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# RELATIONSHIP BETWEEN SOIL OXIDIZABLE CARBON AND PHYSICAL, CHEMICAL AND MINERALOGICAL PROPERTIES OF UMBRIC FERRALSOLS<sup>(1)</sup>

Flávio Adriano Marques<sup>(2)</sup>, Márcia Regina Calegari<sup>(3)</sup>, Pablo Vidal-Torrado<sup>(4)</sup> & Peter Buurman<sup>(5)</sup>

## SUMMARY

The occurrence of Umbric Ferralsols with thick umbric epipedons ( $\geq 100$  cm thickness) in humid Tropical and Subtropical areas is a paradox since the processes of organic matter decomposition in these environments are very efficient. Nevertheless, this soil type has been reported in areas in the Southeast and South of Brazil, and at some places in the Northeast. Aspects of the genesis and paleoenvironmental significance of these Ferralsols still need a better understanding. The processes that made the umbric horizons so thick and dark and contributed to the preservation of organic carbon (OC) at considerable depths in these soils are of special interest. In this study, eight Ferralsols with a thick umbric horizon (UF) under different vegetation types were sampled (tropical rain forest, tropical seasonal forest and savanna woodland) and their macromorphological, physical, chemical and mineralogical properties studied to detect soil characteristics that could explain the preservation of high carbon amounts at considerable depths. The studied UF are clayey to very clayey, strongly acidic, dystrophic, and Al-saturated and charcoal fragments are often scattered in the soil matrix. Kaolinites are the main clay minerals in the A and B horizons, followed by abundant gibbsite and hydroxyl-interlayered vermiculite. The latter was only found in UFs derived from basalt rock in the South of the country. Total carbon (TC) ranged from 5 to 101 g kg<sup>-1</sup> in the umbric epipedon. Dichromate-oxidizable organic carbon represented nearly 75 % of TC in the thick A horizons, while non-oxidizable C, which includes recalcitrant C (e.g., charcoal), contributed

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to the remaining 25 % of TC. Carbon contents were not related to most of the inorganic soil variables studied, except for oxalate-extractable Al, which individually explained 69 % ( $P < 0.001$ ) of the variability of TC in the umbric epipedon. Clay content was not suited as predictor of TC or of the other studied C forms. Bulk density, exchangeable  $Al^{3+}$ , Al saturation, ECEC and other parameters obtained by selective extraction were not suitable as predictors of TC and other C forms. Interactions between organic matter and poorly crystalline minerals, as indicated by oxalate-extractable Al, appear to be one of the possible organic matter protection mechanisms of these soils.

**Index terms:** Ferralsols, tropical soils, soil total carbon, soil organic carbon, pyrogenic carbon, soil charcoal, umbric epipedon

**RESUMO:** *RELAÇÕES ENTRE O CARBONO OXIDÁVEL DO SOLO E ATRIBUTOS FÍSICOS, QUÍMICOS E MINERALÓGICOS DE LATOSSOLOS COM HORIZONTE A HÚMICO*

A ocorrência de Latossolos com horizonte A húmico hiperdesenvolvido ( $\geq 100$  cm de espessura) nos trópicos e subtropicais úmidos é um paradoxo, pois os processos de decomposição da matéria orgânica nesses ambientes são bastante eficientes. Apesar disso, esses solos têm sido documentados nas regiões Sudeste e Sul do Brasil, com algumas ocorrências na região Nordeste. Aspectos da gênese e do significado paleoambiental desses Latossolos aguardam por melhor entendimento. Os processos que levaram o horizonte A a ser tão espesso e escuro e contribuíram para preservação de C orgânico (CO) em profundidades consideráveis nesses pedons são de especial interesse. Neste trabalho, oito Latossolos com horizonte A húmico hiperdesenvolvido (Lh) sob diferentes fitofisionomias (Floresta Ombrófila, Floresta Estacional e Savana Arborizada) foram amostrados e os seus atributos macromorfológicos, físicos, químicos e mineralógicos estudados, com o objetivo de relacioná-los com a preservação de CO em profundidade. Esses Lh são argilosos a muito argilosos, fortemente ácidos, distróficos, álicos e muitos possuem fragmentos de carvão vegetal dispersos na matriz do solo. Caulinita é o principal mineral da fração argila nos horizontes A e B, seguido em abundância por gibbsita e por vermiculita com hidróxi entrecamadas. Este último argilomineral é identificado apenas nos Lh derivados de rochas basálticas da região Sul. Os teores de C total (CT) variam de 5 a  $101 \text{ g kg}^{-1}$  no horizonte A húmico. Carbono oxidado por via úmida com dicromato de potássio constitui, em média, 75 % do CT dos horizontes A húmicos, enquanto o C não oxidável com dicromato (C-res), que inclui formas de C recalcitrantes (como carvões), contribui para os restantes 25 % do CT. Os conteúdos de C foram independentes da maioria das variáveis inorgânicas do solo, exceto do Al extraído com oxalato de amônio ácido (OAA), que individualmente explica 69 % ( $P < 0,001$ ) da variabilidade de CT do horizonte A húmico. Os conteúdos de argila não foram estimadores eficazes do CT e de outras formas de C estudadas, como também não foram: densidade do solo,  $Al^{3+}$  trocável, saturação por Al, capacidade de troca de cátions efetiva e outros parâmetros obtidos por extrações seletivas com OAA e ditionito-citrato-bicarbonato. Interações entre materiais orgânicos e minerais pobremente cristalinos, como indicado pelo Al extraído com OAA, apresentam-se como um dos mecanismos possíveis para proteção da matéria orgânica nesses solos.

**Termos de indexação:** Latossolos, solos tropicais, carbono total, carbono orgânico do solo, carvão do solo, carbono pirogênico, horizonte A húmico.

## INTRODUCTION

In Umbric Ferralsols with thick epipedons (A horizon  $> 100$  cm) (UF) the content of organic matter (OM) in deeper layers is significant. Umbric Ferralsols are commonly found in the Southeast and South of Brazil, and less frequently in the Northeast

(Ker, 1997). According to FAO-UNESCO (1971-1981) these soils cover an area of  $144,000 \text{ km}^2$  of the territory (equivalent to the State territory of Ceará). These soils characteristically have thick surface horizons, a dark color (value and chroma  $\leq 4$ ) and significant organic carbon (OC) contents, overlying the Bw diagnostic horizon of Latosols (Embrapa, 2006).

The genesis and paleoenvironmental significance of UF are not completely understood. Most authors suggest they are soils relic in the landscape of a favorable climate for OC accumulation in the past, preserved due to several specific soil and environmental factors (Queiroz Neto & Castro, 1974; Lepsch & Buol, 1986; Ker 1997; Buol & Eswaran, 2000; Calegari, 2008) such as high acidity, low-base saturation, relatively cold altitude climate, stable geomorphic surfaces and complex organomineral formations. Additionally, Silva & Vidal Torrado (1999) suggested that the humus-rich horizons could be a result of surface addition of charred material (charcoal) that had been partially altered, decomposed into microparticles, and distributed in the soil over time by biological activity.

The presence of charcoal fragments scattered in the soil matrix suggests that in addition to other formation factors, the frequency of natural fires affected the organic matter (OM), and possibly played an important role in the pedogenesis of some of these Brazilian UFs, similarly to the mollic (chernozemic) soils in Germany (Schmidt et al., 1999) and volcanic-ash-rich soils in Japan (Shindo et al., 2004). These charred materials are considered resistant to organic decomposition and chemical change, and can therefore remain in soils for thousands of years (Masiello et al., 2007). However, it is accepted nowadays that the presence of oxygen and moisture cause some degradation of part of the charcoal fragments, although this is a very slow process (Bird et al., 1999; Knicker et al., 2008).

Similarly to the Terras Pretas de Índio (TPI), UFs have dark and thick surface horizons, with large OC reserves and the presence of charcoal fragments. The formation processes, chemical properties and environments of occurrence, however, are quite different. The TPI were formed mainly under human influence, with irregular vertical and horizontal distribution of OC, a high phosphorus content (P) (200–400 mg kg<sup>-1</sup>) and a cation exchange capacity controlled by Ca<sup>2+</sup> and Mg<sup>2+</sup> (Novotny et al., 2007). The UFs on the other hand are a natural phenomenon (charcoal fragments are not associated with lithic artifacts or pieces of pottery), frequently found at the top of slopes, with gradual reduction in the OC content with increasing depth and toward adjacent nearby soils, low P concentrations and exchange complex and often predominance of exchangeable Al<sup>3+</sup> (Ker, 1997).

