Sociedade Brasileira de
Ciência do Solo

Organic Matter Stocks and the Interactions of Humic Substances with Metals in Araucaria Moist Forest Soil with Humic and Histic Horizons

Daniel Hanke[(1)*] **and Deborah Pinheiro Dick**[(2)]

[(1)] Universidade Federal do Pampa, *Campus* Dom Pedrito, Dom Pedrito, Rio Grande do Sul, Brasil.

[(2)] Universidade Federal do Rio Grande do Sul, Instituto de Química, Porto Alegre, Rio Grande do Sul, Brasil.

*Corresponding author:
E-mail: hankesolos@gmail.com

ABSTRACT: Soils with humic and histic horizons in tropical and subtropical ecosystems play an important role in determining the atmospheric C stock and its stabilization, climate regulation, water holding capacity, and environmental filtering, due to the different functions of soil organic matter (SOM). However, the processes and mechanisms that regulate SOM dynamics in these soils are not clear. The objectives of this study were: i) determine the C and N stocks and ii) investigate the SOM chemical fractions and their interactions with Fe and Al ions in soils with humic and histic horizons of a toposequence under Araucaria moist forest in southern Brazil. The soils sampled were classified as Humic Hapludox (top - not hydromorphic), Fluvaquentic Humaquepts (lower third - hydromorphic), and Typic Haplosaprists (floodplain - hydromorphic). The C and N contents were determined in bulk soil samples and SOM chemical fractions; in these fractions, Fe and Al co-extracted contents were also determined. The chemical composition of humin and humic acid fractions was investigated by FTIR spectroscopy. The C content in the toposequence increased from the top to the lowest position. The differences observed in SOM content and SOM chemical composition were defined by the differences in soil water regime. The amount of C stored in the subsurface horizons is about 70 % of total organic C. The carbohydrate-like structures in the humin fraction were protected from solubilization through interaction with iron oxides, which may represent an important mechanism for labile organic compound preservation in these soils. The soluble humic substances showed the highest Fe and Al contents, and their compartments have different affinities for Fe and Al.

Keywords: carbon, stabilization, complexation, organo-mineral, histosol.

INTRODUCTION

Soils with humic and histic horizons in tropical and subtropical ecosystems play an important role in the stocking and stabilization of atmospheric C, climate regulation, hydrological flow distribution (Rieley et al., 2008), and water holding capacity. In addition, these soil act as an environmental filter due to the high density of electrical charges formed by the deprotonation of organic functional groups (Simas et al., 2005; Benites et al., 2007). These factors influence types of soil that support specific vegetation, and preservation of these soils is important for maintaining endemic groups of local fauna and flora (Scheer et al., 2011).

These environments are usually associated with two conditions: i) soil relief patterns that contribute to the orographic condensation of intercepted moist air masses, which can form a local microclimate characterized by low temperatures, high humidity, and cloudiness (Scheer et al., 2011), and ii) hydromorphic terrains associated with high biomass production by vegetation.

Accumulation of soil organic matter (SOM) in C-rich soils has been attributed to conditions unfavorable to its decomposition. Such conditions would be low temperatures, high water content, and low O_2 diffusion. Another condition would be high Al^{3+} saturation of cation exchange capacity, which is toxic to heterotrophic microorganisms (Zech et al., 1997; Chimner and Ewel, 2005; Simas et al., 2005; Benites et al., 2007; Don et al., 2007; Potes et al., 2010).

Although climate and geomorphological conditions may be prominent factors in organic C accumulation in these soils, there may be other aspects related to SOM stabilization. These factors could be related to SOM chemical composition, as well as the interaction of organic compounds with minerals and metals in solution (Krull et al., 2003) that influence organic C dynamics in pedogenetic environments. However, the processes and mechanisms that regulate SOM dynamics in C-rich soils are still not well understood.

In southern Brazil, these environments occur in specific sites of the drainage basin of the Iguaçu River and in the upper montane areas of Paraná, as well as in the higher altitude positions of the eruptive plateau of Paraná, Santa Catarina, and Rio Grande do Sul (Maack, 2002; Potes et al., 2010; Sarante et al., 2011; Scheer et al., 2011). Some of these regions associated with rivers and hydromorphic conditions have been considered priority areas for inclusion in the ecological-economic zoning defined by the new Brazilian forest code (Brasil, 2012) because of their capacity to provide ecosystem services. The major services related to C-rich soils are the capacity to stock SOM and water. However, more information is needed regarding SOM stocks and their distribution in the landscape, as well as the mechanisms related to organic C preservation, for ecological-economic zoning. This information is important for determining soil use and management practices because modifications of the original conditions can affect SOM stabilization mechanisms, which can cause soil C loss.

In subtropical environments under natural conditions, humic and histic soils, whose natural morpho-structural conditions are determined by high organic C content, represent important niches in the investigation of SOM dynamics once SOM stabilization mechanisms have reached equilibrium. Understanding how these factors act at the profile level can support strategies for the conservation and restoration of similar profiles degraded by anthropic action.

The interaction of SOM chemical compartments with metal ions may alter the mobility of organic compounds and metals in the soil profile (Buurman and Jongmans, 2005; González-Pérez et al., 2008). In aerobic soils, the increase in Fe and Al oxides and in C content in subsurface horizons is due to the formation of low molecular weight SOM-metal complexes. Thus, the organo-mineral complexes can percolate through the profile, a process also known as podzolization.

