

Division - Soil in Space and Time | Commission - Soil Genesis and Morphology

Calcination as an alternative method to classify Spodosols on the second categorical level

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ABSTRACT: The classification of Spodosols on the second categorical level (suborder), according to the Brazilian Soil Classification System (SiBCS), is done by observing the colors of genetic horizons in the field. The presence or absence of iron oxides is the main factor for this classification, and the color of the horizon is the criterion currently adopted. However, the simple observation of color in the field can be mistaken and cause an error in the definition of the second categorical level. This occurs when spodic horizons that do not contain iron oxides show high chroma color, or dark color due to the organic matter content, which masks the presence of illuviated Fe produced by podzolization. This can lead to errors, such as classifying *Humiluvico* horizons as *Ferriluvico*, and *Ferri-humiluvico* horizons as *Humiluvico*. These misunderstandings are currently solved through complex analyses using specific extractors and sophisticated equipment. Thus, obtaining a simple, fast, and inexpensive method to confirm the presence or absence of iron oxides in samples of spodic horizons is needed. This study tested an alternative method to assist in the determination of the second categorical level of the class of coastal plain Spodosols. The method consists of calcining samples in a muffle at 600 °C for 6 h. The calcination enabled to identify spodic horizons with and without presence of iron quickly; the result was compared with selective extraction analyses carried out using three different extractors: sodium pyrophosphate, ammonium acid oxalate, and sodium dithionite-citrate. The results obtained from these methods (calcination in muffle and selective extraction of iron oxides) enabled the identification of samples presenting colors varying from yellow to reddish, indicating the presence of iron, whereas those with the whitish color indicated absence or very low iron oxide levels. The 12 profiles of Spodosols were described and classified according to the SiBCS, and six profiles needed to be reclassified after the calcination procedure, which proved to be efficient.

Keywords: Podzol, spodic B horizon, soil classification, Podzolization.

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INTRODUCTION

Podzolization is the process responsible for the formation of spodic horizons, the main pedogenetic process involved with the genesis of Spodosols. This process consists of translocation of organic compounds associated or not with Al and/or Fe, with consequent accumulation of amorph and/or low-crystallinity compounds in the spodic horizons in the subsurface (Lundström et al., 2000; Schaetzl and Anderson, 2005). This accumulation is usually interpreted as a result from the vertical transport process (Andriessse, 1969; Anderson et al., 1982; Lundström et al., 2000); however, studies have shown that this transport and accumulation can occur by lateral fluxes (Jankowski, 2014; Bourgault et al., 2015) or combined with vertical fluxes.

Spodosols are found in Brazil mainly in the plains by the Rio Negro River, in the state of Amazonas, and in plains with sandy sediments in the states of Roraima and Acre. Its occurrence is also reported in the Tabuleiros Costeiros region, and over the coastal region between the states of Bahia and Rio Grande do Sul (Oliveira et al., 1992). Most Spodosols developed from sandy sediments of coastal plains have shown that the thick dark spodic horizons are formed by humus accumulation due to lateral fluxes of water. These soils occur, in general, in plain areas connected by the water table; the moving of water laterally transports colloidal particles constituted of dissolved organic carbon, which increasingly saturate the pores of the sandy source material in the fluctuation zone of the water table (Vidal-Torrado and Ferreira, 2017).

The Spodosol order in the Brazilian Soil Classification System (SiBCS) is divided into three suborders: Humiluvico, Ferri-Humiluvico, and Ferriluvico (Santos et al., 2018), indicating, respectively, Spodosols with humus accumulation (identified by the presence of Bh and/or Bhm genetic horizons); humus with iron compounds (Bhs and/or Bhsm); and only iron accumulation (Bs and/or Bsm) in the spodic horizons. In any of these cases, aluminum is always present and is essential for their formation (Santos et al., 2018).

More cemented spodic horizons, described as Bhm, Bsm, and Bhsm, are also called *ortstein*. The Bhm horizons are strongly cemented by organic matter that fills interstitial spaces and coats the sandy material, filling the porosity between grains and forming stable polymers that are more or less saturated by Al and/or Fe after successive wetting and drying cycles (Andriessse, 1969; De Coninck, 1980; Buurman and Jongmans, 2005).

The fit of Spodosols in the respective suborder of the SiBCS is done, in general, through the identification of the genetic horizons in the field by a pedologist; and the denomination is done by interpretation of probable organometallic compounds accumulated and present in the horizons spodic. The presence of iron, combined or not with humus and cementation (Bhs and Bhsm or Bs and Bsm, respectively), is identified based on the color of the horizons because of the lack of a quantitative criterion related to the minimum iron content required to qualify the genetic horizons. When the horizons present dark colors combined with ochre shades (reddish, yellowish-red, reddish-brown, etc.), they are usually identified as Bhs, or Bhsm horizon (when more cemented); when they present only dark colors, as Bh or Bhm; and when they present brighter colors, but with very little or no darkening by organic matter, they are identified only as Bs or Bsm.

In many cases, when dealing with hydromorphic or non-hydromorphic Spodosols, field observations have not shown correspondence with results of laboratory analyses. Several soils, whose dark spodic horizons were identified as Bh (or Bhm), presented expressive iron contents, but were classified as *Espodossolos Humiluvicos*. In other soils, the dark colors with ochre shades apparently indicate high Fe contents, the genetic horizon is identified as Bhs, and the soils end up being classified as *Espodossolos Ferri-Humiluvicos*, when in fact, the Fe contents are very low and the ochre color is due to organic compounds present in the soil.

The high variation in Fe oxide and organic carbon contents in spodic horizons, the uncertainties on the identification of genetic horizons based only on the morphology observed in the field, and their consequences for the classification of Spodosols to the second categorical level show the importance of defining simple and practical methods that enable to distinguish spodic horizons with humus accumulation (Bh or Bhm) from those with humus accumulation associated with iron (Bhs or Bhsm) or from those with only iron accumulation (Bs or Bsm).

Calcination of samples from spodic horizons enables the elimination of all impregnated organic matter, and samples that have organic matter complexed with Fe oxides will present colors with shades varying from light yellow to reddish after calcination. Samples that contain only organic matter complexed with Al oxide will show whitish colors, indicating absence of Fe oxide complexed with organic matter.

The objective of this study was to test a method that involves the calcination of samples of spodic horizons of 12 Spodosol profiles in the northern Santa Catarina Coastal Plain, Brazil, with variation of morphology and classification of B spodic horizons in the field, by eliminating the organic carbon and, based on the evaluation of the resulting color, confirming the presence or absence of Fe; thus, ensuring a more precise classification of Spodosols to the second categorical level used by the SiBCS.

