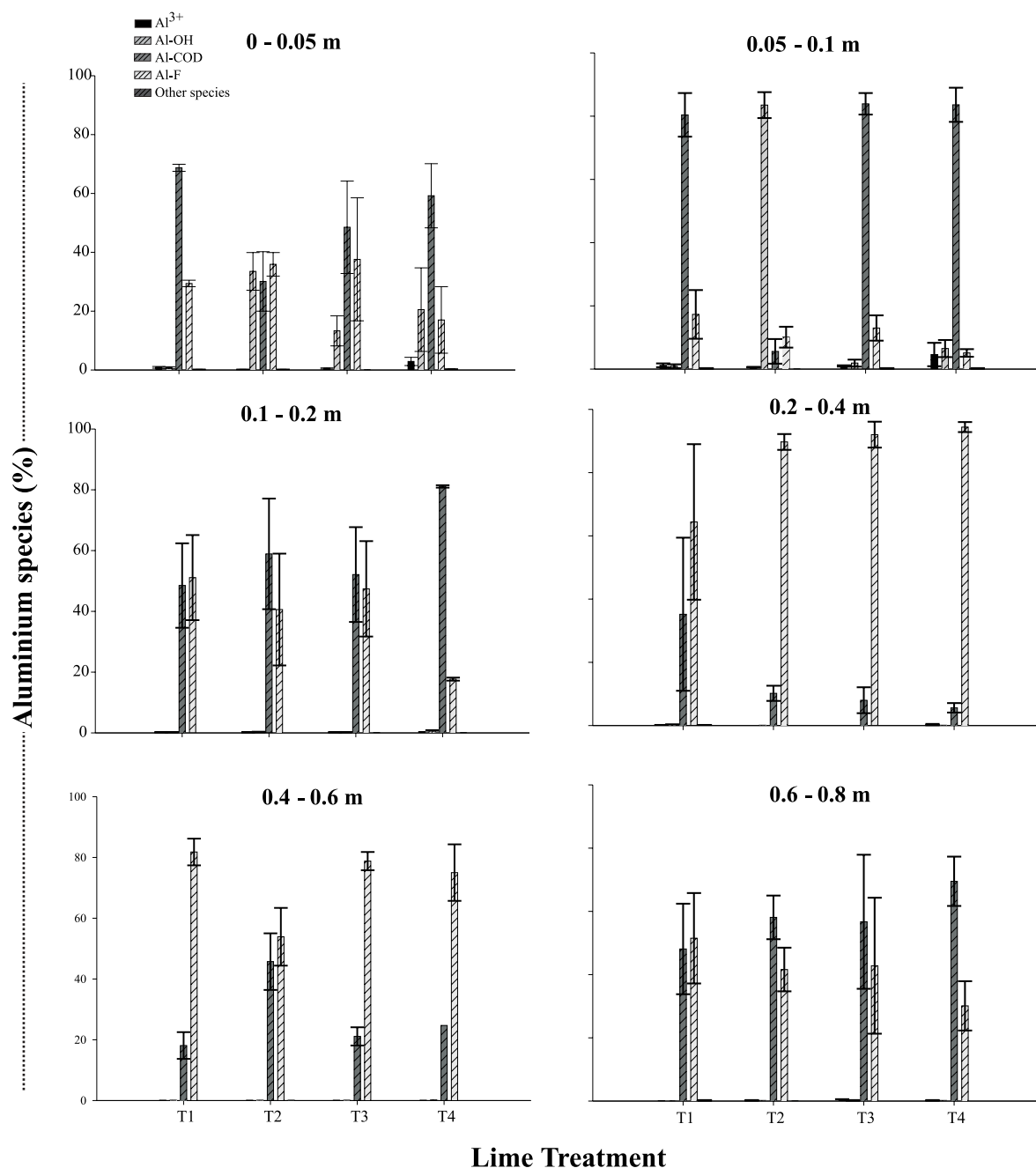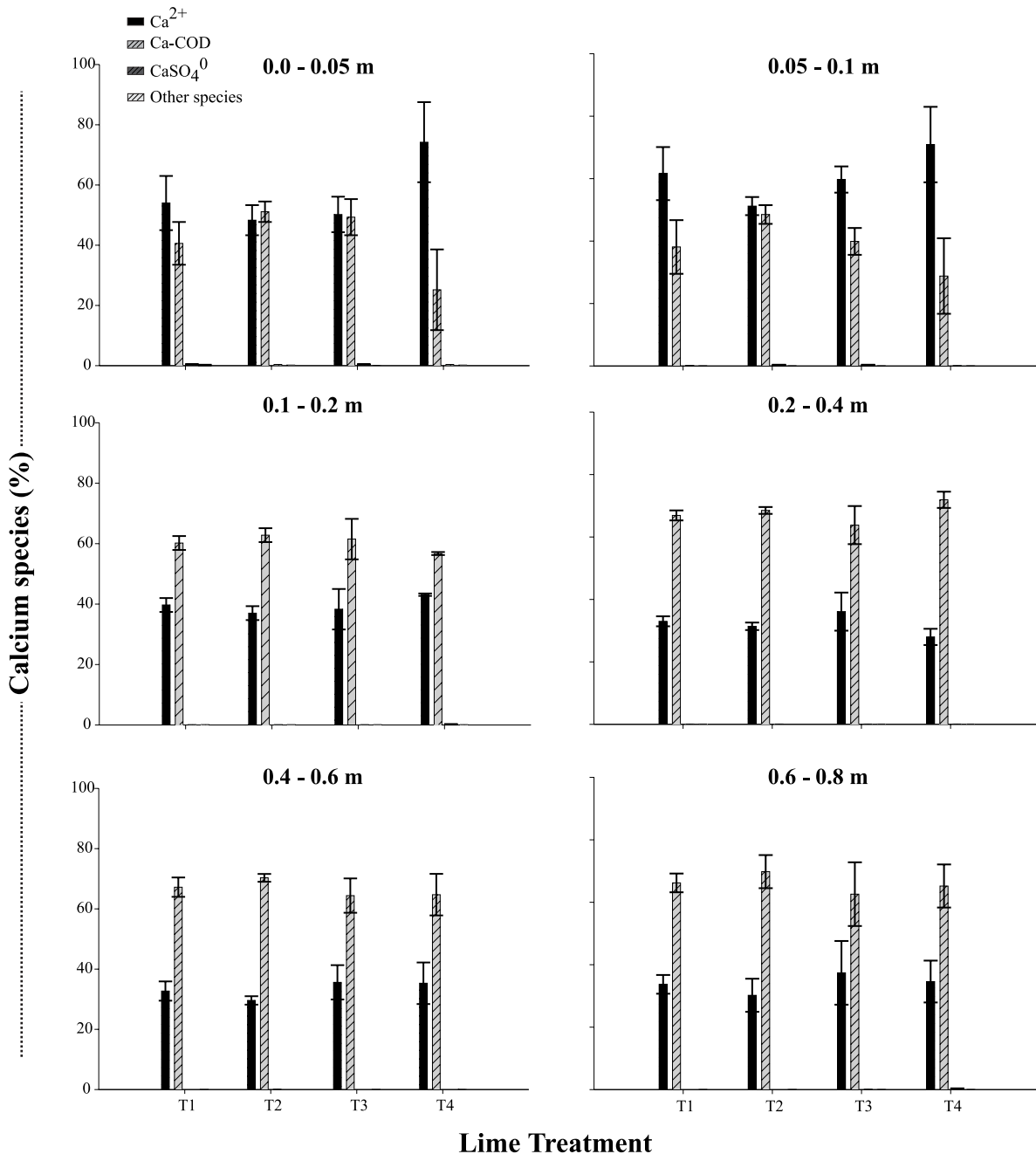
Figure 1 - Lime treatments, and chemical species of aluminum in the solution of an Oxisol under no-till system. T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth. Vertical bars represent the mean deviation (n = 3). Al-OH = Al(OH)$^{2+}$ + Al(OH)$_2^+$ + Al(OH)$_3^0$; Al-F = Al(F)$^{2+}$ + Al(F)$_2^+$ + Al(F)$_3^0$ + Al(F)$_4^-$. Other species: AlHPO$_4^+$ + Al$_2$PO$_4^{3+}$ + AlSO$_4^+$.