Some of the organic ligands can be mineralized, resulting in metal release to the soil solution (Buurman and Jongmans, 2005). However, in acidic or hydromorphic soils, mineralization of the organic ligands can be inhibited by complexation with Fe and Al

(Silva et al., 2008; Dick et al., 2009). Thus, the interaction of the SOM fractions with metals can control the organic C distribution in C-rich soil profiles. In addition, organo-mineral complexes may be responsible for stabilization of the organic compounds in these environments. This approach can assist in understanding the processes involved in increasing the depth of humic and histic horizons, as well as in increasing organic C content in subsurface layers.

Considering that organo-mineral interactions can change SOM dynamics (Dick et al., 2009), they may be responsible for changes in the SOM content and its chemical composition. This process can be a very important factor for controlling SOM dynamics in C-rich acid soils, in which low crystalline iron oxides with high reactivity and high exchangeable Al contents are found. In addition, the mobility of the metal-organic complexes may determine the enrichment of C stocks at depth. The objectives of this work were to determine the C and N stocks and to characterize the SOM chemical compartments and their interactions with Fe and Al in soils with humic and histic horizons of a toposequence in an Araucaria moist forest in southern Brazil.

MATERIALS AND METHODS

Study area and sampling

Soil was sampled in a toposequence beneath Araucaria moist forest in the Curitiba sedimentary basin in the "Primeiro Planalto Paranaense" (roughly translated: 'first plateau of Paraná'), Brazil, in the Iraí conservation area (*APA-Iraí*) - in the hydrographic microbasin of the Canguiri River. The soils sampled were derived from sedimentary rocks (Argillite and Arcosian deposits) of the Guabirotuba Formation from the Cenozoic Era - Pleistocene (Salamuni and Stellfeld, 2001; Salamuni et al., 2004). The climate is Cfb - subtropical humid with moderate winters and mild summers - according to the Köppen classification system, with annual average rainfall ranging from 1,500 to 1,600 mm and average annual temperature of 19.1 °C (Maack, 2002).

Three different soil classes were sampled: *Latossolo Bruno Alumínico rúbrico - LBa* (Santos et al., 2013), a Humic Hapludox (OX); *Gleissolo Melânico Ta Distrófico organossólico - GMvd*, a Fluvaquentic Humaquepts (FH), and *Organossolo Háplico Sáprico típico - OXs*, a Typic Haplosaprists (TS) (Table 1). In the landscape, the soil profile positions correspond to the top of the slope (non-hydromorphic site), the lower third of the slope (hydromorphic site - subsurface hydromorphism), and floodplain (hydromorphic site - surface water table for a short period of the year), respectively. In each site, three soil pits were dug at a distance of approximately 15 m from one to another and different layers were sampled (0.0-0.05, 0.05-0.10, 0.10-0.15, 0.15-0.20, 0.20-0.30, 0.30-0.40, 0.40-0.60, 0.60-0.80, 0.80-1.00, 1.00-1.20, 1.20-1.40, 1.40-1.60, and 1.60-1.80 m) using triplicate sampling per soil type. In OX, sampling was performed from the soil surface to the deepest layer (1.80 m - soil/rock interface). In the other two soils, sampling was performing from the surface to the depth of the water table (1.0 m for FH and 0.6 m for TS).

Soil pH (in distilled water) was determined during soil sampling. In OX the pH values ranged from 4.0 to 4.9. In FH, these values ranged from 4.5 to 4.9, and in TS, from 3.7 to 4.0.

To determine the C and N contents, undisturbed soil monoliths of approximately 2 dm^3, in replicates, were collected and transported to the lab in closed containers. The monoliths were later gently crushed manually, with field moisture intact, and sieved (9.51 mm). After air drying, the samples were separated into different aggregate classes using sieves of 4.00, 2.00, 1.00, and 0.25 mm. The aggregate classes were properly weighed and packed in plastic containers. The purpose of this procedure was to recompose the soil samples based on the weight ratio of each class in the bulk sample. This was done to limit problems from the natural variability of C content due to the distribution of the organic

particulate material. Undisturbed samples were collected in steel cylinders of determined weight, diameter, and height for determination of soil bulk density and water content.

Soil chemical and physical properties

The exchangeable forms of Ca, Mg, and Al ions were extracted with KCl solution (1 mol L^{-1}). Exchangeable K$^+$ was extracted with Mehlich-1 solution. These ions were evaluated using inductively coupled plasma - atomic emission spectrometry (ICP-AES) (Perkin Elmer 7200). Based on these results, the effective cation exchange capacity (CEC) was calculated by adding up the exchangeable bases and the Al^{3+}. In addition, the Al saturation percentage of the exchange sites was calculated.

Soil particles were dispersed by ultrasonic energy application. The sand fraction was separated using a 0.053 mm sieve. The silt and clay fractions were separated by sedimentation according to Stokes' Law. Quantification of the soil particle size was performed according to the pipette method, as described by Gee and Bauder (1986).

The steel cylinders with the OX and FH samples were dried at a temperature of 105 °C, while for the TS samples, the temperature was 65 °C. This was done to reduce thermal degradation of organic compounds. Soil bulk density (Sd) was calculated by dividing the weight of the dry soil by the cylinder volume.

Pedogenic Fe oxides (Fed) were extracted with dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960). Low-crystalline Fe oxides (Feo) were extracted from bulk soil samples by the ammonium oxalate method (AO) (0.2 mol L^{-1}, pH 3.0 - in the dark) (McKeague, 1978). After extractions, Fe contents were determined by flame atomic absorption spectrometry (Perkin Elmer, Lambda 25).

