

# QUANTIFICATION OF ALUMINIUM IN SOIL OF THE SOLIMÕES FORMATION, ACRE STATE, BRAZIL<sup>(1)</sup>

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## SUMMARY

The variety of soils in the State of Acre is wide and their chemical profiles are still not fully understood. The nature of the material of origin of these soils is indicated by the high aluminium (Al) content, commonly associated with high calcium (Ca) and magnesium (Mg) contents. The study objective was to use different methods to quantify Al in soils from toposequences formed from material of a sedimentary nature originating from the Solimões Formation, in Acre, Brazil. Trenches were opened at three distinct points in the landscape: shoulder, backslope and footslope positions. Soil samples were collected for physical, chemical, mineralogical analyses. The Al content was quantified using different methods. High Al contents were found in most of these horizons, associated with high Ca and Mg levels, representing the predominant cations in the sum of exchangeable bases. The mineralogy indicates that the soils are still in a low weathering phase, with the presence of significant quantities of 2:1 minerals. Similar Al contents were determined by the methods of NaOH titration, xylenol orange spectrometry and inductively coupled plasma optical emission spectrometry. However, no consistent data were obtained by the pyrocatechol violet method. Extraction with KCl overestimated the exchangeable Al content due to its ability to extract the non-exchangeable Al

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present in the smectite interlayers. It was observed that high Al contents are related to the instability of the hydroxyl-Al smectite interlayers.

**Index terms:** exchangeable aluminium, sedimentary material, smectite, western Amazonia.

## RESUMO: QUANTIFICAÇÃO DO ALUMÍNIO EM SOLOS DA FORMAÇÃO SOLIMÕES, ESTADO DO ACRE, BRASIL

*Há grande variedade de solos no Acre cujos perfis químicos não são ainda totalmente compreendidos. A natureza do material de origem desses solos pode ser observada a partir do teor de alumínio elevado (Al), normalmente associada com níveis elevados de cálcio (Ca) e magnésio (Mg). O objetivo deste estudo foi utilizar diferentes métodos para quantificar o alumínio em solos de topossequências formadas, a partir de um material de natureza sedimentar proveniente da Formação Solimões, Estado do Acre. Foram abertas trincheiras em três pontos distintos: terço superior (P1), terço médio (P2) e terço inferior (P3) da elevação. As amostras de solo foram coletadas para a realização de análises física, química e mineralógica e caracterização do teor de Al. A mineralogia da fração argila foi identificada e o teor de alumínio, quantificado, utilizando diferentes métodos. Na maioria dos horizontes, foram encontrados altos teores de Al, associados a elevados teores de Ca e Mg, os cátions predominantes na soma de bases trocáveis. A mineralogia indica que os solos estão ainda numa fase de baixo intemperismo, com a presença de quantidades significativas de minerais 2:1. O teor de Al determinado pelos métodos de titulação com NaOH, alaranjado de xilenol e espectrometria de plasma, indutivamente acoplado à espectrometria de emissão óptica, foram semelhantes. No entanto, o método de violeta de pirocatecol não apresentou dados consistentes. A extração com KCl superestimou os teores de Al trocável, em razão da sua capacidade de extrair o Al presente em formas não trocáveis nas intercamadas das esmectitas. Observou-se que o teor de Al elevado está relacionado com a instabilidade das intercamadas das esmectitas hidroxil-Al.*

*Termos de indexação:* alumínio trocável, material sedimentar, esmectita, Amazônia ocidental.

## INTRODUCTION

The wide variety of soils in the State of Acre is the result of geological processes related to tectonic reactivations, historic climatic changes induced by variations of the relative sea level and climate (Rossetti & Toledo, 2007), as for example in the arid period in the last ice age (Mayle & Power, 2008). The soils also, received contributions from deposits of materials with different particle size, often associated with the orogeny of the Andean range (Cavalcante, 2006b). The Solimões Formation is noteworthy amongst the various geological formations in the Acre Basin, which covers more than 80 % of the state area of Acre, Brazil. The soils of this region are closely related to the material of origin, with particular physical, chemical and mineralogical characteristics (Möller & Kitagama, 1982; Möller et al., 1982).

The Andean sediments are suggested as the main factors explaining the presence of minimally weathered clays in these soils (Lima et al., 2006). Smectite, interlayered vermiculites and illites, associated with kaolinites, are common in these soils (Volkoff et al., 1989; Marques et al., 2002), although the contents of aluminium oxides (gibbsites) are either zero or low (Silva, 1999). Due to the presence of this clay type, the soils typically have a cation exchange

capacity (CEC) of over 27 cmol<sub>c</sub> kg<sup>-1</sup> clay. In general, the soil calcium (Ca) and magnesium (Mg) contents are high, often associated with high aluminium (Al) levels, so that some may have aluminic or alitic characteristics (Embrapa, 2006).

Another aspect of the high Al contents is that the element can be in non-exchangeable form. It is also questionable whether the titration method is effective to determine exchangeable Al. In a study of samples of different soils from the Northeast and region of Jaguariúna, in São Paulo State, Boeira et al. (2004) observed that the titration method determined significantly higher Al contents than the xylenol orange spectrophotometry method. The authors attribute these results to titrating with NaOH, which neutralises other acid forms in addition to those resulting from Al hydrolysis.

Unbuffered neutral salt solutions have been used to extract Al from soil samples since the 1960s (Brauner, 1966). A solution of 1 mol L<sup>-1</sup> KCl has been considered the most suitable extractant for quantifying Al (Raij et al., 1987; Hiradate et al., 1998). This solution is also less susceptible to ion interference (Coscione et al., 1998).