MATERIALS AND METHODS

Study Area

The study area is in the municipalities of Araquari and Balneário Barra do Sul, in the northern coast of the state of Santa Catarina, Brazil (Figure 1), an extensive coastal plain area, formed by Pleistocene sandy sediments from marine transgressions and regressions.

Analytical procedures

Samples from profiles of 12 Spodosols and four Quartzipsamments were collected, as described by Santos et al. (2015). The prospectations were done by surveys using a manual auger, followed by opening of trenches with the aid of a backhoe. In environments where the water table level was very close to the surface, water pumps were used for draining to enable the profile descriptions. All samples were collected, placed in plastic bags, and then dried in an oven at 50 °C.

Soil samples were then disaggregated with a wood roll over a rubber sheet and sieved in a 2-mm mesh sieve. Subsequently, they were homogenized and split with the aid of a 16-channel splitter made of galvanized metal sheets. All samples were then stored in 1-liter plastic pots. The aliquots used for the analyses of characterization were also obtained by splitting the samples up to fractions of approximately 50 g and placing them in 50-mL plastic containers, aiming to obtain aliquots that best represented the sample.

The classification of Spodosol profiles to the second categorical level of the Brazilian Soil Classification System (SiBCS) (Santos et al., 2018) was done by two methods: 1) identification of genetic horizons based on the morphology observed in the field, mainly the color; 2) based on results of analyses of calcination of samples at 600 °C, considering the resulting color after the calcination, supported by the iron contents found.

The calcination technique used was adapted from a method of the Santos et al. (2018) to determine organic matter contents in Histosols (*Organossolos*), according to Lynn et al. (1974). The samples were placed in porcelain capsules containing 20 grams of bulk soil, then they were kept in a muffle for 6 h at 600 °C.

After the calcination, the samples were placed in 10-mL transparent acrylic containers, which were arranged side by side to containers containing samples in their natural

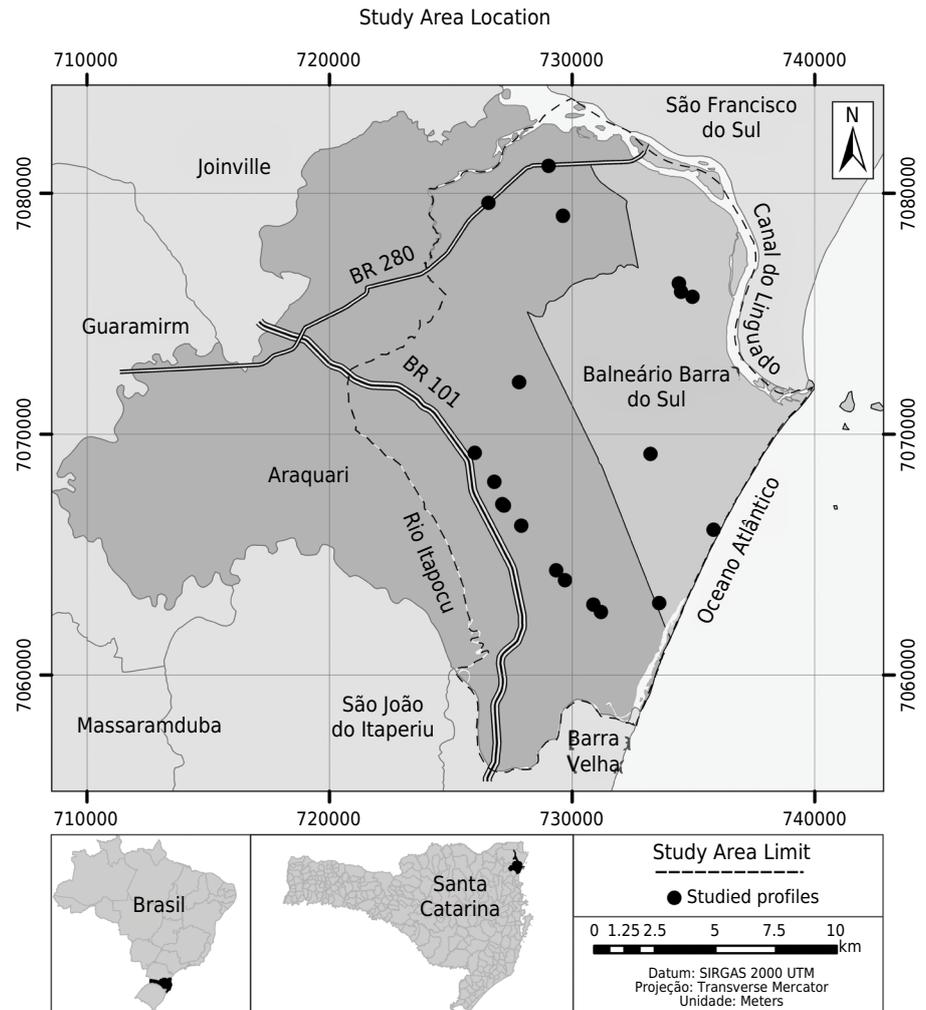


Figure 1. Location of the study area in the northern coast of the state of Santa Catarina, Brazil.

state. The samples were subjected to color classification using a Munsell's chart, and photographed with a digital camera (Nikon D5200) coupled to a tripod and using a dark background to highlight the differences between the samples. All samples were calcined and compared with results obtained from analysis of Fe content extracted with sodium pyrophosphate, ammonium oxalate, and dithionite-citrate-bicarbonate, according to Buurman et al. (1996).

Total carbon was determined using a carbon analyzer (Multi/NC 2100; Analytik Jena, Jena, Germany) coupled to a module for solids. The samples were ground, sieved (0.250 mm), homogenized and, then, maintained in dryers for 24 h. A certified soil sample (LUF4, 1.77 % carbon) was used for the readings in the device to evaluate its precision. The readings were made in quartz cuvettes with approximately 8 mg of the sample, in three replications, using an analytical balance with precision of 0.0001 mg (ATX 224; Shimadzu, Kyoto, Japan).