The study of Umbric Ferralsols with thick epipedons is particularly interesting because of the significant amount of accumulated OC (300 t/ha in the first 1 m), five times higher than in other Ferralsols classes (Andrade et al., 2004) and the potential to studies of paleoenvironmental reconstruction (Calegari, 2008). In many of these polycyclic Ferralsols (Lepsch & Buol, 1986; Calegari, 2008) past climate changes are recorded and fossil carbon (charcoal) is found. Moreover, there is little information on the supposedly stabilized OM

accumulation that contributes to maintain the thick epipedons.

The aim of this study was to characterize general properties of eight UF pedons from different regions of Brazil under distinct plant physiognomy and relate them to carbon preservation in depth.

## MATERIAL AND METHODS

### Selection of pedons

The pedons studied are representative of three UF sets defined by Calegari (2008) (Figure 1). These groups were established based on a factor analysis of a set of 39 pedons. The properties considered in the statistical analysis were climate, altitude, relief, parent material, clay content, A horizon thickness, exchangeable Al<sup>3+</sup>, extractable Fe fractions in the sulfur extract, organic carbon, pH (H<sub>2</sub>O), and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. The groups were defined as:

Group 1: Latossolos Brunos (LB) and Latossolos Vermelhos (LV) on top surfaces of Southern Brazil, with greater CO and Fe<sub>2</sub>O<sub>3</sub> contents and more oxidic clay mineralogy than the others;

Group 2: Latossolos Vermelho-Amarelo (LVA) and Latossolos Amarelos (LA) on old geomorphic surfaces in the Southeast, associated with mountain vegetation and climate, with intermediate CO values; and

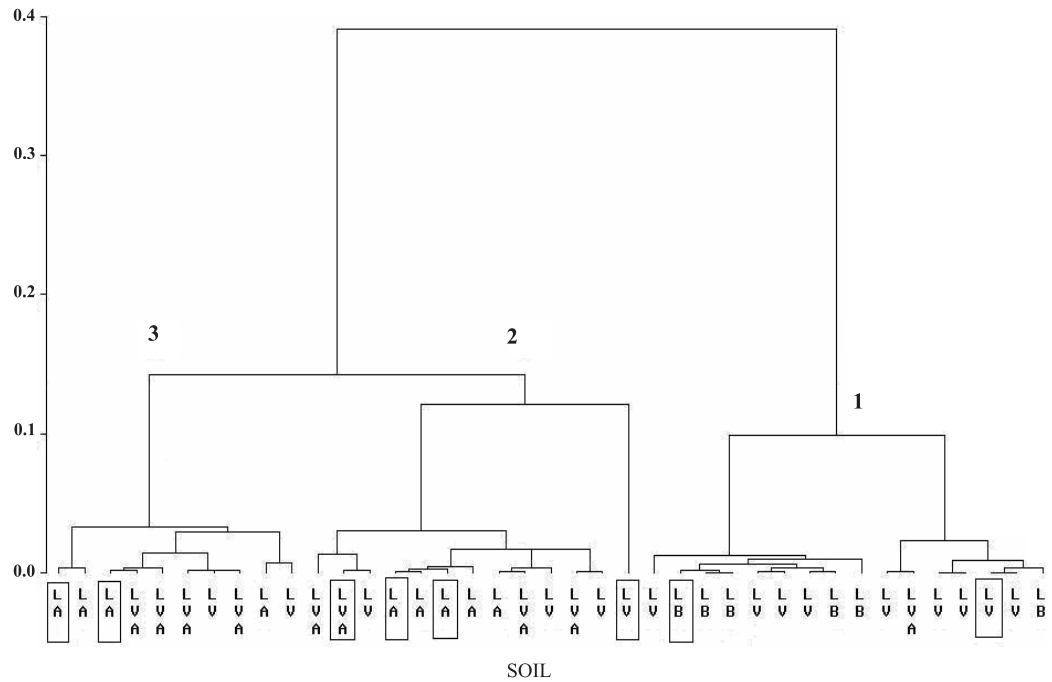
Group 3: LVA and LA with thicker epipedon (> 150 cm), found on higher surfaces of intermediate areas (peripheral depression in São Paulo and Coastal plain region in the Northeast), with the lowest CO contents and essentially kaolinitic mineralogy.

Based on this classification, eight pedons under different plant physiognomy were selected (Mixed Mountainous Ombrophylous Forest, Dense Mountainous Ombrophylous Forest, Semideciduous Mountainous Seasonal Forest, Savanna woodland, and Deciduous Submountainous Seasonal Forest) (Veloso et al., 1991; IBGE, 2004a). All belong to the Atlantic Forest biome, except the Savanna woodland, which belongs to the Cerrado biome (IBGE, 2004b).

The Mixed Mountainous Ombrophylous Forest covers vast areas in Southern Brazil, between the latitudes 24° and 30° S, at 1,000 to 1,400 m asl (Dümig et al., 2008), and, in smaller areas, in the Southeast in fragments of the Serra do Mar and Mantiqueira (IBGE, 1992). This forest is composed of deciduous and conifer trees, among which the arboreal mass of the species *Araucaria angustifolia* (Bertol.) Kuntze (Paraná Pine) is predominant. The predominant climate is subtropical (Cw), characterized by temperatures < 18 °C in the winter and high rainfall distributed evenly throughout the year. Under this

vegetation, two typical UFs derived from basalt of the Serra Geral Formation (Cretaceous) (representative of Group 1) were selected, one in Xanxerê-SC (LV) and the other in Guarapuava-PR (LB) (Table 1).

The Dense Mountainous Ombrophylous Forest is characterized by mild temperatures and high precipitation (> 1,200 mm). This vegetation type was almost completely destroyed by the expansion of



**Figure 1. Hierarchical cluster analysis of the physical, chemical and environmental conditions of 39 pedons of UF. 1: Group 1; 2: Group 2 and 3: Group 3. LVA: Latossolo Vermelho-Amarelo; LA: Latossolo Amarelo; LB: Latossolo Bruno and LV: Latossolo Vermelho. Rectangles indicate the base soils selected for study.**

**Table 1. Vegetation, location, soil classification, altitude (m), climate and parent material of the pedon sampling areas**

Vegetation	Location	Coordinates	Soil <sup>(1)</sup>	Altitude	Climate <sup>(2)</sup>	Parent material
Mixed Mountainous Ombrophylous Forest	Xanxerê (SC)	26°52'44" S 52°26'26" O	LVdf	m 810	Cfa	Basalts
	Guarapuava (PR)	25°21'09" S 51°28'01" O	LBw	1080	Cfb	
Dense Mountainous Ombrophylous Forest	Nova Friburgo (RJ)	22°13'19" S 42°30'23" O	LAd	850	Cwb	Gneiss
Semidecidual Mountainous Seasonal Forest	Machado (MG)	21°38'07" S 45°56'16" O	LVAAd	1155	Cwb	Gneiss-Migmatite
	Manhuaçu (MG)	20°15'04" S 42°10'36" O	LAd	895	Cwa	Charnokites
Deciduous Submountainous Seasonal Forest	Paudalho (PE)	07°51'41" S 35°12'21" O	LAd	180	As'	Sediments <sup>(3)</sup>
Savanna woodland	Campinas (SP)	23°00'58" S 45°56'15" O	LAd	660	Cwa	Sediments <sup>(3)</sup>
	Salinas (MG)	16°16'16" S 42°58'50" O	LVd	910	Aw	Phyllite-Schist

<sup>(1)</sup> LVAAd: Latossolo Vermelho-Amarelo distrófico; LAd: Latossolo Amarelo distrófico; LBw: Latossolo Bruno árico, LVdf: Latossolo Vermelho distrófico and LVd: Latossolo Vermelho distrófico. <sup>(2)</sup> Köppen climate classification. <sup>(3)</sup> Clayey-sandy Sediments.

human occupation (agriculture and deforestation) in the last century and only small patches remain in the Northeast and Southeast regions. One area still under native vegetation was chosen in Nova Friburgo-RJ, where a pedon (LA) was collected and described as belonging to Group 2.

Under the Semideciduous Mountainous Seasonal Forest, two Ferralsols were selected (Group 2), a pedon in Machado-MG (LVA) and another in Manhuaçu-MG (LA) derived from highly weathered metamorphic rocks (Precambrian gneiss or charnokites). Under the Deciduous Submountainous Seasonal Forest, which covers a narrow area in the Northeast (NE) between the humid forest and the Caatinga (dry forest in the Northeast), a Ferralsol of Group 3 was selected (LA in Paudalho-PE) derived from sedimentary rocks and sediments of the Tertiary period (Barreiras Formation).