Aluminium determined by these extractants may overestimate the non-exchangeable species (hydroxyl-Al) in dissolution. The dissolution of hydroxyl-Al is affected by pH, concentration, the chemical

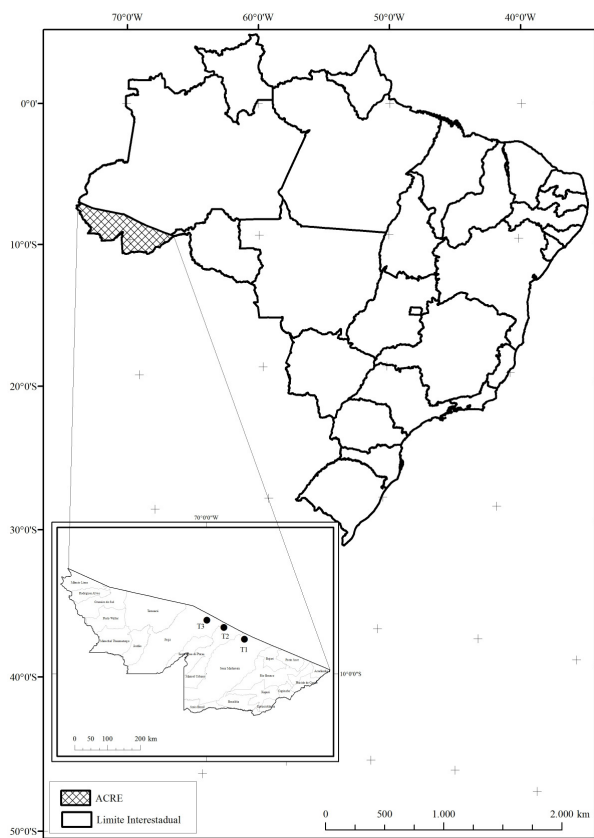
characteristics of the extractant and the extraction time (Kissel et al., 1971; Oates & Kamprath, 1983). While extraction with KCl removes both exchangeable and non-exchangeable Al (Oates & Kamprath, 1983), the contribution of non-exchangeable Al can be considered insignificant in acid soils in Brazil (Pavan, 1983). However, the exchangeable Al method did not appear promising to estimate the lime requirement of 2:1 clay soils in a region of North Carolina, USA (Kamprath, 1970). Gama & Kielh (1999) found low Al phytotoxicity, indicating that the exchangeable Al would not be suitable to test the acidity in these soils.

Based on the above considerations, the present study had the objective of using different methods to quantify Al in soils from three toposequences formed from material of a sedimentary nature originating from the Solimões Formation, Acre State, Brazil.

## MATERIAL AND METHODS

### Physical environment

The areas studied are located in the counties of Sena Madureira (S9 03.237 W68 57.796), Manoel Urbano (S8 43.740 W69 31.242) and Feijó (S8 31.985 W69 59.184), in the State of Acre, Brazil (Figure 1).



**Figure 1.** Localization of the toposequences in each county.

The regional climate is characterised by high temperatures, with a mean temperature of 24.5 °C, and high rainfall, with an annual mean of over 1,600 mm. It is defined by the Köppen system as Aw, tropical climate with dry winter season, and Am, tropical wet (Brasil, 1976). The geology is typical of the Solimões Formation, with pelitic and psammitic sediments from Cenozoic deposits. The predominant materials of the formation are carbonate and gypsiferous concretions, occasionally with carbonized material (peat and lignite), sparse pyrite concentrations, and a large quantity of vertebrate and invertebrate fossils. Subordinately, there are siltites, siltic-argillaceous limestones, ferruginous sandstones, and plomitic conglomerates (Cavalcante, 2006a).

Trenches were opened at three points in the toposequence (T1, T2 and T3) of each location: shoulder position (P1), backslope (P2) and footslope (P3). The toposequences are located in areas of undulated tops in the local relief, with convex and concave sides. The slope length varies from 150 to 250 m. The profiles were characterized according to the Manual for Describing and Collecting Soil in the Field (Santos et al., 2005). Soil samples from each horizon were collected for physical and chemical characterisation. Subsequently the soils were classified according to the Brazilian Soil Classification System (Embrapa, 2006) and Soil Taxonomy (Soil Survey Staff, 1999), as given in table 1. After the soil profiles had been characterised and classified, representative subsurface horizons were selected for study.

### Laboratory analysis

The material was air-dried after collection and sieved (mesh 2.00 mm), thus producing air-dried fine soil (FADS). The physical analysis consisted of: particle size, using the dispersion method and 0.1 mol L<sup>-1</sup> sodium hydroxide. The chemical characterization involved the quantification of the Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup>, extracted with 1 mol L<sup>-1</sup> KCl. Extraction of H+Al was achieved with a 0.5 mol L<sup>-1</sup> solution of calcium acetate at pH 7.0. The P, Na<sup>+</sup> and K<sup>+</sup> contents were extracted with a solution of 0.0125 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 0.05 mol L<sup>-1</sup> HCl. The Ca<sup>2+</sup> and Mg<sup>2+</sup> contents were determined by titration with 0.0125 mol L<sup>-1</sup> EDTA solution; Na<sup>+</sup> and K, by flame photometry; P by colourimetry; and Al<sup>3+</sup> and H+Al, by titration with 0.025 mol L<sup>-1</sup> NaOH. The pH in H<sub>2</sub>O and in KCl (1:2.5 weight) was determined by means of a potentiometer. The organic carbon (C.org) content was determined by wet oxidation. From these data we calculated: aluminium saturation (m); S value (sum of exchangeable bases); T value (soil CEC), clay CEC and V% value. The above procedures were carried out as described by Embrapa (1997).