with chloride and nitrate in this study are in accordance with Adams (1971), who stated that ionic pairs with these anions do not occur or are negligible, while sulfates can have a more expressive association. Nevertheless, the complexation of soluble Ca by DOC was not considered by Adams (1971) and other authors (Carvalho & Raij, 1997; Nogueira & Mozeto, 1990;

Chaves et al., 1991 e Csillag & Kapoor, 1987). Such complexation plays an important role in soils where OM was accumulated due to soil management practices.

The complexation of calcium by organic anions has been related to a vertical mobilization of Ca in soils which received or accumulated surface organic residues, since these anions, after complexing
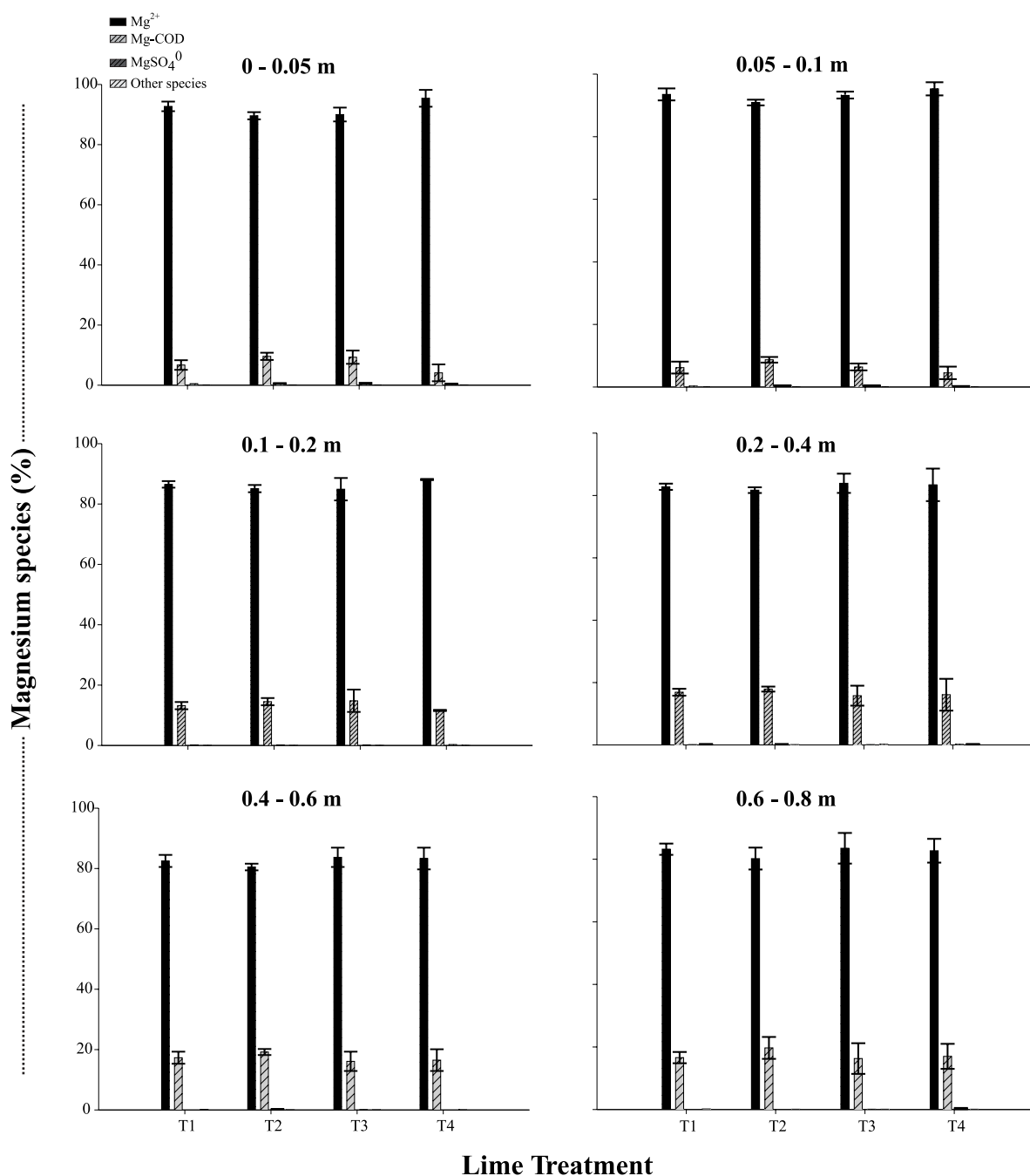
Figure 2 - Lime treatments, and chemical species of calcium in the solution of an Oxisol under no-till system. T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth. Vertical bars represent the mean deviation (n = 3). Other species: $CaCl^+$; $CaNO_3^+$; CaF^+; $CaHPO_{4(aq)}$; $CaH_2PO_4^+$.

