

PEDOGENESIS ON COASTAL TABLELANDS AREA WITH LOW RANGE ALTIMETRY IN PARAÍBA STATE¹

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ABSTRACT - Small variations of relief may change drainage and runoff and hence promote the formation of sandy surface horizons and hardened subsurface horizons (fragipans and/or duripans) in Coastal Tablelands soils. This study aimed to investigate the pedogenesis on Coastal Tablelands area with low range altimetry in Paraíba state; secondly, we also sought to contribute to the improvement of the Brazilian Soil Classification System (BSCS). Four soil profiles were described and collected to be submitted to routine physical and chemical analysis, determination of Fe, Al and Si extracted by sulfuric acid digestion, sodium citrate-bicarbonate-dithionite and acid ammonium oxalate, sodium pyrophosphate, and mineralogical analysis in the sand and clay fractions by X-ray diffractometry. Optical density of the oxalate extract (ODOE) was also determined; the results were statistically evaluated using the R software. Micrelief variations conditioning differentiated water flows, along with the sandy texture of the surface horizons (A and E) and the lower coarse sand/fine sand ratio in the subsurface horizon, seem to promote clay accumulation in depth in the Spodosols developed on Coastal Tablelands environments. For this soils, the argilluvic (*argissólico*) character at the subgroup level of the BSCS should be incorporated. In addition, Al amorphous mineral phases and/or poorly crystalline play an important role in the formation of strongly cemented horizons (duripans) of the Spodosols, as also reported by other authors. Finally, the ODOE showed to be an efficient indicator of soils under podzolization process, being possible its use as a taxonomic criterion for classification of Spodosols by the BSCS.

Keywords: Podzolization. Barreiras Formation. Kaolinite. Cemented Horizons.

PEDOGÊNESE EM ÁREA DE TABULEIROS COSTEIROS COM BAIXA AMPLITUDE ALTIMÉTRICA NO ESTADO DA PARAÍBA

RESUMO - Pequenas variações de relevo influenciam na drenagem e no escoamento superficial, contribuindo para a formação de horizontes superficiais arenosos e subsuperficiais endurecidos (fragipás e, ou, duripás) em solos dos Tabuleiros Costeiros. Este trabalho investigou a pedogênese em área de Tabuleiros Costeiros com baixa amplitude altimétrica no Estado da Paraíba; secundariamente, buscamos contribuir para o aprimoramento do Sistema Brasileiro de Classificação de Solos (SiBCS). Quatro perfis de solos foram descritos e coletados para a realização das análises físicas e químicas de rotina, extrações de Fe, Si e Al por digestão sulfúrica, por ditionito-citrato-bicarbonato de sódio, por oxalato ácido de amônio e por pirofosfato de sódio, e as análises mineralógicas das frações areia e argila por difratometria de raios X. A densidade ótica do extrato de oxalato (ODOE) também foi determinada; os resultados obtidos foram estatisticamente avaliados utilizando o programa R. As variações do microrrelevo condicionando fluxos diferenciados de água, juntamente com a textura arenosa dos horizontes superficiais (A e E) e a menor relação areia grossa/areia fina no horizonte subsuperficial, parece favorecer o acúmulo de argila em profundidade nos Espodossolos desenvolvidos no ambiente dos Tabuleiros Costeiros. Para esses solos, o caráter argissólico em nível de subgrupo do SiBCS deveria ser incorporado. Além disso, fases mineralógicas amorfas e, ou, de baixa cristalinidade de Al têm importante participação na formação de horizontes fortemente cimentados (duripás) dos Espodossolos. Finalmente, a ODOE mostrou-se eficiente como indicador de solos sob processo de podzolização e poderia ser utilizada como critério taxonômico para classificação de Espodossolos pelo SiBCS.

Palavras-chave: Podzolização. Formação Barreiras. Caulinita. Horizontes Cimentados.

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INTRODUCTION

Coastal Tablelands are distributed along the coast of Brazil, from Rio de Janeiro to Amapá, and are formed predominantly by plain surfaces usually interspersed by deep valleys. These plains are associated with the sediments of the Barreiras Formation, dating from the Tertiary, and occupy approximately 200,000 km² (CARVALHO et al., 2013; CORRÊA et al., 2008; FILIZOLA et al., 2001). Coastal Tablelands are usually composed of strongly weathered, clayey, sandy-clayey, or sandy soils that are predominantly kaolinitic and iron-poor. Plains containing sandy sediments predominate in the states of Paraíba and Rio Grande do Norte (CORRÊA et al., 2008).

In the northeast region, Coastal Tablelands occupy an area of approximately 10,000,000 ha, corresponding to approximately 16% of the territory occupied by the states of Bahia, Sergipe, Alagoas, Pernambuco, Paraíba, Rio Grande do Norte, and Ceará (LIMA NETO et al., 2009). Considering the proximity to large urban centers, these plains are of high socioeconomic importance because they are used for cultivating sugarcane and other crops. The states of Alagoas, Pernambuco, Paraíba, and Rio Grande do Norte are used primarily for planting sugarcane (LIMA NETO et al., 2009).

The predominant soils in Coastal Tablelands are Yellow Latosols, Yellow Ultisols, Quartzarenic Neosols and, to a lesser extent, Spodosols, Gray Ultisols, and Plinthosols. The depressions between the plains are formed by Gleysols and, to a lesser extent, by Spodosols and Organosols (NASCIMENTO et al., 2004).

Because of the nature of the parent material (pre-weathered sediments of the Barreiras Formation), the typical soils of Coastal Tablelands are very deep and weathered, and usually well drained. However, small relief variations affect water drainage and surface flow, contributing to the formation of hardened pedogenic horizons, including fragipan (weak cementation) and duripan (strong cementation), which may contain cementing agents such as Fe, Si, and/or Al (CARVALHO et al., 2013; CORRÊA et al., 2015; FILIZOLA et al., 2001; MOREAU et al., 2006). Hardened horizons limit water percolation in depth, limiting water drainage in deeper areas of the landscape. Authors have shown that the spatial variability of the soil chemical attributes and the distribution of granulometric fractions are affected by the water dynamics, which is dictated by the microrelief (OLIVEIRA et al., 2013; SOUZA et al., 2006).

The physical and chemical limitations of

these soils warrant implementing adequate land use and management systems. The limitations include the occurrence of cohesive pedogenic horizons, sandy texture, low cation exchange capacity and consequent low natural fertility, and the presence of hardened pedogenic horizons (CORRÊA et al., 2008, 2015; LIMA NETO et al., 2009).

Yellow or Gray Ultisols and Spodosols are common in the Coastal Tablelands of the state of Paraíba, particularly in the north of the municipality of João Pessoa (BRASIL, 1972; COELHO et al., 2017). These plains, with a predominance of Atlantic Forest vegetation (IBGE, 2012), are poorly studied, and the yield of sugarcane, which occupies most of the agricultural areas of Paraíba, is low. The objective of this study was to investigate the pedogenesis in Coastal Tablelands with a small altitude range in an Ultisol-Spodosol transition to adequately guide management practices to optimize crop production in this geomorphological domain in Paraíba state. The second objective is to improve the Brazilian Soil Classification System (BSCS).

MATERIAL AND METHODS

The study was carried out in an area located in the municipality of Rio Tinto, state of Paraíba, northeast Brazil, in the Atlantic Forest biome (Figure 1). The relief varies from flat to smooth undulating with an altitude range from 57 to 63 m above sea level (a.s.l.).