The analytical procedures used for the Al and Fe extractions were done following the methods described by Buurman et al. (1996). The Fe extraction with sodium pyrophosphate (Fe_p) was done using 0.5 g of ground soil, which was sieved in a 0.250-mm mesh sieve and subjected to extraction with 50 mL of a 0.1 mol L⁻¹ Fe_p solution (pH 10) and shaken for 16 h. The Fe and Al extraction with acid ammonium oxalate (Fe_{ox}) was done using 0.7 g of ground soil, which was sieved in a 0.250-mm mesh sieve in 35 mL of a Fe_{ox} solution (pH 3) and shaken for four hours in the dark. The Fe extraction with dithionite-citrate-bicarbonate

(Fe_d) was done using 1.00 g of ground soil, which was sieved in a 0.250-mm mesh sieve in 60 mL of sodium citrate and sodium dithionite solution and shaken for 16 h. All these suspensions were centrifuged for 15 min at 2.500 rpm, with four drops of coagulant (Superfloc[®], Kemira, Helsinki, Finland) at 0.2 %, followed by filtration of the supernatant using filter paper (11 µm).

Iron and Al concentrations were determined in atomic absorption spectroscopy (AAS) using a spectrometer (AAnalyst 200; PerkinElmer, Waltham, USA). The results for these elements were expressed as mean of two analyses that differed by less than 10 %. After calibrating the AAS, the limits of quantification were calculated according to the equation $LQ = Fd \times (M \pm t \times s)$, in which Fd is the factor of dilution of samples; M is the mean of blank tests; t is the value of the Student t test at a confidence interval of 99 %, as a function of number of degrees of freedom of replicated measurements; and s is the standard deviation of the blanks.

RESULTS

The analytical data of the 12 Spodosol profiles evaluated are presented in table 1. All horizons were initially described and classified in the field, and after the analyses of calcination, they were reclassified when necessary. Among the evaluated profiles, the spodic horizons of the profiles P2, P10, P12, P13, P15, and P17 presented no Fe by any of the extractors used (Table 1), differing from the profiles P4, P6, P7, P8, P14, and P16.

The taxonomical classification of Spodosols presented in table 1 was done according to the SiBCS, based on the results of Fe contents. The spodic horizons of the profiles P6, P8, P12, P14, P15, and P17 were reclassified to the second categorical level.

The analytical data (Table 1) were compared with data of a color spreadsheet obtained with calcination, which resulted in different colors for each calcined sample. These samples were compared qualitatively in an arrangement termed comparison table (Figure 2). The comparison table showed that some samples presented different shades of white. This color indicates very low amounts of Fe compounds in the samples. The samples that presented different shades, with yellowish to reddish colors, indicated the presence of Fe compounds.

The samples of Spodosols of the profiles P4, P10, P12, P13, P15, and P17 presented whitish colors after calcination, some slightly yellowish, indicating no or few Fe compounds associate with humus in the spodic horizons. The opposite occurred for the profiles P6, P7, P8, and P14, which presented dark color in the field (masking the color of Fe compounds), but presented bright colors (Table 1) after calcination. Specifically, the samples from the horizons Bhs1, Bhs2, and Bhsm of the profile P6; Bhsm of the profile P7; Bhsm and Bhs of the profile P8; and Bhs1 and Bhs2 of the profile P14.

In the profile P16, where the podzolization was confirmed by humus accumulation due to lateral fluxes (Heberle, 2017), horizons that were classified in the field as Bh1, Bh2, and Bh3 presented yellowish-red colors after calcination, indicating the presence of Fe associated with humus. Therefore, the Fe compounds were probably from the parent material and did not fit to the typical podzolization process of accumulation of organometallic complexes with iron.

Other soil class that assisted in the understanding of the functionality of the calcination of samples is the Quartzipsamment (*Neossolo Quartzarênico*) (Table 2). After calcination, the samples of subsurface horizons, whose Fe contents were higher than those in upper horizons, presented increases in shades of yellowish-red color (Figure 2). The surface horizons of the profiles P1 and P5, where the Fe contents quantified by the three extractors were low or very low, showed white (P1) or very white (P5) colors after calcination. In the

Table 1. Analytical data of total carbon (TC) and Fe contents in soil samples (Spodosols) extracted with sodium pyrophosphate (Fe_p), acid ammonium oxalate (Fe_{ox}), dithionite-citrate-bicarbonate (Fe_d); and their colors obtained in wet basis, dry basis, and after calcination procedure

