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# SPODOSOLS PEDOGENESIS UNDER BARREIRAS FORMATION AND SANDBANK ENVIRONMENTS IN THE SOUTH OF BAHIA<sup>(1)</sup>

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#### **SUMMARY**

Morphologically differentiated Spodosols usually occur in the Coastal Plain of the South of Bahia and North of Espírito Santo. They are found in profiles known as "muçungas", i.e. sandy soils that accumulate water. In these areas, two kinds of Spodosols, different from those in the Restinga area, can be found: Spodosols with E albic horizon (white mucunungas) and without this horizon (black mucunungas). Eight soil profiles with spodic characteristics were collected and described in order to evaluate differences in the formation process of Barreiras and Restinga Spodosols in the South of Bahia. The soil profiles were also characterized chemically, physically and mineralogically. Additionally, texture and chemical analysis, Fe and Al extraction by sodium dithionite-citrate-bicarbonate (DBC), acid ammonium oxalate and sodium pyrophosphate, ammonium oxalate extract optic density (DOox), sulphuric acid attack, and X ray difractometry of the clay fraction were performed. In the Spodosols of the Barreiras area, fragipan was found the spodic layers. Cemented B spodic horizon were observed in the white mucunungas, and granular structure and dark color from the surface in the black mucunungas. There was no fragipan or hard spodic horizon in the Restinga Spodosol. This soil is acid, dystrophic and alic, with sandy texture and high clay percentages in the spodic horizons. The CEC, based on H + Al, is predominantly represented by the organic matter. The most representative components of the mineral phase of the clay fraction are kaolinite and possibly vermiculite traces with interlayered hydroxy.

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Chemical, physical, morphological and mineralogical differences were observed between the Barreiras and Restinga environments. The black and white muçunungas differ in morphologic and chemical properties only.

Index terms: soil classification, soil organic matter, sand soils, muçunungas.

## **RESUMO**: PEDOGÊNESE DE ESPODOSSOLOS EM AMBIENTES DA FORMAÇÃO BARREIRAS E DE RESTINGA DO SUL DA BAHIA

Nos domínios dos Tabuleiros Costeiros do sul da Bahia e norte do Espírito Santo é comum a ocorrência de Espodossolos morfologicamente diferenciados, que ocorrem em depressões popularmente conhecidas como muçunungas - terras arenosas que acumulam água. Nessas áreas, observam-se Espodossolos com horizonte E álbico (mucunungas brancas) e sem este horizonte (muçunungas pretas), que apresentam características diferenciadas entre si e em relação àqueles encontrados em áreas de Restinga. Com o objetivo de avaliar as possíveis diferenças nos processos de formação dos Espodossolos da Formação Barreiras e da Restinga no sul da Bahia e caracterizá-los química, física e mineralogicamente, foram descritos e coletados oito perfis de solos com materiais espódicos e realizadas análises textural, químicas de rotina, extração de Fe e Al pelo ditionito-citrato-bicarbonato de sódio (DCB), oxalato ácido de amônio e pirofosfato de sódio, densidade ótica do extrato do oxalato de amônio (DOox), ataque sulfúrico e difratometria de raios-x das frações areia, silte e argila. No ambiente Barreiras, os Espodossolos apresentam fragipã abaixo dos horizontes espódicos. As muçunungas brancas apresentam horizonte Bespódico cimentado, enquanto as pretas possuem estrutura pequena granular e coloração escura desde a superfície. No Espodossolo de restinga não se observou horizonte espódico endurecido nem fragipã. Os solos apresentam textura arenosa e aumento dos teores de argila nos horizontes espódicos. São solos ácidos, distróficos e álicos. A CTC, dominada por H + Al, é quase exclusivamente representada pela matéria orgânica. Os principais componentes da fase mineral da fração argila dos horizontes espódicos são caulinita e, possivelmente, traços de vermiculita com hidroxi entre camadas (VHE). Foram constatadas diferenças químicas, físicas, morfológicas e mineralógicas entre os Espodossolos da Formação Barreiras e os da Restinga. As muçunungas pretas e brancas apresentaram apenas diferenças morfológicas e químicas entre si.

Termos de indexação: classificação de solos, matéria orgânica do solo, solos arenosos, muçunungas.

#### INTRODUCTION

In Brazil, Spodosols are found in coastal environments, both of the Barreiras Formation (Tertiary) and the Restingas (Quaternary), with different characteristics, be it in terms of the source material, the morphology or the genesis (Gomes, 1995; Moura Filho, 1998; Corrêa et al., 1999; Moreau, 2001).

In coastal tableland areas, one of the main representatives of the sediments of the Barreiras Formation, the main soil classes are Oxisols and Ultisols, often cohesive, and less pronounced, Ultisol, Spodic Ultisols, and Spodosols Plinthosols. In the southern state of Bahia a special kind of environment is observed in the Tableland depressions, locally called "muçunungas", which are characterized by sandy, moist and loose soils (Souza, 1927) that are flooded or where water brims over the surface in the rainy period (Ferreira, 1986). Spodosols with E horizon occur at

these sites, called white muçunungas, and with no horizon and very dark from the surface, called black muçunungas, either sandy or sandy loam and usually with fragipan or duripan. Spodosols and Quartzipsamments are the main soil classes under the shoal environment that is common in the coastal regions of Brazil. These soils are sandy, chemically poor and were formed from fluvial-marine sediments dating from the Quaternary. The Quartzipsamments often consist of white sands of aeolian deposition (Araújo & Lacerda, 1987).

Existing studies on the class of Spodosols in Brazil are still insufficient to establish analytical criteria for a definition of the spodic B horizon and, consequently, for the classification of the Spodosols that occur here. Thus, the concepts for spodic horizons in Brazil have been adapted from the American Classification - Soil Taxonomy, which generally do not apply to the Spodosols in Brazil and other tropical regions (Moura Filho, 1998).

In SiBCS (Embrapa, 2006), the Spodosol order is divided into Humiluvic Spodosols when there is a predominant accumulation of organic C in the spodic horizon (Bh); Ferrohumiluvic Spodosols, with accumulation of organic C, Fe and Al (Bhs) and Ferroluvic Spodosols, which are characterized by Fe accumulation (Bs).

This designation of the suborders suggests the dominance of Fe-organic complexes in the spodic B horizon of Spodosols along the Brazilian coast, despite finding of greater portion of Al compared to Fe in Brazil and worldwide (Andriesse, 1969; Embrapa, 1975; Anderson et al., 1982; Farmer et al., 1983a; Gomes, 1995; Moreau, 2001; Gomes, 2005).

This study aimed to characterize the chemical. physical and mineralogical properties of the Spodosols of the Barreiras Group (muçununga environments) and the Restinga environment of southern Bahia, to deepen the understanding of its genesis, aside from refining the definition of the spodic B horizon and subdividing this order in the Brazilian System of Soil Classification.

#### MATERIAL AND METHODS

The study area is located in the south of the state of Bahia, between latitudes 17 °S and 18 ° 15 'S and longitudes 39 °W and 40 ° 30 'W. According to Köppen's classification, the prevailing climate is Afwarm climate with annual rainfall > 2.000 mm and average monthly rainfall > 60 mm in all months of the year and average temperatures > 18 °C in most cold months. It is characterized by the presence of sediments of the Barreiras Group, Tertiary, along the coastline or followed by sandy sediments of the Quaternary (Restinga) toward the coast, covering part of the municipalities of Alcobaça, Caravelas, Mucuri, Nova Viçosa, and Teixeira de Freitas, all in the state of Bahia.