The Cerrado biome covers about 2 million km<sup>2</sup> of the national territory and is characterized by well-defined wet and dry seasons. The vegetation, less dense than the preceding vegetation type, is mostly composed of relatively short shrubs and trees (5–15 m) with twisted trunks and deep roots, and grasses. The occurrence of natural fires in this Brazilian ecosystem is common, particularly in the dry season (April–September) (Roscoe et al., 2001). Two pedons were chosen under Savanna woodland, a LA in Campinas-SP (Group 3) and a LV in Salinas-MG (Group 2).

### Study areas and sampling

The location of the pedons, vegetation types, climate of the studied sites, parent material and soil classification up to the 3<sup>rd</sup> category level according to SiBCS (Embrapa, 2006) are summarized in table 1 and figure 2. The pedons are distributed between 7° and 27° southern latitude. Mean annual temperatures and rainfall of the selected sites are shown in figure 3.

Trenches were dug (depth 200 cm) on the top or upper part of slopes and the pedons were morphologically described according to Santos et al. (2005). Deformed samples were collected from all horizons and air-dried, crumbled and sieved (2 mm mesh) to obtain the air-dried fine earth (ADFE). Fragments > 1 cm of rock (gravel and pebbles), charcoal and roots were removed. The ADFE represents 96–100 % of the soil mass. Additional samples were collected with an auger to a depth of 300 cm, in cases where the epipedons were thicker than 150 cm (Embrapa, 2006).

### Mineralogical, physical and chemical properties of UFs

The mineralogical analysis of the clay fractions were performed by means of X ray diffractometry (XRD), using CuK $\alpha$  radiation in samples of A and Bw horizons of all pedons but from Guarapuava-PR, in which the clay mineralogy was detailed by Ghidin et al. (2006a). The samples were previously treated with



Figure 2. Location of the pedons studied in Brazil.

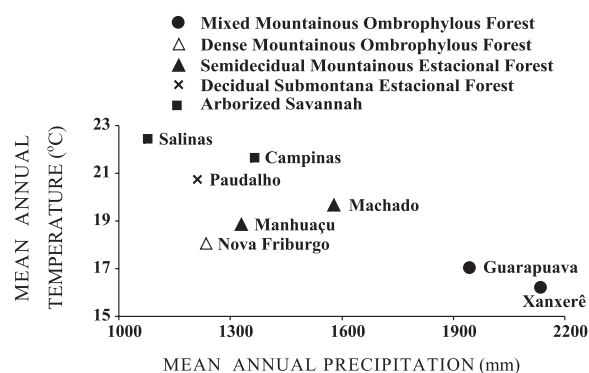


Figure 3. Mean Annual precipitation and temperatures of the studied locations. Source: <http://www.bdclima.cnpm.embrapa.br/resultados/index.php> (access on May 20, 2009).

hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and dithionite-citrate-bicarbonate (DCB) to remove OM and iron oxides, respectively (Jackson, 1956), and oriented on glass slides. The potassium-saturated slides were irradiated at room temperature (25 °C) and afterwards heated to 350 and 500 °C, whereas those saturated with Mg-glycerol were irradiated at room temperature only. The XRD patterns were obtained by a Phillips diffractometer model PW 3710 at the Research Center of Geochemistry and Geophysics of the Lithosphere (NUPEGEL/USP), with a span of 3 to 65 ° 2 $\theta$ , and interpreted according to Brown & Brindley (1980).

The sand mineralogy of UF was not identified in this study because it was described in other papers. The pedons studied were selected based on a database



that contain only UF analyzed and classified in surveys, theses, dissertations and articles. These studies reveal easily alterable quantities of minerals in the sand fraction within the limits established for the order of Latossolos (Embrapa, 2006).

The particle size analysis of ADFE was performed after dispersion with 0.01 mol L<sup>-1</sup> NaOH solution. Fractions of coarse sand (0.2–2.0 mm) and fine sand (0.053 to 0.2 mm) were measured by gravimetry, while the clay fraction (< 0.002 mm) was measured by a hydrometer. The silt fraction (0.002 to 0.053 mm) calculated as the difference (Embrapa, 1997). Soil bulk density (BD) was determined by the amount of dry soil (grams) contained in 100 cm<sup>3</sup> cylinders collected from the field in triplicate (Embrapa, 1997).

Soil pH was measured in H<sub>2</sub>O and KCl 1 mol L<sup>-1</sup> solutions (ratio soil:solution 1:2.5). The cation exchange capacity (CEC) (in cmol<sub>c</sub> kg<sup>-1</sup>) was calculated through the sum of exchangeable cations Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> extracted with solution of KCl 1 mol L<sup>-1</sup>, of K<sup>+</sup> and Na<sup>+</sup> extracted with a solution of 0.05 mol L<sup>-1</sup> HCl, and of H + Al, extracted with buffer solution of calcium acetate pH 7.0. From these values, the effective CEC, base saturation (V value) and aluminum saturation (m %) were also calculated.

For the soil classification according to SiBCS (Embrapa, 2006), 1 g of ADFE was digested with 20 mL of H<sub>2</sub>SO<sub>4</sub> 1:1 and the contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> were determined in the extract of sulfuric acid (Embrapa, 1997). From these concentrations, molecular ratios Ki and Kr (Resende & Santana, 1988) were calculated, which are also used as weathering indexes.

The forms of poorly-crystallized iron and aluminum (Al<sub>o</sub> and Fe<sub>o</sub>, respectively) were extracted with solution of acid ammonium oxalate (AAO) (Schwertmann & Taylor, 1989) and free iron and aluminum (Al<sub>d</sub> and Fe<sub>d</sub>) were extracted with DCB solution (Coffin, 1963). The Al and Fe contents in the extracts were determined by atomic absorption spectrophotometry.

### Carbon and nitrogen

Contents of total carbon (TC) and total nitrogen (TN) were determined in duplicate by dry combustion (950 °C) in an elemental analyzer (NCS Soil Analyzer Flash EA 1112), while organic carbon (OC) contents were analyzed by wet oxidation with potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) 0.4 mol L<sup>-1</sup> (Embrapa, 1997), in triplicate. The labile carbon (C-labile), which contains more easily decomposable organic compounds, such as the microbial materials, was determined, in triplicate, by oxidation with potassium permanganate solution of 0.2 mol L<sup>-1</sup> (Blair et al., 1995). ADFE samples were ground and sieved (0.2 mm mesh) and used in the analysis of these carbon fractions.

The difference between TC and OC contents was denominated oxidation-resistant carbon (C-res). This fraction presumably includes pyrogenic C (black carbon), which has high resistance to chemical and biological decomposition due to its formation/transformation by fire (Knicker et al., 2007), besides carbon forms strongly associated with clay.

### Amounting and dating of charcoals

About 5 kg of soil were collected at different depths in three pedons (LAd in Campinas-SP and in Manhuaçu-MG and LVd in Salinas-MG) to determine the mass of charcoal. Soil samples were weighed and then sieved (1 mm mesh), and the charcoal fragments retained on the sieve were collected with tweezers, rinsed with water, dried and weighed. Charcoal fragments arranged in two distinct rows (60–75 cm and 200–210 cm) of LVd of Salinas-MG were dated by <sup>14</sup>C. This dating was performed using mass spectrometry coupled to a particle accelerator at the Center for Applied Isotope Studies at the University of Georgia, USA. The <sup>14</sup>C age was expressed in years BP (before present), normalized to -25 ‰ (PDB) and calibrated to the present, year 1950.

### Statistical analysis

Analyses of linear correlation were performed between soil C content (TC, OC, C-res and C-labile) and between these and some UF properties (chemical and physical properties) using STATISTICA 5.0 software, to study the relationship of these properties with carbon preservation.

## RESULTS AND DISCUSSION

### Soil position in the landscape

As suggested by the position in the landscape (top or upper third of the slope) morphology and Ti/Zr ratio (Calegari, 2008), the colluvial process was not the primary factor causing the thick epipedons in the pedons studied. Evidence of this process is found in the UFs described in Nova Friburgo-RJ and Machado-MG, both located in the upper third of slopes in mountainous areas with declivity > 25 %. In the first, the A2 and A3 horizons have slightly darker colors than the overlying horizon, which suggests colluvial deposition, while in Machado-MG, a recent 10 cm thick deposit of reworked material (colluvium) was clearly identified in the upper epipedon. However, the ratio Ti/Zr of these and other UFs reported by Calegari (2008), shows that the formation and development (thickening) of the A horizon of pedons occurred after colluvial deposition.