the cation, cause a change in charges and favor leaching (Pavan, 1994; Ziglio et al., 1999; Franchini et al., 1999, 2001; Cassiolato et al., 2000). In the present study, there was high complexation of Ca by DOC down to the 0.8 m depth (Figure 2). So, there are indicators that this form of leaching does occur in areas under NT. Nevertheless, the ionic pairs between Ca and inorganic anions (sulfate, chloride, and nitrate) in the soil solution are also significant agents

of cation mobilization along the soil profile (Soprano & Alvarez, 1989; Pavan et al., 1984; Piirainem et al., 2002). The sulfate content in solution is directly related to the cation leaching potential (Piirainem et al., 2002). In the present study, the soluble sulfate content in the 0.1 - 0.2 and 0.2 - 0.4 m layers was positively correlated to the calcium content in solution (r = 0.60; P = 0.04 and r = 0.62; P = 0.03, respectively), indicating that the Ca movement

from the surface layers was, at least in part, related to sulfates.

DOC was the main ligand of Mg in the soil solution (Mg-DOC), but the free form Mg^{2+} was predominant (Figure 3). Among the inorganic anions, the interaction with sulfate ($MgSO_4^0$) occurred in proportions close to 1%. When performing ionic speciation in the solution of several soils with distinct chemical