Eight representative soil profiles were selected with spodic and transitional characteristics of spodic materials (Figure 1), seven from the environment Barreiras and only one (P7) from the Restinga. The morphological profiles were described and the horizons determined according to Santos et al. (2005) in April

The collected material was dried and crushed, if necessary, and sieved (2 mm mesh), to obtain air-dried fine earth (ADFE), which was analyzed chemically and physically, by methods recommended by Embrapa (1997). Granulometry was analyzed by the dispersion method (Ruiz, 2005). The following properties were determined: water pH and 1 mol L-1 KCl, using a potentiometer, both in the ratio soil: solution of 1:2.5 with an hour of contact and shaking of the suspension at reading; available P, exchangeable Na and K by Mehlich-1, P being determined spectrophotometrically, Na and K by flame emission photometry and the micronutrients Zn, Fe, Mn, Cu, by atomic absorption spectrophotometry, Ca and Mg by atomic absorption spectroscopy and exchangeable Al by titration after extraction with 1 mol L-1 KCl in the ratio 1:10; potential acidity (H + Al) by titration after extraction with 0.5 mol L-1 Ca acetate, pH 7.0, and soluble sulfate by spectrophotometry after extraction with acetic acid monocalcium phosphate in the proportion 1:2.5 (v/v). The total organic C of ADFE was determined by titration with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> remaining 0.2 mol L-1 Fe (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O after wet oxidation treatment (Yeomans & Bremner, 1988).

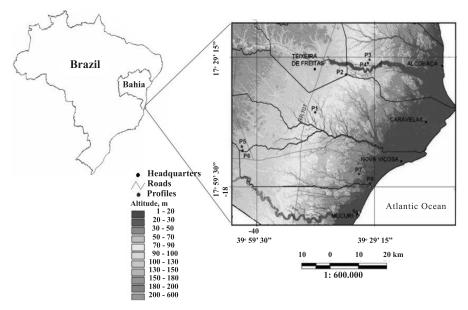


Figure 1. Location of study area showing the profiles P1, P2, P3, P4, P5, P6, P7 and P8.

Different fractions of Fe and Al were determined after grinding and passing the samples through a 0.15 mm sieve and these elements extracted by dithionite-citrate-bicarbonate - DCB (Mehra & Jackson, 1960), acid ammonium oxalate (Schwertmann, 1973), and sodium pyrophosphate (Wang, 1978; Schwertmann & Taylor, 1989), with the determination of Fe and Al by atomic absorption spectrophotometry. In the extract of ammonium oxalate, the optical density (DOox) by spectrophotometry was read at a wavelength of 430 nm (USDA, 1996).

In the mineralogical analysis, the clay and silt fractions were separated from the ADFE by sedimentation and sand fraction by sieving (Embrapa, 1997). In the clay fraction the Fe and Al oxides were removed using DCB (Mehra & Jackson, 1960), and then,  $Mg^{2+}$  and  $K^{+}$  saturation treatments were carried out. The glass slides were mounted, oriented by scraping. The  $Mg^{2+}$  saturated clays were solvated with glycerol and the  $K^{+}$  saturated were read at room temperature, after heating to 550 °C for three hours. Slides of natural clay saturated with  $Mg^{2+}$  only were mounted as well. The silt and sand slides were mounted on non-oriented powder, using scraped slides.

The minerals were identified by X ray diffraction at a voltage of 40 kV and 30 mA, using Co-K $\alpha$  radiation in the range from 2 to 45 °20 at steps of 0.02 °20, at a speed of 1 step s<sup>-1</sup>.

#### RESULTS AND DISCUSSION

#### Morphological properties

The soils have different propertys in color, structure, depth and thickness of the horizons (Table 1). The Spodosol profiles P1, P2, P3, P4 and P8 had an albic E horizon, followed by cemented spodic horizon with massive structure, featuring ortstein with different thicknesses and depths. This cementation according to Farmer et al. (1983b) occurred due to the fallout between the quartz grains of organic compounds before solution. In the Spodosols in the Barreiras Formation, the presence of fragipan was always observed below the spodic horizon. The extremely hard consistency when dry and very firm when moist, of the hardened spodic horizon as much as of the fragipan, are common features of Spodosols found in other areas of the Coastal Plains (Embrapa, 1975a,b; 1980; 2000) and are both impediments to water and root penetration. Some authors state that this property is quite common in other Spodosols of the world under different climatic conditions and contributes substantially to the podzolization process, preventing organic compounds dissolved or suspended in water from leaving the system (Andriesse, 1969; Mokma & Evans, 1999). Perhaps this is reason for the meaning of the term muçununga: sandy soil that accumulates water. However, the fragipan or cemented spodic B are not always solid, as observed in some of the profiles collected for this study and in other Spodosols in areas of tablelands in southern Bahia (Moreau, 2001; Corrêa, 2005).

In the profiles P5 and P6, aside from dark color and "coffee powder" structure from the surface, the spodic B was loose, very friable, with weak, small granular structure, despite the texture being sand clay and sand clay loam. In this case, round shaped organometallic complexes cover the quartz grains, but do, however, not characterize single grains. In this respect, Mokma & Evans (1999) pointed out that as the organometallic complexes are immobilized in the B horizon, they recovered the quartz grains, occluding them.

In the most coastal (P7) from a typical Restinga, the morphological differentiation between the Spodosols studied was greatest, interestingly loose all long its length, with a single-grain structure. It was also the only profile with a characteristic Bs horizon and without fragipan, even when extending the observation up to 200 cm depth. Although this finding cannot be generalized for all Restinga Spodosols, some soil examples with morphological features similar to those of this study were described in such environments, from the state of Alagoas (Moura Filho, 1998) to Paraná (Embrapa, 1980; Oliveira et al., 1992), sometimes classified as intermediate marine Quartzipsamment for Podzol and/or Parapodzol (Gomes, 2005).

Except for the fragipan horizons (Cx), which are slightly sticky, the consistency of the horizons of these soils is invariably not sticky and non-plastic when wet.

The transition between the spodic and the overlying horizon ranged from flat to undulating and abrupt to clear, suggesting variations in the soil water flow (Mokma et al., 2004). The transition of profile P7 to the E horizon for Bhs was wavy and abrupt, which is probably due to the incipient pedogenesis, in other words, the time of formation of this soil was insufficient for the homogenization of the morphological properties.

It was observed that the greater the distance of the profiles from the sea, the greater is the development and the evidence of the podzolization process. Thus, the little expressive color development and structure of the spodic P7 is due to the younger character of the sandy (Quaternary) sediments and to the sandy granulometry with predominance of coarse sand, which, in turn, reduces the retention capacity. This favors the leaching of organic compounds linked to Al and Fe ions, which percolate or leach in the profile, remaining only partly accumulated in the Bhs horizon.