The situation of these pedons in the landscape is quite different from the Ferralsols found in middle and lower slopes, where the epipedon thickening is clearly due to the accumulation of reworked material derived from upstream positions (Silva et al., 2007; Calegari, 2008).

### Soil morphology

The Ferralsols studied are very deep, well to markedly drained and have a dark and OC-rich A horizons in depth, all classified as humic by the SiBCS (Embrapa, 2006). The epipedon thickness of the selected pedons ranged from 100 to 220 cm, indicating huge OC reserves (Calegari, 2008). The LAd described in Campinas-SP has the thickest A horizon (220 cm) of all studied pedons.

Some of the epipedons have conspicuous morphological features, such as: (a) randomly distributed brownish spots (Campinas-SP) and; (b) clearly formed vertical channels (pedotubules) with a diameter of at least 2 cm in and variable length (Machado-MG, Salinas-MG, Xanxerê-SC and Guarapuava-PR). These Pedotubules are filled with small to very small granular aggregates, well-rounded and reddish or dark materials originating from overlying horizons. It was not possible to identify the organisms responsible for these features; however, they seem to be a result from the intense activity of arthropods (mainly termites and ants). The occurrence of biological channels in Brazilian Ferralsols, particularly those with high clay content that seem to preserve these features for a long period, is widely documented in the literature (Silva & Vidal-Torrado, 1999; Schaefer, 2001; Zinn et al., 2007).

Clear lines of macroscopic charcoal fragments were identified in the pedons located in Campinas-SP (between 65–80 and 95–110 cm) and in Salinas-MG (between 60–75 and 200–210 cm), both under Cerrado vegetation. The charcoal lines of the LVd of Salinas-MG were dated by  $^{14}\text{C}$  to ages of  $1,660 \pm 73$  (60–75 cm) and  $7,895 \pm 59$  (200–210 cm) years Cal. AP. These ages are consistent with those found by Gouveia et al. (1999) and Silva & Vidal-Torrado (1999) in soils from the southeastern region and show a period of fires associated with drier climatic periods in the Middle Holocene (Pessenda et al., 1996, 2004).

Once most of the charred material is deposited on the surface, the occurrence of charcoal lines in depth indicates that, similarly to the formation of stonelines, a selective vertical transport through the soil fauna of materials from deeper to surface horizons (pedoturbation) occurred for a considerable period of time (Gouveia et al., 1999).

Based on the ages obtained by  $^{14}\text{C}$  dating of charcoal lines of the LVd of Salinas-MG, the mobilization rates in the pedon were calculated, which were 0.41 and 0.26 mm year $^{-1}$ , for the lines of 60–75 cm and 200–210 cm respectively. These charcoal mobilization rates are in agreement with those found for other Ferralsols classes by Miklós (1992) and Gouveia et al. (1999) in São Paulo. The charcoal mass in the soils at different depths (Table 2) ranged from 7.0 to 35.3 g in the pedons under Cerrado vegetation (Campinas, SP and Salinas-MG – Savanna woodland) and from 1.3 to 1.6 g in the LAd of Machuaçu-MG, under

Semideciduous Mountainous Seasonal Forest. The highest charcoal concentration in soils under Cerrado is due, presumably, to the greater frequency of fires in this ecosystem, compared to the others (Czimczik & Masiello, 2007). These charcoal contents are within the ranges documented by Silva & Vidal-Torrado (1999) (0.5 to 125.7 g) and Gouveia et al. (1999) (up to 121.9 g) for Ferralsols.

There were no charcoal fragments in pedons described in the South (Xanxerê-SC and Guarapuava-PR), located in areas under higher rainfall volumes. This may be due to: (a) absence of regular and intense fires, (b) vegetation predominantly of grasses in the past and/or (c) erosion of burned residues. In the other pedons, except for the LVAd of Machado-MG, charcoal fragments were found in small numbers, scattered on the ground.

All pedons have dark colors near the surface, gradually transitioning to yellow, red, yellowish red or brown subsurface layers. The Latossolo Bruno ácido (LBw) described in Guarapuava-PR, however, deserves special emphasis due to its distinct polychrome. This Ferralsol shows dark colors in the humic A horizon (2.5YR 3/1 and 5YR 3/3), brownish tone in an intermediate layer (120–140 cm) and red hue (2.5YR 3/6) at the trench base (180–200 cm). The brownish overlying the red layer indicates goethite formation (xanthization process) and a record of bioclimatic changes (Schwertmann, 1971). Supposedly it represents a milestone in the transition from a dry and warm to a cooler and wetter climate, where milder temperatures, more rainfall and OM accumulation in the soil favor the formation of goethite in detriment of hematite (Kämpf & Schwertmann, 1983). Ghidin et al. (2006a) documented the predominance of goethite (Gt) over hematite (Hm) in the transitional horizon AB (90–120 cm) of this pedon (Table 6). The signature of  $\delta^{13}\text{C}$  of the soil OM in this pedon reported by Calegari (2008) suggests a change of vegetation of the photosynthetic pathway from  $\text{C}_4$  to  $\text{C}_3$  (from -17 ‰ to -24 ‰) during the Holocene. Moreover, this pedoenvironment with mild climate, high precipitation regularly distributed throughout the year, and rich

**Table 2. Charcoal mass in g 10 kg $^{-1}$  UF soil from different depths**

Location	Soil	Depth	Charcoal
		cm	g 10 kg $^{-1}$ soil
Manhuaçu (MG)	LAd	60– 80	1.6
		100–120	1.3
Campinas (SP)	LAd	80–100	10.0
		160–180	9.4
		200–220	10.3
Salinas (MG)	LVd	0– 30	12.3
		60– 75	35.3
		160–210	7.0



in OM supports the formation of goethites in the LBw (Kämpf & Schwertmann, 1983).

Compared with the LBw of Guarapuava-PR, xanthization is much less significant in the LVdf of Xanxerê-SC (about 230 km southwest of the LBw). Although these soils are derived from the same parent material (basalt), the LVdf has higher Fe contents as evidenced by digestion with sulfuric acid and extraction with DCB (Table 6). The reduced significance of the xanthization process in the LVdf of Xanxerê-SC may be related to (a) richer pedon in iron oxides, (b) better soil drainage, reducing water activity, (c) unfavorable local microclimate and/or (d) no significant paleoenvironmental change in the past, including the Holocene.

### Physical properties

The UF studied vary from clayey to very clayey, a result of intense desilication (Buol & Eswaran, 2000) that preceded OC accumulation in the soil. The clay content ranged from 314 to 704 g kg<sup>-1</sup> in the epipedon and these values tend to increase with depth (Table 3). Except for pedons in the South (LVdf and LBw), silt contents are little significant and the distribution among horizons irregular (Table 3).

The silt content in the LVdf of Xanxerê-SC and in the LBw of Guarapuava-PR varied from 21 to 34 % among horizons, and was higher than of other Ferralsol classes also developed from basic effusive rocks (basalts) in the South (Ghidin et al., 2006b). The high stability of microaggregates, resulting from the cementing action of OM and Fe and Al oxides made the complete dispersion of clay minerals by the traditional granulometric methods of analysis impossible, particularly in clayey soils (Donagemma et al., 2003). Although the nature of the silt fraction has not been investigated, it is supposed that, along with it, there are also very stable still preserved clay-microaggregates, which resulted in an overestimation of the content of this fraction (silt) in these Ferralsols. Nevertheless, the silt/clay ratio was low (< 0.6), and tended to decrease with depth, corroborating the idea of intense weathering and successive pedogenesis cycles, besides indicating a strong predominance of secondary minerals.

Compared to clay, the sand content was low, particularly in UFs described in Xanxerê-SC and Guarapuava-PR, where the parent material had undergone significant changes (Calegari, 2008) and contained low amounts of weathering-resistant minerals, e.g., quartz. In the sand fraction, the contents of fine sand are predominant over those the coarse sand fraction in most UFs studied (Table 3).

In general, the bulk density (BD) in the humic epipedons was lower than 1.0 t m<sup>-3</sup>, remaining constant or increasing slightly with depth (Table 3), while the OM content decreased. The oscillation in BD between horizons may be associated with soil

compaction on the soil surface or variations in texture and/or soil structure in depth (Calegari, 2008). Ghidin et al. (2006b) studied the influence of clay mineralogy on the physical properties of the LBw of Guarapuava-PR. These authors observed that the contents of kaolinite and gibbsite were significantly correlated ( $r = 0.92^{**}$  and  $-0.93^{**}$ , respectively) with the BD of subsurface horizons.