The specific surface of the ground and sieved (60-mesh) FADS was determined. Adsorption was measured using ethylene glycol monomethyl ether (EGME), as proposed by Carter et al. (1965), Heilman et al. (1965) and modified by Cihacek & Bremner

**Table 1. Classification of the soil profiles studied using the Brazilian Soil Classification System (SiBCS) and Soil Taxonomy**

Toposequence/profile	SiBCS <sup>(1)</sup>	Soil Taxonomy <sup>(2)</sup>
T1P1	Typic haplic orthic Vertisol	Chromic Hapluderts
T1P2	Typic haplic Ta eutrophic Cambisol	Typic Dystrudepts
T1P3	Typic haplic Ta eutrophic Cambisol	Typic Dystrudepts
T2P1	Plinthic Red-Yellow alitic Argisol	Typic Plinthudults
T2P2	Typic haplic Ta eutrophic Cambisol	Typic Dystrudepts
T2P3	Typic haplic Ta eutrophic Gleysol	Typic Udorthents
T3P1	Plinthic Red Alitic Argisol	Typic Plinthudults
T3P2	Typic Grey dystrophic Argisol	Typic Plinthudults
T3P3	Typic haplic Ta eutrophic Cambisol	Vertic Dystrudepts

<sup>(1)</sup> Embrapa (2006); <sup>(2)</sup> Soil Survey Staff (1999).

(1979). A 1.0 g sample mass was weighed and then 3.0 mL EGME was added. The soil material was subjected to vacuum in a desiccator with CaCl<sub>2</sub>, and weighed at pre-established intervals, until constant weight. Total specific surface (S.s.) was calculated using the equation: S.s. = gEGME g<sup>-1</sup> (sample) x 2.86x10<sup>-4</sup> g m<sup>-2</sup>.

Sulphuric attack was applied to the clay fraction to quantify the Fe, Al and Ti contents, and silica in the residue was subsequently analysed. The method consisted of boiling the clay in a 1:1 solution of H<sub>2</sub>SO<sub>4</sub> for 30 min under reflux, cooling and filtering. The Fe, Al and Ti contents in the filtrate were determined, and Si in the residue (Embrapa, 1997). The SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents were quantified and expressed as percentages and used to calculate the molecular ratios ki (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) and kr (SiO<sub>2</sub>/R<sub>2</sub>O<sub>3</sub>).

The minerals in the clay fraction were identified by X-ray diffraction (XRD), obtained by sedimentation after dispersion with 1 mol L<sup>-1</sup> NaOH. The fresh samples were analysed with the following treatments: deferrification by CBD (citrate-bicarbonate-sodium dithionite), in accordance with Mehra & Jackson (1960); K saturation and, after mounting on a slide, heating for 2 h at 110, 350 and 550 °C; saturation with Mg and solvation with ethylene glycol, as described by Embrapa (1997) and Calderano et al. (2009). Smearing was used to prepare oriented slides.

The clay fraction was mounted on oriented slides with a suspension of total clay (<2.0 µm). Analyses were conducted with a Rigaku diffractometer, model Miniflex II, using Kα radiation with λ 0.15405 nm, produced by a copper tube, 30 kv and 15 mA, with a sweep amplitude from 2 to 45°2θ.

The diffractograms were produced using the Microcal Origin 6.0 software and presented in the following order: untreated sample (Am. total); iron-free sample saturated with magnesium (Mg) and subsequently solvated with ethylene glycol (MgEG); iron-free sample saturated with K, with sweeps at room temperature (K25) and, after heating, at the

indicated temperatures (K350 and K550). The diffractograms were interpreted based on the tables and criteria of Thorez (1976), Brindley & Brown (1984) and Moore & Reynolds Jr. (1997). The orthography of the mineral names is in conformity with Branco (1987).

To quantify exchangeable aluminium, extracts were produced using 1 mol L<sup>-1</sup> KCl at a ratio of 1:10. The exchangeable Al content in the extracts was determined using: titration (Al\_Na), with 0.025 mol L<sup>-1</sup> NaOH solution as titrate and bromothymol blue as the turning point indicator (Embrapa, 1997); xylenol orange colourimetry (Al\_AX) with UV-Vis spectrophotometer colour reading at 555 nm, as described by Coscione et al. (2000); pyrocatechol violet colourimetry (PVC), allowing discrimination of monomeric (Al\_VPM) and total (Al\_VPT) aluminium forms, with spectrophotometry absorbance readings at 577 nm, as described by Dougan & Wilson (1974) and; inductively coupled plasma optical emission spectrometry - ICP-OES (Al\_P1). The ICP-OES method was also used to determine the water-soluble aluminium (Al<sub>sol</sub>) content, following Embrapa (1997).

The equipment for ICP-OES was a Perkin-Elmer model OPTIMA 3000 of Embrapa-Solos, with the operating conditions: radiofrequency power 1500 W, plasma argon flow 15 L min<sup>-1</sup>, auxiliary argon flow 0.5 L min<sup>-1</sup>, nebulizer argon flow 0.7 L min<sup>-1</sup>, and sample aspiration rate of 2.0 mL min<sup>-1</sup>.

Conclusions on the data were drawn on the basis of the Pearson correlation and the F test.

## RESULTS AND DISCUSSION

### Chemical and physical characteristics

The chemical analysis results are presented in table 2. It was observed that the organic carbon (C.org) contents in the horizons were low (0.7-4.6 g kg<sup>-1</sup>). These values are probably related to the high