Table 1. General soil characterization: geomorphology and soil morphological description

Geographic coordinate	Altitude	Relief	Horizon	Thickness	Color (wet)	Predominant structure
	m			m		
Latossolo Bruno Alumínico rúbrico (*LBa*) - Humic Hapludox (OX)						
22.5° 24' 3" S	951	Flat - Slightly rolling	A	0.42	10YR 3/4	Moderate, small and granular
49° 7' 34" W			AB	0.17	5YR 4/6	Moderate, small, subangular blocky and granular
			BA	0.10	2.5YR 3/6	Moderate, small, subangular blocky and granular
			Bw1	0.51	5YR 4/6	Strong, small to very small, granular
			Bw2	0.48	10YR 6/8	Strong, small to very small, granular
			C	0.21	10YR 7/4	Massive and angular blocky
Gleissolo Melânico Ta Distrófico organossólico (*GMvd*) - Fluvaquentic Humaquepts (FH)						
25° 24' 39" S	918	Slightly rolling - Rolling	A1	0.26	2.5YR 2.5/1	Moderate, small and granular
49° 7' 17" W			A2	0.15	10YR 2/1	Moderate, small and granular
			C1g	0.52	10YR 4/1	Strong, large and prismatic
			C2g	0.07	10YR 3/1	Massive
Organossolo Háplico Sáprico típico (*OXs*) - Typic Haplosaprists (TS)						
25° 24' 40" S	913	Flat	H1	0.21	10YR 3/1	Strong, small and crumbly
49° 7' 13" W			H2	0.39	10YR 2/1	Strong, small and crumbly

Organic C and N content

The C and N contents were determined by dry combustion ("Variol El" elemental analyzer) of bulk soil samples. The soil samples were first ground and sieved through a 0.2 mm mesh. The C and N stocks in each sample were calculated based on the contents of these elements and the soil mass, which is defined according to equation 1:

$$Sm = Sd \times Lt \times A \qquad\qquad\qquad\qquad Eq. 1$$

where Sm = soil mass (Mg ha^{-1}); Sd = soil bulk density (Mg m^{-3}); Lt = layer thickness (m); and A = area of 1 m^2.

The C and N stocks were then calculated by multiplying Sm by the C and N contents in each layer.

SOM chemical fractions and determination of co-extracted Fe and Al

SOM chemical fractions were extracted according to the solubilization method in aqueous acid/alkaline media (Dick et al., 1998). Approximately 1 g of soil sample was recomposed from the mass of the different aggregate classes. This sub-sample was milled in an agate jar, passed through a sieve (2.0 mm), and subjected to SOM chemical fractionation. Initially the water-soluble fraction was extracted by weighing 1 g of the sample in a centrifuge tube (100 mL) and adding 30 mL of deionized H$_2$O. The suspension was shaken on a horizontal orbital shaker for 2 h. After this procedure, the tube was centrifuged for 10 min (relative centrifugal force = 1050) and the separated extract was preserved in a plastic container. The container was refrigerated to avoid organic compound degradation. This procedure was repeated three times and the total volume of the extract was quantified. After the extraction of water-soluble compounds, three extractions were performed with HCl solution (0.1 mol L^{-1}) in the same way as the previous extractions (shaken for 2 h followed by centrifugation). The acid extract was also preserved in a container and refrigerated. The total extracted volume was quantified.

Subsequently, the soluble humic substances were extracted using a NaOH solution (0.5 mol L^{-1}). Then, 30 mL of alkaline solution was added to the soil remaining after extractions with H$_2$O and HCl, followed by horizontal orbital shaking (3 h). This procedure was repeated until the supernatant became colorless (about 5 to 6 extractions). The volume of the alkaline extract containing the soluble humic substances (HSs) was measured and an aliquot (10 mL) was taken to determine C concentration. The alkaline extract was acidified to pH 2.0 using HCl solution (4 mol L^{-1}) and allowed to stand for about 24 h. After resting, the extract was centrifuged for separation of fulvic acids (FA - supernatant) and humic acids (HA - precipitate). The C content in the water extract (C$_{H2O}$), acid extract (C$_{HCl}$), extract of soluble humic substances (C$_{HSs}$), and fulvic acid extract (C$_{FA}$) was determined by ultraviolet and visible spectrometry (absorbance 580 nm) (Shimadzu - UV-160 A) after C oxidation with potassium dichromate in an acidic medium (60 °C for 4 h) (Dick et al., 1998).

The C content for humic acids (C$_{HA}$) was calculated from the equation: C$_{HA}$ = C$_{HSs}$ - C$_{FA}$. The C content in the humin fraction (C$_{HU}$) was calculated by: C$_{HU}$ = C - (C$_{HSs}$ + C$_{HCl}$), where C is the total soil organic carbon content, which was previously determined by dry combustion.

The FA extract was purified in a column containing DAX-8 resin. After retention of this fraction, the column was washed with two volumes of HCl (0.1 mol L^{-1}), and the FAs were eluted with NaOH solution (0.1 mol L^{-1}). The FA extract was acidified to pH 2 with HCl (0.1 mol L^{-1}) and shaken (1 h) to ensure the protonation of the carboxylic groups and release of complexed metals. Subsequently, dialysis was performed with deionized water in 1 kDa cut-off membranes until testing negative for chloride with AgNO$_3$. An aliquot (2.5 mL) was used for determination of Fe and Al concentrations in this fraction (PFA), and the suspension was oven dried at 50 °C.

The Fe and Al contents in the HSs and FA extracts (before and after purification) were determined by atomic absorption spectroscopy (Perkin-Elmer 240). The Fe and Al contents associated with HA were obtained by the difference between the content of these elements in the HSs extract and the content determined in the FA extract.

SOM chemical composition

Purification of humic acids and humin fractions

The humic acids (HA) fraction was purified using 30 mL of HF/HCl solution (5 %, v/v). The samples were mechanically shaken (2 h) and centrifuged for 10 min (relative centrifugal force = 1050); the procedure was repeated six times. At the end, the solid residue was washed three times with distilled water and oven dried at 50 °C. The humin fraction (HU) was purified using 30 mL of HF solution (10 %, v/v). Similar to the procedure for the HA fraction, the HU samples were mechanically shaken (2 h) and then centrifuged for 10 min (relative centrifugal force = 1050). The procedure was repeated eight times. At the end, the solid residue was washed three times with distilled water and oven dried at 50 °C (Dick et al., 2003).

