Depth distribution of exchangeable aluminum in acid soils: A study from subtropical Brazil

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ABSTRACT. Due to potential crop toxicity, high aluminum (Al) availability requires increased attention when preparing agricultural soils. However, research examining the relationship between depth distribution of Al and soil weathering has received little priority in Brazil, particularly regarding the number of soil profiles investigated. This study analyzed 38 acid soils selected from Soil Surveys in southern Brazil to identify and isolate the effects of organic and mineral components on depth distribution of exchangeable Al extracted with KCl (Al_{KCl}). These soil profiles were divided into the following three groups based on Al_{KCl} depth distribution: Group I – decrease with depth; Group II – little variation with depth; and Group III – increase with depth. High Al_{KCl} found near the surface of well-developed soils (Group I) was influenced by organic matter content, while mineral fraction quality defined the occurrence of high Al_{KCl} in subsurface horizons of Group III. The depth distribution of Al_{KCl} was defined by the degree of weathering in these subtropical soils. Possessing a knowledge of these soil groupings may aid in soil acidity management to optimize crop productivity in southern Brazil.

Keywords: Ki index; organic matter; smectite; kaolinite; Al oxides; lime requirement.

Distribuição de alumínio trocável em profundidade nos solos ácidos: um estudo em áreas subtropicais do Brasil

RESUMO. Alta disponibilidade de Al demanda maiores cuidados para tornar os solos aptos para a agricultura devido a toxidez para as plantas cultivadas. Contudo, as pesquisas sobre a relação entre a distribuição de Al em profundidade e o intemperismo do solo têm sido pouco priorizadas, principalmente aquelas conduzidas com um maior número de perfis de solos. O presente estudo analisou-se 38 solos ácidos selecionados dos levantamentos de solos da região Sul do Brasil, com o objetivo de identificar e isolar o efeito dos componentes orgânicos e minerais na distribuição em profundidade do Al trocável extraído com KCl (Al_{KCl}). A seleção resultou na formação de três grupos de solos em relação aos teores de Al_{KCl} em profundidade: Grupo I – diminuição; Grupo II – inexpressiva variação e; Grupo III – aumento. A matéria orgânica foi mais importante para determinar os altos teores de Al_{KCl} na superfície dos solos mais intemperizados (grupo I) e a qualidade da fração mineral definiu os elevados teores de Al_{KCl} nos horizontes subsuperficiais do grupo III. A distribuição de Al_{KCl} em profundidade foi definida pelo grau de intemperismo do solo. O conhecimento desses agrupamentos de solo pode auxiliar no manejo da acidez do solo para otimizar a produtividade das culturas no sul do Brasil.

Palavras-chave: índice Ki; matéria orgânica; esmectita; caulinita; óxidos de Al; necessidade de calagem.

Introduction

Acidic soils have a pH lower than 7; however, much of the pedosphere has higher acidity (pH < 5.5) that favors increased toxic forms of aluminum (particularly Al^{3+}) in soil solution. Most agricultural plant species do not attain maximum production potential when grown in high acidity soils due to Al toxicity and nutritional deficiency (Kochian, Piñeros, Liu, & Magalhães, 2015; Goulding, 2016; Sade et al., 2016; Barbosa, Motta, Consalter, & Pauletti, 2017a). Acidic soils directly affect the health and nutrition of people living in rural and urban areas by constraining production of cultivated species.

Aluminum extraction with KCl (Al_{KCl}) is a method that has been adopted worldwide to evaluate Al availability in mineral soils that can be affected by soil pH, organic matter content, and soil clay mineralogy (Marques, Teixeira, Schulze, & Curi, 2002; Zolotajkin, Ciba, Kluczka, Skwira, & Smoliński, 2011; Bernini et al., 2013; Eimil-Fraga, Álvarez-Rodriguez, Rodrígues-Soalleiro, & Fernández-Sanjurjo, 2015; Barbosa, Poggere, Dalpisol, Motta,

Serrat, & Bittencourt et al., 2017b). Organic matter has the following two distinct actions influencing the amount of Al_{KCl} in soil: i) reductions due to complexation reactions, ii) increases due to organic matter, which is the primary source of CEC in well-developed soils (Motta & Melo, 2009). Weathering of 2:1 minerals results in release and buffering of Al_{KCl} in soil. However, soil evolution naturally tends to stabilize Al_{KCl} in secondary minerals such as kaolinite and gibbsite (Lindsay, 2001; Vendrame et al., 2013).