According to Köppen's classification, the climate of the region is As', tropical rainy with dry summer and a rainy season from March to September (ALVARES et al., 2013). The average annual rainfall is 1,635 mm; the wettest months are April, May, and June, the driest months are October, November, and December, and the mean annual temperature is 25 °C. The primary vegetation is dense ombrophilous forest, with segments of seasonal semideciduous forest, and Restinga, which was almost completely replaced by sugarcane crops, except for preservation and legal reserve areas (IBGE, 2012). The area is inserted in the Coastal Tablelands domain and is dominated by sediments of the Barreiras Formation, with a predominance of strongly weathered, clayey, clayey-sandy, or sandy soils of Cenozoic origin, typically kaolinitic and iron-poor. Sediment thickness varies according to the undulations of crystalline rocks (granites and biotite and/or garnet-hornblende gneisses of the Paraíba do Sul Complex, Precambrian), which are occasionally outcropped, leading to variations in relief forms (SCHOBENHAUS et al., 1995).

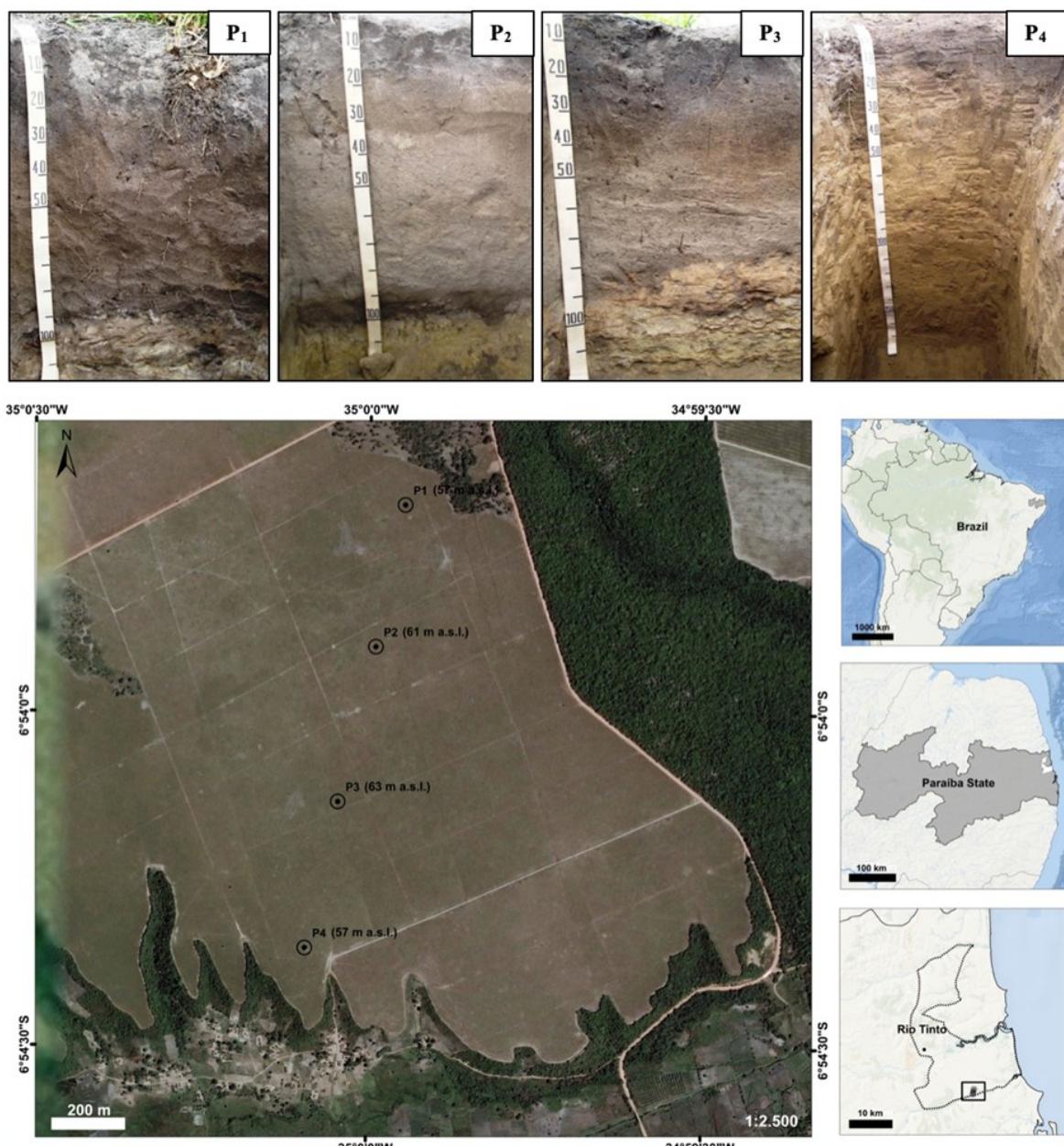


Figure 1. Studied soil profiles and sampling sites.

On the basis of cartographic data obtained by a detailed soil survey performed in the study area, four soil profiles were selected in an Ultisol-Spodosol transition area with a small altitude range. The trenches were opened at four landscape positions, including coastal tableland depression (P_1 , 57 m a.s.l.), gentle slope of depression (P_2 , 61 m a.s.l.), flat top (P_3 , 63 m a.s.l.), and middle third of slope (P_4 , 57 m a.s.l.) (Figure 1). The morphological description (color, structure, and consistency) of the profiles was made according to the recommendations of Santos et al. (2015). After that, the deformed and undeformed samples were collected in each horizon for analyzing physical, chemical, and mineralogical characteristics. The soils were classified according to the BSCS (SANTOS et al., 2018).

The air-dried fine earth (ADFE) samples were subjected to granulometric analysis by the densitometric method and determination of soil density (D_s) using the volumetric ring method (TEIXEIRA et al., 2017). The chemical analyses included pH in water (ratio 1: 2.5); potential acidity in a 1 mol L⁻¹ calcium acetate solution; Na and K extracted using Mehlich-1 extractant and measured by flame photometry; exchangeable Ca, Mg, and Al extracted in 1 mol L⁻¹ KCl and measured by atomic absorption spectrophotometry, and total organic carbon (TOC) using the Walkey-Black method (TEIXEIRA et al., 2017). The obtained results allowed calculating the sum of exchangeable bases (SB), cation exchange capacity (CEC), percentage of base saturation (V%), and percentage of Al

saturation (m%).

In addition to these chemical analyses, Fe, Al, and Si were extracted in the ADFE by sulfur digestion (Fe_s , Al_s , and Si_s) and quantified by atomic absorption spectrophotometry to determine the weathering index (Ki) (TEIXEIRA et al., 2017). The ADFE samples were subjected to three sequential extractions with sodium citrate-bicarbonate-dithionite (d) (MEHRA; JACKSON, 1960), a single extraction with acid ammonium oxalate (o) (McKEAGUE; DAY, 1966), and a single extraction with sodium pyrophosphate (p) (COURCHESNE; TURMEL, 2008). The concentrations of Fe (Fe_d , Fe_o , and Fe_p), Al (Al_d , Al_o , and Al_p), and Si (Si_d , Si_o , and Si_p) in the extracts were measured by atomic absorption spectrophotometry.

The optical density of the oxalate extract (ODOE) was measured by spectrophotometry according to (BURT, 2004). After the reaction time with the soil samples, the acid ammonium oxalate extracts were transferred to glass cuvettes with a cross-sectional area of 1.0 cm^2 and read in a visible spectrophotometer model BIOESPECTRO SP-22 at a wavelength of 430 nm, as recommended by the Keys to Soil Taxonomy for Spodosols (SOIL SURVEY STAFF, 2014).