**Table 2. Chemical and physical properties of the soil horizons**

Profile/horizon	pH		H+Al	Al <sup>3+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	CTC <sup>(1)</sup>	V	m	C.org.	Sand	Silt	Clay	S.s.
	H <sub>2</sub> O	KCl														
	cmol <sub>c</sub> kg <sup>-1</sup>							%		g kg <sup>-1</sup>				m <sup>2</sup> g <sup>-1</sup>		
T1P1 Cv <sub>3</sub>	5.3	4.0	5.4	1.5	18.0	21.5	0.5	0.2	87	88	4	1.8	31	442	527	260
T1P1 2Cv	8.0	6.9	0.2	0.0	21.4	22.6	0.8	0.1	97	100	0	0.7	182	355	463	315
T1P2 2Bi <sub>2</sub>	4.0	3.8	18.5	11.8	1.5	9.9	0.1	0.2	43	39	51	4.5	103	197	700	209
T1P2 2C	4.2	3.8	18.3	13.5	1.4	16.3	0.2	0.3	81	50	43	1.9	120	432	448	213
T1P3 Bi <sub>1</sub>	4.3	3.8	13.4	8.4	3.5	15.0	0.0	0.2	88	58	31	2.7	372	265	363	161
T1P3 2C <sub>2</sub>	5.9	3.9	3.1	0.6	13.8	7.5	0.2	0.2	168	87	3	0.4	240	612	148	125
T2P1 Bt	3.9	3.5	21.3	14.0	1.2	7.6	0.0	0.2	44	30	61	4.6	61	242	697	219
T2P1 Btf <sub>3</sub>	4.3	3.6	19.0	13.6	1.4	9.7	0.1	0.2	81	38	55	1.5	123	500	377	223
T2P2 Bi <sub>1</sub>	4.1	3.5	17.7	12.1	4.5	9.5	0.1	0.2	58	45	46	3.2	98	349	552	245
T2P2 C <sub>2</sub>	5.5	3.7	4.0	1.3	16.7	5.4	0.4	0.1	162	85	6	0.7	371	465	164	79
T2P3 2Bg	6.0	4.0	1.8	0.6	16.0	6.3	0.5	0.5	98	93	3	1.2	169	574	257	201
T2P3 2Cg <sub>1</sub>	6.6	4.5	1.5	0.0	23.2	11.8	0.7	0.4	105	96	0	1.2	284	357	359	254
T3P1 2Bt	4.7	3.6	15.8	10.8	1.1	2.0	0.0	0.3	29	18	78	3.0	99	230	671	200
T3P2 Btf <sub>1</sub>	4.9	3.5	20.5	13.2	1.5	8.7	0.0	0.5	51	34	56	2.1	180	210	611	274
T3P3 Bi	5.3	3.6	15.5	9.6	16.3	12.3	0.5	0.2	89	65	25	2.0	46	448	506	217
T3P3 Cv <sub>2</sub>	6.1	4.8	4.0	1.0	22.5	14.9	1.1	0.6	77	91	3	1.0	112	329	560	266

<sup>(1)</sup> Clay CEC; V: saturation indicator; m: aluminium saturation indicator; C.org.: organic carbon; S.s.: specific surface.

mineralisation rates of organic matter in the soil surface, due to the soil-climatic conditions of the region, ie., the high temperature, air humidity and rainfall (Acre, 2000).

Generally, the pH values in H<sub>2</sub>O were low, but higher than those determined in KCl solution, indicating the predominance of negative charges. High base saturation was observed, ranging from 18 % in the 2Bt horizon of the P1 profile of T3 to 100 % in the 2Cv horizon of the P1 profile of T1. The values for Al saturation in these horizons were, respectively, 78 and 0 %. The majority of horizons were found to have high Al content and predominance of Ca and Mg in the sum of exchangeable bases, as in the 2C horizon of the P2 profile of T1. In some horizons the Mg were higher than the Ca contents. This pattern of variation and high Ca and Mg contents was also observed by Amaral (2003), in soils of the Solimões Formation in the Iaco-Acre river basin.

In spite of the high active acidity of these soils (low pH in H<sub>2</sub>O) and high exchangeable Al contents, no phytotoxic effect or response to acidity correction has been proven in pot experiments or for varieties of Al-sensitive plants (Gama & Kiehl, 1999), due to the combination of two factors: the soil Ca content may be mitigating the Al toxicity. Also, the standard method of Al extraction (1 mol L<sup>-1</sup> KCl) may not be suitable for these soils (Gama & Kiehl, 1999), as it may be extracting part of the Al that is strongly retained at the adsorbent surface rather than the Al in equilibrium with the soil solution (Wadt, 2002).

In the profiles studied, the silt and clay were predominant over the sand fraction (Table 2). The specific surface (S.s.) values were relatively high

(79 - 315 m<sup>2</sup> g<sup>-1</sup>), associated with high cation exchange capacity (CEC) values in the clay fraction (Table 2). These results are characteristic of the presence of clay minerals, such as illite and smectite, with high S.s. and high activity. Similar results were found by Gama (1986), with S.s values ranging from 120 to 386 m<sup>2</sup> g<sup>-1</sup>, demonstrating the close relationship between this value and the soil CEC. According to Volkoff et al. (1989), the material of origin of some soils of the State of Acre is clay composite with high montmorillonite content, with variable illite and vermiculite and low kaolinite levels, resulting in high S.s values.

The values for the molecular ratios ki and kr (Table 3) suggest a lower degree of weathering in these horizons, with predominance of SiO<sub>2</sub> and low Fe<sub>2</sub>O<sub>3</sub> values. The low Fe<sub>2</sub>O<sub>3</sub> content may be due to the high rainfall together with the low soil permeability, creating favourable conditions for iron reduction and removal from the soil (Araújo et al., 2004).

### Mineralogy of the clay fraction

The X-ray diffraction results obtained for the clay fraction are given in table 4 and some example diffractograms in the figure 2. The presence of the following clay minerals was confirmed: smectite and kaolinite, with the greatest contents, together with quartz and lepidocrocite, in smaller proportions and absent in some samples. The presence of interlayered kaolinite-smectite was observed in the 2Bt horizon of the P1 profile of the T3.

Smectite is very evident, predominant in nearly all analysed horizons, except for the sample from the 2Bt horizon of the P1 profile of the T3. The clay mineral is indicated by its main reflection in the 6.5° (2θ) region

of ~1.40 nm, in the sample saturated with magnesium (Mg), which is shifted (indicating expansion) after treatment with ethylene glycol (MgEG). The intensity and shape of this reflection in the diffractograms for the Mg-saturated sample are noteworthy. The large occurrence of smectite demonstrates that the soils are still in a low weathering phase.