The effects of lime, management system/land use practices, and organic residue addition on Al_{KCl} levels have been widely evaluated (Brunetto et al., 2012; Barcellos, Motta, Pauletti, Silva, & Barbosa, 2015; Costa, Crusciol, Ferrari Neto, & Castro, 2016; Baquy, Li, Xu, Mehmood, & Xu, 2017; Barbosa et al., 2017b; Machado, Camara, Sampaio, Pereira, & Ferraz, 2017; Rocha et al., 2017). These data were obtained from the most superficial soil layers, excluding less weathered deep horizons with organic matter contents close to zero. In contrast, there are limited studies on Al_{KCl} as a function of soil weathering, organic matter, and clay mineralogy. Quesada et al. (2010) studying surface layers (0 – 30 cm) of 71 tropical forest soils (i.e., Brazil, Venezuela, Bolivia, Colombia, Peru, and Ecuador) noted higher Al_{KCl} values in Chernozems, Cambisols, and Plinthosols than those in Acrisols and Ferralsols. Cunha, Almeida, and Barboza (2014) reported high values of Al_{KCl} due to 2:1 minerals in Brazilian soils. However, little attention has been given to explaining variations of Al_{KCl} in both superficial and subsurface layers of such acid soils. Understanding factors that govern depth distribution of Al_{KCl} in soil can contribute to the knowledge base concerning the nature and management of acidic soils.

The aim of this study was to identify and isolate the effects of organic and mineral components on the depth distribution of Al_{KCl} in acid soils with different degrees of weathering. Our goal was not to correlate lithology or climate with Al_{KCl} levels because consistent variations in Al_{KCl} within soil profiles occurred independent of these factors.

Material and method

Study areas

This study was developed based on the following three soil surveys of the southern region of Brazil: 1) Soil Recognition Survey of the Paraná (Embrapa, 1984); 2) Soil Recognition Survey of the Santa Catarina (Embrapa, 1998); and 3) Soil Recognition Survey of the Rio Grande do Sul (Brasil, 1973). These surveys were conducted between the 1960s and 1990s and covered the territory of each southern Brazilian state. Soils were carefully chosen to adequately represent the taxonomic unit in terms of morphological, chemical, and physical attributes along the profile for classification. Regarding soil characterization, it is important to note that standard methodologies were used to evaluate soils in all surveys.

Data collection

Mineral soil profiles were selected to evaluate the potential for creating acidity. Distribution profiles of Al_{KCl} were the only selection criterion. In selecting acid soil profiles, one of the horizons typically had Al_{KCl} higher than 4 $cmol_c$ kg^{-1}, but all profiles had at least one horizon in which Al_{KCl} was higher than 2 $cmol_c$ kg^{-1}. The profiles were divided into the following three Groups: (I) decrease of Al_{KCl} with depth (12 profiles), (II) insignificant variation of Al_{KCl} with depth (9 profiles), and (III) increase of Al_{KCl} with depth (17 profiles) (Figure 1; Tables 1, 2, and 3). The following soil profile variables were also considered: depth, clay content, organic carbon (C), Ki index, H (potential non-exchangeable acidity), cation exchange capacity (CEC) at pH 7.0, pH in KCl (pH_{KCl}), and Al_{KCl} saturation (m).

Survey analyses were conducted on fine air dry soil (FADS) using the following methodologies (Embrapa, 1984; Brasil, 1973; Embrapa, 1998): clay content, dispersion with NaOH 5% (m/v) [in special cases, $(NaPO_3)_6$ or Calgon] and determination by the Bouyoucos hydrometer method; pH_{KCl}, equilibrium with 1 mol KCl L^{-1} (soil/solution ratio of 1:2.5); exchangeable Al (Al_{KCl}), extraction with 1 mol KCl L^{-1} and determination by titulometry (blue bromothymol indicator); C, oxidation of organic material with 0.2 mol L^{-1} potassium dichromate; SiO_2 and Al_2O_3, sulfuric attack with concentrated H_2SO_4 and Na_2CO_3 (5% m/v), with Si determined by colorimetry (blue molybdenum indicator) and Al by Titriplex IV; and H (potential non-exchangeable acidity), extraction with calcium acetate (0.5 mol L^{-1}, pH 7.0) and determination by titulometry (phenolphthalein indicator).