For mineralogical analyses, the ADFE samples were treated with hydrogen peroxide to remove organic matter and then subjected to separation of the fine sand, coarse sand, silt, and clay fractions (TEIXEIRA et al., 2017). The measurements were made using an X-ray diffractometer model Shimadzu XRD 6000 coupled to a graphite crystal monochromator, with $\text{CuK}\alpha$ radiation at a voltage of 40 kV and current of 20 mA. The scanning range was 5° to $65^\circ 2\theta$ for the non-oriented samples, and 3° to $35^\circ 2\theta$ for the samples oriented on a glass slide, all at a recording speed of $1^\circ 2\theta \text{ min}^{-1}$. The coarse sand and fine sand fractions were analyzed by light microscopy. The clay fraction was analyzed in non-oriented slides (powder mount) and oriented slides (smear mount). The oriented slides were prepared with the clay fraction after pretreatment for removing Fe oxides, saturated with KCl, analyzed before heating and after heating

at 350° C and 550° C , and analyzed with MgCl_2 without heating (TEIXEIRA et al., 2017).

The physical and chemical results of the samples from the horizons of the four soil profiles were evaluated by both basic statistical analysis [regressions and Pearson correlations] and multivariate analysis [principal component analysis (PCA)] using software R.

RESULTS AND DISCUSSION

Soil morphological properties

P_1 (Spodosol) presented the horizon sequence Ap, E, and spodic B (Table 1), with morphological properties indicative of a significant increase in clay content in the B horizon (Table 2) associated to the accumulation of organic matter (inferred by its dark yellowish brown color) and a high degree of cementation, characterizing a Bsm-type spodic B horizon. The BSCS has not created classifications at lower categorical levels to indicate the significant increase in clay in depth in Spodosols. In this study, the inclusion of argilluvic (*argissólico*) character at the subgroup level for this soil class is suggested. Therefore, the podzolization process, forming the spodic B horizon, would define the soil class (taxonomic precedence over the textural B horizon) independently of the intensity of textural differentiation and chronology/hierarchy of active pedogenic processes.

P_2 (Spodosol) showed the horizon sequence Ap, E, and Bsm (Table 1), and its morphological properties indicated an increase in clay content in the spodic B horizon, with levels slightly higher than those found in P_1 (Table 2). The eluvial horizon (E) was thicker, with a sandy texture, conferring a spessarenic (*espessarénico*) character. The Bsm horizon had a grayish color with strong yellow and brown mottling, indicating the occurrence of oxidation-reduction processes, which are common in Coastal Tablelands soils, especially in those with hardened horizons (fragipan and duripan) (FILIZOLA et al., 2001; MOREAU et al., 2006).

Table 1. Morphological properties of the soils.

Horiz.	Depth (m)	Transition ⁽¹⁾	Munsell Soil Color (moist)		Structure ⁽³⁾	Consistence ⁽⁴⁾		
			Soil matrix	Mottle ⁽²⁾		Dry	Moist	Wet
Profile 1 (coastal tableland depression) – Duric Arenic Orthic Ferriluvic Spodosol								
Ap	0 – 0.20	cl, wa	10 YR 3/2	-	we, fi, gr / sg	lo	lo	npl, nst
E ₁	0.20 – 0.67	gr, sm	10 YR 4/2	-	ma-wce	so	vfr	npl, nst
E ₂	0.67 – 0.90	gr, wa	2.5 Y 5/2	-	ma-mce	sha	vfr	npl, nst
Bsm	0.90 – 1.10+	-	2.5 Y 6/4	10 YR 3/4 co, fi-me, dt	ma-sce	eha	efm	npl, sst
Profile 2 (gentle slope of depression) – Spessarenic Orthic Ferriluvic Spodosol								
Ap	0 – 0.17	cl, wa	10 YR 4/2	-	we, fi, gr / sg	lo-so	lo-vfr	npl, nst
E ₁	0.17 – 0.36	gr, sm	10 YR 5/3	-	we, fi, gr / sg	so	vfr	npl, nst
E ₂	0.36 – 0.75	di, sm	10 YR 5/3	-	ma-wce	so	vfr	npl, nst
E ₃	0.75 – 1.05	ab, wa	10 YR 5/3	-	ma-sce / we, fi, sb	so	vfr	npl, nst
Bsm	1.05 – 1.10+	-	10 YR 6/3	2.5 YR 6/6 abn, me, dt 7.5 YR 5/8 fe, fi, dt,	ma-sce	eha	efm	spl, sst
Profile 3 (flat top) – Duric Arenic Orthic Ferriluvic Spodosol								
Ap	0 – 0.25	ab, wa	10 YR 3/2	-	ma-wce / we, fi, gr	so	vfr	npl, nst
E ₁	0.25 – 0.55	gr, sm	10 YR 4/3	-	ma-wce	so	vfr	npl, nst
E ₂	0.55 – 0.80	ab, ir	10 YR 5/3	-	ma-wce / we, vfi- fi, sb	so	vfr	npl, nst
Bsm	0.8 – 1.20+	-	10 YR 5/4	10 YR 4/6 co, me-cs, dt	ma-sce	eha	efm	npl, nst
Profile 4 (middle third of slope) – Typical Dystrocohesive Yellow Ultisol								
Ap	0 – 0.15	cl, wa	10 YR 3/2	-	ma-wce / we, fi, gr	vha	fr	spl, sst
AB	0.15 – 0.37	gr, sm	10 YR 4/3	-	ma-mce	vha	fr	spl, sst
BA	0.37 – 0.65	gr, sm	10 YR 4/4	-	ma-mce	eha	fm	spl, sst
Bt ₁	0.65 – 1.05	gr, sm	10 YR 6/6	-	ma-mce	eha	fm	pl, st
Bt ₂	1.05 – 1.45	gr, sm	10 YR 6/6	2.5 YR 4/6 co, fi-me, pr	we, fi-me, sb	vha	fm	pl, st
Bt ₃	1.45 – 1.75+	-	10 YR 6/6	-	we, fi-me, sb	vha	fm	pl, st

⁽¹⁾ab = abrupt, cl = clear, gr = gradual, di = diffuse, sm = smooth, wa = wavy, ir = irregular. ⁽²⁾ fe = few, co = common, abn = abundant, fi = fine, me = medium, cs = coarse, dt = distinct, pr = prominent. ⁽³⁾ we = weak, vfi = very fine, gr = granular, sb = subangular blocky, sg = single grain, ma = massive, wce = weakly cohesive, mce = moderately cohesive, sce = strongly cohesive. ⁽⁴⁾ lo = loose, so = soft, sha = slightly hard, vha = very hard, eha = extremely hard, vfr = very friable, fr = friable, fm = firm, efm = extremely firm, npl = non-plastic, spl = slightly plastic, pl = plastic, nst = non-sticky, st = sticky.

The P₃ (Spodosol) had a horizon sequence similar to that of the other profiles, differing only in the absence of accumulation of the clay fraction in the Bsm horizon (Table 2). The Bsm horizon in this profile presented yellow color a bit more intense with strong brown mottling, indicating poor drainage, but less pronounced than the profiles P₁ and P₂ probably because of the slope.

P₄ (Ultisol) presented the horizon sequence Ap, AB, BA, Bt₁, Bt₂, and Bt₃ (Table 1), and the morphological properties (color, structure, and consistency) were considerably different from those of other soils, with clayey texture in the subsurface.

The characteristic feature of P₄ was the

absence of aggregation in the horizons AB, BA, and Bt₁ up to a depth of 1.05 m, resulting in a moderately cohesive massive structure with a wide variation in dry and wet consistency. These characteristics define cohesive soils (SANTOS et al., 2018). Cohesive soils are usually found in Yellow Ultisols and Oxisols in Coastal Tablelands (CORRÊA et al., 2008, 2015; DANTAS et al., 2014; LIMA NETO et al., 2009; MOREAU et al., 2006). Studies reported that these characteristics reduced the vertical flow of water (CORRÊA et al., 2008, 2015; LIMA NETO et al., 2009). However, the proximity to natural drain conditions seems to promote more efficient water drainage than the other studied profiles (Figure 1).

even when compared to the profile with a similar height in the landscape (P_1), with a consequent reduction in oxidation-reduction Fe reactions, and formation of hardened horizons (fragipan and duripan).