The smectite reflections vary in intensity and width, demonstrating, respectively, variation in the

**Table 3. Contents of Si, Al, Fe and Ti, determined by sulphuric attack on clay, and molecular ratios ki and kr for the horizons under study**

Profile/horizon	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	ki <sup>(1)</sup>	kr <sup>(2)</sup>
	g kg <sup>-1</sup>					
T1P1 Cv <sub>3</sub>	306	204	53	5.4	2.55	2.19
T1P1 2Cv	294	193	56	4.9	2.59	2.18
T1P2 2Bi <sub>2</sub>	276	210	50	5.3	2.23	1.94
T1P2 2C	282	205	57	5.3	2.34	1.99
T1P3 Bi <sub>1</sub>	256	204	55	5.3	2.13	1.82
T1P3 2C <sub>2</sub>	256	197	66	4.2	2.21	1.82
T2P1 Bt	254	211	66	5.3	2.05	1.71
T2P1 Btf <sub>3</sub>	310	200	63	5.4	2.64	2.19
T2P2 Bi <sub>1</sub>	254	196	63	5.0	2.2	1.83
T2P2 C <sub>2</sub>	288	185	62	4.9	2.65	2.18
T2P3 2Bg	288	187	69	5.0	2.62	2.12
T2P3 2Cg <sub>1</sub>	294	186	65	5.2	2.69	2.20
T3P1 2Bt	278	211	70	5.8	2.24	1.85
T3P2 Btf <sub>1</sub>	278	196	67	4.9	2.41	1.98
T3P3 Bi	250	195	57	4.9	2.18	1.84
T3P3 Cv <sub>2</sub>	308	180	67	5.2	2.91	2.35

<sup>(1)</sup> ki = (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) x 1.7; <sup>(2)</sup> kr = (SiO<sub>2</sub> x 1.7)/[(Al<sub>2</sub>O<sub>3</sub> + (0.64 x Fe<sub>2</sub>O<sub>3</sub>)]

relative proportion and crystallinity degree of the mineral. The presence of larger reflections, that is, a lower crystallinity degree, may be associated with Al polymers filling the space between the smectite layers, denominated hydroxyl-Al interlayered smectite (HIS), but may also be due to the presence of interlayered kaolinite/smectite.

Mica (an inclusive term for illite) occurs in all horizons, as indicated by its diagnostic reflections at ~8.85°, 17.65° and 26.70° (2θ), which remained stable under the applied treatments. The increase in intensity, observed after heating to 350° and 550 °C, was due to the collapse of the other 2:1 clay minerals. Its occurrence is quite significant in all horizons, with apparent predominance over kaolinite in nearly all of them.

Evaluating the mineralogy of the western Amazonian region, Marques et al. (2002) observed that clay consisted of smectite, vermiculite and smectite with interlayered hydroxyl resulting from the addition of sediments, solution precipitation and transformation of the primary minerals.

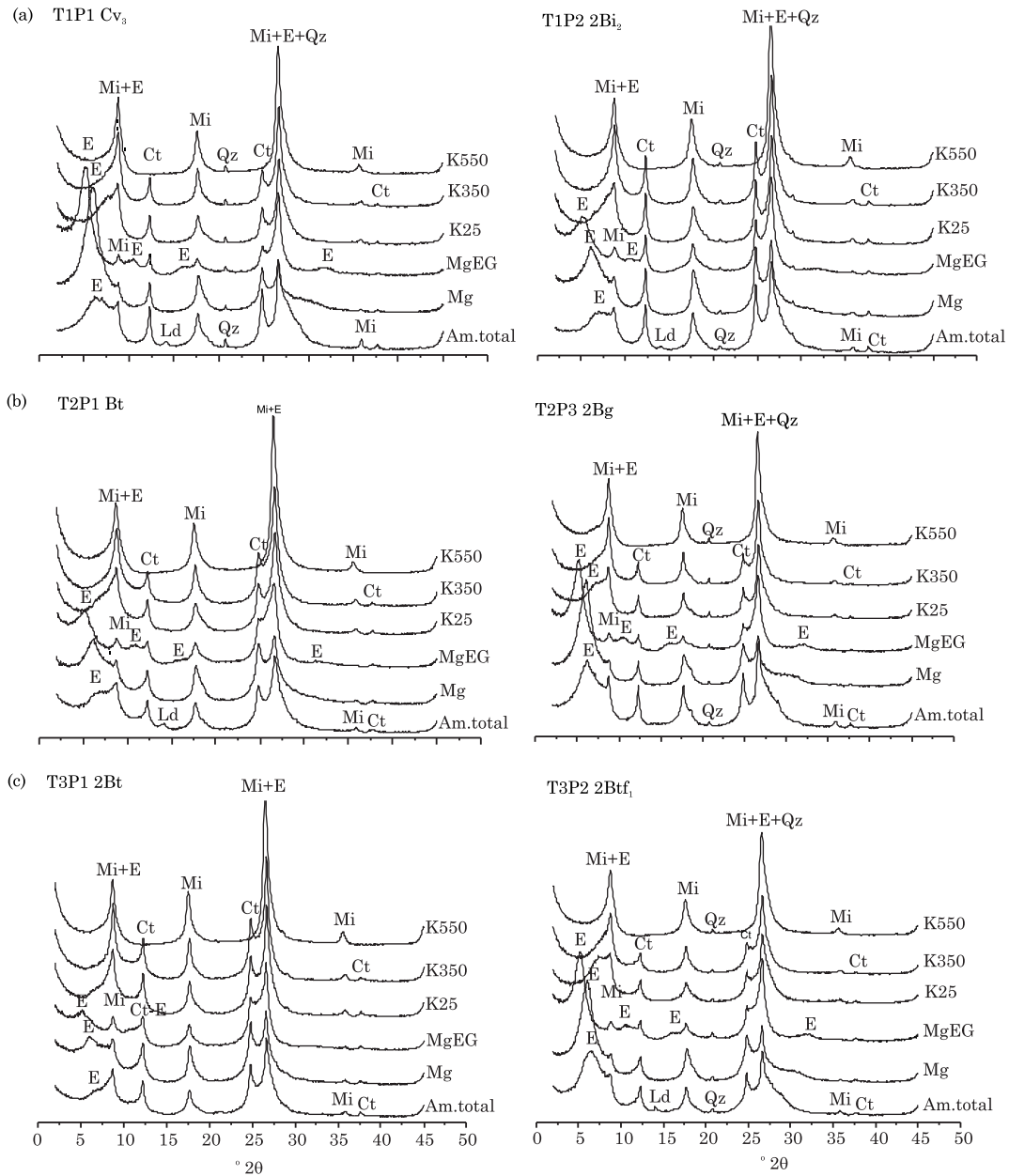
Kaolinite also occurs in all horizons analysed at lower proportions than those mentioned above. Evidence for its presence are well-formed reflections in the regions 12.3°, 24.8° and 37.7° (2θ), which disappear after the sample is heated to 550 °C.