Samples ⁽¹⁾		Fe_p	Fe_{ox}	Fe_d	TC	Color (Munsell)		
Lab.	Field					Wet ⁽²⁾	Dry ⁽³⁾	Calcined ⁽⁴⁾
g kg ⁻¹								
<i>P2 - Espodossolo Humilúvico Órtico típico</i> Albic Carbic Podzols (Arenic, Drainic, Hyperspodic) ⁽⁵⁾								
A	A	nd	nd	0.24	6.09	10YR 5/1	10YR 4/1	7.5YR 8.5/2
AE	AE	nd	nd	0.03	0.06	10YR 6/1	10YR 5/1	7.5YR 9/1
E	E	nd	nd	nd	0.08	7.5YR 7/0	7.5YR 7/1	N9.5/
Bh	Bh	nd	nd	0.06	7.62	7.5YR 5/1	7.5YR 3/1	10YR 9/2
Bhm	Bhm	nd	nd	0.07	33.6	10YR 4/3	7.5YR 2.5/2	10YR 9/1
<i>P4 - Espodossolo Humilúvico Órtico dúrico</i> Albic Carbic Ortsteinic Podzol (Arenic, Drainic, Hyperspodic) ⁽⁵⁾								
A	A	nd	nd	0.13	6.26	7.5YR 5/1	10YR 4/1	7.5YR 8.5/2
E1	E1	nd	nd	0.00	0.13	10YR 7/2	10YR 7/2	7.5YR 9.5/1
Bh	Bh	nd	nd	0.11	31.2	10YR 5/1	10YR 3/1	10YR 9/2
Bhm	Bhm	0.43	0.66	0.86	52.2	10YR 4/3	7YR 2.5/1	10YR 8.5/2
BhE	BhE	nd	nd	0.03	5.31	7.5YR 4/1	7.5YR 3/1	7.5YR 9.5/1
EBh	EBh	nd	nd	nd	4.14	7.5YR 5/1	7.5YR 3/1	10YR 9/1
E2	E2	nd	nd	nd	0.17	7.5YR 7/1	7.5YR 6/2	7.5YR 8.5/1
BhBhm	BhBhm	nd	nd	nd	22.5	7.5YR 2.5/2	10YR 2/0*	10YR 9/1
<i>P6 - Espodossolo Ferri-humilúvico Órtico dúrico</i> Albic Ortsteinic Podzols (Arenic) ⁽⁵⁾								
Ap	Ap	nd	nd	0.03	28.4	7.5YR 5.5/1	7.5YR 4/1	7.5YR 8.5/2
A	A	nd	nd	nd	3.38	7.5YR 5.5/1	7.5YR 4/1	10YR 8.5/1
E	E	nd	nd	nd	0.124	7.5YR 7/1	10YR 7/2	10YR 8.5/1
Bh1	Bh1	0.54	0.66	0.74	11.1	7.5YR 5/2	7.5YR 3/2	7.5YR 8.5/2
Bhs1	Bh2	2.26	4.75	4.14	31.6	10YR 3/2	7.5YR 3/1	5YR 6/8
Bhsm	Bhm	12.78	9.55	20.43	42.7	10YR 4/4	7.5YR 3/1	2.5YR 4/8
Bhs2	Bh3	2.17	3.81	3.68	33.1	7.5YR 4/2	7.5YR 3/2	5YR 7/6
BhBhm	BhBhm	nd	nd	nd	8.54	7.5YR 4/1	7.5YR 3/1	10YR 9.5/1
Bh2	Bh4	nd	0.31	0.15	3.23	10YR 5/3	10YR 3/4	10YR 8.5/2
<i>P7 - Espodossolo Ferri-humilúvico Hidromórfico dúrico</i> Albic Ortsteinic Podzols (Arenic, Oxyaquic) ⁽⁵⁾								
A	A	nd	nd	nd	28.7	10YR 6/1	10YR 5/1	7.5YR 8.5/1
EA	EA	nd	nd	nd	0.79	7.5YR 6/1	10YR 6/1	7.5YR 9/1
E	E	nd	nd	nd	0.17	7.5YR 7/1	10YR 7/1	7.5YR 8.5/1
Bh	Bh	0.31	0.27	0.20	45.1	7.5YR 3/2	10YR 2/2	2.5YR 9/2
Bhsm	Bhsm	8.34	7.97	13.25	34.9	10YR 4/4	5YR 2.5/2	2.5YR 9/8
Bhm	Bhm	0.21	nd	0.04	46.9	10YR 3/2	10YR 2/0	10YR 8.5/1
BhE	BhE	nd	nd	nd	8.05	10YR 6/1	10YR 2/0	10YR 8.5/2
<i>P8 - Espodossolo Ferri-humilúvico Hidromórfico típico</i> Albic Podzols (Arenic, Drainic, Oxyaquic) ⁽⁵⁾								
A	A	0.28	0.35	0.54	13.6	10YR 5/1	10YR 3/1	5YR 8/4
EA	EA	nd	nd	nd	2.51	7.5YR 7/1	10YR 5/1*	7.5YR 9.5/1
BhE	BhE	nd	nd	0.02	6.16	7.5YR 7/1	10YR 5/2*	10YR 8.5/2
Bh	Bh1	0.27	0.24	0.30	24.4	10YR 3/2	10YR 2/1	10YR 8.5/2
Bhsm	Bhm	2.54	0.70	0.36	29.4	10YR 4/2	10YR 2/2	5YR 6/8

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Samples ⁽¹⁾		Fe _p	Fe _{ox}	Fe _d	TC	Color (Munsell)		
Lab.	Field					Wet ⁽²⁾	Dry ⁽³⁾	Calcined ⁽⁴⁾
g kg ⁻¹								
Bhs	Bh2	0.79	0.62	1.06	7.59	10YR 4/2	10YR 3/1*	5YR 7/6
C	C	nd	nd	nd	1.09	2.5YR 7/3	2.5YR 5/4	7.5YR 8.5/1
P10 - <i>Espodossolo Humilúvico Hidromórfico típico</i> Albic Carbic Podzols (Arenic, Oxyaquic) ⁽⁵⁾								
A1	A1	nd	nd	nd	35.5	7.5YR 6/1	7.5YR 4/1	7.5YR 8.5/1
A	A	nd	nd	nd	4.92	7.5YR 7/1	7.5YR 5/1	10YR 8/1
E1	E1	nd	nd	nd	0.12	7.5YR 7/0	7.5YR 6/1	10YR 8/1
Bh1	Bh1	nd	nd	0.10	16.7	10YR 4/3	10YR 2/1	7.5YR 8.5/1
Bh2	Bh2	nd	nd	nd	3.54	7.5YR 5/1	7.5YR 3/1	10YR 8/1
E2	E2	nd	nd	nd	0.11	7.5YR 7/0	7.5YR 6/1	2.5Y 8/1
P12 - <i>Espodossolo Humilúvico Hidromórfico dúrico</i> Albic Carbic Ortsteinic Podzols (Arenic, Drainic, Oxyaquic) ⁽⁵⁾								
Ap	Ap	0.75	0.82	1.49	66.4	10YR 5/1	10YR 2/1	2.5YR 7/6
A	A	nd	nd	0.15	99.25	7.5YR 4/1	7.5YR 2.5/1	2.5YR 8/1
E1	E1	nd	nd	nd	10.8	7.5YR 6/1	7.5YR 3/1	N9/
Bh1	Bh	nd	nd	nd	18.1	10YR 4/1	10YR 2/0	10YR 8.5/1
Bh2	Bs	nd	nd	nd	7.66	10YR 4/4	10YR 2/2	N9/
E2	E2	nd	nd	nd	1.45	10YR 6/3	10YR 4/3	N9.5/
Bhm	Bhm	nd	nd	nd	38.6	10YR 3/2	10YR 2/1	N9/
P13 - <i>Espodossolo Humilúvico Hidromórfico dúrico</i> Albic Carbic Ortsteinic Podzols (Arenic, Drainic, Oxyaquic) ⁽⁵⁾								
Ap	Ap	nd	nd	nd	44.7	10YR 6/1	10YR 4/1	7.5YR 8.5/1
A	A	nd	nd	0.06	128	7.5YR 5/1	7.5YR 2.5/1	10YR 8.5/2
EA	EA	nd	nd	nd	49.1	10YR 5/2	10YR 2/2	7.5YR 8.5/1
E	E	nd	nd	nd	1.08	10YR 6/1	10YR 3/2	10YR 9.5/1
Bh1	Bh1	nd	nd	nd	34.7	10YR 4/1	10YR 2/2	10YR 9/1
Bh2	Bh2	nd	nd	nd	92.2	10YR 3/1	10YR 2/0	10YR 8.5/1
Bhm	Bhm	nd	nd	nd	51.7	2.5YR 3/2	10YR 2/0	7.5YR 8.5/1
P14 - <i>Espodossolo Ferri-humilúvico Órtico típico</i> Albic Podzols (Arenic, Hyperspodic) ⁽⁵⁾								
A	A	nd	nd	0.06	32.6	10YR 5/1	10YR 4/1	7.5YR 8/2
EA	EA	nd	nd	nd	2.42	7.5YR 6/1	10YR 5/2	7.5YR 8/1
E	E	nd	nd	nd	0.715	7.5YR 6/1	10YR 6/2	7.5YR 8/1
Bhs1	Bh1	5.84	8.40	6.63	31.1	10YR 3/2	7.5YR 3/1	5YR 7/4
Bhs2	Bh2	0.93	1.09	1.76	42.1	10YR 2/2	10YR 2/1	10YR 9/2
Bh	Bh3	nd	0.26	0.34	12.6	7.5YR 3/1	10YR 2/1	10YR 8.5/2
P15 - <i>Espodossolo Humilúvico Órtico típico</i> Albic Carbic Ortsteinic Podzol (Arenic, Drainic, Hyperspodic) ⁽⁵⁾								
A	A	nd	nd	nd	32.9	7.5YR 5/1	10YR 2/1	N
EA	EA	nd	nd	nd	6.10	10YR 6/1	10YR 6/2	10YR 8/1
E	E	nd	nd	nd	0.39	10YR 3/2	10YR 7/1	10YR 8.5/1
Bh1	Bh1	nd	nd	nd	22.6	7.5YR 3.5/2	7.5YR 2/1	7.5YR 8/2
Bhm1	Bhm	nd	nd	nd	57.8	7.5YR 3/2	10YR 2/1	7.5YR 8/1
Bh2	Bh2	nd	nd	nd	43.9	7.5YR 4/2	10YR 2/1	7.5YR 8/1
Bhm2	Bhsm	nd	nd	nd	37.4	10YR 6/1	10YR 2/2	7.5YR 8.5/1