Soil physical attributes

The sand, silt, and clay fractions varied in the soils along the studied area, with a decrease in the sand fraction and an increase in the silt and clay fractions in depth, and the highest clay content was found in Ultisol (Table 2). Studies reported that a decrease in the clay fraction in Spodosols, especially

in superficial horizons, were due to the destruction of this fraction by strong hydrolysis and acidolysis reactions (CORRÊA et al., 2015; FILIZOLA et al., 2001); however, the podzolization process usually occurs in soils whose parent materials are predominantly sandy. Subsequently, the elements that make up the minerals of the clay fraction migrate as free ions (H_4SiO_4) or organometallic compounds (Al and Fe - hummus), forming weak and/or strong bonds between the fractions that compose the underlying horizons, resulting in the formation of the spodic B horizon, fragipan, and/or duripan (CORRÊA et al., 2015; MOREAU et al., 2006).

Table 2. Physical and chemical attributes of the soils.

Horiz.	Sand				Silt	Clay	Ds	pH _{H2O}	SB	Al ³⁺	H + Al	CEC	V	m	TOC								
	Coarse	Fine	Total	Coarse Fine																			
$g\ kg^{-1}$				$Mg\ m^{-3}$				$cmol_c\ kg^{-1}$				%		$g\ kg^{-1}$									
Profile 1 (coastal tableland depression) – Duric Arenic Orthic Ferriluvic Spodosol																							
Ap	696	223	919	3.12	8	73	1.58	5.7	2.1	0.1	4.2	6.3	33	5	11.20								
E ₁	683	247	930	2.77	5	65	1.50	5.7	0.4	0.2	3.7	4.1	10	32	5.62								
E ₂	626	268	894	2.34	30	76	1.44	5.8	0.3	0.1	3.5	3.8	7	27	6.19								
Bsm	415	224	639	1.85	186	175	1.62	5.3	0.3	0.3	8.0	8.3	4	51	11.95								
Profile 2 (gentle slope of depression) – Spessarenic Orthic Ferriluvic Spodosol																							
Ap	658	265	924	2.48	4	72	1.65	5.8	1.2	0.0	2.1	3.3	36	0	6.01								
E ₁	643	286	929	2.25	6	65	1.69	6.1	0.6	0.0	1.4	2.0	28	0	1.54								
E ₂	641	286	927	2.24	8	65	1.63	6.1	0.5	0.0	1.8	2.3	22	0	2.71								
E ₃	569	312	881	1.82	43	76	1.56	6.0	0.4	0.0	1.9	2.3	17	0	1.98								
Bsm	309	273	582	1.13	203	215	1.73	5.5	0.3	0.2	7.3	7.8	4	39	8.50								
Profile 3 (flat top) – Duric Arenic Orthic Ferriluvic Spodosol																							
Ap	570	343	913	1.66	14	73	1.48	5.9	3.0	0.0	4.3	7.3	41	0	12.06								
E ₁	517	361	878	1.43	42	80	1.46	5.3	0.5	0.3	6.1	6.6	7	40	10.05								
E ₂	510	355	864	1.44	56	80	1.50	5.4	0.6	0.2	6.1	6.7	8	27	10.36								
Bsm	504	286	790	1.76	92	118	1.42	5.6	1.8	0.3	11.1	12.9	14	15	32.67								
Profile 4 (middle third of slope) – Typical Dystrocohesive Yellow Ultisol																							
Ap	472	332	804	1.42	56	140	1.65	4.4	1.9	0.0	4.1	6.0	31	0	12.81								
AB	366	320	686	1.14	66	248	1.57	4.2	1.2	0.2	4.3	5.5	22	14	11.38								
BA	302	268	570	1.13	73	357	1.38	4.1	0.9	0.6	4.8	5.7	16	39	10.29								
Bt ₁	261	238	499	1.10	47	454	1.50	4.0	0.7	0.7	3.7	4.4	17	49	6.53								
Bt ₂	298	228	526	1.30	55	419	1.58	4.0	0.4	0.8	3.8	4.2	09	67	3.48								
Bt ₃	311	254	565	1.23	38	397	1.54	4.0	0.3	0.8	2.8	3.1	10	71	2.27								

Most of the studied Spodosols presented a sandy texture, with the total sand content higher than $864\ g\ kg^{-1}$ for the surface horizons (A and E); but we highlight an intermediate texture for the spodic B horizons of the soils P_1 and P_2 with total sand content equal to 639 and $582\ g\ kg^{-1}$, respectively (Table 2). The increase in the clay content in the spodic B horizons of the soils P_1 and P_2 was sufficiently high to satisfy the B/A textural ratio higher than $1.80\ g\ kg^{-1}$, a criterion established by the BSCS for

soils with clay contents less than $150\ g\ kg^{-1}$ in the A horizon, indicating a conjugated textural B horizon. However, the argilluvic (*argissólico*) character is not considered at lower categorical levels in the order of Spodosols by the BSCS (SANTOS et al., 2018).

The effect of microrelief variations on water drainage and surface flow together with the sandy texture of the surface horizons (A and E) seems to favor argilluviation and/or differential erosion of clay (elutriation), with subsequent occurrence of B/A

textural ratios in Spodosols (P_1 and P_2). Oliveira et al. (2010) analyzed a Spodosol in the south of Bahia with characteristics intermediate to Ultisol and classified it as Argilluvic Orthic Humiluvic Spodosol based on the presence of a spodic B horizon (Bhs) overlying a textural B horizon (Bt). In Coastal Tablelands, under the influence of the pre-weathered sediments of the Barreiras Formation, the destruction of the clay fraction with the consequent increase in the migration of its constituent elements through the sandy horizons (A and E) and subsequent accumulation of these elements in the clayey subsurface horizon (Bh, Bs, or Bhs) appear to determine the genesis of these Spodosols, as reported by Filizola et al. (2001) and Corrêa et al. (2015). However, we highlight the possibility of occurrence of other processes of textural differentiation (SILVA et al., 2012), considering that the clay fraction was not increased in the spodic B horizon of the P_3 because of the relief condition (flat top). Similarly, Oliveira et al. (2013) emphasized the effect of microrelief on the production of specific water flows along different surface forms (convex, rectilinear, and concave), resulting in significant variations in the distribution of granulometric fractions in Cambisols of limestone origin.

In addition, the coarse sand fraction was much more expressive in all soils except for the Bsm horizons of the soils P_1 and P_2 and in the Bt₁ of the soil P_4 , where the coarse sand/fine sand ratios were lower. This characteristic may have favored the increase of the clay content in subsurface in the Spodosols, especially by argilluviation and/or elutriation. The retention of the fine particles in the zones whose fine sands is distributed between the porosity of the larger sand grains may result in packaged zones that act as sieves of fine materials transported through the water flows; thus incipient bands are formed representing barriers to water descending movement (DIJKERMAN et al., 1967). Silva et al. (2012) conducted micromorphological

studies and confirmed the occurrence of argilluviation (not identified in the field) in Spodosols of the northeast region of Brazil associated with the dominant podzolization process.