Two of the studied Spodosol profiles have no E horizon (P5 and P6), suggesting that in these soils the podzolization process is still going on. The

Table 1. Morphological properties of the soil profile

Horizon	Donth (one)	Estavotumo(1)	(	Consisten	$\mathrm{cy}^{(2)}$	Co(3)	Color (Munsell)		
norizon	Depth (cm)	Estructure <sup>(1)</sup>	Dry Moist Wet		Wet	Cementation <sup>(3)</sup>	Moist	Dry	
		P1- Duric Hydror	norphic F	errohumil	uvic Spodosol	. – Barreiras			
A	0-14	sg	dl	ml	wpo /wso	nc	10YR 7/1	10YR 7/1	
AE	14-28	sg	dl	ml	wpo /wso	nc	10YR 5/1	10YR 5/1	
E	28-53	sg	dl	ml	wpo /wso	nc	$10 { m YR} \ 4.5/1$	7.5YR 5/2	
EBh	53-80/90	wk m sbk	dl	$_{ m ml}$	wpo /wso	nc	$10 { m YR} \ 3/1.5$	7.5YR 5/2	
Bhm	80/90-94/101	st mc	dvh	mefi	wpo /wso	cs	$5YR\ 2.5/2$	7.5YR 3/4	
Bhsm	94/101-120	st mc	dvh	mefi	wpo /wso	cs	5YR 3/3	7.5YR 4/6	
Cx	120-130+	st m/g sbk	dvh	mefi	wpo /wss	cs	10YR 6/3	7.5YR 7/4	
		P2 - Duric Hydro	morphic l	Ferrohumi	luvic Spodoso	l – Barreiras			
A	0-3	sg	dl	ml	wpo /wso	nc	10YR 2/1	10YR 3/1	
AE	3-11	sg	dl	ml	wpo /wso	nc	10YR 4/1	10YR 6/1	
E	28-70	sg	dl	ml	wpo /wso	nc	2.5Y 7/2	5Y 8/1	
Bhsm	70-90	st mc	deh	mefi	wpo /wso	cs	7.5YR 3/4	7.5YR 4/	
	P3	- Arenic Hapludal	f Hydrom	orphic Fer	rohumilivic S	Spodosol – Barreira	s		
A	0-16	sg	dl	$_{\mathrm{ml}}$	wpo /wso	nc	10YR 3/1	10YR 6/1	
E	16-68	sg	dl	ml	wpo /wso	nc	2.5Y 7/2	5Y 8/1	
Bhg	68-71/90	sg	dl	ml	wpo /wso	nc	$10 \mathrm{YR}~4/2$	10YR 5/2	
Bhsm	71/90+	st mc	deh	mefi	wpo /wso	cs	7.5YR 3/4	7.5YR 4/	
		P4 - Typical Or	thic Ferro	ohumiluvio	Spodosol – E	Barreiras			
A	0-13	sg	dl	$_{ m ml}$	wpo /wso	nc	10YR 4/1	10YR 5/	
E	25/59-65	sg	dl	ml	wpo /wso	nc	7.5YR 6/1	7.5YR 6/	
Bhsm	70-82	st mc	dh	mvfi	wpo /wso	cw	5YR 3/4	10YR 3/6	
2B	170 - 190	st m/g sbk	dh	mefi	wpo /wso	cw	$7.5 { m YR}~4/4$	10YR 5/2	
Cx	160	st m/g sbk	dh	mefi	wpo /wss	cw	2.5Y 7/3	2.5Y 7/4	
		P5 - Typical	Orthic H	umiluvic S	podosol – Bai	rreiras			
A1	0-8	sg; wk m/g gr	dl	mvfi	wpo /wso	nc	$10\mathrm{YR}\ 2/1$	10YR 3/	
A2	8-21	sg; wk m/g gr	dl	mvfi	wpo /wso	nc	10YR 2/1	10YR 4/	
A3	21-32	sg; wk m/g gr	dl	mvfi	wpo /wso	nc	$10\mathrm{YR}\ 2/2$	10YR 3/	
Bh1	32-53	md p gr	dl	mvfi	wpo /wso	nc	$10 { m YR} \ 3/1.5$	10YR 4/	
Bh2	53-85	md p gr	dl	mvfi	wpo /wso	nc	$10 { m YR} \ 2.5/1$	10YR 4/	
Bh3	85-111	md p gr	dl	mvfi	wpo /wso	nc	$10 { m YR} \ 3/1.5$	10YR 4/	
Cx1	114 - 134	md g sbk	ds	mvfi	wpo /wss	cw	2.5Y 5/6	2.5Y 7/4	
		P6 – Argilluv	ic Orthic	Humiluvic	Spodosol – E	Barreiras			
A1	0-21	sg; md m gr	$^{\mathrm{ds}}$	$_{ m fr}$	wpo /wso	nc	10YR 2/2	10YR 3/	
A2	21 - 46	wk m bs	$^{\mathrm{ds}}$	mfi	wpo /wso	nc	10YR 3/3	10YR 4/	
Bhs	46-83	wk m sbk	$^{\mathrm{ds}}$	mfi	wpo /wss	nc	10YR 4/3	10YR 5/	
Placic board	83-95	md m/g sbk	dh	mvfi	wpo /wss	cw	10YR 4/6	10YR 6/	
2Bt	120 - 150	st m/g sbk	dsh	mfi	wp/ws	nc	10YR 5/6	10YR 6/	
	I	P7 - Arenic Haplud	alf Orthi	e Ferrohun	nilivic Spodos	ol – Restinga			
A	0-26	sg nc	dl	ml	wpo /wso	nc	7.5YR 3/2	7.5YR 5/	
E	45-68/80	sg nc	dl	ml	wpo /wso	nc	7.5YR 4/2	7.5YR 5/	
Bs1	68/80-110	sg nc	dl	ml	wpo /wso	nc	7.5YR 4/3	7.5YR 6/	
Bs2	110 - 150 +	sg nc	dl	ml	wpo /wso	nc	7.5YR 4/4	10YR 5/4	
	I	P8 - Duric Hydrom	orphic Fe	rrohumilu	vic Spodosol -	- Barreiras			
A	0-15	sg	dl	ml	wpo /wso	nc	10YR 3/1	10YR 3/2	
E	25-40	sg	dl	ml	wpo /wso	nc	$10\mathrm{YR}~5/2$	10YR 6/1	
Bhsm	40+	st mc	Deh	mefi	wpo /wso	cs	7.5YR 2.5/3	10YR 4/4	

<sup>(1)</sup> Structure: Development level: wk: weak, md: moderate, st: strong. Size: vf: very fine, f: fine, m: medium, g: large, mg: extra large. Form: sg: single grain, gr: granular, sbk: subangular blocky, lm: laminar, mc: massive. (2) Consistency: Dry: dl: loose, ds: delta large. soft, dsh: Slightly hard, dh: hard, dvh: Very hard, deh: Extremely hard, nod.: nodules. Moist: ml: loose, mvfr: very friable, mfr: friable, mfi: firme, mvfi: very firm, mefi: extremely firm. Wet: wpo: Nonplastic, wps: Slightly plastic, wp: plastic; wso: Nonsticky, ws: Slightly sticky, ws: Sticky. (3) Cementation: nc: no cemented, cw: Weakly cemented, cs: Strongly cemented.

observation of a dark spodic B horizon, but already with a certain development of dark gray color immediately above the hardened suggests that this process is ongoing and may even lead to the appearance of the E horizon.

When existing, the E horizon is generally easy to identify because it differs from the others in color with two possibilities: almost white (albic) or light gray (not albic). The high color values of the horizon E and are caused mainly by the scarcity of organic material and iron oxides, and the color is determined by the remaining sand and silt particles, predominantly quartz.