In the 2Bt horizon of the P1 profile of the T3, the presence of kaolinite-smectite was confirmed. Evidence for their presence is given by a band alongside the kaolinite reflections in the sample with Mg after treatment with ethylene glycol (MgEg), best seen in the reflection at 12.3° (2θ). This reflection should not be confused with the second smectite reflection that also occurs in this region.

The presence of lepidocrocite was also observed in some samples, whose reflection is only perceptible in untreated samples, disappearing after disferriification

**Table 4. Estimates of the relative proportions of the mineral constituents of the clay fraction of the analysed horizons**

Toposequence/profile	Horizon	Mineralogy
T1P1	Cv <sub>3</sub>	Smectite > mica > kaolinite, lepidocrocite, quartz
T1P2	2Bi <sub>2</sub>	Smectite > kaolinite > mica, lepidocrocite, quartz
T1P2	2C	Smectite > mica > kaolinite, lepidocrocite, quartz
T1P3	Bi <sub>1</sub>	Smectite > mica > kaolinite, lepidocrocite, quartz
T2P1	Bt	Smectite > mica > kaolinite, lepidocrocite
T2P1	Btf <sub>3</sub>	Smectite > mica > kaolinite, quartz
T2P2	Bi <sub>1</sub>	Smectite > mica > kaolinite, quartz
T2P2	C <sub>2</sub>	Smectite > mica > kaolinite, quartz
T2P3	2Bg	Smectite > mica > kaolinite, quartz
T2P3	2Cg <sub>1</sub>	Smectite > mica > kaolinite, quartz
T3P1	2Bt	Smectite > mica > kaolinite > interlayered kaolinite-smectite
T3P2	Btf <sub>1</sub>	Smectite > mica > kaolinite, lepidocrocite, quartz
T3P3	Bi	Smectite > kaolinite > mica, lepidocrocite, quartz
T3P3	Cv <sub>2</sub>	Smectite > mica > kaolinite, quartz



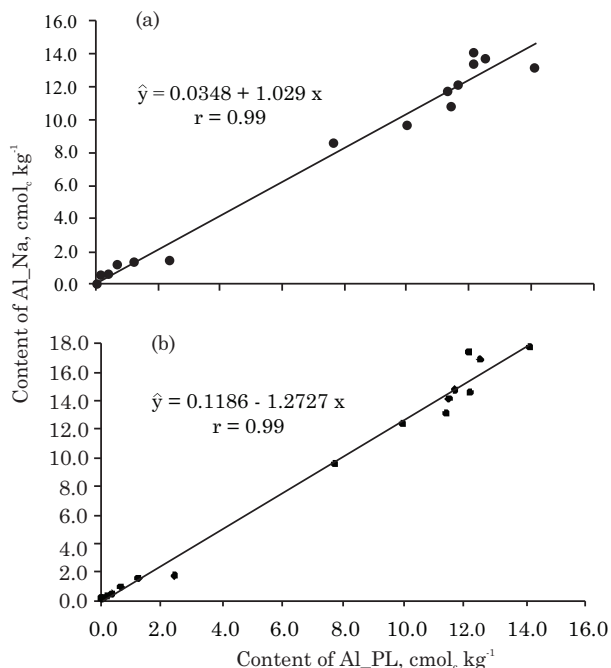
**Figure 2.** X-ray diffractograms of the clay fraction of the horizons of the T1 (a), T2 (b) and T3 (c) toposequences. E: smectite, Mi: mica, Ct: kaolinite, Ct-E: interlayered kaolinite-smectite, Ld: lepidocrocite, Qz: quartz.

(with dithionite citrate bicarbonate). Quartz is also present, and both in reduced proportions.

There was a tendency for more intense smectite reflections in the spectra of the deepest horizons in all profiles, suggesting the presence of a greater quantity of large and well-crystallised particles. The crystallinity degree of smectite was lower in the shallower horizons. These results demonstrate that the deeper smectites are more protected from weathering processes. According to Lima et al. (2006), the occurrence of smectite may be attributed to the high base (Ca and Mg) content and of sufficient silica for this mineral to be synthesised and stabilised.

The weathering processes are more intense in better drained environments, favouring Al release, and together with the great frequency of wetting and drying cycles, promote the formation of HIS, expressed by the wider reflections (Figure 3).

Moreover, the high Al content in these soils may be due to the presence of 2:1 clay minerals with interlayered hydroxyl. The filling of the smectite interlayer spaces with Al-OH modifies the properties of these minerals, such as: reducing the permanent charge and increasing the variable charge, reducing the internal surface areas (Barnhisel & Bertsch, 1989) and the capacity for expansion and contraction, as



**Figure 3. Correlation between aluminium contents determined by ICP-OES (Al\_PL) and by titration with NaOH (Al\_Na) (a) and by spectrometry with xylenol orange (Al\_AX) (b).**

well as, under certain environmental conditions, being the cause of very high Al levels (Kämpf & Curi, 2003).