### Chemical properties

Regardless of the vegetation type or the parent material, all Ferralsols studied were highly acidic, dystrophic and highly Al<sup>3+</sup> saturated. The water pH ranged from 4.1 to 5.6 and exceeded the pH in KCl in all horizons, except in the Bw horizon of the LBw of Guarapuava-PR, demonstrating that despite the intense weathering, negative charges still predominate in the exchange complex (Table 4).

As suggested by the significant precipitation (> 1,000 mm, Figure 3), the long exposure time and landscape position, these soils are poor in bases. Contents of exchangeable Na<sup>+</sup> were virtually nonexistent, whereas cations K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> had slightly larger values in the epipedon than the other subsurface horizons, which is typical of nutrient cycling by vegetation in highly leached soils (Simas et al., 2005) (Table 4). In the humic LVd, which is currently located in a transition area between the Cerrado and Caatinga vegetation (Northern Minas Gerais state), under sub-humid climate (Aw), the Na contents were much higher (0.52–0.58 cmol<sub>c</sub> kg<sup>-1</sup>), possibly due to a drier climate, resulting in less Na leaching.

The CEC decreased sharply with depth in all soils, along with the carbon contents. The Al<sup>3+</sup> saturation (m %) was high in all pedons, mainly in the humic epipedon, probably due to the effect of partial destabilization of clay minerals by the acidifying action of OM, resulting in Al<sup>3+</sup> release. A similar geochemical behavior was reported by Simas et al. (2005), Schaefer et al. (2002), Silva & Vidal Torrado (1999) and Volkoff et al. (1984) for Brazilian Ferralsols and other soils in mountainous areas.

### Carbon and nitrogen

As indicated by the low soil pH, carbonates are absent in these soils and all total carbon (TC) determined was organic. The TC contents determined by dry combustion ranged from 5 to 101 g kg<sup>-1</sup> between horizons and decreased gradually with depth in the pedons. This trend was also observed in contents of total nitrogen (TN) and of oxidizable C fractions (OC and C-labile) (Table 5).

Total C contents at a depth of 1 m in the pedons studied were > 15 g kg<sup>-1</sup>, indicating large carbon stocks in the subsurface horizons (Andrade et al., 2004; Dick et al., 2005). The lowest TC and TN contents in the humic epipedon were recorded in the LAd of

**Table 3. Some physical and morphological properties of UF pedons studied**

Horizon	Depth	Color humid	Sand		Silt	Clay	Silt	BD
			Coarse	Fine			Clay	
	cm		g kg <sup>-1</sup>				tm <sup>-3</sup>	
Xanxerê-SC								
A	0– 20	5YR 2.5/2	6	50	328	616	0.5	0.7
A2	20– 50	5YR 3/2	8	44	295	653	0.4	0.6
A3	50– 70	5YR 3/3	7	37	252	704	0.4	0.7
AB	70–100	5YR 3/3	7	44	268	681	0.4	0.7
BA	100–120	2.5YR 3/4	6	33	245	716	0.3	0.8
Bw1	120–160	2.5YR 3/6	6	39	245	710	0.3	0.8
Bw2	160–200	2.5YR 4/6	7	47	207	739	0.3	0.8
Guarapuava-PR								
A	0– 35	2.5YR 3/1	15	37	339	609	0.6	0.8
A2	35– 60	5YR 2.5/3	14	30	295	661	0.4	0.8
A3	60– 90	5YR 3/3	14	29	297	660	0.4	0.8
AB	90–120	5YR 3/3	11	28	313	648	0.5	0.8
BA	120–140	4YR 3/4	13	28	284	675	0.4	0.9
Bw	140–205	2.5YR 3/6	14	33	237	716	0.3	1.2
Nova Friburgo-RJ								
A	0– 25	7.5YR 3/1	194	194	246	366	0.7	0.7
A2	25– 70	7.5YR 2.5/1	187	433	66	314	0.2	0.7
A3	70–100	7.5YR 2/1	186	247	116	451	0.3	0.8
AB	100–120	7.5YR 3/3	222	235	102	441	0.2	0.9
BA	120–160	7.5YR 4/3	172	252	101	475	0.2	1.0
Bw	160–210	7.5YR 5/6	177	249	108	466	0.2	1.1
Machado-MG								
A	0– 10	5YR 3/2	264	142	139	455	0.3	0.8
A2	10– 60	5YR 2.5/2	153	173	176	498	0.4	0.8
A3	60– 85	5YR 2.5/2	162	140	131	567	0.2	0.9
AB	85–120	5YR 2.5/2	164	120	176	540	0.3	1.0
BA	120–140	5YR 4/4	118	137	147	598	0.2	1.1
Bw1	140–170	5YR 4/6	107	134	136	623	0.2	1.1
Bw2	170–200	5YR 5/8	112	150	88	650	0.1	1.0
Manhuaçu-MG								
A	0– 25	7.5YR 2.5/1	183	208	137	472	0.3	1.0
A2	25– 60	7.5YR 2.5/1	128	211	128	533	0.2	0.8
A3	60– 82	7.5YR 2.5/2	121	177	133	569	0.2	0.8
AB	82–100	7.5YR 2.5/3	124	170	100	606	0.2	0.9
BA	100–130	7.5YR 4/4	132	166	106	596	0.2	0.9
Bw1	130–180	7.5YR 5/6	130	172	61	637	0.1	1.0
Bw2	180–210	7.5YR 5/8	123	171	69	638	0.1	1.0
Paudalho-PE								
A	0– 30	10YR 2/1	174	370	111	345	0.3	1.2
A2	30– 54	10YR 2/1	186	319	76	419	0.2	1.3
A3	54– 90	10YR 3/2	159	329	94	418	0.2	1.4
AB	90–140	10YR 3/3	160	281	78	481	0.2	1.4
BA	140–180	10YR 4/4	144	261	77	518	0.2	1.3
Bw	180–210	10YR 5/6	137	252	71	540	0.1	1.2
Campinas-SP								
A	0– 15	7.5YR 2/1	275	224	71	430	0.2	1.2
A2	15– 40	7.5YR 3/1	247	194	44	515	0.1	1.0
A3	40– 70	7.5YR 3/2	244	174	81	501	0.2	1.0
A4	70–100	7.5YR 3/2	238	192	35	535	0.1	1.0
A5	100–150	7.5YR 3/2	232	191	32	545	0.1	1.0
AB	150–220	7.5YR 3/3	238	185	31	546	0.1	1.0
BA	220–260	7.5YR 3/3	224	202	21	553	0.04	1.0
Bw	260–300	7.5YR 4/6	219	192	6	583	0.01	...
Salinas-MG								
A	0– 30	5YR 3/3	37	250	133	580	0.2	0.9
A2	30– 60	5YR 3/2	32	236	101	631	0.2	0.8
A3	60– 75	5YR 3/3	31	234	103	632	0.2	0.8
A4	75–100	5YR 3/4	33	228	82	657	0.1	0.9
AB	100–130	5YR 4/4	29	232	80	659	0.1	0.9
BA	130–160	2.5YR 4/4	30	233	77	660	0.1	1.0
Bw	160–210	2.5YR 4/6	27	222	66	685	0.1	0.9