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Samples ⁽¹⁾		Fe _p	Fe _{ox}	Fe _d	TC	Color (Munsell)		
Lab.	Field					Wet ⁽²⁾	Dry ⁽³⁾	Calcined ⁽⁴⁾
g kg ⁻¹								
P16 - <i>Espodosolo Humilúvico Órtico típico</i> Entic Podzols (Arenic) ⁽⁵⁾								
A	A	2.40	3.83	32.12	40.4	10YR 6/1	10YR 3/1	5YR 7/4
AE	AE	4.72	5.31	6.66	23.5	10YR 5/2	10YR 3/2	5YR 6/6
Bh1	Bh1	6.00	7.70	9.29	18	10YR 5/3	10YR 3/3	5YR 6/6
Bh2	Bh2	4.83	5.81	7.17	19.0	10YR 4/3	7YR 2.5/2	7.5YR 6/6
Bh3	Bh3	5.12	7.21	9.17	21.7	10YR 3/2	10YR 2/1	7.5YR 6/8
P17 - <i>Espodosolo Humilúvico Órtico típico</i> Albic Carbic Ortsteinic Podzols (Arenic) ⁽⁵⁾								
A	A	nd	nd	0.14	60.2	10YR 4/1	10YR 2/1	7.5YR 8.5/1
E	E	nd	nd	nd	1.42	10YR 6/1	10YR 5/1	10YR 8.5/1
Bh1	Bh1	nd	nd	nd	11.4	7.5YR 4/1	10YR 3/1	N
Bh2	Bh2	nd	nd	nd	30.6	10YR 2/2	10YR 2/1	7.5R 8.5/1
Bhm	Bhsm	nd	nd	nd	8.20	10YR 4/4	7.5YR 2.5/3	7.5YR 8.5/1
C	C	0.28	0.29	0.27	2.45	2.5Y 5/3	10YR 3/3	7.5YR 8/2

⁽¹⁾ Lab. refers to identification of horizons in laboratory, after calcination; and Field refers to identification of horizons done in the field. nd: non-detected.
⁽²⁾ Wet color described during the morphological analyses done in the field. ⁽³⁾ Dry color described after air drying the bulk soil before calcination.
⁽⁴⁾ Color described after calcination (unground sample) at 600 °C for 6 hours. ⁽⁵⁾ Classified according to World Reference Base for Soil Resources (2014).