and physical characteristics in São Paulo State, Brazil, Nogueira & Mozeto (1990) observed that the ionic pair $MgSO_4^0$ represented up to 1.5% of the total Mg species. Although on a smaller scale, there were interactions of magnesium with other inorganic anions, such as fluoride (MgF^+), phosphate ($MgHPO_{4(aq)}$), nitrate ($MgNO_3^+$), and chloride ($MgCl^+$), always under 0.5% of the total species of this cation, designated as
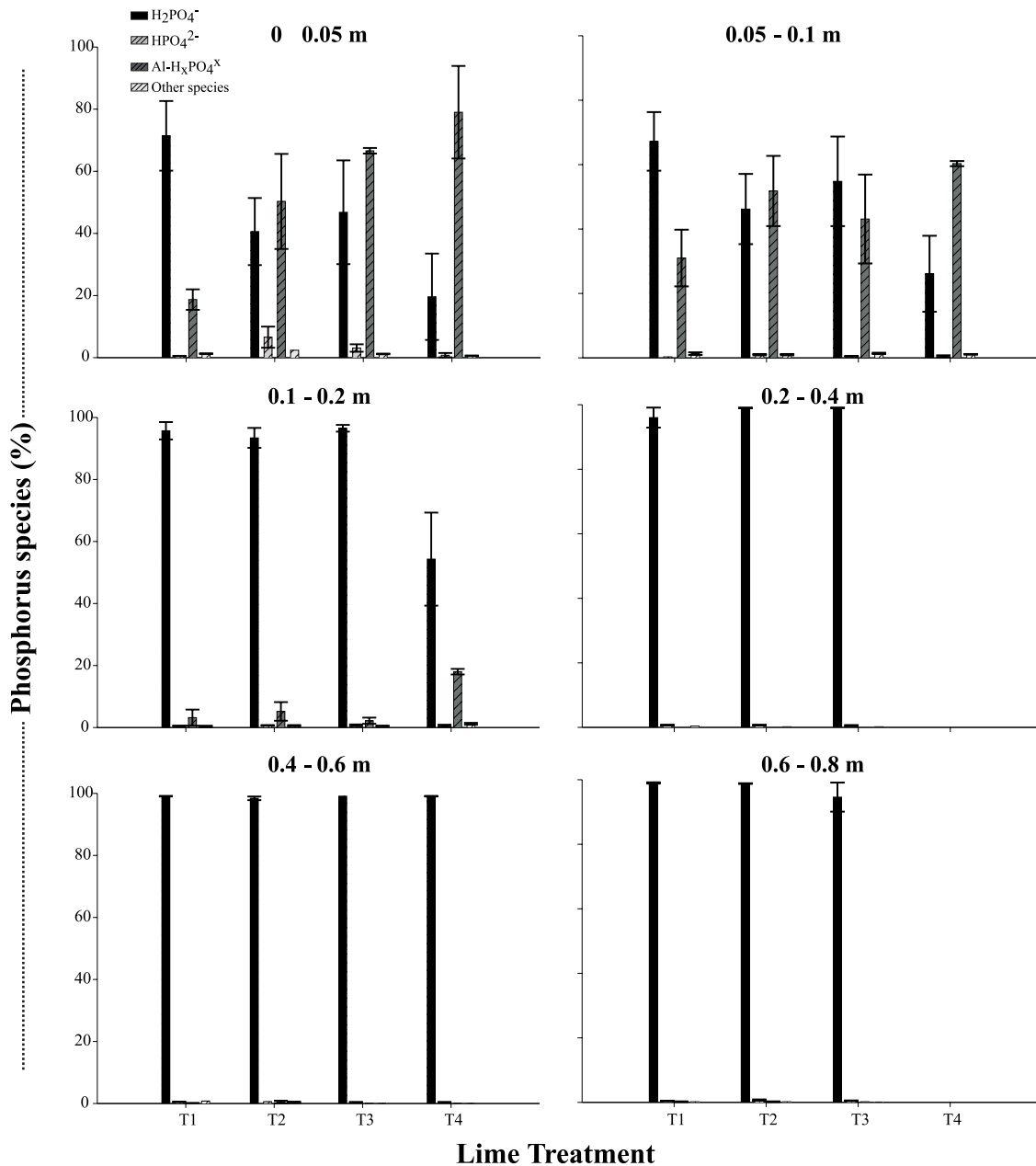

Figure 3 - Lime treatments, and chemical species of magnesium in the solution of an Oxisol under no-till system. T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth. Vertical bars represent the mean deviation (n = 3). Other species: $MgCl^+$; $MgNO_3^+$; MgF^+; $MgHPO_{4(aq)}$.

"other species" in Figure 3. The magnesium complexes with chloride and nitrate have similar stability constants, but occupy insignificant proportions regarding the activities of these two anions in solution (Lindsay, 1979). Thus, just as with calcium, the contents of magnesium and sulfate in solution were positively correlated in the 0.1 - 0.2 m (r = 0.67; P = 0.01) and 0.2 - 0.4 m (r = 0.66; P = 0.02) layers, which could be related to the joint leaching of these elements.

Potassium, unlike calcium and magnesium, was not complexed by organic anions in solution, being found mainly as a free ion (K^+). The percentage of ionic pairs for K ($KCl_{(aq)}$, KNO_3, and KSO_4^-) represented a maximum of 0.2% of the total, regardless of the liming treatment or the sampling depth. In well drained soils, K complexes are usually of little relevance (Lindsay, 1979). However, the interaction of potassium with anions in the soil solution is important for leach-

Figure 4 - Lime treatments, and chemical species of phosphorus in the solution of an Oxisol under no-till system. T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth. Vertical bars represent the mean deviation (n = 3). Al-H$_x$PO$_4^x$ = AlHPO$_4^+$ + Al$_2$PO$_4^{3+}$. Other species: FeHPO$_4^+$; MnHPO$_4^+$; CaHPO$_{4(aq)}$; CaH$_2$PO$_4^+$; MgHPO$_{4(aq)}$; KH$_2$PO$_{4(aq)}$.

ing - even though it is a monovalent cation, potassium needs accompanying anions to move along the soil profile (Rosolem et al., 2006). In this work, positive correlations were observed between potassium and chloride in the 0.1 - 0.2 m (r = 0.56; P = 0.05) and 0.2 - 0.4 m (r = 0.51; P = 0.05) layers, suggesting that a possible movement of potassium from the soil surface layers would be related to this anion. Potassium leaching, though, depends mainly on

its content and on the water content in the soil profile (Rosolem et al., 2006).