Fourier Transform Infrared Spectroscopy (FTIR)

The purified samples of HA and HU fractions were analyzed by Fourier transform infrared spectroscopy (FTIR) (Shimadzu 8300) in KBr pellets (1:100) using 32 scans and a resolution of 4 cm^{-1} in the spectral range of 4000 to 400 cm^{-1}.

The absorption bands were attributed according to Farmer (1974) and Tan (1996). From the FTIR spectra we calculated the aromaticity index (AI) (Chefetz et al., 1996) where $I_{C=C}$ is the absorption intensity around 1630 cm^{-1} and I_{C-H} is the absorption intensity around 2920 cm^{-1}, after establishing the baseline between 1800 and 1500 cm^{-1} and between 3000 and 2800 cm^{-1}.

The relative intensities (RI) of the main absorption bands were calculated following Gerzabek et al. (2006) by dividing the corrected peak intensity (2950, 1710, 1630, 1540, 1430, 1250, and 1075 cm^{-1}) by the sum of the intensities of all peaks, multiplied by 100 %. The parameters to determine the peak intensities were base1/peak/base2 (cm^{-1}): 3000/2950/2800; 1800/1710/1500; 1800/1630/1500; 1800/1540/1500; 1500/1430/900; 1500/1250/900, and 1500/1075/900.

Statistical analysis

Results were first subjected to statistical descriptive analysis (mean and standard deviation) to verify natural sample variability with respect to the three replicates. The data set was subjected to simple linear regression analysis to study correlation between the variables.

RESULTS AND DISCUSSION

Soil chemical and physical properties

The clay contents of OX (303 to 497 g kg^{-1}) and FH (320 to 487 g kg^{-1}) were similar, but lower in TS (123 to 187 g kg^{-1}) (Table 2). Soil bulk density (Sd) values were higher in mineral soils and lower in TS (Table 2). The Sd mean values were 1.5, 1.4, and 0.8 Mg m^{-3} for OX, FH, and TS, respectively. In OX and FH, the Sd values increased from the surface horizon to depth. In TS, the Sd is about 0.8, which is due to the high C content. However, compared to other organic soils under non-hydromorphic conditions, the Sd values observed in TS were higher (Scheer et al., 2011), which is probably due to the occurrence of a more compact soil structure.

Table 2. Clay content, soil bulk density, chemical properties, pedogenic iron oxide contents, carbon and nitrogen contents of three soils in a toposequence under Araucaria moist forest in southern Brazil