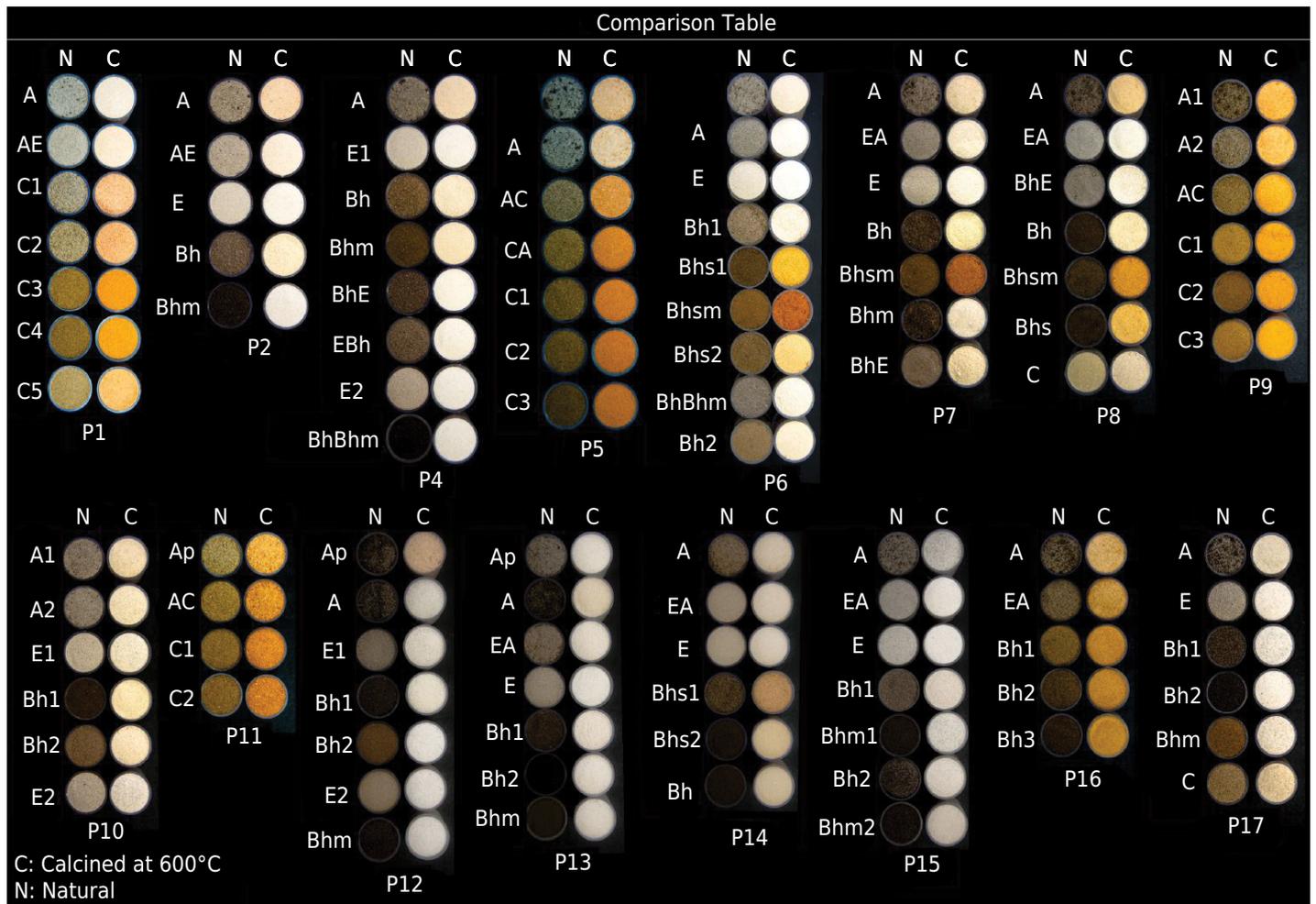


Figure 2. Comparison table of all soil samples before and after calcination at 600 °C. The names of the horizons are in accordance with the reclassification after the application of the calcination technique.

Table 2. Analytical data of total carbon (TC) and Fe contents in soil samples (Quartzipsamments) extracted with sodium pyrophosphate (Fe_p), acid ammonium oxalate (Fe_{ox}), dithionite-citrate-bicarbonate (Fe_d), and their colors obtained in wet basis, dry basis, and after calcination procedure

Sample	Fe_p	Fe_{ox}	Fe_d	TC	Color (Munsell)		
					Wet ⁽¹⁾	Dry ⁽²⁾	Calcined ⁽³⁾
g kg ⁻¹							
<i>P1 - Neossolo Quartzarênico Órtico espodossólico Lamellic Sideralic Arenosols (Aeolic)⁽⁴⁾</i>							
A	nd	nd	0.17	3.74	10YR 4/1	10YR 6/1	2.5YR 8/2
EA	nd	nd	0.31	0.04	10YR 5/2	10YR 6/2	2.5YR 8/3
C1	3.81	6.21	5.93	6.40	7.5YR 3/2	7.5YR 5/2	2.5YR 7/6
C2	4.17	8.28	8.58	7.84	10YR 3/4	10YR 5/3	2.5YR 6/6
C3	2.44	3.22	3.51	4.94	10YR 4/4	10YR 5/4	5YR 5/8
C4	1.53	1.89	2.91	5.56	10YR 3/4	10YR 4/4	5YR 6/8
C5	0.58	0.46	0.93	0.41	10YR 5/3	10YR 6/3	5YR 5/8
<i>P5 - Neossolo Quartzarênico Órtico típico Sideralic Arenosols (Aeolic)⁽⁴⁾</i>							
Ap	0.43	0.43	0.63	23.3	10YR 5/2	10YR 6/1	2.5YR 7/3
A	0.41	0.51	0.75	31.2	10YR 3/1	10YR 4/1	2.5YR 8/4
AC	2.87	3.55	3.51	8.25	10YR 4/2	10YR 5/2	2.5YR 6/6
CA	3.24	4.45	4.32	6.6	10YR 4/4	10YR 5/4	2.5YR 5/8
C1	3.86	4.49	4.20	6.1	10YR 4/6	10YR 5/4	2.5YR 5/8
C2	2.59	3.84	3.90	5.42	7.5YR 3/3	10YR 5/4	2.5YR 5/8
C3	2.29	2.36	3.30	4.62	7.5YR 3/3	10YR 4/4	2.5YR 5/8
<i>P9 - Neossolo Quartzarênico Órtico típico Sideralic Arenosols (Aeolic)⁽⁴⁾</i>							
A1	2.67	3.23	4.29	37.9	7.5YR 4/2	7.5YR 5/1	2.5YR 6/6
A2	3.60	4.15	5.42	34.2	7.5YR 3/2	7.5YR 4/1	2.5YR 6/6
CA	5.30	5.55	7.41	28.8	7.5YR 4/3	10YR 4/3	2.5YR 5/6
C1	4.87	5.86	8.13	7.55	7.5YR 5/8	10YR 5/6	2.5YR 5/8
C2	3.91	5.72	7.22	6.79	7.5YR 4/3	10YR 5/4	2.5YR 5/8
C3	2.56	2.13	4.79	0.79	7.5YR 5/6	10YR 5/6	5YR 6/8
<i>P11 - Neossolo Quartzarênico Órtico típico Sideralic Arenosols (Aeolic)⁽⁴⁾</i>							
A	1.43	1.86	3.89	4.83	7.5YR 5/3	7.5YR 6/3	2.5YR 6/6
AC	3.46	4.39	6.38	5.48	7.5YR 4/4	7.5YR 5/4	2.5YR 5/8
C1	2.66	3.41	5.67	5.86	7.5YR 4/6	10YR 5/6	2.5YR 5/8
C2	2.06	1.99	3.42	3.64	7.5YR 4/6	10YR 5/6	2.5YR 5/8

nd: non-detected. ⁽¹⁾ Wet color described during the morphological analyses done in the field. ⁽²⁾ Dry color described after air drying the bulk soil before calcination. ⁽³⁾ Color described after calcination (unground sample) at 600 °C for 6 hours. ⁽⁴⁾ Classified according to World Reference Base for Soil Resources (2014).

other surface samples (P9 and P11), where the Fe contents were higher and the original colors were darker, the elimination of organic matter by calcination resulted in soils with brighter colors (2.5YR 5/8).