**Table 4. Some chemical properties of UF pedons studied**

Horizon	Depth	pH (1:2.5)		K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	H <sup>+</sup>	CEC <sup>(1)</sup>	m <sup>(2)</sup>
		H <sub>2</sub> O	KCl								
	cm						cmol <sub>c</sub> kg <sup>-1</sup>				%
Xanxerê-SC											
A	0– 20	4.1	3.8	0.15	0.02	0.50	0.30	6.68	7.23	14.88	87
A2	20– 50	4.2	3.8	0.07	0.03	0.11	0.07	6.14	5.40	11.82	96
A3	50– 70	4.3	3.9	0.02	0.02	0.09	0.06	5.16	3.78	9.13	97
AB	70–100	4.4	3.9	0.01	0.00	0.06	0.04	4.76	3.37	8.25	98
BA	100–120	4.5	4.0	0.00	0.00	0.06	0.04	3.88	3.23	7.21	97
Bw1	120–160	4.4	4.1	0.00	0.00	0.06	0.03	2.38	2.77	5.24	96
Bw2	160–200	4.4	4.2	0.00	0.00	0.10	0.09	1.32	2.15	3.66	87
Guarapuava-PR											
A	0– 35	4.6	4.1	0.11	0.00	0.41	0.56	2.03	6.53	9.65	65
A2	35– 60	4.9	4.2	0.02	0.02	0.06	0.79	1.17	4.56	6.61	57
A3	60– 90	4.9	4.3	0.01	0.02	0.00	0.54	0.63	4.41	5.61	53
AB	90–120	5.0	4.6	0.03	0.02	0.00	0.23	0.20	4.03	4.51	42
BA	120–140	5.4	5.1	0.34	0.03	0.00	0.02	0.06	2.80	3.26	13
Bw	140–205	5.4	5.4	0.21	0.02	0.01	0.03	0.07	1.87	2.21	21
Nova Friburgo-RJ											
A	0– 25	4.9	4.3	0.03	0.03	0.25	0.15	1.91	7.80	10.16	81
A2	25– 70	5.4	4.5	0.01	0.02	0.02	0.02	1.18	7.97	9.22	94
A3	70–100	5.6	4.5	0.12	0.01	0.01	0.01	0.99	3.69	4.83	87
AB	100–120	5.4	4.5	0.04	0.01	0.01	0.01	0.82	2.40	3.29	93
BA	120–160	5.5	4.5	0.06	0.00	0.02	0.01	0.59	1.73	2.40	88
Bw	160–210	5.5	4.6	0.12	0.01	0.01	0.01	0.45	1.54	2.14	76
Machado-MG											
A	0– 10	4.2	4.1	0.14	0.03	0.12	0.09	2.88	4.93	8.19	88
A2	10– 60	4.7	4.3	0.03	0.03	0.04	0.03	2.43	5.49	8.05	95
A3	60– 85	5.0	4.3	0.02	0.01	0.03	0.01	2.48	4.93	7.47	97
AB	85–120	5.0	4.3	0.01	0.01	0.03	0.01	2.19	4.64	6.89	97
BA	120–140	4.9	4.3	0.01	0.01	0.03	0.01	1.74	2.73	4.53	97
Bw1	140–170	5.5	4.3	0.01	0.01	0.03	0.01	1.17	1.83	3.06	95
Bw2	170–200	4.2	4.1	0.02	0.01	0.03	0.01	0.48	1.67	2.22	88
Manhuaçu-MG											
A	0– 25	4.3	4.0	0.12	0.02	0.50	0.40	2.69	6.41	10.13	72
A2	25– 60	4.3	4.1	0.03	0.01	0.16	0.11	2.85	5.18	8.35	90
A3	60– 82	4.7	4.2	0.03	0.01	0.08	0.07	1.69	4.68	6.55	90
AB	82–100	4.9	4.2	0.11	0.01	0.06	0.06	1.54	4.05	5.83	87
BA	100–130	5.0	4.3	0.03	0.01	0.05	0.02	1.49	3.35	4.95	93
Bw1	130–180	5.3	4.6	0.02	0.01	0.05	0.01	0.30	1.68	2.07	77
Bw2	180–210	5.6	5.3	0.10	0.05	0.04	0.03	0.03	1.30	1.55	12
Paudalho-PE											
A	0– 30	4.5	4.0	0.21	0.04	2.68	0.99	0.95	3.60	8.46	20
A2	30– 54	4.4	3.9	0.15	0.04	0.93	0.30	1.87	2.90	6.18	57
A3	54– 90	4.6	3.9	0.04	0.04	0.94	0.27	1.53	2.39	5.21	54
AB	90–140	4.5	3.9	0.00	0.03	1.01	0.30	1.12	1.34	3.80	45
BA	140–180	4.4	3.9	0.00	0.03	0.82	0.27	1.07	0.91	3.09	49
Bw	180–210	4.5	4.0	0.00	0.04	0.91	0.36	0.58	0.94	2.84	31
Campinas-SP											
A	0– 15	4.9	4.2	0.10	0.02	0.29	0.15	1.94	4.14	6.64	78
A2	15– 40	4.8	4.2	0.03	0.01	0.06	0.03	1.84	3.17	5.13	94
A3	40– 70	4.8	4.2	0.02	0.01	0.04	0.02	2.42	3.07	5.57	97
A4	70–100	4.9	4.2	0.05	0.01	0.05	0.01	1.98	2.94	5.04	94
A5	100–150	5.1	2.2	0.02	0.01	0.08	0.01	1.66	3.19	4.97	93
AB	150–220	5.3	4.2	0.01	0.02	0.02	0.01	1.41	2.44	3.91	96
BA	220–260	5.2	4.2	0.03	0.01	0.02	0.01	1.23	2.53	3.83	94
Bw	260–300	5.6	4.6	0.01	0.01	0.01	0.01	0.28	1.19	1.51	87
Salinas-MG											
A	0– 30	5.0	4.0	0.11	0.53	0.24	0.18	3.35	5.25	9.66	76
A2	30– 60	4.5	4.3	0.06	0.56	0.05	0.02	2.28	4.02	6.99	77
A3	60– 75	4.7	4.4	0.06	0.52	0.04	0.02	1.86	3.52	6.01	75
A4	75–100	4.8	4.4	0.05	0.58	0.03	0.01	1.61	3.17	5.45	71
AB	100–130	5.0	4.5	0.04	0.56	0.03	0.00	1.29	3.11	5.04	67
BA	130–160	5.1	4.5	0.04	0.56	0.03	0.00	1.06	2.60	4.29	63
Bw	160–210	5.0	4.6	0.03	0.54	0.04	0.00	0.56	2.11	3.28	48

<sup>(1)</sup> CEC: cation exchange capacity. <sup>(2)</sup> m %: Al saturation.

**Table 5. Contents of carbon (TC, OC, C-res and C-labile) and TN, and C/N ratio in the UF studied. Rows in bold refer to charcoal fragment lines**

Horizon	Depth	TC	TN	C/N	C-labile	OC	C-labile <sup>(1)</sup>	OC <sup>(1)</sup>	C-res <sup>(1)</sup>
	cm	g kg <sup>-1</sup>			g kg <sup>-1</sup>		%		
Xanxerê-SC									
A	0– 20	55.7	3.9	14	15.3	42.5	28	76	24
A2	20– 50	35.0	1.8	19	9.7	31.0	27	88	12
A3	50– 70	23.7	1.3	18	6.3	17.1	26	69	31
AB	70–100	20.8	1.5	14	5.1	15.5	24	74	26
BA	100–120	18.7	1.1	17	4.3	16.4	23	88	12
Bw1	120–160	12.9	0.9	14	2.7	10.2	21	79	21
Bw2	160–200	5.4	0.6	10	1.2	4.1	8	76	23
Guarapuava-PR									
A	0– 35	41.4	2.2	19	10.4	30.2	25	73	27
A2	35– 60	24.9	1.3	20	4.8	16.6	19	63	33
A3	60– 90	21.1	0.9	23	4.2	13.4	20	64	36
AB	90–120	17.8	0.9	20	3.1	13.0	17	73	27
BA	120–140	12.2	0.6	20	5.4	9.1	44	74	26
Bw	140–205	4.9	0.3	16	2.1	4.7	43	96	4
Nova Friburgo-RJ									
A	0– 25	100.7	7.5	13	33.6	62.8	33	62	38
A2	25– 70	98.9	6.9	14	16.3	64.0	16	65	35
A3	70–100	28.2	1.8	16	5.2	23.0	18	85	15
AB	100–120	18.2	1.3	14	3.4	13.0	18	76	24
BA	120–160	12.3	1.0	12	2.1	9.9	17	81	19
Bw	160–210	10.0	0.9	11	1.5	8.0	15	80	20
Machado-MG									
A	0– 10	46.9	3.5	13	4.6	43.9	10	94	6
A2	10– 60	45.6	2.8	17	11.9	35.2	26	77	23
A3	60– 85	33.4	1.7	20	8.4	33.6	25	100	0
AB	85–120	29.0	1.4	20	6.8	22.7	24	78	22
BA	120–140	18.7	1.0	18	4.3	16.7	23	89	11
Bw1	140–170	12.5	0.8	16	2.8	9.7	22	77	23
Bw2	170–200	9.3	0.7	13	2.0	7.0	22	75	24
Manhuaçu-MG									
A	0– 25	57.5	4.6	13	27.7	41.2	48	72	28
A2	25– 60	44.8	3.5	13	10.4	33.9	23	76	24
A3	60– 82	32.0	2.4	13	6.4	26.6	20	83	17
AB	82–100	27.6	2.0	14	4.9	19.4	18	70	30
BA	100–130	22.3	1.6	14	4.7	15.4	21	69	31
Bw1	130–180	9.7	0.9	11	1.8	8.6	18	88	12
Bw2	180–210	6.5	0.7	10	1.2	6.5	18	100	0
Paudalho-PE									
A	0– 30	28.6	2.0	14	5.5	15.6	19	55	45
A2	30– 54	19.1	1.1	18	3.5	13.6	18	71	29
A3	54– 90	14.8	0.9	17	2.6	10.3	18	69	31
AB	90–140	8.6	0.6	14	1.3	5.9	15	68	32
BA	140–180	6.4	0.5	12	0.9	5.1	14	80	20
Bw	180–210	5.4	0.5	11	0.8	5.0	15	93	7
Campinas-SP									
A	0– 15	41.1	2.6	16	10.0	28.8	24	70	30
A2	15– 40	27.8	1.5	18	6.4	26.0	23	94	6
A3	40– 70	24.8	1.3	19	5.0	21.0	20	85	16
A4	70–100	25.0	1.0	25	5.2	19.0	21	76	24
A5	100–150	21.3	0.9	23	4.7	16.8	22	79	21
AB	150–220	16.2	0.7	24	7.0	14.3	43	88	12
BA	220–260	16.2	0.7	23	3.4	12.4	21	77	23
Bw	260–300	7.1	0.4	17	1.5	5.8	21	81	19
Salinas-MG									
A	0– 30	43.9	2.0	22	...	26.5	...	60	40
A2	30– 60	27.4	1.2	23	...	20.0	...	73	27
A3	60– 75	22.3	1.1	20	...	16.0	...	72	28
A4	75–100	19.3	0.8	24	...	14.5	...	75	25
AB	100–130	17.7	0.7	25	...	14.2	...	80	20
BA	130–160	13.9	0.6	23	...	11.8	...	85	15
Bw	160–210	9.7	0.5	19	...	8.6	...	88	12