### Physical, chemical and mineralogical properties

In most soils in this study the texture of the Spodic B horizon was sandy loam and sand. The higher clay levels in the spodic B of profile P6 were particularly interesting, because of the intermediate character to Ultisol (Table 2). This finding is consistent with analytical results from Spodosols in restinga areas or Barreiras depressions, Brazil (Embrapa, 1975a,b; 1977, 1980; Gomes, 1995; Moura Filho, 1998; Moreau, 2001; Gomes, 2002; Gomes, 2005) and, consequently, with the definition of the spodic B horizon SiBCS (Embrapa, 2006).

Table 2. Physical properties of soil samples

Horizon	Coarse sand	Fine sand	$\mathbf{Silt}$	Clay	Texture Class
		g kg-1			
	P1- Duric Hydro	morphic Ferrohumi	luvic Spodo	sol – Barreiras	
A	760	140	60	40	Sand
ĀE	790	150	20	40	Sand
E	780	160	40	20	Sand
EBh	700	200	20	80	Sand
Bhm	650	200	20	130	Loamy sand
Bhsm	700	130	30	140	Sandy loam
Cx	390	100	30	480	Sandy Clay
OA		norphic Ferrohumily			Sandy Clay
A	430	360	110	100	Sandy loam
AE AE	820	130	20	30	Sandy loain Sand
E E	750	200	20 30	20	Sand Sand
Bhsm		200 150	50 50		
	650			150	Sandy loam
	P3 - Arenic Hapludalf				
A	800	150	20	30	Sand
E	750	210	20	20	Sand
Bhg	650	210	60	80	Loamy sand
Bhsm	760	150	10	80	Sand
	P4 - Typical C	rthic Ferrohumiluvi	ic Spodosol	– Barreiras	
A	750	180	10	60	Sand
$\mathbf{E}$	660	250	30	60	Sand
Bhsm	640	210	40	110	Loamy sand
2Bs	670	230	50	50	Sand
Cx	390	140	60	410	Sandy clay loam
	P5 - Typical	Orthic Humiluvic S	podosol – B	Sarreiras	
A1	780	100	20	100	Loamy sand
A2	790	100	20	90	Loamy sand
A3	730	120	30	120	Loamy sand
Bh1	710	120	30	140	Sandy loam
Bh2	690	140	40	130	Sandy loam
Bh3	710	140	30	120	Loamy sand
Cx1	460	100	30	410	Sandy clay loam
0111		ic Orthic Humiluvic			Sarray oray roun
A1	700	120	50	130	Sandy loam
A2	580	140	70	210	Sandy clay loam
Bhs	490	160	60	290	Sandy clay loan
Placic board	480	150	70	300	Sandy clay loam
2Bt	340	100	70	490	Clay
200		dalf Orthic Ferrohu			
A	930	20	10	40	Sand
A E	930	50 50	10	40 10	Sand Sand
Bs1	930 950	30	10	10 10	Sand Sand
				10 10	
Bs2	920 De Dunio Hydn	60 omovnia Formaliumi	10		Sand
Α.		omorphic Ferrohumi	-		T
A	670	180	90	60	Loamy sand
E	650	240	80	30	Sand
$\operatorname{Bhsm}$	650	210	120	20	Sand

The highest proportion of the coarse sand fraction in all horizons of these soils was striking. This property strongly favors the percolation of organometallic complexes with the consequent formation of the spodic B horizon (van Wambeke, 1992). The already low clay levels of the spodic decrease in the E horizons and tend to increase in the spodic B horizons, possibly due to vertical movement (Table 2). As the clay content increases, there is a tendency of adsorption of these complexes by inhibiting or even preventing their percolation. This justifies the contribution of texture change in the profile to the podzolization process (Mokma & Evans, 1999). The components present in organic and organometallic illuviation horizons are intimately associated with inorganic phases (Brydon & Shimoda, 1972), which also contribute to cementing the horizons. Only in the profiles P7 and P8 this trend was not observed (Table 4).

The pH values in H<sub>2</sub>O indicate acidic (Table 3), in agreement with results obtained for other studied in Restinga areas and Barreiras depressions of the country (Gomes, 1995; Moura Filho, 1998; Moreau, 2001; Rossi & Queiroz Neto, 2001; Gomes, 2002, 2005). The pH in H<sub>2</sub>O, higher than the values obtained with 1 mol L-1 KCl, indicates the predominance of negative charges in the spodic horizon soils.