Layer	Clay	Sd	CEC	m	Fed	Feo	Feo/Fed	C	N	C/N
m	g kg^{-1}	Mg m^{-3}	cmol$_c$ dm^{-3}	%	———— g kg^{-1} ————			———— g kg^{-1} ————		
				Humic Hapludox (OX)						
0.00-0.05	325 ±10	1 ±0.1	21.9 ±0.6	9 ±1	35 ±2.4	6.9 ±0.1	0.20	54.2 ±2.2	3.8 ±2.2	14
0.05-0.10	303 ±6	1.1 ±0	19.2 ±0.3	30 ±1	36.9 ±2.7	5.5 ±0	0.15	39.2 ±2.3	2.8 ±2.3	14
0.10-0.15	311 ±6	1.3 ±0.1	15.5 ±0.1	48 ±0	37.5 ±1.0	3.3 ±1.2	0.09	34.4 ±1.6	2.4 ±1.6	15
0.15-0.20	331 ±4	1.3 ±0.1	19.9 ±0.3	55 ±0	39.6 ±3.2	3.2 ±1.3	0.08	32.4 ±1	2.2 ±1	15
0.20-0.30	317 ±2	1.5 ±0.1	18.2 ±0	79 ±0	47.9 ±3.9	3 ±0.6	0.06	29.6 ±0.7	1.8 ±0.7	16
0.30-0.40	329 ±8	1.6 ±0.1	14.3 ±0	84 ±1	56 ±2.6	3.1 ±0.3	0.05	24.6 ±0.2	1.9 ±0.2	13
0.40-0.60	341 ±7	1.6 ±0.1	8.5 ±0.1	87 ±1	62.1 ±3.8	3.3 ±0.8	0.05	17.4 ±0.1	0.9 ±0.1	18
0.60-0.80	463 ±11	1.7 ±0	9.2 ±0.1	84 ±2	86.8 ±1.9	5 ±0.7	0.06	8.9 ±0.6	0.6 ±0.6	15
0.80-1.00	491 ±13	1.6 ±0.1	7.9 ±0	88 ±1	90.9 ±3.1	5.4 ±0.8	0.06	8.2 ±0.3	0.8 ±0.3	10
1.00-1.20	497 ±7	1.7 ±0	5.8 ±0.2	81 ±1	67.3 ±3.8	5.8 ±1.0	0.09	4.4 ±0	0.4 ±0	12
1.20-1.40	365 ±2	1.8 ±0	3.3 ±0	79 ±0	50.8 ±3.8	4 ±0.7	0.08	2.2 ±0.5	0.2 ±0.5	11
1.40-1.60	361 ±2	1.8 ±0	4.1 ±0	84 ±2	24.4 ±4.1	2.9 ±0.7	0.12	1.6 ±0.1	0.2 ±0.1	8
1.60-1.80	403 ±8	1.9 ±0	3.3 ±0.1	85 ±2	20.7 ±1.7	2.3 ±0.4	0.11	0.9 ±0.1	0.1 ±0.1	6
				Fluvaquentic Humaquepts (FH)						
0.00-0.05	351 ±7	1.1 ±0	32.4 ±3.2	5 ±3	15.2 ±2.6	8.2 ±1.9	0.53	70.4 ±4.3	3.5 ±0.1	20
0.05-0.10	385 ±5	1.2 ±0	29.6 ±2	19 ±4	15.1 ±2.6	6.8 ±0.4	0.46	70.4 ±4.2	3 ±0.2	23
0.10-0.15	383 ±9	1.2 ±0	26.8 ±3.1	36 ±4	14.6 ±2.5	8 ±1.2	0.55	79.5 ±2.9	3.7 ±0.4	21
0.15-0.20	320 ±7	1.4 ±0	26.1 ±0.2	30 ±3	14.9 ±2.6	8.7 ±1.4	0.58	70 ±3.7	3.4 ±0.7	21
0.20-0.30	439 ±13	1.5 ±0	29 ±0.7	35 ±6	12.6 ±2.2	8.4 ±1.0	0.68	77.2 ±5.5	3.3 ±0.2	24
0.30-0.40	443 ±9	1.6 ±0	26.1 ±1.4	30 ±2	14.4 ±2.5	10.4 ±1.5	0.72	67.4 ±8.6	3.2 ±0.3	21
0.40-0.60	375 ±9	1.6 ±0	32.9 ±0.1	7 ±2	13 ±2.2	10.9 ±2.5	0.83	67.9 ±1.4	4 ±0.1	17
0.60-0.80	371 ±4	1.8 ±0	26.6 ±2.6	13 ±2	10.5 ±1.8	10.6 ±1.5	1.02	74.3 ±3.8	4.3 ±0.3	17
0.80-1.00	487 ±11	1.7 ±0.1	24.7 ±3.7	33 ±4	8.7 ±1.5	7.9 ±0.9	0.92	89.8 ±3.9	4.5 ±0.3	20
				Typic Haplosaprists (TS)						
0.00-0.05	175 ±8	0.8 ±0.1	50.5 ±4.8	84 ±7	5.1 ±0.3	4.8 ±0.2	0.95	142.6 ±5.3	9.1 ±0.4	16
0.05-0.10	123 ±7	0.8 ±0	39.3 ±3.1	93 ±9	4.9 ±0.3	4.8 ±0.2	0.97	168.9 ±3.7	11.1 ±0.3	15
0.10-0.15	177 ±12	0.7 ±0	49.3 ±2.7	94 ±2	4.6 ±0.3	4.4 ±0.2	0.96	169.2 ±1.9	10.9 ±0.4	16
0.15-0.20	159 ±14	0.7 ±0	43.8 ±4.2	95 ±9	4 ±0.2	4 ±0.2	0.98	176.2 ±2.9	10.7 ±0.2	16
0.20-0.30	127 ±9	0.7 ±0	39 ±2	96 ±9	3 ±0.2	2.8 ±0.2	0.94	167.2 ±0.5	9.5 ±0	18
0.30-0.40	149 ±9	0.7 ±0	24.7 ±0.8	96 ±7	3 ±0.2	2.9 ±0.2	0.97	159.3 ±2	8.6 ±0.1	19
0.40-0.60	187 ±8	0.9 ±0.1	31.1 ±1.2	96 ±5	2.9 ±0.2	2.7 ±0.2	0.94	100.9 ±0.4	5.1 ±0	20

Sd: soil bulk density calculated by: soil mass/cylinder volume; CEC: effective cation exchange capacity, calculated by adding up Ca^{2+}, Mg^{2+}, and Al^{3+}, extracted with KCl solution (1 mol L^{-1}); and K^+: extracted with Mehlich-1 solution. The ions were measured by ICP-AES ; m = Al^{3+} saturation of effective CEC; Fed: total pedogenic Fe oxide contents, extracted with dithionite-citrate-bicarbonate and FeO: low crystallinity Fe oxide contents, extracted with ammonium oxalate (0.2 mol L^{-1}, pH 3.0), both determined by flame atomic absorption spectrometry; Feo/Fed: mass ratio between the low crystallinity Fe oxides and total pedogenic Fe oxides; C and N: C and N contents determined by dry combustion in a CN elemental analyzer; and C/N: C/N ratio.

Effective CEC was generally higher in TS, followed by FH and OX (Table 2), while Al saturation (m) decreased in the order TS > OX > FH. In OX, the m values increased with depth, which is usually observed in weathered soils. During weathering, the release of Al^{3+} from minerals into the soil solution is responsible for the relative enrichment of this ion in the system. In addition, weathering is also responsible for progressive removal of the exchangeable alkaline cations from the soil. In FH, the lower saturation of CEC by Al^{3+} compared to OX is probably due to the lower degree of weathering of this soil. In this profile, clay activity was higher than 27 cmol$_c$ kg^{-1} (data not shown), indicating the presence of 2:1 minerals in this fraction. These minerals indicate a less evolved

mineralogical matrix, where an expressive part of Al is still in the aluminosilicate structure. In TS, m values were high in all profiles, indicating the presence of SOM-Al complexes, which are also extracted by 1 mol L^{-1} KCl solution and determined by ICP-AES.