The Ki index was obtained by the following equation:

$$Ki = 1.7 \, X \left(\frac{SiO_2}{Al_2O_3}\right) \qquad (1)$$

where: SiO_2 and Al_2O_3 were obtained by sulfuric attack (g kg^{-1}).

The relationship between potential exchangeable acidity (Al_{KCl}) and non-exchangeable potential acidity (H) was determined as Al_{KCl}/H.

The CEC at pH 7.0 was obtained by the following equation:

$$CEC = Ca^{2+} + Mg^{2+} + K^+ + Na^+ + (H + Al^{3+}) \quad (2)$$

where: Ca^{2+}, Mg^{2+}, K^+, Na^+, and Al^{3+} represent the contents ($cmol_c\ dm^{-3}$) of these elements extracted using

KCl solution; H represents the content ($cmol_c\ dm^{-3}$) of this element extracted using calcium acetate.

Saturation by Al_{KCl} (m) was obtained by the following equation:

$$m = Al^{3+} \ X\ 100/(Ca^{2+} + Mg^{2+} + K^+ + Na^+ + Al^{3+}) \quad (3)$$

where: m in percentage; Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+ represent the contents ($cmol_c\ dm^{-3}$) of these elements extracted using KCl solution.
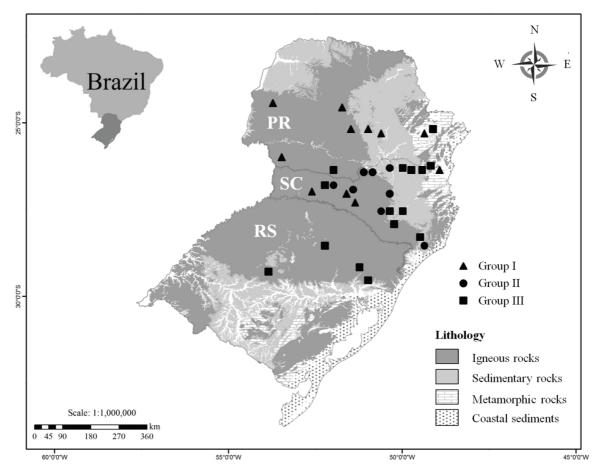

Figure 1. Distribution of acid soil profiles used to form Groups I, II, and III in southern Brazil. PR – Paraná State; SC – Santa Catarina State; RS – Rio Grande do Sul State.

Table 1. Acid soils used to form Group I (decrease of Al_{KCl} with depth) in southern Brazil.

State[1]	Page[2]	Profile[3]	SiBCS[4]	WRB[5]
PR	119	002	Latossolo Vermelho-Amarelo distrófico úmbrico	Rhodic Ferralsol
PR	197	015	Latossolo Vermelho distrófico típico	Rhodic Ferralsol
PR	282	030	Latossolo Vermelho distroférrico típico	Rhodic Ferralsol
PR	286	032	Latossolo Vermelho distroférrico típico	Rhodic Ferralsol
PR	325	037	Latossolo Bruno distroférrico típico	Dystric Ferralsol
PR	328	038	Latossolo Bruno distroférrico típico	Dystric Ferralsol
PR	442	056	Nitossolo Bruno alumínico típico	Dystric Nitisol
SC	143	021	Latossolo Vermelho distroférrico típico	Rhodic Ferralsol
SC	193	070	Latossolo Bruno distrófico típico	Dystric Ferralsol
SC	194	072	Latossolo Bruno distroférrico típico	Dystric Ferralsol
SC	360	015	Argissolo Vermelho-Amarelo distrófico típico	Ferric Acrisol
SC	520	033	Cambissolo Húmico distrófico típico	Dystric Cambisol

[1] PR – Paraná; SC – Santa Catarina State; RS – Rio Grande do Sul State. Soil Recognition Survey of the Paraná (Embrapa, 1984), Santa Catarina (Embrapa, 1998), and Rio Grande do Sul (Brasil, 1973). [2] Page number in each soil survey. [3] Number of soil profiles collected in each survey. [4] Brazilian system of soil classification (Embrapa, 2013). [5] Corresponding global classification system (IUSS Working Group WRB, 2015); classification adopted in the present study.