Table 3. Chemical properties of soil samples

	pН		_													
Horizon	$\overline{\mathbf{H}_{2}\mathbf{O}}$	KCl	Ca <sup>2+</sup> Mg <sup>2</sup>		$\mathbf{K}^{+}$	Na⁺	$Al^{3+}$	H + Al	$SB^{(1)}$	$\mathbf{T}^{(2)}$	$V^{(3)}$	m <sup>(4)</sup>	$\mathbf{S}$	P	oc	Prem
						— cmo	l <sub>e</sub> dm <sup>-3</sup> –					%	— mg	dm-3 —	dag kg-1	mg L <sup>-1</sup>
						P1	- Durio	Hydromo	orphic Ferr	o-humilu	vic Spoo	losol				
A	5.14	3.74	1.44	0.54	0.10	0.02	0.40	8.80	2.10	10.90	19.3	16.0	1.20	3.30	1.95	55.6
$\mathbf{E}$	5.31	3.99	0.35	0.05	0.02	0.00	0.30	2.60	0.42	3.02	13.9	41.7	1.20	0.90	0.38	54.4
EBh	4.98	3.76	0.38	0.09	0.02	0.00	2.67	13.60	0.49	14.09	3.5	84.5	24.50	1.60	0.98	38.2
Bhm	4.77	3.76	0.12	0.22	0.00	0.00	7.80	65.20	0.34	65.54	0.5	95.8	71.40	0.90	3.53	10.0
Bhsm	4.86	3.99	0.00	0.10	0.00	0.00	6.81	59.20	0.10	59.30	0.2	98.6	96.10	0.40	4.84	6.2
Cx	4.87	4.25	0.01	0.03	0.00	0.00	2.57	19.60	0.04	19.64	0.2	98.5	71.50	0.10	1.68	15.7
						$P_2$	2 - Duri	c Hydrom	orphic Fer	rohumilu	ivic Spoo	losol				
A	5.19	4.40	4.42	1.94	0.26	0.05	0.00	16.10	6.67	22.77	29.3	0.0	1.20	7.70	5.69	53.3
AE	5.17	4.08	1.16	0.15	0.03	0.00	0.20	2.80	1.34	4.14	32.4	13.0	1.20	1.80	0.55	57.4
E	5.80	4.82	0.21	0.00	0.01	0.00	0.00	1.00	0.22	1.22	18.0	0.0	2.00	0.30	0.13	57.4
Bhsm	4.86	3.86	2.08	0.17	0.03	0.05	7.70	80.70	2.33	83.03	2.8	76.8	117.10	1.40	5.90	5.3
						P9	R. Dur	ic Hydron	norphic Fe	rrohumil	uvie Sno	doeol				
A	6.14	4.54	1.08	0.33	0.02	0.00	0.10	4.10	1.43	5.53	25.9	6.5	8.10	3.30	0.77	62.3
E	5.85	5.12	0.01	0.01	0.01	0.00	0.00	0.00	0.03	0.03	100.0	0.0	7.30	0.50	0.03	60.5
Bhg	5.76	4.75	1.57	0.08	0.04	0.00	0.10	6.40	1.69	8.09	20.9	5.6	23.70	0.90	0.60	44.5
Bhsm	5.38	4.02	1.58	0.16	0.03	0.00	3.36	37.80	1.77	39.57	4.5	65.5	45.90	2.20	1.99	13.2
									hic Ferroh							
A	5.37	4.33	1.31	0.19	0.00	0.00	0.10	7.30	1.50	8.80	17.0	6.3	23.30	86.30	0.88	51.9
E	5.96	5.09	1.03	0.13	0.03	0.00	0.00	2.80	1.20	4.00	30.0	0.0	21.10	8.30	0.49	55.0
Bhsm	5.47	4.42	3.74	0.36	0.00	0.00	1.98	40.90	4.11	45.01	9.1	32.5	97.10	1.40	3.80	11.0
2Bs	5.27	4.42	1.14	0.11	0.01	0.00	0.49	9.90	1.26	11.16	11.3	28.0	31.00	19.10	1.04	48.0
Cx	5.16	4.54	0.13	0.02	0.05	0.00	0.89	10.60	0.20	10.80	1.9	81.7	73.00	1.80	0.84	20.8
011	0.10	1.01	0.10	0.02	0.00	0.00	P5		Orthic Hu				10.00	1.00	0.01	20.0
A 1	5.17	4.24	1.54	0.46	0.04	0.00	0.89	13.20	2.04	15.24	3pouosoi 13.4	30.4	30.20	4.70	2.06	39.8
A1	5.21	4.16	1.22	0.40 $0.37$	0.04	0.00	1.48	16.00	1.62	17.62	9.2	47.7	24.20	4.30	1.83	32.9
A2	4.88	4.13	0.61	0.16	0.03	0.00	3.16	20.40	0.79	21.19	3.7	80.0	38.20	1.30	$\frac{1.03}{2.08}$	25.4
A3	4.98	4.13	0.01	0.10	0.02	0.00	2.27	24.80	0.18	$\frac{21.19}{24.98}$	0.7	92.7	88.60	1.60	$\frac{2.08}{2.30}$	11.9
Bh1 Bh2	5.21	4.54	0.13	0.04	0.00	0.00	0.99	14.80	$0.13 \\ 0.24$	15.04	1.6	80.5	89.10	0.80	1.53	13.3
Bh3	5.80	4.79	0.10	0.23	0.00	0.00	0.30	9.10	0.68	9.78	7.0	30.6	82.30	1.30	0.90	19.8
Cx1	5.71	4.94	0.17	0.29	0.04	0.00	0.20	13.90	0.50	14.40	3.5		135.40	1.70	1.55	11.3
CXI	0.11	1.51	0.17	0.25	0.04	0.00							155.40	1.70	1.00	11.0
A 1	F C0	4 77	0.05	0.45	0.00	0.00			Humiluvi				11 10	0.70	1 10	40.0
A1	5.68	4.77	2.65	0.45	0.02	0.00	0.00	6.50	3.12	9.62	32.4	0.0	11.10	0.70	1.13	48.0
A2	5.68	4.66	2.29	$0.29 \\ 0.23$	0.01	0.00	0.20	9.90	2.59	12.49	$20.7 \\ 27.2$	7.2	29.90	0.60	1.05	33.4
Bhs	5.99	4.93	2.63		$0.02 \\ 0.00$	0.00	0.10	7.70	2.88	10.58		3.4	31.30	0.30	0.91	29.7
Placic board	5.66	$4.77 \\ 4.21$	$\frac{1.24}{0.23}$	$0.09 \\ 0.03$	0.00	0.00 $0.00$	$0.20 \\ 2.57$	8.30 8.00	$\frac{1.33}{0.26}$	$9.63 \\ 8.26$	$13.8 \\ 3.1$	13.1 90.8	48.80 $41.30$	$0.40 \\ 0.40$	$0.79 \\ 0.48$	18.3 20.8
2Bt	4.76	4.21	0.25	0.05	0.00	0.00							41.50	0.40	0.46	20.6
		0.00	0.00	0.10	0.00	0.01			ludalf Orth				F F0	4.50	1.00	
A	4.44	3.08	0.06	0.19	0.03	0.01	1.98	11.40	0.29	11.69	2.5	87.2	5.50	4.70	1.36	55.9
E	4.69	3.72	0.00	0.02	0.01	0.00	0.49	3.30	0.03	3.33	0.9	93.2	3.50	0.70	0.30	57.0
Bs1	4.92	4.37	0.00	0.00	0.00	0.00	0.40	3.40	0.00	3.40		100.0	20.60	0.60	0.20	52.8
Bs2	4.91	4.12	0.00	0.00	0.00	0.00	0.79	5.70	0.00	5.70		100.0	18.30	0.40	0.27	49.6
				0.46					omorphic F					0.0-		22 -
A	5.11	4.17	0.05	0.16	0.02	0.00	2.67	17.80	0.23	18.03	1.3	92.1	49.10	3.20	1.77	26.2
E	5.25	4.15	0.00	0.80	0.01	0.00	0.69	5.10	0.09	5.19	1.7	88.5	23.40	1.30	0.39	55.1
Bhsm	5.08	4.23	0.00	0.04	0.01	0.01	4.84	47.40	0.06	47.46	0.1	98.8	102.20	1.00	4.72	5.2

<sup>(1)</sup> SB: sum of bases, (2) T: CEC pH 7.0. (3) V: base saturation. (4) m: aluminum saturation.

The sum of bases (SB) is higher in the top surface of the profiles indicating the importance of nutrient cycling even in desaturated soils as these. Because of the proximity to the sea, saline sprays may also be contributing to the nutrient supply at the soil surface. SB values tend to decrease in depth with a slight increase in spodic B horizons, which normally constitute an impediment to the water flow or leaching of Na, K,  $Ca^{2+}$  and  $Mg^{2+}$ .

The H + Al values were positively correlated with organic C when considering only the spodic horizons (r=0.95, p < 0.001) or all horizons (r=0.85, p < 0.001) and fitted well linearly to the spodic horizons (Figure 2), indicating that  $CEC_{\rm pH~7.0}$  is almost exclusively due to the organic fraction.

The soils are dystrophic or alic. In the latter case, Al $^{3+}$  values are considerably higher than  $4.0~\rm cmol_c~dm^{-3}$  (Table 3), one of the SiBCS requirements for an aluminic character. Another requirement for this character would be the value of the clay activity, (100  $\rm CTC_{pH~7.0}$  / % clay) > 20  $\rm cmol_c~kg^{-1}$  clay, a criterion that is not adequate for sandy soils.

A positive correlation between the concentrations of organic C and  $Al^{3+}$  was found for both spodic B (r=0.88, p<0.001) and for all horizons (r=0.72, p<0.01) (Figure 2). Although in Spodosols Al is generally complexed to organic material in the spodic horizons, the amount of exchangeable Al in these horizons may be increasing since the microbial degradation of organic compounds is sufficient for the release of the Al then connected to them (van Breemen & Buurman, 1998).

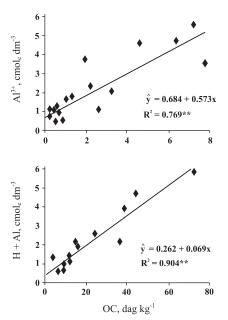


Figure 2. Relationship between organic C (OC) and exchangeable Al, and organic carbon and H+Al horizons Spodic soils.