DISCUSSION

The study was conducted in a toposequence that comprises lateral transformations of Quartzipsamments-Spodosols; thus, the understanding of the relationship between soil and relief and the formation of coastal plains subsidized the understanding of the dynamics

of Fe compounds over the toposequence. This information enabled the understanding of the response of each soil sample to the effects of calcination.

Sediments from the Pleistocene in well-drained marine-eolic terraces are subjected to higher Fe compound accumulation and oxidation over time, naturally enriching the parent material and leading to the expression of brighter colors, as shown by Suguio and Tessler (1984). The reddening of sands intensifies as the distance from the coast increase. This process of reddening is known as rubefaction (Norris, 1969; Folk, 1976; Williams and Yaalon, 1977), and it represents a pedogenesis stage in which Fe is released from primary minerals and forms Fe oxides that coat quartz particles in soils as a reddish thin film (Buol et al., 1973).

During the evolution of coastal plains, the shoreline retreat and erosive processes promoted a gradual deformation of originally formed beach ridges, leading to the formation of a practically plain relief, which has small altitude variations that are sufficient for the formation of well-drained terraces (beach ridges), where Quartzipsamments predominate, as well as poor-drained areas (between beach ridges) with different hydromorphism levels where Spodosols predominate.

Spodosols present variation in hydromorphism levels, not only due to their lower topographic position, but also due to the genesis and typology of spodic horizons. In many cases, strongly cemented horizons defined as ortsteins (Bm, Bhm, Bhsm, or Bsm) modify the vertical and lateral water flows. These horizons change the local water dynamics, causing situations in that profiles at the same elevation present different morphological variations.

The morphological diversity of the Spodosols in the present study made the classification of profiles to the second categorical level of the SiBCS (*Humiluvico*, *Ferri-Humiluvico*, and *Ferriluvico*) more difficult because of the deficient criteria currently proposed by the SiBCS for identification of these genetic horizons (Bh, Bhs, and Bs) and their cemented correspondents (Bhm, Bhsm, and Bsm). The dark color of spodic horizons is not always related only to accumulation of organic matter, since Fe compounds associated with it can be found; and ochre colors may not result from the presence of expressive Fe contents, but from the type of organic compounds present in them.

Chemical analysis of Fe contents can contribute to a safer identification of genetic horizons and, thus, to their adequate fit to the suborder level; however, the SiBCS does not define limits for Fe contents for the fitting of these soils to the second categorical level.

Moreover, the quantitative determination of Fe oxide contents in samples of spodic horizons is laborious and requires several reagents and time-consuming procedures. Therefore, the qualitative estimation of presence of Fe compounds by calcination of soil samples is a faster and more practical procedure for identification of presence of significant amounts of Fe, associated or not with organic compounds, which enable a more certain fit of Spodosols to the suborder level in the SiBCS.

Profiles that presented horizons with high chroma in spodic horizons (Figure 3), such as the profiles P12 and P17, showed no presence of Fe when analyzed with selective extractors; however, they presented colors that indicated presence of Fe. After the calcination of the samples, the resulting colors were whitish, confirming the absence of iron (Figure 2).

The inverse was also observed: profiles presenting dark colors, such as the horizons Bhsm and Bhs of P8, and Bhs1 and Bhs2 of P14 (Figure 3), when analyzed chemically and by calcination, showed expressive iron contents (Table 1) and high chroma (Figure 2), respectively.

Some profiles of Spodosols initially classified as *Espodosolos Ferrilúvicos* or *Humilúvicos* needed to be changed to *Humilúvicos* or *Ferri-Humilúvicos* after calcination and chemical analysis of the samples (Table 3).

The development of the fast and practical test of calcination for identification of horizons with or without accumulation of Fe compounds avoided a mistaken classification, for example, of a horizon as Bs or Bhs exclusively based on its morphology, as described by the SiBCS. The principle of the test is the removal of the organic matter present in the samples by means of burning.

The samples that had been morphologically erroneously classified as Bs or Bhs could be redefined as Bh horizons; and samples that presented no morphological characteristics of horizons with presence of iron oxides were reclassified as Bhs (Table 3), as done for the profiles P6, P8, and P14.

The profiles P6, P8, and P14 presented spodic horizons with high contents of Fe_{ox} (Table 1), as described in the SiBCS. However, the horizons Bhs1 and Bhsm of the profile P6 did not present the typical color that indicates presence of Fe oxides. The presence of Fe in these samples was clearly observed only after calcination. The same occurred for the profiles P8 and P14.

Profiles with morphological characteristics that indicate Bs horizons showed very low Fe contents after calcination, which was not shown by the color of the samples (Table 1). Samples from P12 Bh2 and P17 Bhm presented characteristics of Bs with brownish color in the field (Figure 3), but the calcination showed that this color was due to the presence of organic matter, since the colors after calcination changed to whitish.

The indicative color of presence of Fe compounds by calcination could be identified by a slightly intense reddening, and by colors that vary from yellow to orange (Figure 2). Considering only samples that had high chroma colors after calcination - Bhs1, Bhsm, and Bhs2 of the profile P6, Bhsm of the profile P7, Bhsm and Bhs of the profile P8, and Bh1, Bh2, and Bh3 of the profile P16 - and the data in table 1, the ranges of Fe contents by the three extractors used were calculated, showing expression of high chroma colors after calcination, resulting in the following ranges of iron contents: $Fe_p = 0.79$ to 12.78 g kg^{-1} ; $Fe_{ox} = 0.62$ to 9.55 g kg^{-1} ; $Fe_d = 0.36$ to 20.43 g kg^{-1} . The ranges of Fe contents for the three extractors would be: $Fe_p = 2.26$ to 12.78 g kg^{-1} ; $Fe_{ox} = 3.81$ to 9.55 g kg^{-1} ; $Fe_d = 3.68$ to 20.43 g kg^{-1} .

Based on these ranges and considering the pertinence of establishing minimum Fe contents for the characterization of *Espodossolos Ferri-Humilúvicos* or *Ferrilúvicos*, these minimum values found can be considered for these assessments.