These results show that a reducing environment favours the greatest concentration of smectite, as in the 2Bg and 2Cg<sub>1</sub> horizons of the P3 profile of T2. On the other hand, environments with better drainage favour HIS, illite and interlayered illite/smectite. In a study of two Cambisols of clay origin from the Guabirotuba Formation in the Curitiba Sedimentary Basin (Paraná State), Melo et al. (2009) identified smectite with interlayered hydroxyl-Al in the horizons closest to the surface (A and Bi) and smectite in the samples from the C horizon. The same authors emphasized that even with the limited occurrence of 2:1 minerals in the A horizon, HIS was maintained, which may be due to the presence of hydroxyl-Al in the smectite interlayers, stabilising the 2:1 minerals, which are thermodynamically unstable under conditions of greater weathering and silica removal.

In a study of the soils of Rio Branco and Manuel Urbano in Acre, Volkoff et al. (1989) observed that smectites are predominant in younger and deeper horizons, as is characteristic of Inceptisol, and illite predominates in the more developed horizons, as in Argisol, probably due to smectites being degraded.

According to Kämpf & Curi (2003), smectites are generally saturated with Ca and Mg. However, Al is released from the structure upon acidification of the medium, forming Al-OH polymers that precipitate in the interlayers, producing smectites with hydroxyl-Al interlayers.

### Aluminium contents determined by different methods

Table 5 shows the Al content in the horizons studied, extracted with KCl and water, determined by different methods. It can be observed that the water-soluble Al contents are very low, demonstrating that practically all Al determinations by the different methods used in this study was based on KCl extraction. In general, the Al contents quantified by xylenol orange spectroscopy (Al\_AX) were higher in comparison to values from the other methods (0.2 - 17.8 cmol<sub>c</sub> kg<sup>-1</sup>, on average 8.5 cmol<sub>c</sub> kg<sup>-1</sup>).

Aluminium determination by pyrocatechol violet spectrometry was found to be ineffective with little variation or consistency between the values for monomeric Al (Al\_VPM) and total Al (Al\_VPT). In Bi of the P3 profile of T3 (Table 5), the values for monomeric Al were higher than those for total Al. This result may be due to the method being incapable of determining high Al concentrations since a significant dilution of the extract is required, which can lead to errors. In a study of Histosols from various regions of Brazil with Al-rich soils, Ebeling (2006) observed that the Al contents quantified by pyrocatechol violet were not consistent with the results of the other methods: titration with NaOH, xylenol orange and ICP-OES.

Lower Al values were recorded in the 2Cv horizon of the P1 profile of T1 and the deeper horizons of the (P3) profile, probably due to the poor drainage and the less intense weathering process, increasing the stability of smectite with Al in its structure.

The correlation analysis between the Al values determined by different methods (Al\_Na, Al\_AX, and Al\_PL) and the pH in H<sub>2</sub>O and KCl, and for Ca<sup>2+</sup>, clay CEC, ki and kr (Table 6), showed a significant and negative correlation, with higher pH values in H<sub>2</sub>O and clay CEC. The correlations between the different Al and clay methods were positive and significant. The results indicate that the higher the content of clay and the lower the values for clay CEC, ki and kr, the higher the Al content. That is, the greater the weathering degree of the soil, the greater the Al content. In studies of soils in the same region of Acre, Volkoff et al. (1989) stated that the distribution of exchangeable Al content follows the variation in the clay content, suggesting that a possible explanation for the high Al content is the destabilisation and destruction of clay, with subsequent Al release.

In a study of the mineralogy of three soils from a toposequence in Western Amazonia, Lima et al. (2006) observed the occurrence of smectite in an Ultisol with high CEC and Al contents, especially in the (deeper) 2C2 horizon, where the high content of bases and silica are sufficient for this mineral to be synthesised and stabilised, unlike in the surface horizons, where the activity of bioclimatic agents is more intense and the acidity is higher. Smectite becomes unstable under these conditions, degrading and releasing Al to the



**Table 5. Aluminium contents of the horizons determined by different methods**

Toposequence/profile/horizon	Alsol <sup>(1)</sup>	Al_Na	Al_AX	Al_PL	Al_VPM	Al_VPT
	cmol <sub>c</sub> kg <sup>-1</sup>					
T1P1 Cv <sub>3</sub>	0.02	1.5	1.7	2.5	0.7	0.8
T1P1 2Cv	-	0.0	0.2	0.0	0.1	0.2
T1P2 2Bi <sub>2</sub>	0.02	11.8	13.1	11.4	6.7	7.5
T1P2 2C	0.06	13.5	14.6	12.2	7.7	8.2
T1P3 Bi <sub>1</sub>	0.01	8.4	9.6	7.8	6.6	6.3
T1P3 2C <sub>2</sub>	0.03	0.6	0.5	0.4	0.3	0.5
T2P1 Bt	0.02	14.0	17.3	12.1	8.0	7.1
T2P1 Btf <sub>3</sub>	0.02	13.6	16.8	12.5	5.1	7.1
T2P2 Bi <sub>1</sub>	-	12.1	14.7	11.7	7.9	8.0
T2P2 C <sub>2</sub>	0.23	1.3	1.6	1.2	0.7	0.8
T2P3 2Bg	0.11	0.6	0.3	0.2	0.3	0.4
T2P3 2Cg <sub>1</sub>	0.29	0.0	0.2	0.1	0.2	0.2
T3P1 2Bt	0.05	10.8	14.1	11.5	7.0	8.2
T3P2 Btf <sub>1</sub>	0.02	13.2	17.8	14.2	5.3	8.0
T3P3 Bi	0.04	9.6	12.4	9.9	5.8	8.1
T3P3 Cv <sub>2</sub>	0.07	1.0	1.0	0.6	7.7	7.7
Mean	0.06	7.0	8.5	6.8	4.4	4.9

<sup>(1)</sup> Al<sub>sol</sub>: water-soluble aluminium; Al\_Na: aluminium determined by titration with NaOH; Al\_AX: aluminium determined by xylenol orange spectrometry; Al\_PL: aluminium determined by plasma emission (ICP-OES); Al\_VPM: monomeric aluminium determined by pyrocatechol violet spectrometry; Al\_VPT: total aluminium determined by pyrocatechol violet spectrometry.