The Ds ranged from 1.42 to 1.73 g cm⁻³, and the highest values were observed in hardened horizons (duripans – duric character) in the Spodosols (Table 2), as reported in other studies (CORRÊA et al., 2008; LIMA NETO et al., 2009; MOREAU et al., 2006; OLIVEIRA et al., 2010). The high Ds of duric horizons may be a consequence of the packaging of its components. This hypothesis was confirmed by comparing the granulometry of these horizons with the Bt horizons of soil P_4 , with similar composition but lower Ds. This packaging is favored by the lower coarse sand/fine sand ratio of the duripans, leading to higher water retention and accumulation of cementing elements resulting from acidolysis. In P_4 , the Ds was slightly higher in the surface horizons because of the compaction caused by soil management activities during sugarcane production. In the other horizons, the effect of sandy granulometry on compaction resistance may have been stronger, limiting the degradation caused by management practices.

The principal component analysis of physical variables indicated that the Bsm horizons of the Spodosols P_1 and P_2 as well as the horizons Bt₁, Bt₂, and Bt₃ of the Ultisol P_4 presented stronger associations with the silt and clay fractions, mainly with the clay fraction because of the longer vector length of this variable (Figure 2). In contrast, the surface horizons (A and E) and the Bsm horizon of Spodosol P_3 , where the clay content was not increased significantly, had a stronger association with coarse sand, fine sand, and the coarse sand/fine sand ratio. This result confirms the need to consider the argilluvic (*argissólico*) character at the subgroup level for the taxonomic distinction of Spodosols with marked effect of the clay fraction on the spodic B horizon.

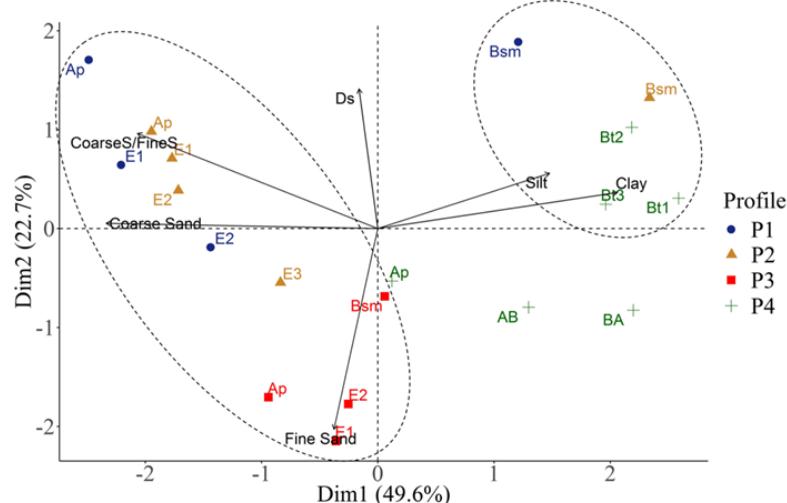


Figure 2. Principal component analysis of the soil physical attributes. CoarseS/FineS = coarse sand/fine sand ratio.

Soil chemical attributes

All studied soils were acidic and dystrophic, and the highest SB values were found in superficial horizons probably because of soil management with correctives and fertilizers during the crop cycles (Table 2). Acidity and dystrophy are due to the fact that these soils are developed from sediments of the Barreiras Formation, with a low reserve of cations and predominance of kaolinite (CORRÊA et al., 2008; DANTAS et al., 2014; LIMA NETO et al. 2009; MOREAU et al., 2006). In addition to the

lithogenic effect, pedogenic development is strongly affected by the leaching process in view of the high rainfall in the region.

The CEC values presented a significant correlation ($r = 0.93, p < 0.01, n = 13$) with the TOC, suggesting that the CEC of the studied soils was predominantly derived from organic matter (Figure 3). Similar results were obtained by Corrêa et al. (2008) and Oliveira et al. (2010) for Ultisols and Spodosols originating from sediments of the Barreiras Formation.

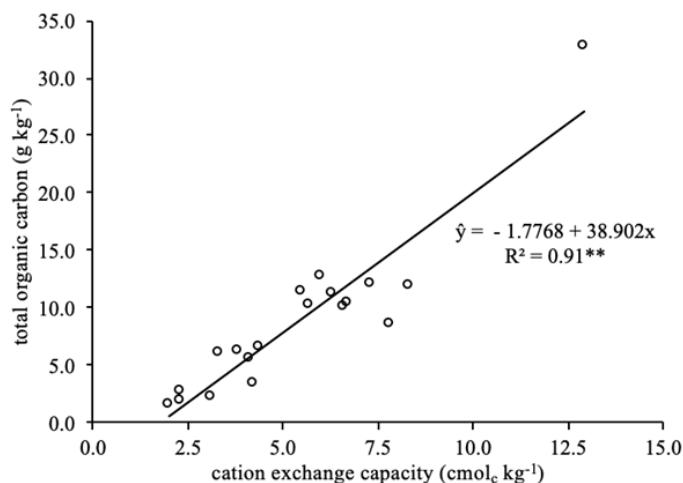


Figure 3. Linear adjustment between the cation exchange capacity and total organic carbon. **significant at a level of significance of 1 %.

The exchangeable aluminum (Al^{3+}) of Spodosols was low, varying from 0 to 0.3 $\text{cmol}_c \text{kg}^{-1}$, and the highest values were found in the spodic B horizons (Table 2). Although Al^{3+} in these horizons is usually complexed with organic compounds, microbial degradation may promote an increase in this element under conditions of better water drainage and aeration (LOPEZ-MAZZETTO et al., 2018; OLIVEIRA et al., 2010). Furthermore, during the extraction of Al^{3+} with 1 mol L^{-1} KCl, the dissolution of poorly crystalline forms of Al hydroxides present in these horizons may occur (CUNHA et al., 2015). The highest values were found in Ultisol, with 0.8 $\text{cmol}_c \text{kg}^{-1}$ in the horizons Bt_2 and Bt_3 .

The TOC levels ranged from 1.54 to 32.67 g kg^{-1} , with an increase in depth in Spodosols, indicating carbon illuviation in the subsurface and

corroborating the morphological findings obtained in the field. In the Ultisol, the TOC varied from 2.57 and 12.81 g kg^{-1} , and the highest values were found in the surface layer. In view of the higher clay content of this soil, there was greater protection of soil organic matter, which limited clay mobility in the profile.

The soils presented a low Fe_s content ($< 50 \text{ g kg}^{-1}$) in all analyzed horizons (Table 3), as reported in other studies in soils derived from pre-weathered sediments of the Barreiras Formation (CORRÊA et al., 2008; LIMA NETO et al., 2009; MOREAU et al., 2006; OLIVEIRA et al., 2010). The Ki index was close to 2.0, indicating that the mineralogical composition of the clay fraction was predominantly kaolinitic, and this result was confirmed by X-ray diffraction analysis.

Table 3. Sulfuric digestion (s), selective dissolution using sodium citrate-bicarbonate-dithionite (d), acid ammonium oxalate (o), sodium pyrophosphate (p), optical density of the oxalate extract (ODOE), and mineralogical composition of the soils.