Table 2. Acid soils used to form Group II (insignificant variation of Al_{KCl} with depth) in southern Brazil.

State[1]	Page[2]	Profile[3]	SiBCS[4]	WRB[5]
SC	211	031	Latossolo Bruno distrófico típico	Humic Ferralsol
SC	212	047	Latossolo Vermelho-Amarelo distrófico húmico	Rhodic Ferralsol
SC	256	056	Nitossolo Bruno distroférrico típico	Dystric Nitisol
SC	257	066	Nitossolo Bruno distroférrico típico	Dystric Nitisol
SC	278	064	Nitossolo Bruno alumínico húmico	Dystric Nitisol
SC	279	071	Nitossolo Bruno aluminoférrico húmico	Dystric Nitisol
SC	522	046	Cambissolo Húmico aluminoférrico típico	Humic Cambisol
SC	524	063	Cambissolo Húmico alumínico típico	Humic Cambisol
SC	555	006	Argissolo Vermelho-Amarelo alumínico abrúptico	Chromic Acrisol

[1] PR – Paraná State; SC – Santa Catarina State; RS – Rio Grande do Sul State. Soil Recognition Survey of the Paraná (Embrapa, 1984), Santa Catarina (Embrapa, 1998), and Rio Grande do Sul (Brasil, 1973). [2] Page number in each soil survey. [3] Number of soil profiles collected in each survey. [4] Brazilian system of soil classification (Embrapa, 2013). [5] Corresponding global classification system (IUSS Working Group WRB, 2015); classification adopted in the present study.

Table 3. Acid soils used to form Group III (increase of Al_{KCl} with depth) in southern Brazil.

State[1]	Page[2]	Profile[3]	SiBCS[4]	WRB[5]
PR	570	071	Cambissolo Húmico Alítico típico	Humic Cambisol
PR	572	072	Cambissolo Húmico Alítico típico	Humic Cambisol
PR	774	087	Neossolo Litólico distroúmbrico típico	Lithic Leptosol
SC	238	054	Nitossolo Bruno aluminoférrico típico	Dystric Nitisol
SC	289	059	Nitossolo Bruno aluminoférrico típico	Dystric Nitisol
SC	329	005	Argissolo Vermelho-Amarelo alumínico típico	Ferric Acrisol
SC	331	013	Argissolo Vermeho-Amarelo distrófico típico	Rhodic Acrisol
SC	408	052	Argissolo Bruno-Acinzentado alítico típico	Haplic Acrisol
SC	409	074	Argissolo Bruno-Acinzentado alítico	Haplic Acrisol
SC	476	043	Cambissolo Háplico alumínico úmbrico	Haplic Cambisol
SC	521	042	Cambissolo Húmico alumínico típico	Humic Cambisol
SC	544	038	Cambissolo Háplico alítico típico	Haplic Cambisol
SC	688	051	Neossolo Litólico húmico típico	Lithic Leptosol
RS	140	050	Argissolo Vermelho-Amarelo alumínico típico	Chromic Acrisol
RS	157	150	Argissolo Vermelho alumínico abrúptico	Rhodic Acrisol
RS	188	127	Argissolo Bruno Acinzentado alítico abrúptico	Haplic Acrisol
RS	239	154	Planossolo Háplico alítico gleissólico	Dystric Planosol

[1] PR – Paraná State; SC – Santa Catarina State; RS – Rio Grande do Sul State. Soil Recognition Survey of the Paraná (Embrapa, 1984), Santa Catarina (Embrapa, 1998), and Rio Grande do Sul (Brasil, 1973). [2] Page number in each soil survey. [3] Number of soil profiles collected in each survey. [4] Brazilian system of soil classification (Embrapa, 2013). [5] Corresponding global classification system (IUSS Working Group WRB, 2015); classification adopted in the present study.

Data processing and analysis

Selected data were entered into Microsoft® Excel spreadsheets and organized according to each soil group. Because of wide depth variability between soil profiles and soil horizons, the following average ranges (cm) were used: 0 – 10; 10 – 20; 20 – 30; 30 – 40; 40 – 50; 50 – 70; 70 – 100; 100 – 150; and > 150 (average depth of 225 cm). The soil profile was evaluated based on horizon analysis, and the reported depth was considered to be half the depth of each horizon. Mean values and standard deviations for each attribute per depth range were calculated. All data were subjected to Pearson's simple correlation analysis using Sisvar statistical software (Ferreira, 2014).