**Table 6. Pearson correlation between Al content and properties of the horizons**

Property	Al_Na	Al_AX	Al_PL
pH H <sub>2</sub> O	-0.84*	-0.81*	-0.82*
pH KCl	-0.58*	-0.57*	-0.58*
Ca <sup>2+</sup>	-0.91 <sup>ns</sup>	-0.89 <sup>ns</sup>	-0.90 <sup>ns</sup>
Clay	0.59*	0.60*	0.61*
Clay CEC	-0.68*	-0.69*	-0.70*
ki	-0.60*	-0.59*	-0.60*
kr	-0.58*	-0.58*	-0.57*

\* significant at 1 %; ns: not significant.

medium, which can lead to high exchangeable Al contents.

According to Coscione et al. (1998), the titration method is the least sensitive for exchangeable Al<sup>3+</sup> determination. Bertsch & Bloom (1996) stated that spectrophotometric methods for Al determination, e.g., ICP-OES, are doubtlessly the most sensitive and reliable. From the analysis of correlation of Al\_PL with Al\_Na and Al\_AX, high correspondence was observed between the methods (r = 0.99, at 5 % significance) (Figure 3), demonstrating that these methods are mutually comparable. However in general, the difference between the Al\_Na and Al\_PL values is less than the difference between the Al\_Na and Al\_AX values. This result may be due to the greater dilution of the extract required for

determination by xylenol orange spectrometry, increasing the possibility of analytical error. The observed pattern does not disqualify this method for Al determination.

According to Pérez et al. (2009), the procedure of extraction with KCl and titration with NaOH determines H<sup>+</sup>, identified as exchangeable acidity (Sposito, 1989). Therefore, in this context, there is no differentiation between “exchangeable H<sup>+</sup>” and the H<sup>+</sup> produced by the hydrolysis of Al. This finding indicates that practically all of the H<sup>+</sup> determined by titration with NaOH originated from the hydrolysis of Al, without much interference from other sources of H<sup>+</sup>, such as the pH-dependent charges, due to the predominance of 2:1 clay minerals and the low organic matter content. The results demonstrate that the exchangeable acidity was mainly due to Al, even at pH lower than 4.5.

When determining Al contents in 18 horizons of mineral soils with kaolinite and/or iron/aluminium oxyhydroxides as the main clay fraction minerals, Pérez et al. (2009) concluded that most protons quantified in the extracts of the mineral soils, i.e., the exchangeable acidity, originated from the hydrolysis of exchangeable Al.

Despite the similar results, the different methods for determining Al were not capable of quantifying exclusively exchangeable Al, which is toxic to plants, due to the ability of KCl to extract non-exchangeable Al forms (Abreu Jr. et al., 2003). According to Ross et al. (2008), the repeated extraction with a neutral salt

continuously removes Al in quantities according to the pH of the soil and solution combination. According to Wadt (2002) and Marques et al. (2002), this distortion in the exchangeable Al content, as an indicator of soil acidity, is exacerbated because KCl as extractant causes the dissolution of the low crystallinity forms of Al and of the interlayered Al, which are non-exchangeable forms and, therefore, have a very tenuous equilibrium with the soil solution. Accordingly, the presence of 2:1 clay minerals with interlayered hydroxyl-Al leads to an overestimation of exchangeable Al, i.e., the extract consists mainly of non-phytotoxic non-exchangeable Al.

To explain the effect of the non-phytotoxicity of Al, Wadt (2002) stated that in the case of the soils of Acre, the adsorbent surface has high electronegativity and attracts cations with smaller hydrated ionic radius and greater valence more effectively. The cations adsorbed in this way are less active in the soil solution. On the other hand, other cations with larger hydrated ion radius and lower valence are released to the soil solution, where they have greater activity. In practice, these mechanisms reduce the quantity of Al that can reach the plant root systems and, therefore, its phytotoxic effect.

According to Araújo (2008), for the conditions of some of the soils of Acre, which have high Ca, Mg and exchangeable Al contents, root development is not harmed because of the high Ca activity in solution, which can reduce the problems arising from acidity.

The smectite surface (2:1 clay minerals) has a permanent negative charge, which allows hydroxyl-Al, positively-charged polymers, to be adsorbed (Kämpf & Curi, 2003). Due to its low stability, subject to release by weathering, the hydroxyl-Al can be indicated as the cause of the high Al contents. Therefore, smectites may play an important role in the adsorption of Al, reducing its activity in the soil solution.

In the acidic mineral soils, the titrated  $H^+$  in the non-buffered KCl solution does not represent the exchangeable acidity of the soil, but the low stability of the hydroxyl-Al forms, except in soils with high organic matter contents (Raij et al., 2001).

## CONCLUSIONS

1. The Al contents determined by titration with NaOH, xylenol orange spectrometry and ICP-OES were similar. However, the pyrocatechol violet method did not obtain consistent data. Extraction with KCl overestimated the exchangeable Al content due to its ability to extract the non-exchangeable Al present in the smectite interlayers.

2. It was observed that a high Al content is related to the instability of the hydroxyl-Al smectite

interlayers. The horizons with the lowest degree of weathering, demonstrated by relatively low values for clay CEC, ki and kr, and by the mineralogy with most intense smectite reflections, have lower Al contents.

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