Horiz.	Sulfuric digestion ⁽¹⁾				<u>Fe_o</u>	<u>Al_o</u>	<u>Al_p</u>	ODOE	<u>Al_o + 0,5Fe_o</u>	Mineralogical composition ⁽³⁾			
	Si _s	Fe _s	Al _s	Ki ⁽²⁾	Fe _d	Al _d	Al _p			Clay fraction	Sand fraction		
	----- g kg ⁻¹ -----												
Profile 1 (coastal tableland depression) – Duric Arenic Orthic Ferriluvic Spodosol													
Ap	n.d.	n.d.	n.d.	n.d.	0.34	0.79	0.41	0.32	0.17	K, An, Gt, Fd, Gb, Qz	Qz, Tm, Zr		
E ₁	n.d.	n.d.	n.d.	n.d.	1.24	0.41	0.82	0.30	0.01	n.d.	n.d.		
E ₂	n.d.	n.d.	n.d.	n.d.	1.26	0.48	0.86	0.26	0.01	n.d.	n.d.		
Bsm	143.0	12.0	137.8	1.76	0.11	1.86	1.21	0.41	0.50	K, An, Gt, Gb, Qz	Qz		
Profile 2 (gentle slope of depression) – Spessarenic Orthic Ferriluvic Spodosol													
Ap	n.d.	n.d.	n.d.	n.d.	0.04	1.00	0.36	0.26	0.11	K, An, Gt, Fd, Qz	Qz, Tm, Ilm		
E ₁	n.d.	n.d.	n.d.	n.d.	0.68	0.62	0.40	0.06	0.01	n.d.	n.d.		
E ₂	n.d.	n.d.	n.d.	n.d.	1.15	0.63	0.67	0.14	0.02	n.d.	n.d.		
E ₃	n.d.	n.d.	n.d.	n.d.	0.79	0.58	0.58	0.09	0.01	n.d.	n.d.		
Bsm	181.0	35.5	168.4	1.82	0.00	10.39	1.86	0.26	0.74	K, An, Gt	Qz		
Profile 3 (flat top) – Duric Arenic Orthic Ferriluvic Spodosol													
Ap	n.d.	n.d.	n.d.	n.d.	0.07	2.84	0.60	0.22	0.20	K, An, Gt, Fd, Gb, Qz	Qz, Tm, Ilm, Zr		
E ₁	n.d.	n.d.	n.d.	n.d.	0.91	0.82	0.43	0.28	0.01	n.d.	n.d.		
E ₂	n.d.	n.d.	n.d.	n.d.	1.38	0.47	0.44	0.25	0.02	n.d.	n.d.		
Bsm	34.0	9.1	37.3	1.54	0.24	15.59	0.97	0.85	0.91	K, An, Gt, Gb, Qz	Qz		
Profile 4 (middle third of slope) – Typical Dystrocohesive Yellow Ultisol													
Ap	56.0	19.2	36.1	2.64	0.06	1.91	0.80	0.13	0.18	K, An, Gt, Qz	Qz, Tm, Ilm		
AB	n.d.	n.d.	n.d.	n.d.	0.01	1.81	0.62	0.14	0.17	n.d.	n.d.		
BA	152.0	26.1	136.5	1.89	0.01	1.69	0.84	0.13	0.19	n.d.	n.d.		
Bt ₁	n.d.	n.d.	n.d.	n.d.	0.01	1.86	0.87	0.07	0.20	n.d.	n.d.		
Bt ₂	156.5	45.3	157.1	1.69	0.01	1.40	0.80	0.05	0.16	K, An, Gt	Qz		
Bt ₃	n.d.	n.d.	n.d.	n.d.	0.01	0.86	0.85	0.05	0.13	n.d.	n.d.		

n.d. not determined. ⁽¹⁾ The Si_s, Fe_s e Al_s contents are expressed in their oxide form SiO₂, Fe₂O₃ and Al₂O₃. ⁽²⁾ Molar ratio Si_s / Al_s x 1.7. ⁽³⁾ An = anatase, K = kaolinite, Gt = goethite, Fd = feldspar, Gb = gibbsite, Ilm = ilmenite, Qz = quartz, Tm = tourmaline, Zr = zircon.

The results obtained from the selective dissolution indicated significant differences in the distribution of Fe, Al, and Si in all profiles (Figure 4). The results in Spodosols evidenced an accumulation of these elements in the spodic B horizons (Bsm), especially of Al associated with

organic compounds (Al_p) and poorly crystalline forms (Al_o), and these characteristics are typical of soils undergoing podzolization process (COELHO et al., 2010a, 2010b; CORRÊA et al., 2008, 2015; MOREAU et al., 2006; OLIVEIRA et al., 2010; SILVA et al., 2013).

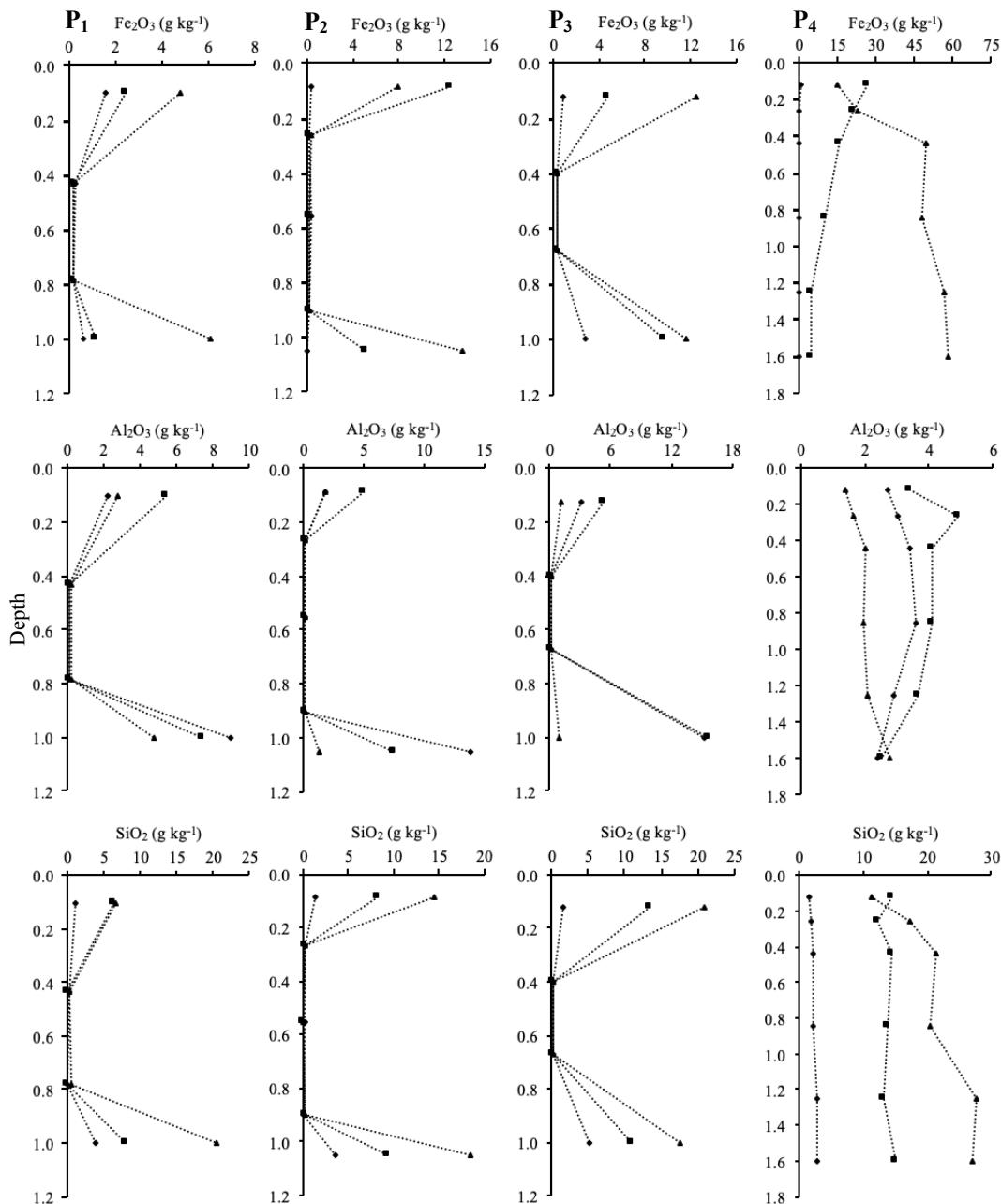


Figure 4. Fe, Al, and Si expressed as oxides, determined by selective dissolution with sodium citrate-bicarbonate-dithionite (▲), acid ammonium oxalate (◆), and sodium pyrophosphate (■).