Result and discussion

Climate (Alvares, Stape, Sentelhas, Gonçalves, & Sparovek, 2013) and lithology (Figure 1) were variable within each soil group and were similar across groups. For this reason, climate and lithology were not considered in the discussion data. In Group I, the average Al_{KCl} content was close to 5 $cmol_c dm^{-3}$ in the 0 – 10 cm layer and was reduced to ~1.5 $cmol_c dm^{-3}$ at the greatest depth. For Group II, a lower Al_{KCl} variation (4.6 to 3.2 $cmol_c dm^{-3}$) was observed from the most superficial soil layer to the deepest layer. In Group III, a clear increase occurred in average Al_{KCl} with depth, which varied from 3 to 11 $cmol_c dm^{-3}$ (Figure 2).

Comparing the two groups of highest contrast, Group I was predominantly Ferralsols (Table 1), while Group III (Table 3) included soils with moderate weathering and diagnosed as having incipient developed B horizons or B horizons with clay accumulation (Brasil, 1973; Embrapa, 1984; Embrapa, 1998). Additionally, when comparing contrasting Ki index values (Group I: from 1.2 to 2; Group III: from 2 to 3.3), well-developed soils have Ki indices < 2.0 (IBGE, 2015). Dalović et al. (2012) also found a clear increase in average Al_{KCl} content in low-developed soils (102 profiles) from a basin in Serbia. Similar results are reported for tropical and subtropical Brazilian soils (Marques et al., 2002; Motta & Melo, 2009; Cunha et al., 2014). The increased level and buffering of Al_{KCl} with depth are even more significant for low-developed soils that have high levels of amorphous minerals of allophane and imogolite types, high Al/Si molar ratios, and low environmental stability. This is observed under conditions of extremely low soil weathering, such on the Peninsula Keller (Antarctica) where soil profiles were developed from sulfide-bearing andesites (rich in amorphous minerals) having high Al_{KCl} contents of 18.2 $cmol_c kg^{-1}$ in the A horizon and 27.8 $cmol_c kg^{-1}$ in the B horizon (Poggere, Melo, Francelino, Schaefer, & Simas, 2016).
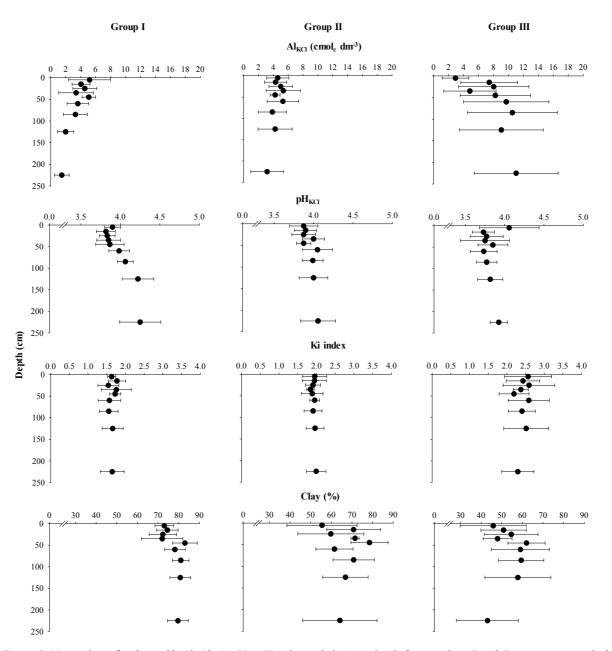
Figure 2. Mean values of exchangeable Al (Al_{KCl}), pH_{KCl}, Ki index, and clay in acid soils from southern Brazil. Bars represent standard deviation.