Table 3. Classification of profiles before (morphological description in the field) and after application of the calcination procedure

Profile	Horizon in the field	Classification in the field	Horizon after the calcination	Classification after calcination
P6	Bh2	<i>Espodossolo Humilúvico Órtico dúrico</i>	Bhs1	<i>Espodossolo Ferri-Humilúvico Órtico dúrico</i>
	Bh3		Bhs2	
P8	Bhm	<i>Espodossolo Humilúvico Hidromórfico típico</i>	Bhsm	<i>Espodossolo Ferri-Humilúvico Hidromórfico típico</i>
	Bh2		Bhs	
P12	Bs	<i>Espodossolo Ferrilúvico Hidromórfico típico</i>	Bhs2	<i>Espodossolo Humilúvico Hidromórfico típico</i>
P14	Bh1	<i>Espodossolo Humilúvico Órtico típico</i>	Bhs1	<i>Espodossolo Ferri-Humilúvico Órtico típico</i>
	Bh2		Bh2	
P15	Bhsm	<i>Espodossolo Ferri-Humilúvico Órtico típico</i>	Bhm2	<i>Espodossolo Humilúvico Órtico típico</i>
P17	Bhsm	<i>Espodossolo Ferri-Humilúvico Órtico dúrico</i>	Bhm	<i>Espodossolo Humilúvico Órtico dúrico</i>

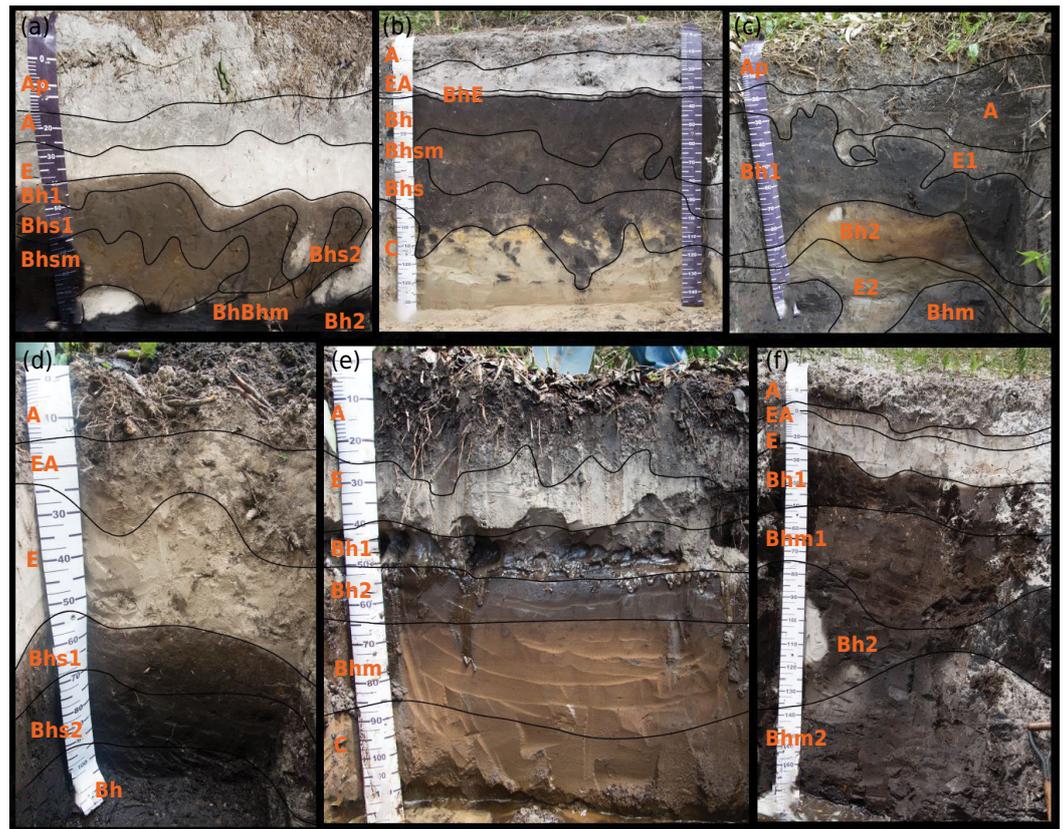


Figure 3. Profiles reclassified after calcination procedure: profile 6 reclassified from EK to ESK (a); profile 8 reclassified from EK to ESK (b); profile 12 reclassified from ES to EK (c); profile 14 reclassified from EK to ESK (d); profile 17 reclassified from ESK to EK (e); and profile 15 reclassified from ESK to EK (f).

The effects of calcination the organic matter resulted in the whitening of samples that did not contain Fe oxides, slightly yellowing of samples with very low Fe contents, and intense yellowing or even reddening of those that contained more Fe. Thus, samples containing Fe compounds that were masked by the dark color of organic matter showed, after the calcination process, presence of Fe by intensification of their yellowish or yellowish-red colors.

The color intensity (high chroma) is related to the form of Fe oxides present in the soil samples and to the level of topotactic transformations of Fe compounds during the calcination procedure. According to Scwtermann (1971), in sandy and hydromorphic soils, hematite is dissolved may reprecipitate as goethite or lepidocrocite, but never as hematite. Thus, their heating and consequent transformation can produce materials with different colors depending on the new oxides formed.

The thermal dehydration of goethite and lepidocrocite by increasing the temperature originates hematite and maghemite, respectively, by topotactic transformations (Cudennec and Lecerf, 2006). Goethite is directly transformed into hematite without any intermediate phase; contrastingly, after heating the lepidocrocite, it is transformed first into maghemite and then, at higher temperatures, into hematite, depending on the crystallinity and size of the particles (Cudennec and Lecerf, 2005).

According to Fang et al. (2003), the temperature for the formation of maghemite is approximately 249 °C; and for the formation of well-crystalized hematite from maghemite, it is above 599 °C. Considering the removal of organic matter and, additionally, the highlight of the expression of contents and form of Fe oxides present in the sample, it is possible that not all Fe oxyhydroxides are transformed into hematite. However, the temperature of 600 °C was sufficient for the intended application, showing yellowish or

yellowish-red colors, which express the presence of Fe compounds at significant amounts when they are associate with organic compounds, enabling the differentiation of Bh from Bhs horizons, and their cemented correspondents (Bhm and Bhsm).

Considering that the colors of Fe oxides present in the samples are shown after calcination, the use of this calcination technique is recommended for samples of spodic horizons. However, further analyses of processes involved with the genesis of Spodosols can also be used as a tool to assist in the detection of Fe compounds over the whole soil profile, including the parent material.

CONCLUSIONS

The calcination technique enabled the identification of horizons with illuviation of organic matter with or without iron oxides, without the need of analysis of selective extractions.

The use of the calcination technique made the classification of Spodosols to the second categorical level easier and substituted well the use of selective extractors, reducing the costs with chemical reagents, and obtaining fast and precise results.

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