The distribution of free forms of phosphorus ($H_2PO_4^-$ + HPO_4^{2-}), which can be absorbed by plants, is dependent upon the soil solution pH values. There are approximately equal amounts of $H_2PO_4^-$ and HPO_4^{2-} in a pH of 7.2 (Lindsay, 1979). In our study, the pH values of the soil solution were much smaller than 7.2 (Table 1), and thus, the $H_2PO_4^-$ form was predominant
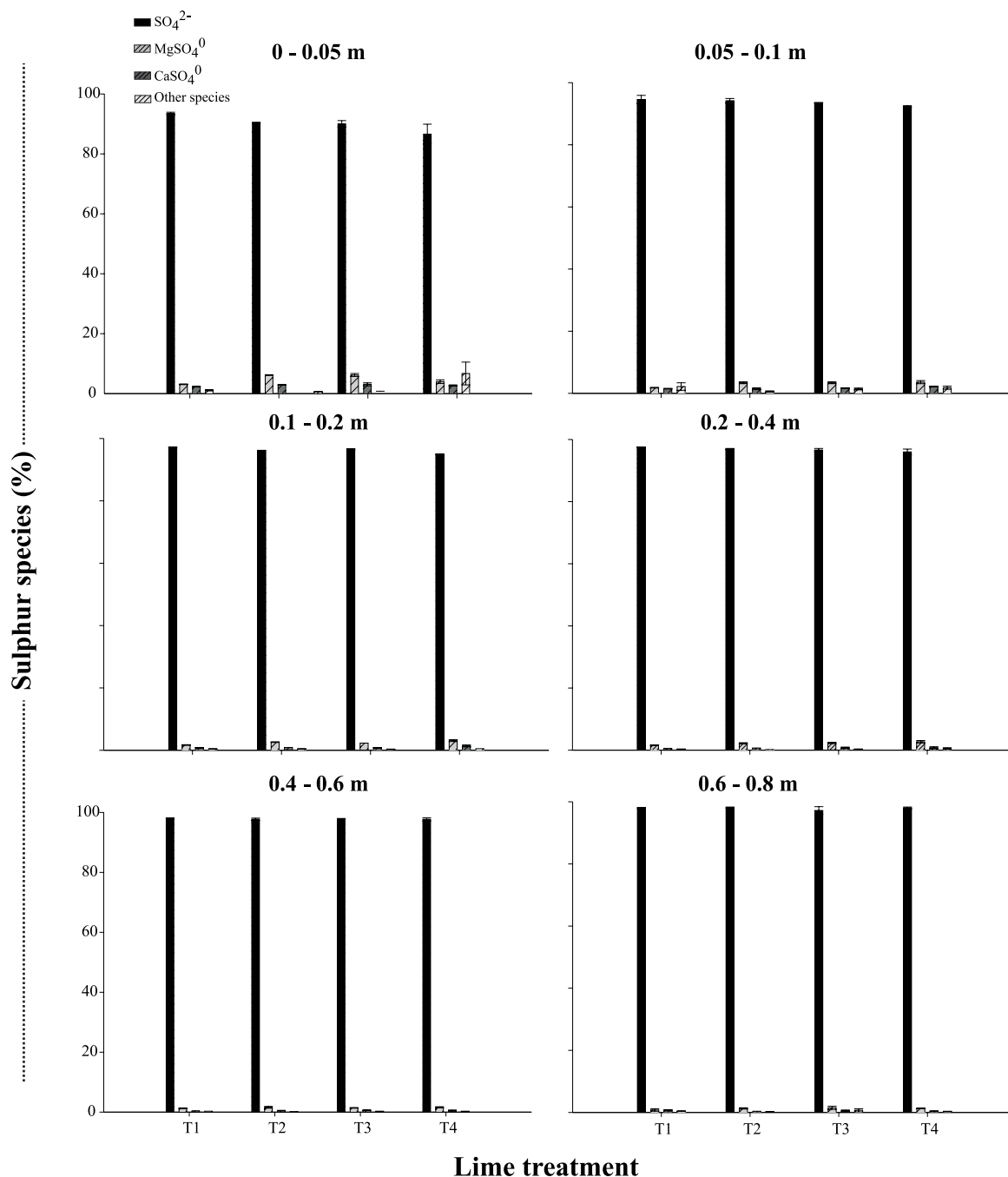