Motta and Melo (2009) established the following relationships for the evolution of Al_{KCl} in subsurface horizons with weathering of tropical and subtropical soils: i) Low weathering soils with 2:1 dioctahedral (smectite) minerals: incipient weathering is not sufficient to release Al from octahedral sheets, and all negative charges of minerals are occupied by bases (V = 100%), ii) Moderate to intense weathering: partial or total dissolution of 2:1 minerals in the B horizon promotes Al release and acidifies soil, iii) Intense weathering: neoformation of kaolinite from Al

and Si released by 2:1 minerals reduces acidity of the B horizon, iv) Very intense weathering: transition to an oxidic system that stabilizes Al in gibbsite structure. Considering chemical equilibrium reactions and equilibrium constants for 2:1 (Mg-montmorillonite) and 1:1 minerals (kaolinite) presented by Lindsay (2001), it is possible to exemplify more solubility and Al release from 2:1 minerals. As an example (using ionic forms of elements), given a pH of 6.0, H_4SiO_4 in soil solution is in equilibrium with quartz (10^{-4} mol L^{-1}) for Mg-montmorillonite and kaolinite, and Fe^{3+} is

in equilibrium with goethite with Mg^{2+} equal to 10^{-3} mol L^{-1} (Lindsay, 2001) for montmorillonite, the following concentrations of Al^{3+} are present in soil solution under equilibrium conditions: Mg-montmorillonite, $Al^{3+} = 10^{-10.0}$ mol L^{-1}; kaolinite, $Al^{3+} = 10^{-11.3}$ mol L^{-1}. At lower pH values, the instability of minerals increases, and the difference in Al^{3+} content in equilibrium solution favoring montmorillonite is even more significant.

According to these premises, the degree of soil weathering was classified intense to very intense for Group I and moderate to intense for Group III, which corroborated Ki index results (Figure 2). The expressed variation in average Ki levels among groups allowed for the establishment of positive correlations with Al_{KCl} content considering all samples (0.53, p < 0.01) or excluding those in the 0–50 cm depth range (0.70, p < 0.01; Table 4). Analysis of only subsurface diagnostic horizons increased the correlation coefficient between Ki index and Al_{KCl} content, since the effect of surface horizon organic matter on Al_{KCl} dynamics in soil was isolated. When soil groups were considered separately, correlation coefficients were less than 0.4, since Ki values were similar along the soil profiles within each group (Figure 2).

The presence of 2:1 soil minerals promotes low CEC variation in subsurface soil, such as that observed in Group III (Figure 3). In Group III, the correlation coefficient for Al_{KCl} and CEC at pH 7.0 was 0.70 (p < 0.01). However, unlike other groups, the low correlation between CEC and C (0.33, p < 0.01) indicated that maintenance of high Al_{KCl} levels in Group III soils was primarily controlled by negative charges of minerals in the clay fraction. As a consequence, more intense adsorption kept Al in the soil and prevented leaching. High Al_{KCl} levels in soils with 2:1 minerals are also associated with the capacity of the extractor (KCl) to solubilize Al amorphous compounds and Al-hydroxy islands between layers of secondary 2:1 minerals (Marques et al., 2002; Cunha et al., 2014).

The correlation coefficient between C and Al_{KCl} was 0.61 (p < 0.01) for Group I (Table 4). For Group III, the correlation coefficient between these same parameters was low (–0.16, p < 0.01). The correlation coefficient between Al_{KCl} and CEC was also high in Group I (0.74, p < 0.01), and soil negative charges were due to humic compounds (correlation coefficient between CEC and C = 0.97, p < 0.01). The average C levels decreased markedly along the profiles within the three groups (Figure 3). However, the CEC at pH 7.0 was reduced with the same intensity only in Groups I and II; ranging from

averages close to 20 $cmol_c$ dm^{-3} near the surface to 6 $cmol_c$ dm^{-3} in the deepest soil layers. By contrast, Group III initial mean values were approximately 20 $cmol_c$ dm^{-3} but remained close to 15 $cmol_c$ dm^{-3} as depth increased. These results indicated that the variation of Al in Group I was most associated with the organic fraction, whereas in Group III, this variation occurred with the mineral fraction of the soil.