This trend of higher Al³+ levels in the spodic B horizon, despite poorly studied, perhaps because of the low agricultural potential of these soils, is a rather common property in coastal Spodosols (Gomes, 1995; Moura Filho, 1998; Moreau, 2001; Gomes, 2002, 2005; Corrêa, 2005) and even the northern region (Brazil, 1975, 1976, 1977a,b, 1978). Thus, it seems advisable to determine lower categorical levels for the alic character of Spodosols.

Higher amounts of P extracted by Mehlich-1 were constant in the A horizon of the soils studied, due to the cycling of nutrients from organic material, since the material of these soils is poor.

A trend of P accumulation was observed in the spodic B horizons. It is likely that P is translocated to the profile complexed with organic matter, which is favored by the sandy texture. Furthermore, the reduction of crystallinity of iron oxides (Schwertmann, 1966; Tan, 1986), in this case, of goethite or ferrihydrite, by organic acids also explains the accumulation of P in spodic B horizons. Only in profile P7 this trend was not observed, due to lower levels of oxides and the higher proportion of coarse sand fraction in this profile.

The values of remaining phosphorus (Prem) in A and E horizons were medium and high (Ribeiro et al., 1999), whereas in the spodic B horizons these values dropped abruptly to low values (Table 3). These results were inversely associated to variations in clay content (Table 2) in the horizons of the soil profile.

The concentrations of S, unlike for P, were lower at the surface with a clear tendency to accumulate in the Spodic B horizon, associated with the pH in this horizon, indicating strong influence of illuvial organic matter in S movement of the Spodosols studied.

Although near the sea, the concentrations in all soils were low. It is noteworthy that the most relevant source of these elements in soil is presumably the input by marine spray, due to the poverty of the source material.

The extractions of Fe and Al with DCB (d), oxalate (o) and pyrophosphate (p) indicated accumulation of these elements in the spodic B horizons (Table 4). These results agree with those obtained by Gomes (1995), Moura Filho (1998) and Gomes (2005) for Spodosols of the Restinga environment in Brazil and were explained by the translocation of Fe and Al complexed with organic compounds (van Wambeke, 1992; van Breemen & Buurman, 1998; Mokma & Evans, 1999).

The Al were higher than those of Fe by DCB as well as oxalate and pyrophosphate in the Spodic B horizons of these soils (Table 4). This suggests a greater involvement of Al forms related to organic acids in the podzolization process than of Fe. The only exception to this trend was observed in P7 (Restinga). In this case, beyond a possible richness of Al in environmental Barreiras, both the hardened

Table 4. Optical density of the extract of ammonium oxalate (DOox), levels of Fe and Al oxides extractable with dithionite-citrate-bicarbonate (DCB), ammonium oxalate and sodium pyrophosphate and ratios between these metals to soils

Horizon	Depth	DO	$\propto rac{Oxalate}{Al_2O_3 \;\; Fe_2O_3 \;\; Al/Fe^{(1)}}$			DCB			Pyı	rophos	phate	TE (TE (2)	A1 /A1 (0)	A1 . 0 = T . (3
		DOox	$\overline{\mathbf{Al}_2\mathbf{O}_3}$	$\mathbf{Fe}_{2}\mathbf{O}_{3}$	Al/Fe <sup>(1)</sup>	$\overline{\text{Al}_2\text{O}_3}$	$\mathbf{Fe}_{2}\mathbf{O}_{3}$	Al/Fe <sup>(1)</sup>	$\overline{\mathbf{Al}_2\mathbf{O}_3}$	$\mathbf{Fe}_{2}\mathbf{O}_{3}$	Al/Fe <sup>(1)</sup>	Fe <sub>o</sub> /Fe <sub>d</sub> (2)	AI <sub>o</sub> /AI <sub>d</sub> <sup>(2)</sup>	Al <sub>0</sub> +0.5 Fe <sub>0</sub> **/
	cm		– dag	g kg-1—		– dag	g kg-1_		— dag	g kg-1—				
			P1	- Duric	Hydromo	rphic l	Ferrohi	ımiluvic S	Spodoso	ol – Bar	reiras			
A	0-14	0.03	0.03	0.00	0.00	0.04	0.01	6.28	0.07		5.50	0.00	1.00	nc
AE	14–28 28–53	0.02	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	nc
$_{ m EBh}$	28-53 80-90	$0.02 \\ 0.59$	$0.03 \\ 0.12$	$0.00 \\ 0.00$	$0.00 \\ 0.00$	$0.05 \\ 0.06$	$0.01 \\ 0.00$	$7.85 \\ 0.00$	$0.00 \\ 0.35$	$0.00 \\ 0.01$	$0.00 \\ 54.94$	$0.00 \\ 0.00$	$0.67 \\ 2.00$	nc nc
Bhm	94–101	2.74	1.62	0.00	254.34	1.15	0.00	180.55	1.52	0.01	238.64	1.00	1.41	0.87
Bhsm	101-120		2.26	0.01	354.82	2.11	0.01	331.27	2.12	0.01	332.84	1.00	1.07	1.21
Cx	120-130	+ 0.56	1.31	0.01	205.67	0.91	0.00	0.00	0.94	0.04	38.90	0.00	1.44	nc
								umiluvic						
A	0-3	0.08	0.02	0.07	0.45	0.10	0.05	3.14	0.05	0.06	1.31	1.40	0.20	nc
AE E	3–11 28–70	$0.02 \\ 0.01$	0.00 $0.00$	$0.01 \\ 0.00$	$0.00 \\ 0.00$	$0.06 \\ 0.08$	$0.01 \\ 0.00$	$9.42 \\ 0.00$	$0.10 \\ 0.13$	$0.01 \\ 0.00$	$15.70 \\ 0.00$	$\frac{1.00}{0.00}$	$0.00 \\ 0.00$	nc nc
E Bhsm	70 <del>-</del> 90	3.14		0.00	84.10	4.28	0.00	48.00	$\frac{0.15}{2.85}$	0.00	28.00	0.64	1.12	2.58
Diisiii	10 50							Ferrohun					1.12	2.00
A	0–16	0.05	0.02	0.01	3.14	0.00	0.01	0.00	0.00	_	0.00	1.00	0.00	nc
Ë	16-68	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	nc
Bhg	68–71	0.21	0.10	0.00	0.00	0.05	0.00	0.00	0.07	0.00	0.00	0.00	1.67	nc
Bhsm	71–90+	1.86	0.84	0.01	131.88	0.53	0.01	83.21	0.71		111.47	1.00	1.57	0.45
					_			iluvic Spo						
A	0-13	0.10	0.11	0.04	4.31	0.69	0.04	27.08	0.02	0.01	3.14	1.00	0.16	nc
$_{ m Bhsm}^{ m E}$	25/59-65 70-82	$0.10 \\ 1.89$	$0.07 \\ 2.40$	$0.02 \\ 0.24$	$5.50 \\ 15.70$	$0.40 \\ 1.98$	$0.02 \\ 0.15$	$31.40 \\ 20.72$	$0.00 \\ 1.62$	$0.01 \\ 0.18$	$0.00 \\ 14.13$	$\frac{1.0}{1.60}$	$0.17 \\ 1.21$	$^{ m nc}_{1.36}$
$2\mathrm{Bs}$	170-190	0.36	0.05	0.24	0.00	0.14	0.13	20.72 $21.98$	0.12	0.13	18.84	0.00	0.43	0.03
Cx	160		1.72	0.03	90.01	0.63	0.03	32.97	0.57	0.03	29.83	1.00	2.76	nc
				P5 - Ty	pical Or	thic Hu	ımiluvi	c Spodosc	ol – Bar	reiras				
A1	0-8	0.12	0.19	0.03	7.85	0.17	0.04	4.71	0.17	0.03	7.07	0.75	1.11	nc
A2	8-21	0.23	0.22	0.04	6.28	0.25	0.04	6.8	0.38	0.04	10.47	1.00	0.92	nc
A3 Bh1	21–32 32–53	$0.35 \\ 0.59$	0.43 $1.10$	$0.08 \\ 0.06$	$\frac{6.01}{22.77}$	$0.48 \\ 0.93$	$0.06 \\ 0.03$	$9.81 \\ 38.47$	$0.85 \\ 1.55$	$0.08 \\ 0.05$	$\frac{11.78}{32.19}$	$\frac{1.33}{2.00}$	$0.92 \\ 1.18$	$_{0.60}^{ m nc}$
Bh2	53 <del>-</del> 85	0.60	1.23	0.05	25.51	0.91	0.03	37.68	0.95	0.03	26.17	1.67	1.35	0.67
Bh3	85-111	0.35	1.00	0.03	41.61	0.63	0.02	51.81	0.59	0.02	48.67	1.50	1.61	0.54
Cx1	114 <del>-</del> 134	0.19	4.16	0.23	21.59	1.49	0.21	0.19	0.72	0.19	4.59	1.10	2.78	nc
								vic Spodo						
A1	0-21	0.12	0.16	0.08	2.09	0.24	0.15	1.86	0.29	0.13	2.62	0.53	0.62	nc
$\frac{A2}{Bhs}$	21–46 46–83	$0.21 \\ 0.15$	$0.37 \\ 0.48$	$0.13 \\ 0.14$	$\frac{3.49}{3.93}$	$0.46 \\ 0.56$	$0.24 \\ 0.25$	$\frac{2.22}{2.62}$	$0.86 \\ 0.7$	$0.27 \\ 0.32$	$\frac{3.80}{2.71}$	$0.54 \\ 0.56$	$0.83 \\ 0.83$	$\overset{ ext{nc}}{0.30}$
	ırd 83 <del>-</del> 95				1.40	0.89	$0.25 \\ 0.45$	$\frac{2.02}{2.31}$	1.30		$\frac{2.71}{2.52}$	1.76	1.04	$0.30 \\ 0.77$
2Bt	120-150				3.93	0.70	0.40	2.07	0.11		11.78	0.35	0.68	nc
			P7 -	Arenic	Hapludal	lf Orth	ic Ferr	humilivi	c Spodo	sol – R	estinga			
A	0–26	0.1	0.03	0.02	3.14	0.07	0.12	0.79	0.00	0.03	0.00	0.17	0.50	nc
$\mathbf{E}$	45-68/80	0.09	0.02	0.02	1.57	0.05	0.16	0.43	0.00	0.02	0.00	0.13	0.33	nc
Bs1	68/80-110		0.04	0.04	1.05	0.11	0.17	0.79	0.00	0.04	0.00	0.24	0.33	0.04
Bs2	110-150+	- 0.10	0.04	0.05	0.79	0.08	0.18	0.48	0.00	0.07	0.00	0.28	0.50	0.06
	0.15	0.40						amiluvie s				1.00	0.70	
A E	0–15 25–40	$0.49 \\ 0.05$	$0.35 \\ 0.04$	$0.02 \\ 0.01$	$29.83 \\ 3.14$	$0.49 \\ 0.10$	$0.02 \\ 0.01$	$\frac{40.82}{7.85}$	$0.33 \\ 0.00$	$0.00 \\ 0.00$	$0.00 \\ 0.00$	$\frac{1.00}{1.00}$	$0.73 \\ 0.40$	nc
Bhsm	40+	2.10	2.88	$0.01 \\ 0.08$	39.77	3.10	$0.01 \\ 0.04$	85.83	2.33	0.00	64.37	$\frac{1.00}{2.00}$	$0.40 \\ 0.93$	$^{ m nc}_{1.55}$
		0				0		(0)					0.00	