Figure 5 - Lime treatments, and chemical species of sulphur in the solution of an Oxisol under no-till system. T1 = control (without lime); T2 = 4.5 t ha^{-1} of surface-applied lime (split in three annual applications of 1.5 t ha^{-1}); T3 = 4.5 t ha^{-1} of surface-applied lime (single application); T4 = 4.5 t ha^{-1} of lime incorporated at 0.2 m depth. Vertical bars represent the mean deviation (n = 3). Other species: $AlSO_4^+$; $NaSO_4^-$; KSO_4^-.

(Figure 4). There was also association of phosphorus with cations in the soil solution (ionic pair Al-$H_xPO_4^x$ + other species) (Figure 4), which can be explained by the fact that phosphate ions in the soil solution are strongly prone to interactions with Al, Fe, Ca, and Mg. The magnitude of bonding of phosphate with each of these cations depends on the soil type, with Al and Fe bonds more predominant in acid soils, and more Ca and Mg bonds in alkaline soils (Lindsay, 1979).

The proportion of Al-$H_xPO_4^x$ + other forms increased with liming, more markedly in the first two soil layers (Figure 4). Liming can reduce the efficiency of phosphorus fertilization in soils under NT due to the interaction between phosphate and Ca^{2+} (Machado & Silva, 2001). It is suggested that liming could have caused an increase in the concentration of cations in solution (Ca^{2+} and Mg^{2+}), and the displacement of Al^{3+} from the soil exchange complex, increasing the formation of ionic pairs with phosphate. Nolla & Anghinoni (2006) observed the presence of chemical species of phosphate with calcium and magnesium in the solution of an Oxisol under NT. Since the phosphate content is low in relation to cation content, the impact of reducing phosphate activity by bonding with cations is much larger than reducing cation activity by bonding with phosphates. Prochnow et al. (2006) pointed out a possible reduction of P availability to plants, due to the decrease in activity of phosphate ions by forming ionic pairs with cations in the soil solution.

Sulfur occurred in the soil solution, regardless of the liming treatments or sampling depth, as free sulfate ion (SO_4^{2-}) (Figure 5), the form it is absorbed by plant roots (Leustek & Saito, 1999). The elements which formed more ionic pairs with sulfate were magnesium ($MgSO_4^0$) and calcium ($CaSO_4^0$). In smaller proportions, there were associations with aluminum ($AlSO_4^+$), sodium ($NaSO_4^-$) and potassium (KSO_4^-), designated as "other species" (Figure 5). On average, in the first two soil layers, the proportion occupied by the free SO_4^{2-} ion varied from 90 to 93%, while the values reached 98% in the other layers, indicating that high cation concentrations tend to reduce the presence of sulfur as SO_4^{2-} in the soil solution.

Nitrate occurred predominantly in the free form (NO_3^-) (average of 99.8%) in the soil solution, regardless of the liming treatment or sampling depth, indicating little interaction with cations in solution. Performing a chemical speciation in a percolated solution, Amaral et al. (1998) reported that the nitrate ion was found only in the free form. Chloride also occurred mainly as free ions (Cl^-) (average of 99.9%), without liming treatment or sampling depth effects.

CONCLUSIONS

Aluminum forms complex mainly with dissolved organic carbon and fluoride in the soil solution under the no-till system. The complexation of aluminum by dissolved organic carbon is not influenced by soil acidity amelioration by liming.

Surface or incorporated application of lime does not affect Ca and Mg speciation in the soil profile solution. Dissolved organic carbon is the main complexing agent with both cations in the soil solution under the no-till system.

The proportion occupied by the free forms of phosphorus ($H_2PO_4^-$ + HPO_4^{2-}) in the soil solution was influenced by liming due to the increment in cation-associated forms, mainly in the soil surface layers.

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