In Group I, organic matter contributed more to higher Al_{KCl} content near the surface, and the decrease in exchangeable potential acidity with depth could be attributed to Al stabilization primarily in the structure of gibbsite (Vendrame et al., 2013). Ghidin, Melo, Lima, and Lima (2006) worked with a toposequence of Ferralsols (similar to profiles 30 and 32 in Group I; Table 1) from Guarapuava (Paraná State) that originated from basalt. They observed a predominance of oxides in the clay fraction of the B horizon (i.e., 322 g kg^{-1} gibbsite, 309 g kg^{-1} hematite, and 294 g kg^{-1} kaolinite). Thus, with much of Al stabilized in the structure of gibbsite and kaolinite, organic matter becomes the source of this element. Despite the strong interaction between Al and organic matter, a KCl solution can extract the most labile fraction (Campos, Silva, Silva, & Vidal-Torrado, 2014; Cunha et al., 2014). However, some authors found Al-hydroxy islands between layers of secondary 2:1 minerals in Ferralsol clay fractions of several Brazilian regions, although these minerals are only residual in well-developed soils (Silva, Motta, Melo, & Lima, 2008; Schaefer, Fabris, & Ker, 2008).

The lowest values for Al_{KCl}/H were observed in deeper layers of Group I profiles (Figure 3). Since C contents in the subsurface were similar between Groups I and III, the low Al_{KCl}/H ratio in Group I was indicative of greater hydroxylated surface groups (pH dependent charge) in soil colloids, higher levels of 1:1 silicate minerals, and Fe and Al oxides in the clay fraction. The aluminol (-AlOH) and ferrol (-FeOH) groups common in these minerals cause low acidity (predominance of CEA over CEC at pH below 7 to 9; Schwertmann & Taylor, 1989), and elevation of natural soil pH to 7.0 during extraction with 0.5 mol L^{-1} Ca acetate results in a high release of H. The reduction of this ratio in Group I was favored by lower Al_{KCl} content.

For the most active clay system (Group III), less H release most likely occurs due to reduced occurrence of aluminol and ferrol; approximately 95% of 2:1 secondary mineral charges are structural or independent of pH changes (Brady & Weil, 1996). In 2:1 clays, a proportion of silanol groups (-SiOH) occur that act as strong acid radicals deprotonating at pH 2 (Tarì, Bobos, Gomes, & Ferreira, 1999). Since each analyzed soil had a pH

above 2, H had been previously released. Thus, these H groups were not computed in the determination of potential acidity since they were not exchangeable using Ca acetate (0.5 mol L^{-1}, pH 7.0). Therefore, in subsurface horizons of Group III soils, the primary component of acidity was the exchangeable potential (high Al_{KCl}/H ratio). The effect of organic matter favoring non-exchangeable potential acidity was evident in the reduction of the Al_{KCl}/H ratio for surface horizons of Group III soils.

The pH_{KCl} also exhibited variation among groups (Figure 2), with a negative correlation coefficient for pH (KCl) and C significant at $p < 0.01$ only for Group I (Table 4). Significant increases in this parameter with depth for Group I reflected reduction of the positive effect of organic matter in forming negative charges near the surface, and the more oxidic mineralogy of Ferralsols favors positive charge formation in subsurface layers (Silva et al., 2008; Serafim, Lima, Lima, Zeviani, & Pessoni, 2012). Increase in the proportion of positive charges with depth of Group I profiles favors the adsorption of OH^- and an increased pH_{KCl} after the exchange of these anions by the Cl^- in solutions of KCl (1 mol L^{-1}).
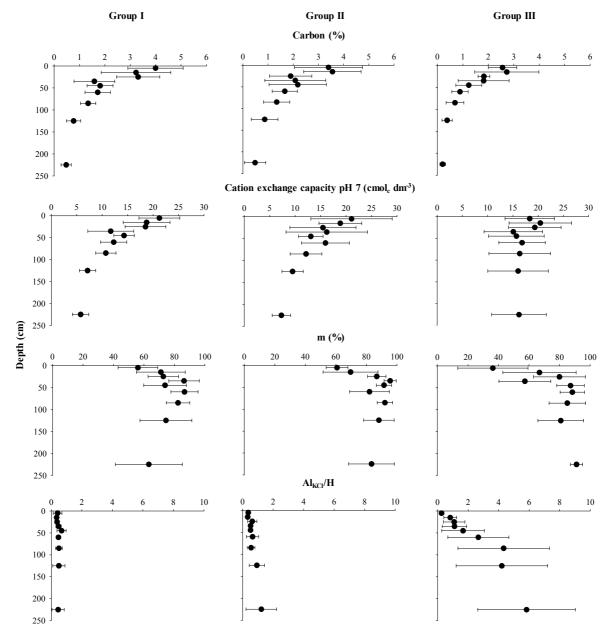

Figure 3. Mean values of carbon (C), cation exchange capacity (CEC) at pH 7, m (Al_{KCl} saturation), and Al_{KCl}/H ratio in acid soils from southern Brazil. Bars represent standard deviation.