In general, Fed content was highest in OX (50.5 g kg^{-1}), followed by FH (13.2 g kg^{-1}) and TS (3.9 g kg^{-1}) (Table 2), as expected, since the higher moisture conditions promoted Fe^{3+} reduction processes. These processes may lead to dissolution of the iron oxides or even prevent their crystallization. The Feo content ranged from 2.3 to 10.9 g kg^{-1} (Table 2). In OX, the ratio of low crystalline Fe oxides (Feo) and total Fe oxides (Fed) (Feo/Fed) was higher at the surface, possibly due to the effect of SOM on the crystallization kinetics of these minerals. The Feo content was higher in FH than in OX. In FH, the Feo/Fed values were higher than 0.90 at depth, whereas in TS, the Feo/Fed values were always greater than 0.94 (Table 2). In these two soils, the more hydromorphic environment and the abundant organic ligands probably retard, or even inhibit, the crystallization of the Fe^{3+} oxides.

Carbon and N content and stock

The C and N contents increased from the top of the slope to the floodplain; they were lower in OX (non-hydromorphic) and increased in FH (hydromorphic) and TS (hydromorphic) (Table 2). The C and N contents ranged from 0.9 to 176.2 g kg^{-1} and from 0.1 to 11.1 g kg^{-1}, respectively (Table 2).

In OX, the C content ranged from 0.9 to 54.2 g kg^{-1} and decreased in the subsurface (Table 2). In TS, the C content of all layers was above 80 g kg^{-1}, the threshold between organic and mineral material (Santos et al., 2013) (Table 2), which confirms the presence of histic horizons in this soil. In FH, the C content ranged from 67.4 to 89.8 g kg^{-1}, increasing in the deeper layers. The increase in C content at depth may be due to the lower mineralization rate of organic compounds, which is controlled by the more frequent hydromorphic conditions.

In general, the C/N ratio was highest in FH (17-24) and decreased in TS (15-20) and OX (6-18) (Table 2). In OX, the C/N ratio exhibited two distinct tendencies: i) an increase from top to depth to the 0.40-0.60 m layer (C/N = 18) and ii) a decrease to 1.80 m (C/N = 6). C/N values lower than 10 indicate predominance of more humified material and microbial products (Christensen, 1992; Moreira and Siqueira, 2006). In FH, the different layers have a similar C/N ratio, whereas in TS, there is an increase at depth, contrary to the trend observed in OX. This difference is caused by the changes in the water regime and in the water table level where these soils occur. Hydromorphic conditions retard SOM decomposition, due to the limitations to heterotrophic growth, which are responsible for SOM degradation. Thus, in this environment, the C/N ratio tends to be higher, due to less humified material compared to the more oxidizing environments (Chimner and Ewel, 2005; Moreira and Siqueira, 2006).

The total C stocks were 32, 120, and 66 kg m^{-2} and N stocks were 2.4, 6.1, and 3.6 kg m^{-2} for OX, FH, and TS, respectively. In OX, C and N stocks decreased with depth, except for the intermediate profile position (0.20-0.80 m) where the increase was caused by the higher Sd. In FH and TS, the C and N stocks increased from the top to lower depths (Figure 1).

Considering all soil layers, the C and N stocks were highest in FH, where values approximately two times greater than TS and three to four times greater than OX were observed (Figure 1). However, comparing the profiles up to 0.60 m (limit for TS sampling depth), we observed the largest stock inTS, followed by FH and OX.

The 0.00-020 m layer contains only 29, 22, and 28 % of the total C stock and 32, 15, and 42 % of the total N stock in OX, FH, and TS, respectively. This is strong evidence that the subsurface horizons are important compartments for SOM storage. However, surface conservation is essential for maintenance of the C and N stocks at depth. In addition,
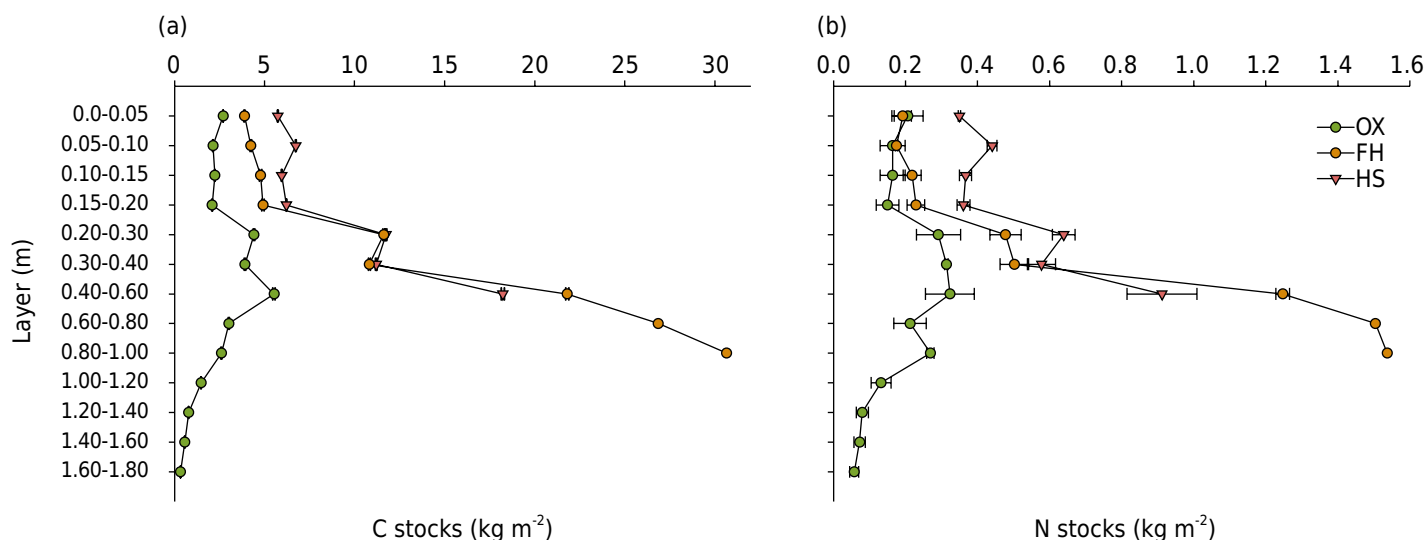
Figure 1. Total carbon (a) and nitrogen (b) stocks in a Humic Hapludox (OX), a Fluvaquentic Humaquepts (FH), and a Typic Haplosaprists (TS).

these surface stocks are more susceptible to losses through erosion and mineralization, which should be considered in environmental management.