<sup>(1)</sup> Percentage in relation to total C.

Paudalho-PE under Deciduous Seasonal Submountainous Forest. The climate of this pedon is tropical with dry summer seasons (As'), which is favorable for a rapid decomposition of soil OM.

A C/N ratio between 12 and 16 of the epipedon reflects the dominance of humidified OM (Stevenson, 1994). The C/N ratio calculated for the humic epipedon of the soils studied was higher than these values (13–25) and increased with depth. These values, however, decreased toward the Bw horizon, which can be explained by the major input of plant material near the surface. Furthermore, in the pedons of Campinas-SP and Salinas-MG, located in regions with less rainfall and with clear lines of charcoal fragments in the soil matrix, the values of the C/N ratio were highest.

The OC oxidation with dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) accounted for an average 75 % of the TC of humic epipedons of Ferralsols. Therefore, 3/4 of the TC reserves in the epipedon is not very recalcitrant and other mechanisms of C stabilization may help to maintain the TC content in depth high in the pedons studied. Carbon compounds resistant to dichromate oxidation (C-res) made up the remaining 25 % of the TC in the epipedon. This fraction (C-res) supposedly includes: (i) highly recalcitrant C forms, including pyrogenic C (black carbon), and/or (ii) organic compounds strongly associated with the clay fraction (kaolinite and Fe and Al oxides).

There are to date no standard methods for an accurate determination of the black carbon (BC) content in terrestrial environments (Masiello et al., 2007). Moreover, results of measurements of the BC concentration in the soil by different methods vary up to 500 times (Schmidt et al., 2001). The fact that soil BC does not stand for a single variable, but rather a *continuum* (different levels of carbonized biomass), makes quantification difficult.

In most horizons, the C-labile fraction represented about 20 % of TC. The surface horizons of LAd of Nova Friburgo-RJ and Manhuaçu-MG, located in a mild mountainous climate, are constantly supplied with fresh material by the Rain Forest (Dense Mountainous Ombrophylous Forest and Semideciduous Mountainous Seasonal Forest) and have the largest labile C reserves.

### Mineralogy and selective extraction

The  $\text{Fe}_o$  and  $\text{Al}_o$  contents ranged from 0.8 to 5.9 g kg<sup>-1</sup>; and from 1.3 to 14.0 g kg<sup>-1</sup>, respectively, in the humic epipedon. The highest  $\text{Fe}_d$  contents were found in UF samples from Xanxerê-SC and Guarapuava-PR, evidencing the nature of the parent material, rich in ferromagnesian minerals. The values of the ratio  $\text{Fe}_o/\text{Fe}_d$  were low (< 8 %) due to the strong predominance of these crystalline forms in these Ferralsols (Table 6). These values decreased with depth indicating a higher degree of crystallinity of Fe oxides in the subsurface horizons. This is in accordance with the distribution and influence of OC

in these pedons, which is an important inhibitor of oxide crystallization (Cornell & Schwertmann, 1996). The lowest  $\text{Fe}_o/\text{Fe}_d$  ratio was recorded in the LAd of Paudalho-PE, which was derived from clayey-sandy sediments and also had the lowest OC content of the soils studied.

Most pedons were classified as kaolinite ( $\text{Ki} > 0.75$  and  $\text{Kr} > 0.75$ ) or kaolinitic-oxidic ( $\text{Ki} > 0.75$  and  $\text{Kr} \leq 0.75$ ), according to Embrapa (2006), while the LAd of Nova Friburgo-RJ and LBw of Guarapuava-PR were classified as gibbsitic-oxidic ( $\text{Ki} \leq 0.75$  and  $\text{Kr} \leq 0.75$ ) (Table 6).

The kaolinite (Kt) was the main clay mineral in all pedons identified by XRD, followed by gibbsite (Gb), absent only in pedons of Salinas-MG and Paudalho-PE, and by hydroxy-interlayered vermiculite (HIV) that was identified in the diffractograms of the LVdf of Xanxerê-SC and LBw of Guarapuava-PR. The identification of HIV is in agreement with other studies of Ferralsols in Southern Brazil (Ker, 1988; Ghidin et al., 2006a).

The XRD patterns obtained were similar, and the Kt peaks were always more intense than those of Gb, except for the LAd in Nova Friburgo-RJ, where the Gb peaks were most intense, in agreement with the low Ki values (0.4 and 0.6 for horizons A3 and Bw, respectively) in this pedon.

The gibbsite formation was favored by intense leaching and alitization, destroying the 1:1 type minerals, especially kaolinite. Direct formation from primary minerals (feldspars and plagioclase) can also occur under intense leaching (Schaefer et al., 2002). However, it must be taken into account that gibbsite crystallization can be completely inhibited by low soil pH and high OM contents (Hsu, 1989). Therefore, for the humic LAd of Nova Friburgo-RJ, gibbsite nucleation is rather unlikely near the surface in the present environmental conditions, where an OM-rich horizon was formed. The gibbsite found in the humic epipedon of this pedon must have therefore been formed in the past in a possibly warmer and more seasonal scenario, prior to OM accumulation. This finding corroborates the model proposed by Simas et al. (2005) and Modenesi Gauttieri & Toledo (1996) for the development of Ferralsols in the Serra da Mantiqueira (MG) and Serra da Itatiaia (RJ), respectively.

### Correlation analysis

With few exceptions, TC contents were independent from most variables tested (Table 7). This variable correlated positively and significantly with OC ( $r = 0.97$ ,  $P < 0.001$ ), with the C non-oxidized with dichromate (C-res) ( $r = 0.90$ ,  $P < 0.001$ ) and with the C-labile fraction ( $r = 0.88$ ,  $P < 0.001$ ). Correlations between TC and OC were also found in other tropical areas, as in Ferralsols of the Colombian Amazon (Buurman & Mosquera, 2008).