Table 4. Pearson correlations between n physical and chemical attributes in acid soils from southern Brazil[1].

	C	Ki	Al_{KCl}/H	Clay	CEC	pH_{KCl}	m
All groups (n = 199)							
Al_{KCl}	–0.06	0.53***(1)	0.72***	–0.25***	0.69***	–0.60***	0.34***
C		–0.18***	–0.36***	0.22***	0.51***	–0.16	–0.18***
Ki			0.41***	–0.48***	0.39***	–0.45***	–0.09
Al_{KCl}/H				–0.35***	0.31***	–0.39***	0.26***
Clay					–0.13	0.24***	0.14***
CEC						–0.54***	–0.02
pH_{KCl}							–0.31***
All groups and without samples from layer 0–50 cm (n = 144)							
Al_{KCl}	–0.16	0.70***	0.76***	–0.34***	0.85***	–0.65***	0.28***
Group I – Al_{KCl} decrease with depth (n = 46)							
Al_{KCl}	0.61***	–0.10	0.55***	–0.32	0.74***	–0.71***	0.42***
C		–0.10	–0.14	–0.36	0.97***	–0.64***	–0.06
Ki			–0.03	–0.01	–0.03	–0.17	–0.05
Al_{KCl}/H				–0.05	–0.01	–0.24	0.50***
Clay					–0.36	0.44***	–0.16
CEC						–0.72***	0.01
pH_{KCl}							–0.39***
Group II – Al_{KCl} insignificant variation (n = 65)							
Al_{KCl}	0.26	0.22	0.44***	–0.12	0.61***	–0.64***	0.47***
C		–0.27	–0.35***	0.32***	0.85***	–0.37***	–0.24
Ki			0.32	–0.39***	–0.14	–0.37***	0.14
Al_{KCl}/H				–0.33	–0.18	–0.32	0.30
Clay					0.07	0.01	0.16
CEC						–0.38***	–0.04
pH_{KCl}							–0.40***
Group III – Al_{KCl} increase with depth (n = 88)							
Al_{KCl}	–0.16	0.38***	0.66***	0.13	0.70***	–0.50***	0.48***
C		–0.06	–0.45***	0.13	0.33	–0.05	–0.20
Ki			0.21	–0.20	0.36***	–0.30***	–0.17
Al_{KCl}/H				–0.15	0.26	–0.30***	0.34***
Clay					0.20	–0.04	0.23
CEC						–0.38***	0.03
pH_{KCl}							–0.35***

[1] *** – correlation coefficient significant at $p < 0.01$.

Regardless of group, saturation by Al_{KCl} (m) increased as a function of soil depth (Figure 3). However, the highest m values occurred through different routes, particularly for more contrasting groups (I and III). For Group I, reduced variation in Al_{KCl} (below 60 cm) indicated increased mean m values up to this layer and was a reflection of reduced CEC with depth. For Group III, the increase in m values with depth followed significant increases in Al_{KCl} along soil profiles.

In practical terms, the differences in Al_{KCl} content and depth distribution patterns in the studied soils require necessary variations in acidity management. When cultivating plants in acid soils with Ki index > 2.2 (usually soils with cambic B or argic B horizons), managing soil acidity in depth will be more intense due to higher Al_{KCl}.

Conclusion

The distribution of Al_{KCl} with depth was defined by the degree of soil weathering in subtropical Brazil. For soils with intense to very intense weathering, the organic fraction increased CEC and Al_{KCl} in superficial horizons, with Al_{KCl} reduction in subsurface layers due to reduced organic matter and probable predominance of minor minerals with lower Ki (1:1 + Al oxides) that reflected higher Al stability in structural forms. By contrast, soils with moderate weathering had higher Al_{KCl} and increased average Al_{KCl} content with depth that indicated greater influence of soil mineral fractions. These soil groupings may aid in soil acidity management.

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