The high Al_o/Al_d (> 1.85) and Al_o/Al_p (> 0.96) ratios demonstrate that the participation of the poorly crystalline forms was higher (Table 3), as observed by Coelho et al. (2010a, 2010b) and Silva et al. (2013) in spodic B horizons. In the Ultisol, although the Al_o/Al_d ratio was > 1.85 in the horizons Ap and Bt₁, the dynamics were different, with a trend of equal distribution of the elements in depth. These findings reinforce the hypothesis of the genesis of fragipans and duripans from chemical cementation by Fe, Si, and/or Al compounds (CARVALHO et al., 2013; CORRÊA et al., 2015; FILIZOLA et al., 2001; MOREAU et al., 2006).

The Fe_d concentration was less than 20 g kg⁻¹

in Spodosols and less than 60 g kg⁻¹ in Ultisol (Figure 4), which may be due to the low concentrations of this element in the pre-weathered sediments of the Barreiras Formation on which these soils developed (CORRÊA et al., 2015). The Fe_o/Fe_d ratio > 0.06 clearly separates Spodosols (P₁, P₂, and P₃) from Ultisol (P₄), indicating the considerable participation of poorly crystalline Fe forms, especially in the eluvial horizons (E) overlying the spodic B horizons with duric character (duripans) that are commonly found in environments with limited drainage (CORRÊA et al., 2008; FILIZOLA et al., 2001). In P₄, the Fe_o/Fe_d ratio < 0.06 indicates the predominance of highly crystalline Fe forms; in

addition, the higher values found in the Ap horizon corroborates the effect of the organic matter on the inhibition of the crystallinity of Fe oxides.

Except for P₁, where the ODOE value in the spodic B horizon was higher than 0.25 but less than double the levels found in eluvial horizons (E₁ and E₂), the values of ODOE and Al_o + 0.5Fe_o of the other Spodosols (P₂ and P₃) agreed with the criteria established by the Keys to Soil Taxonomy for defining spodic B horizons (Table 3) (SOIL SURVEY STAFF, 2014). Oliveira et al. (2010) also reported similar results in Spodosols of the Barreiras Formation in the state of Bahia. The BSCS does not use ODOE as a taxonomic criterion for defining

spodic B horizon, but for the other criteria considered (color, carbon content, cementation by organic matter and Al, and the value of Al_o + 0.5Fe_o), the profiles P₁, P₂, and P₃ have spodic B horizons and are classified in the order of Spodosols.

The ODOE was also significantly correlated with the Al_p ($r = 0.84, p < 0.01, n = 13$), Al_o ($r = 0.71, p < 0.01, n = 13$), H + Al ($r = 0.85, p < 0.01, n = 13$), and TOC ($r = 0.95, p < 0.01, n = 13$) (Figure 5), evidencing its importance for identifying soils with significant participation of humic substances, and indicating that this chemical property may be used to assess the occurrence of podzolization process in soils (OLIVEIRA et al., 2010).

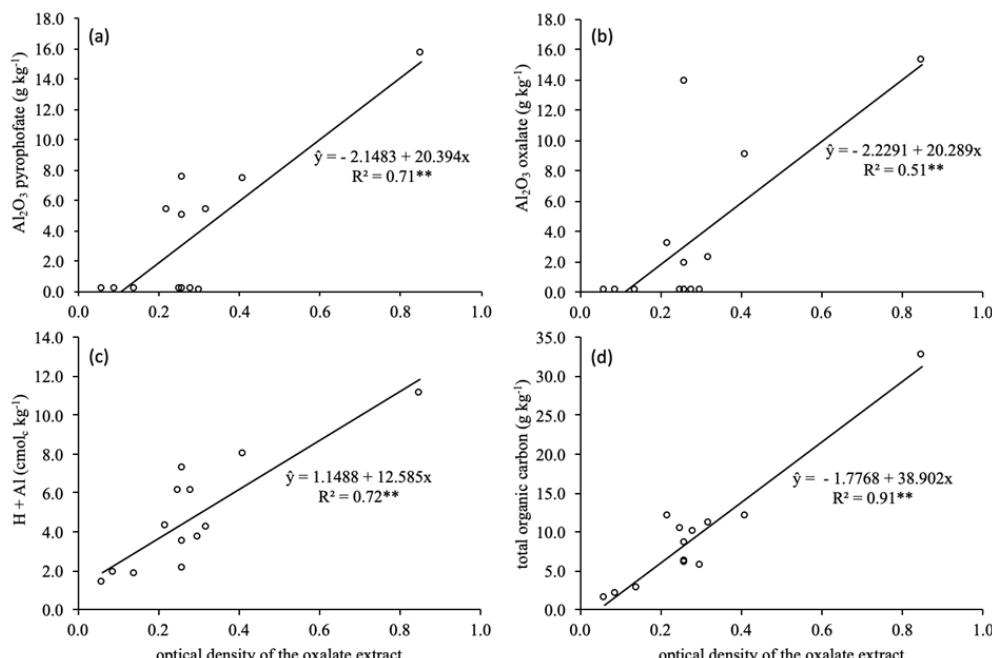


Figure 5. Linear adjustments between the values of optical density of the oxalate extract (ODOE) and the chemical attributes Al₂O₃ extracted using sodium pyrophosphate (a) and acid ammonium oxalate (b), potential acidity (H + Al) (c), and total organic carbon (d). ** significant at a level of significance of 1 %.

Similarly, the principal component analysis indicated a strong relationship between the chemical attributes ODOE, TOC, CEC, Al_o/Al_d, Al_o/Al_p, Al_o + 0.5Fe_o, and the Bsm horizons of Spodosols (Figure 6). The BSCS (SANTOS et al., 2018), and other studies (COELHO et al., 2010a, 2010b; CORRÊA et al., 2008, 2015; MOREAU et al., 2006; OLIVEIRA et al., 2010; SILVA et al., 2013) emphasize the highest levels of Fe_o and Al_o in spodic B horizons. However, the values are highly variable, and hence no quantitative criteria are available to date for defining this horizon. In this study, we highlight the possibility of using ODEO as a taxonomic criterion by the BSCS, as also used by the Keys to Soil Taxonomy to classify Spodosols (SOIL SURVEY STAFF, 2014). Given that it is a spectroscopic measurement, the amplitude of its values is considerably lower than that of the absolute values of Fe and Al extracted by acid ammonium oxalate or

sodium pyrophosphate (Table 3 and Figure 4).

Soil mineralogical attributes

The mineralogical assemblage was simple, with a predominance of kaolinite in the clay fraction and quartz in the sand fraction (Table 3 and Figure 7), as also reported in other studies (CARVALHO et al., 2013; CORRÊA et al., 2008; DANTAS et al., 2014; LIMA NETO et al., 2009; MOREAU et al., 2006; OLIVEIRA et al., 2010; SILVA et al., 2012). Quartz, which is usually found in coarse fractions (sand and silt), was also observed in the clay fraction of all studied soils. However, when present in the clay fraction quartz is usually associated with coarse clay particles (SILVA et al., 2012). Carvalho et al. (2013) evidenced the presence of quartz in the clay fraction of Spodosols in the states of Paraíba and Pernambuco.