**Table 6. Contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, molecular ratios, mineralogy of the clay fraction and Fe and Al contents extracted with DCB or AAO from the studied soils**

Horizon	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Ki	Kr	Mineralogy of the clay fraction <sup>(1)</sup>	Fe <sub>o</sub>	Al <sub>o</sub>	Fe <sub>d</sub>	Al <sub>d</sub>	Fe <sub>o</sub> /Fe <sub>d</sub>
	g kg <sup>-1</sup>							g kg <sup>-1</sup>				%
A	...	...	...	...	...	...	Xanxerê-SC	5.9	5.7	70.5	16.1	8.4
A2	...	...	...	...	...	...	Kt>Gb>HIV	5.5	6.1	71.1	16.3	7.7
A3	...	...	...	...	...	...	...	4.5	5.2	72.2	16.0	6.2
AB	199	229.2	174.1	25.7	1.5	1.0	...	...	...	...	...	...
BA	...	...	...	...	...	...	Kt>Gb> HIV	...	...	...	...	...
Bw2	185	243.9	186.3	26.1	1.3	0.9	...	...	...	...	...	...
							Guarapuava-PR					
A	...	...	...	...	...	...	...	3.6	6.5	63.9	27.9	5.6
A2	...	...	...	...	...	...	...	2.8	5.8	66.8	23.1	4.2
A3	107	291.2	150.2	21.2	0.6	0.5	...	2.7	5.6	67.9	22.3	4.0
AB	...	...	...	...	...	...	Kt>Gb>>Gt>Hm <sup>(4)</sup>	...	...	...	...	...
Bw	131	308.1	152.1	20.2	0.7	0.6	Kt>Gb>>Hm>Gt <sup>(4)</sup>	...	...	...	...	...
							Nova Friburgo-RJ					
A	...	...	...	...	...	...	...	2.5	12.6	44.8	25.5	5.6
A2	...	...	...	...	...	...	...	3.0	14.0	45.1	31.3	6.6
A3	61	231.3	76.1	7.0	0.4	0.4	Kt>Gb	1.3	5.4	48.2	18.9	2.7
Bw	87	245.0	87.6	7.1	0.6	0.5	Kt>Gb	...	...	...	...	...
							Machado-MG					
A2	...	...	...	...	...	...	Kt>Gb	3.4	5.9	51.9	15.0	6.6
A3	...	...	...	...	...	...	...	3.9	5.9	46.7	13.1	8.3
AB	174	247.1	86.7	7.7	1.2	1.0	...	2.8	5.2	51.6	13.3	5.4
BA	...	...	...	...	...	...	Kt>Gb	...	...	...	...	...
Bw2	185	261.8	87.8	7.9	1.2	1.0	...	...	...	...	...	...
							Manhuaçu-MG					
A	...	...	...	...	...	...	...	2.7	3.2	50.5	19.2	5.3
A2	...	...	...	...	...	...	...	3.0	3.8	52.9	17.3	5.6
A3	...	...	...	...	...	...	Kt>Gb	2.8	4.5	55.0	18.0	5.0
AB	121	239.7	91.5	11.5	0.9	0.7	...	...	...	...	...	...
Bw1	...	...	...	...	...	...	Kt>Gb	...	...	...	...	...
Bw2	131	244.4	102.1	11.9	0.9	0.7	...	...	...	...	...	...
							Paudalho-PE					
A	...	...	...	...	...	...	...	1.0	1.3	35.7	3.3	2.8
A2	...	...	...	...	...	...	...	1.0	1.4	39.1	4.0	2.6
A3	148	148.8	32.2	5.6	1.7	1.5	Kt	0.8	1.3	37.4	4.2	2.1
Bw	188	185.0	41.1	6.3	1.7	1.5	Kt	...	...	...	...	...
							Campinas-SP					
A2	...	...	...	...	...	...	Kt>Gb	1.9	4.0	44.1	8.7	4.3
A4	...	...	...	...	...	...	...	1.6	3.3	44.8	9.0	3.6
A5	102	193.5	53.1	5.7	0.9	0.8	...	1.4	4.0	44.0	12.3	3.2
Bw	112	211.3	57.4	5.8	0.9	0.8	Kt>Gb	...	...	...	...	...
							Salinas-MG					
A	...	...	...	...	...	...	...	2.0	4.2	44.3	8.1	4.5
A2	...	...	...	...	...	...	...	2.0	4.4	45.5	8.4	4.4
A3	195	243.9	59.9	11.0	1.4	1.2	Kt	2.0	4.5	44.5	7.6	4.5
A4	...	...	...	...	...	...	...	1.7	4.3	44.4	7.6	3.8
Bw	219	241.8	69.9	11.2	1.5	1.3	Kt	...	...	...	...	...

<sup>(1)</sup> Exclusive for Fe oxides, except for the pedon of Guarapuava-PR. Kaolinite: Kt; Gibbsite: Gb; HIV= Hydroxy-interlayered vermiculite; Goethite: Gt; Hematite: Hm. <sup>(2)</sup> AAO: Ammoniac Acid Oxalate. <sup>(3)</sup> DCB: dithionite-citrate-bicarbonate. <sup>(4)</sup> Obtained from Ghidin et al. (2006a).

These correlations suggest that, in most horizons, the irregular charcoal contents in depth did not interfere with the TC contents, and that part of this fraction must be strongly associated with the soil mineral fraction. If organic compounds derived from charcoal played a role, it would be as a largely humidified fraction and immobilized of TC. Since the

macroscopic charcoal fragments were removed during sample preparation, when retained in the sieve (1 mm mesh), they did not influence the TC content of the ADFe. Considering that the non-oxidized fraction with dichromate (C-res) is obtained by subtraction, the result is supposedly rather misleading, which may be the cause for a lower correlation with TC.

**Table 7. Linear correlation coefficients (r) between C forms in the soil and between these and other variables of A and B horizons**

Parameters	TC	OC	C-res	C-labile
TC (n=47)	1			
OC (n=47)	0.97***	1		
C-res (n=47)	0.90***	0.78***	1	
C-labile (n=47)	0.88***	0.85***	0.83***	1
Clay (n=47)	-0.49***	-0.47***	-0.46***	-0.36*
Sand (n=47)	0.20	0.20	0.17	0.10
Ds (n=46)	-0.45**	-0.47**	-0.34*	-0.37*
pH (n=47)	-0.21	-0.24	-0.12	-0.23
Effective CEC (n=47)	0.03	-0.04	0.16	0.06
Exchangeable Al <sup>3+</sup> (n=47)	0.37*	0.44**	0.17	0.36*
Al <sup>3+</sup> saturation (n=47)	0.27	0.35*	0.08	0.19
Fe <sub>o</sub> (n=21) <sup>(1)</sup>	0.36	0.40	0.12	0.29
Al <sub>o</sub> (n=21) <sup>(1)</sup>	0.83***	0.81***	0.76***	0.58*
Fe <sub>d</sub> (n=21) <sup>(1)</sup>	-0.04	0.00 <sup>(2)</sup>	-0.11	-0.01
Al <sub>d</sub> (n=21) <sup>(1)</sup>	0.63**	0.63**	0.58**	0.49**

<sup>(1)</sup> Only for A horizons. \*, \*\*, \*\*\* Significant at P < 0.05, P < 0.01, and P < 0.001, respectively.

Among the inorganic parameters, poorly-crystalline Al extracted with AAO (Al<sub>o</sub>) is most significantly correlated with TC. It alone explains 69 % (r<sup>2</sup> = 0.69) of the TC variation in epipedons, and 66 % and 58 % of the OC and C-res, respectively. The lower value for C-res again may be explained by its large error. In oxide-rich soils, Al<sub>d</sub> contains part of the amorphous fraction extracted with AAO solution and Al substituted by Fe minerals, such as goethite. Once Al<sub>d</sub> contents were not characterized as a homogeneous fraction, the correlations were not as high as those obtained for Al<sub>o</sub>. Clay content explained only 24 % of the variation in TC content and 20 % of bulk density (BD). Other parameters were not suited as indicators of the different carbon fractions.

The results suggested that for the humic epipedon of Brazilian Ferralsols, organic compounds were predominantly associated with poorly-crystalline minerals represented mainly by Al<sub>o</sub>, once Fe<sub>o</sub> occurred in smaller amounts (Table 6).

## CONCLUSIONS

1. The physical and chemical properties of the pedons, e.g., clayey to very clayey texture, strongly acidic pH, dystrophy, and high Al saturation tend to delay SOM decomposition.

2. Organic compounds that are highly recalcitrant or strongly associated with clay minerals (C-res) account for 6–25 % of TC of the humic epipedon, while the oxidizable fraction (OC) represents the major part of the TC reserves in these Ferralsols. This indicates that the OM of UF is not essentially composed of pyrogenic C.

3. Regardless of the location of the vegetation, the C/N ratio of epipedons increases with depth, indicating a lower degree of OM decomposition in the subsurface.

4. Interactions between different forms of carbon and poorly-crystalline aluminum (Al<sub>o</sub>) represent a mechanism of carbon protection in the humic epipedon.

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