<sup>(1)</sup> Molecular relationship between the levels of oxides of Fe and Al. (2) Based on the levels of oxides of Fe and Al. (3) Based on Fe and Al extracted with ammonium oxalate. Nc: not calculated.

horizon and the fragipan restrict drainage, creating a temporary water-saturated environment, long enough to promote Fe reduction and mobilization (Anderson et al., 1982; Farmer et al., 1983a). This effect was intensified by the sandy texture and low amount of Fe in the system (Andriesse, 1969).

It is noteworthy that the prefix Al has been used by the Soil Taxonomy (U.S., 1999) for Spodosols with less than 0.10 % Fe by ammonium oxalate in 75 % or more of the thickness of the spodic horizon, at the large group level. Thus, the terms Ferriluvic and Ferrihumiluvic do not seem to be the most appropriate in recognition of the SiBCS suborder.

The high values of the Feo/Fed ratios (Table 4) in spodic horizons of the soils (greater than unity in profiles P1, P4, P5, P6 and the placid board termo sem sentido P8) indicate greater involvement of Fe forms with low crystallinity degree in most soils. This result confirms Schwertmann (1966), who reported on the effect of organic matter on the inhibition of Fe crystallization of the presence of ferrihydrite (Schwertmann et al., 1986; Parfitt & Childs, 1988). Ferrihydrite is extremely soluble in ammonium oxalate and was once reported for soils with high CO levels, and can also occur in Spodic horizons.

Unlike in the other profiles, Fe and Al in spodic horizons increased slightly in P7, but in this case, Fe predominated over Al and the values of CO and DOox decreased in these horizons (Table 4). For lying closest to the sea and, therefore, being younger, the profile would have been exposed to reducing conditions for a shorter time, justifying the higher values of Fe than of Al.

Also with the exception of P7, the ratio Alo/Ald (Table 4) of spodic horizons of the other profiles is close to or greater than one, also indicating the involvement of Al forms with poorer crystallinity.

The low Feo/Fed ratios and Alo/Ald indicate effective participation of poorly crystalline oxides and seem to be the most likely explanation for the low values observed in the Prem spodic horizons, except for P7.

Except for the P3 and P7, a relation ship of Alo +  $0.5 \, \mathrm{Feo} \geq 0.5 \, \mathrm{was}$  observed in the soils, meeting the criteria proposed by the Soil Taxonomy (U.S., 1999) to define "Spodic materials", as already studied in other Spodosols of Brazil (Gomes, 1995, 2005; Moura Filho, 1998). The DOox values in soil profiles related to P1, P2, P3, P4 and P8 were clearly above 0.25 (Table 4), another minimum required value for the environment as "Spodic materials" of the Soil Taxonomy (U.S., 1999). Moreover, the DOox values were more than twice as high in the spodic horizons of these profiles than in the overlying horizons (either A or E), thus meeting another criteria determined in the definition of "Spodic materials".

The DOox values of the dark and without E horizon (P5 and P6) in P5 were higher than 0.25, but not the double of the overlying horizon. However, field observations and analytical results, especially regarding the organic C, Fe and Al extracted by oxalate, pyrophosphate and dithionite, confirmed the classification as Spodosols; this type of Spodosol was rarely described in the country. In fact, this result confirms that the double DOox value of the spodic horizon in the overlying horizon would not apply to these soils.