The C stocks observed in this toposequence were higher than other values observed in Brazilian soils (humic and histic profiles). Novaes Filho et al. (2007) found values ranging from 3.4 to 3.9 kg m^{-2} at the 0.00-0.30 m depth in soils under native forest in the state of Rondônia. Batjes and Dijkshoorn (1999) observed C stocks ranging from 4.0 kg m^{-2} in Regolithic profiles to 72.8 kg m^{-2} in Haplosaprists to a depth of 1.0 m in the Amazon forest. In the upper montane region in the state of Paraná ("Serra da Igreja"), Scheer et al. (2011) observed C stocks ranging from 27.4 to 41.1 kg m^{-2} for soils in natural grasslands, and from 19.0 to 23.3 kg m^{-2} for profiles under native forest, at depths ranging from 0.42 to 0.86 m. The higher SD values observed for TS and FH compared to the non-hydromorphic C-rich soils of other studies (Batjes e Dijkshoorn, 1999; Scheer et al., 2011) were responsible for the larger C and N stocks calculated.

To estimate the total C stock in this microbasin, a brief survey of the location of the soil classes in this area was performed. This survey was based on two major documents: i) Soil survey of the state of Paraná (*Levantamento de reconhecimento dos solos do Estado do Paraná*) (Embrapa, 1984) and ii) Preliminar pedological survey from the basin to upstream of the Iraí River reservoir (*Levantamento pedológico preliminar da bacia a montante da represa do Rio Iraí*) (UFPR, 2004).

The Iraí conservation area has an area of approximately 11,536 ha distributed over the Guabirotuba geologic formation. Typic Haplosaprists are located in approximately 10.5 % of the area and Fluvaquentic Humaquepts in 11.3 % of the area. Oxisols and Inceptisols are found in about 50 % of the area. Thus, 71.8 % of the soils are represented by the soil classes examined in this study.

Assuming the values determined in this study, we can infer that in this area there is a C stock of 4.2 × 10^6 Mg, distributed as follows: 19 % - TS (7.95 × 10^5 Mg C - floodplain), 36 % - FH (1.36 × 10^6 Mg C - lower third), and 45 % - OX (1.9 × 10^6 Mg C - top slope). This C stock is twice as high as the stock in upper montane soils in natural grasslands and forests in the state of Paraná (Scheer et al., 2011).

SOM chemical fractions

In general, the proportion of total organic C was significantly higher in the SOM humic fractions (FA, HA, and HU) than in the non-humic fractions (water extract and 0.1 mol L^{-1} HCl solution), with mean values of 94.7 and 5.3 %, respectively (Figure 2).
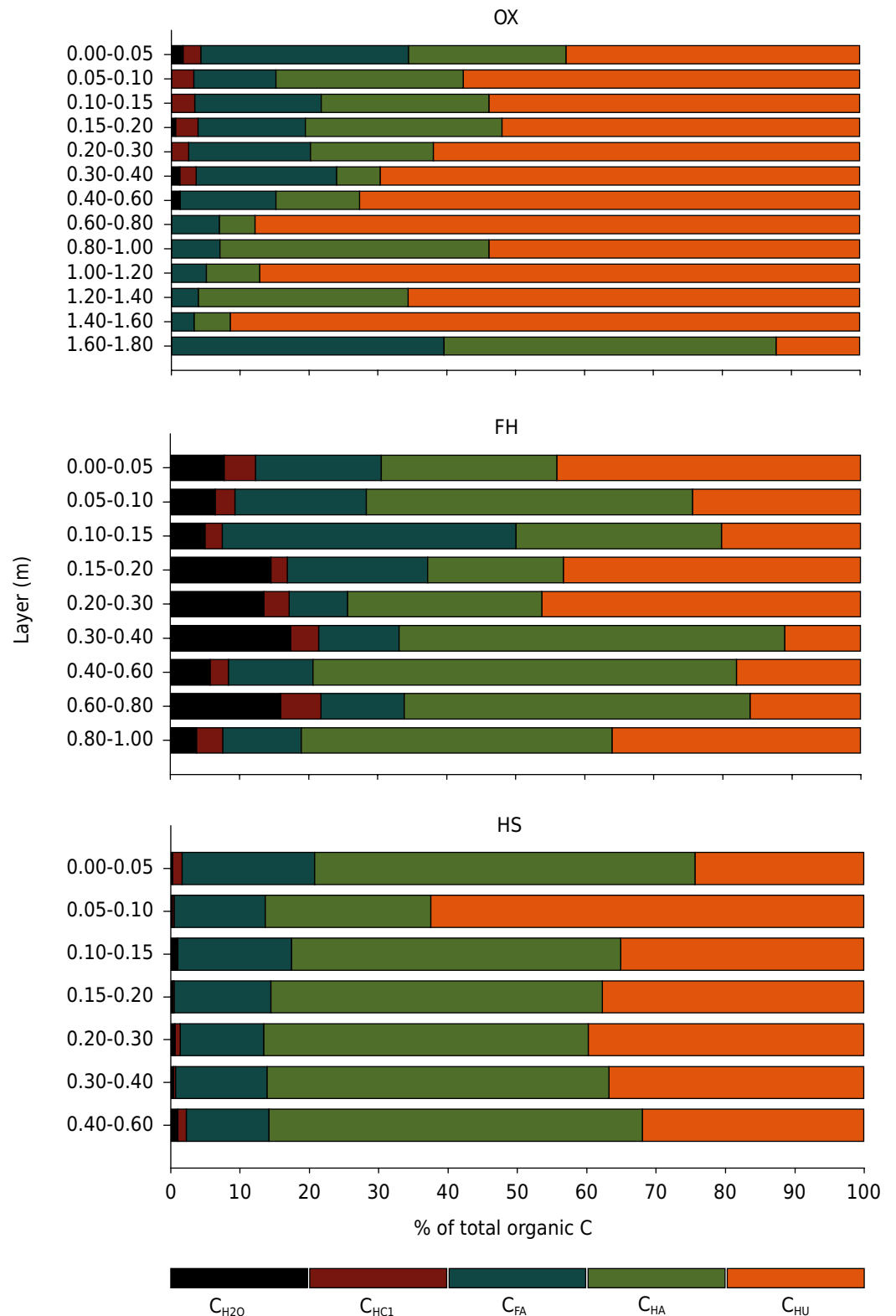
Figure 2. Proportion of soil organic matter fractions in total organic carbon of a Humic Hapludox (OX), a Fluvaquentic Humaquepts (FH), and a Typic Haplosaprists (TS).