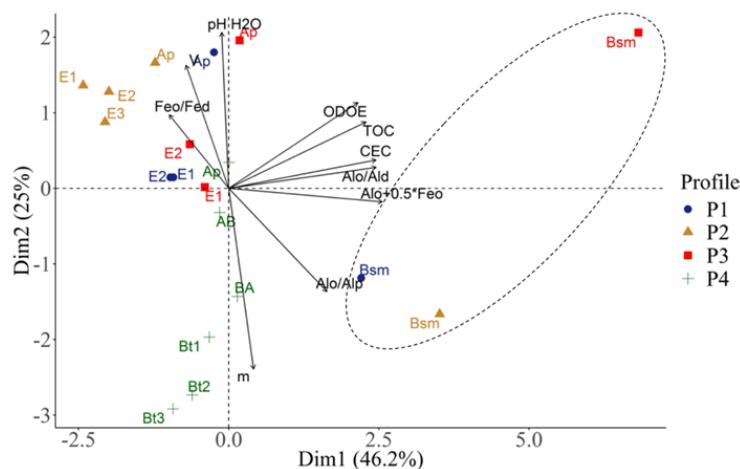


Figure 6. Principal component analysis of the soil chemical attributes.

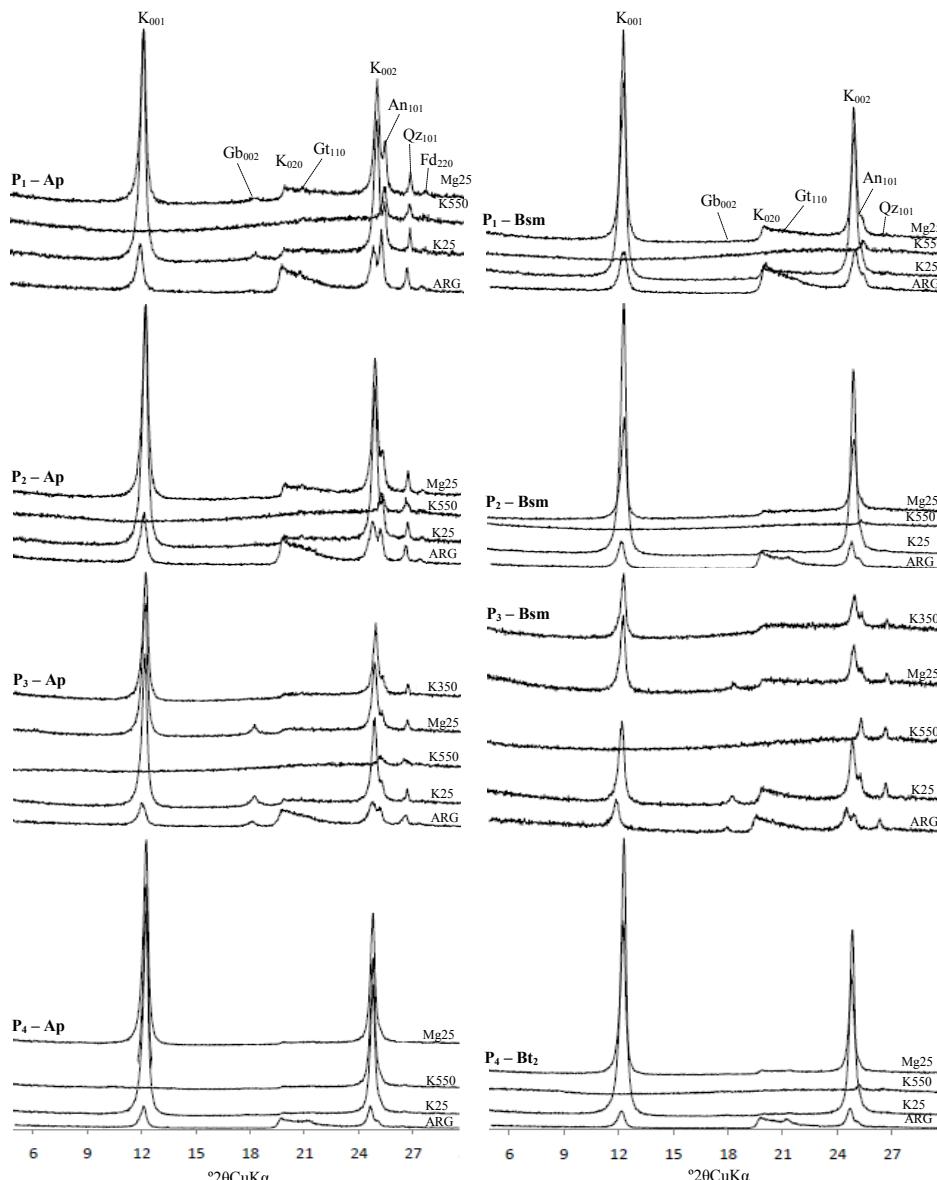


Figure 7. X-ray diffractograms of the clay fraction in the surface and subsurface horizons. ARG = clay without pretreatment, K25 = clay saturated with KCl without heating, K350 = clay saturated with KCl and heated to 350 °C, K550 = clay saturated with KCl and heated to 550 °C, Mg25 = clay saturated with MgCl₂ without heating, K = kaolinite, Gb = gibbsite, Gt = goethite, An = anatase, Qz = quartz, Fd = feldspar.

Trace concentrations of feldspar were found in the clay fraction of Spodosols but were absent in Ultisol (Table 3 and Figure 7). Feldspar is considered the main precursor of kaolinite in soils originating from sediments of the Barreiras Formation (CORRÊA et al., 2008). Goethite and anatase were found in all studied soils (CARVALHO et al., 2013; CORRÊA et al., 2008; OLIVEIRA et al., 2010).

In the top soils (P_1 and P_3), desilication was more intense because of better drainage; therefore, during weathering there might be phases in which SiO_2 activity in solution was lower than that required for producing kaolinite, leading to gibbsite precipitation. Although at low concentrations, gibbsite is common in Coastal Tablelands soils (CARVALHO et al., 2013; CORRÊA et al., 2008).

The coarse sand fraction consisted primarily of quartz (< 95 %), less than 3% of accessory minerals such as ilmenite, tourmaline, and zircon, and typically kaolinitic clay aggregates of gray color. These aggregates were more concentrated in the Bsm horizons of soils P_1 and P_2 , where they reached up to 5% of the coarse sand fraction. The quartz grains were predominantly hyaline in P_1 and P_2 and partially covered by a reddish-brown film, which was more abundant in P_4 (Fe_d levels of 15 - 58 g kg⁻¹) because of the higher Fe oxide concentrations in this soil. In addition, there was no significant difference in the mineralogical nature of the fine sand fraction between the soils; however, there was a slight increase in the number of clay aggregates, corresponding to 6%, 7%, and 4% in the spodic B horizons of soils P_1 , P_2 , and P_3 , respectively.

CONCLUSIONS

Microrelief variations conditioning differentiated water flows, along with the sandy texture of the surface horizons (A and E) and the lower coarse sand/fine sand ratio in the subsurface horizon, seem to favor clay accumulation in depth in the Spodosols developed on Coastal Tablelands environments. Therefore, we suggest incorporating argilluvic (*argissólico*) character at the subgroup level of the Brazilian Soil Classification System (BSCS) to the Spodosols with a B/A textural ratio. In addition, Al amorphous mineral phases and/or poorly crystalline determine the cementation and genesis of spodic B horizons with duripans (duric character), as evidenced in our study and by other authors, considering the higher levels of extracted Al by sodium pyrophosphate (Al_p) and acid ammonium oxalate (Al_o). Furthermore, the optical density of the oxalate extract (ODOE) was an efficient indicator of soils in which podzolization was the main specific process of soil distinction and, therefore, should be considered a criterion for classifying Spodosols by the BSCS.

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