In the profile P6, in turn, despite the dark color, though much lower than in the P5, the DOox values were lower than 0.25 in the Bhs and the placic board (0.15 and 0.13 respectively). Although it is an intermediary soil to the Ultisol with a 2BT horizon (10YR 5/6) appearing at 120 cm, this result confirms that if the DOox should come to be adopted as a criterion for the characterization of the spodic B

horizon in Brazil, the minimum value of 0.25 should be revised, to include the Brazilian Spodosols.

The DOox values were lowest in the P7 profile (0.07 and 0.10 in the Bs1 and Bs2 horizons, respectively), consistent with the low organic C, Al and Fe levels. For the spodic B horizons (Figure 3), there was good correlation and linear adjustment between optical density and organic C (r = 0.92, p < 0.001), Al³+ (r = 0.92, p < 0.0001), H + Al (r = 0.95, p < 0.0001) and Al₂O₃ extracted by oxalate (r = 0.82, p < 0.001), DCB (r = 0.78, p < 0.001) and pyrophosphate (r = 0.79, p < 0.001). Thus, the optical density can be used as a criterion for defining analytical "Spodic materials", although adjustments for the Spodosols of Brazil are still necessary.

We conclude that some criteria adopted by the Soil Taxonomy in the classification of Spodosols do not apply to characterize Spodosols of tropical regions or specifically in Brazil, as reported by some authors (Gomes, 1995, 2002; Moura Filho, 1998; Rossi & Queiroz Neto, 2001). Thus, it is suggested that the criteria for Spodosol classification in the current SiBCS should be reviewed, despite earlier proposals of updates and revisions to the new system (Embrapa, 2006). The problem is that the system does not address the accumulation of organic matter quantitatively in the suborder distinction and does not determine a priority of the criteria used.

The studied soils showed increases in organic C in spodic B horizons (Table 3). Except for the P7, these values met one of the criteria constituting the definition of "Spodic material" proposed by the Soil Taxonomy (U.S., 1999), determining C greater than or equal to 0.6 % in spodic horizons.

The clay fraction of spodic and fragipan horizons studied is largely dominated by kaolinite with minor amounts of quartz and hydroxy vermiculite between layers (data not shown). This fact is consistent with the source material originated from soil sediments of the Barreiras Group (Achá Panoso, 1976; Anjos, 1985; Fonseca, 1986; Ferreira, 1988; Fernandes, 2000) as well as Spodosols formed from Quaternary deposits (Gomes, 1995, 2002, 2005; Moura Filho, 1998) in both tropical and cold zones (Andriesse, 1969). Fonseca (1986) studied Oxisols and Yellow Ultisols cohesive Coastal Tablelands and also mentioned the widespread kaolinite, the low amount of quartz and hydroxy vermiculite between layers, which is a mineral with recognized stability in acidic environments and has been reported in Restinga in Brazil (Gomes, 1995, 2002) and temperate climate (Brydon & Shimoda, 1972).

#### Soil classification

According to the criteria of SiBCS, the profiles P1, P2, P3 and P8 were classified as Duric Hydromorphic Ferrohumiluvic Spodosols, because besides the accumulation of water just above or in the spodic

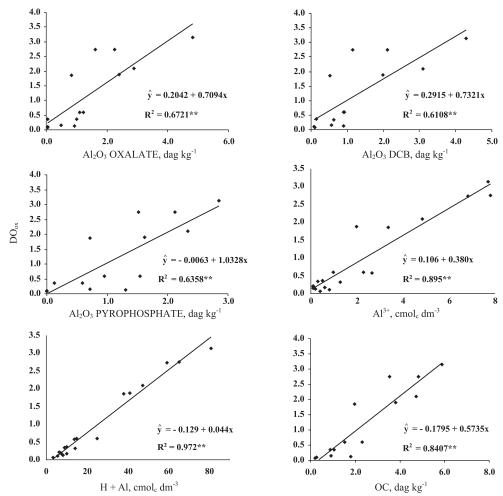


Figure 3. Relations between the values of optical density of the extract of ammonium oxalate (DOox) and  $Al_2O_3$  extracted by ammonium oxalate, DCB and sodium pyrophosphate,  $Al^3$  +, H + Al, organic C spodic horizons of soil profile.

horizon, the Bh and Bhs are hardened (ortstein) within 100 cm of the soil surface. The P4 was classified as Duric Orthic Ferrohumiluvic Spodosol, because no ortstein was observed, nor any signs of water accumulation in a horizon, at least at sampling.

The profile P5 (black muçununga) was classified as Typical Orthic Humiluvic Spodosol, although it is believed to accumulate water in some part of the year. The faint gray staining observed in the layer above the fragipan corroborates this statement, although the soil was not water saturated on two occasions of observation (rainy season - November and early dry season - April).

Despite the dark color, the organic C levels in P6 (black muçununga) were not high in Spodic B. This profile had a "plaque" or discontinuous placic layer just below the Bhs horizon, followed by the horizon color 10YR 5/6, with clay texture (49 % clay) and plastic and sticky consistency, transitioning to Ultisol, resulting in its classification as Argilluvic Orthic

Humiluvic Spodosol. The presence of a yellowish horizon underlying Bhs in P6, similarly to the cohesive Ultisols Bt in the study area, indicates that the podzolization this soil was more recent than the deposition of sediment barriers, and perhaps without silica in solution and a sufficiently long dry period to form the fragipan.

The genesis of the profiles P1, P2, P3, P4, P5 and P8, all with fragipan, seems to be related to clay destruction (Brinkman, 1979), especially kaolinite, in the depression areas where they are found. This statement is anchored by the fact that these soils transit to clay loam cohesive Ultisols within short distances. The frequent observations of placic horizons in the areas surrounding cohesive Ultisols also indicate a lateral import of Fe and certainly also of Al and silica, which could be contributing to the genesis of spodic and fragipan horizons, respectively. The most coastal profile (P7) located in restinga forest, is pedogenetically the least developed, when drawing

conclusions from the colors of the Bs horizon and its single-grain structure. Besides being a younger soil, it has no structural organization, nor any evidence of cementation. The presence of the E horizon together with the podzolization, albeit incipient, allowed the classification of P7 as a Spodosol.

#### **CONCLUSIONS**

- 1. The Spodosols located in the area of the Coastal Plains are chemically, physically and morphologically different from each other and from Spodosols in the Restinga.
- 2. All Spodosols related to the Barreiras sediments have hardened horizon in the subsurface (ortstein and/ or fragipan), suggesting lateral import of silica and aluminum, resulting from the destruction of cohesive Ultisols clay located at higher altitudes.
- 3. The fragmentary nature of the fragipan suggests instability in the current climate conditions. In P7, the recent deposition of sandy (Holocene) and vegetation sediments did not allow the development of fragipan horizons.
- 4. In all soils except P7, higher Al levels were extracted by dithionite, oxalate, and pyrophosphate than of Fe, suggesting the need to reassess the classification of the suborders of the current SiBCS, which emphasizes the illuviation of Fe, as indicated by the nomenclature of two suborders: Ferriluvic and Ferrihumiluvic.
- 5. The optical density values of oxalate extract (DOox) of the spodic B horizons are 0.31 to 3.14, which is higher than the required in Spodic materials, per definition of the Soil Taxonomy. The P7, with values of 0.07 in Bs1 and 0.10 in the Bs2, did not meet this requirement.

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