Considering all soils, the highest C portion in the non-humic fraction was observed in the water extract (3.4 %), whereas in the HCl extract, the proportion was only 1.9 % of the total organic C. These fractions are composed of more labile hydrophilic structures, which are smaller than the FA and HA structures. These organic compounds are soluble in water and acid extract and are derived from microbial activity, as well as root exudates (Potes et al., 2010). The higher solubility of these compounds

can be explained by the lower aliphatic content in their structures. In addition, these groups show a weak association with the mineral fraction, which is mainly due to the mechanism of cation bridges through Ca^{+2} and Mg^{+2} (Dick et al., 1998). In the SOM humic fractions, the C proportion decreased in the following order: C_{HU} (46.1 %) > C_{HA} (33.1 %) > C_{FA} (15.5 %). The humin (HU) fraction and soluble humic (FA + HA) fractions represented approximately 50 % of organic C. However, the SOM fractions show different tendencies in each soil profile.

In OX, the organic C portion of the non-humic substances ranged from 2.5 to 6.1 % and decreased with depth. It was not possible to determine the non-humic fractions in the layers below 0.60 m (Figure 2). The reasons for this were i) the contribution of compounds from litter decomposition, as well as from root exudates, is greater in the surface horizon and ii) the higher availability of reactive sites of Fe oxide surfaces in the subsurface allows a stronger interaction between hydrophilic organic compounds and minerals, preventing their solubilization. In the same profile, the organic C proportion in HU ranged from 12 to 91 % and tended to increase with depth, which may also be due to the higher interaction of this fraction with the minerals, as well as its higher aliphaticity (discussed below). As expected, the opposite behavior was verified for the soluble fraction in alkaline medium (FA and HA), where the C proportion ranged from 8.6 to 87.8 % and decreased with depth (Figure 2).

Organic C in non-humic substances was higher in FH than in OX, ranging from 7.5 to 21.8 %, and it oscillated randomly at depth (Figure 2). A similar trend was observed in TS, although the C proportion in this fraction was lower than in FH, ranging from 0.5 to 2.3 % (Figure 2). The lower proportion of non-humic fractions in TS may be related to lower microbial activity, due to the hydromorphic conditions (Chimner and Ewel, 2005; Beutler et al., 2015).

In general, humic substances soluble in alkaline medium (HA and FA) showed the highest organic C proportion, ranging from 36.6 to 73.6 % in FH and from 37.0 to 73.9 % in TS (Figure 2). This result indicates a higher degree of hydrophilic functionalization of the humic fractions in these soils. The lower organic C proportion in the HU fraction in FH (28.8 %) and TS (38.4 %) than in OX (62 %) suggests that the organo-mineral interactions play an important role in stabilizing SOM from solubilization in acid/alkaline medium. This may be a very important mechanism in aerobic soils, with lower C contents and higher availability of Fe oxide surfaces to interact with SOM. In FH and TS, there were smaller mineral surfaces available and higher C content than in OX, causing surface saturation by SOM. This means that the organic C portion that could be stabilized by organo-mineral interactions in FH and TS was smaller than in OX, decreasing the HU proportion (Schöning et al., 2005; Heckman et al., 2013; Greathouse et al., 2014; Polubesova and Chefetz, 2014). The average proportion of organic C in the HU in TS was higher than in FH. This was due to greater abundance of hydrophobic aliphatic compounds in this fraction. These aliphatic structures can be preserved from anaerobic degradation (Bingham et al., 2010) and they are insoluble in an acid/alkaline medium.

Chemical composition of SOM fractions by FTIR

The FTIR spectra of purified HA and HU from the A horizon of OX (up to 0.40 m) and from all layers of FH and TS had the same pattern. Examples of HA and HU FTIR spectra are shown in figure 3. The absorption bands observed in the spectra were 3420 cm^{-1}, attributed to the O-H stretching in H-bonds; two bands at 2950 and 2840 cm^{-1}, attributed to the C-H stretching of aliphatic groups; 1710 cm^{-1}, attributed to the C=O stretching of carboxyls; 1630 cm^{-1}, attributed to C=C vibration of aromatic groups; 1540 cm^{-1}, attributed to N-H deformation and to C=N stretching; 1245 cm^{-1} attributed to C-O stretching and OH deformation of the carboxyl group; and 1075 cm^{-1}, attributed to the C-O bond of the carbohydrate-like structures (C-O-alkyl).
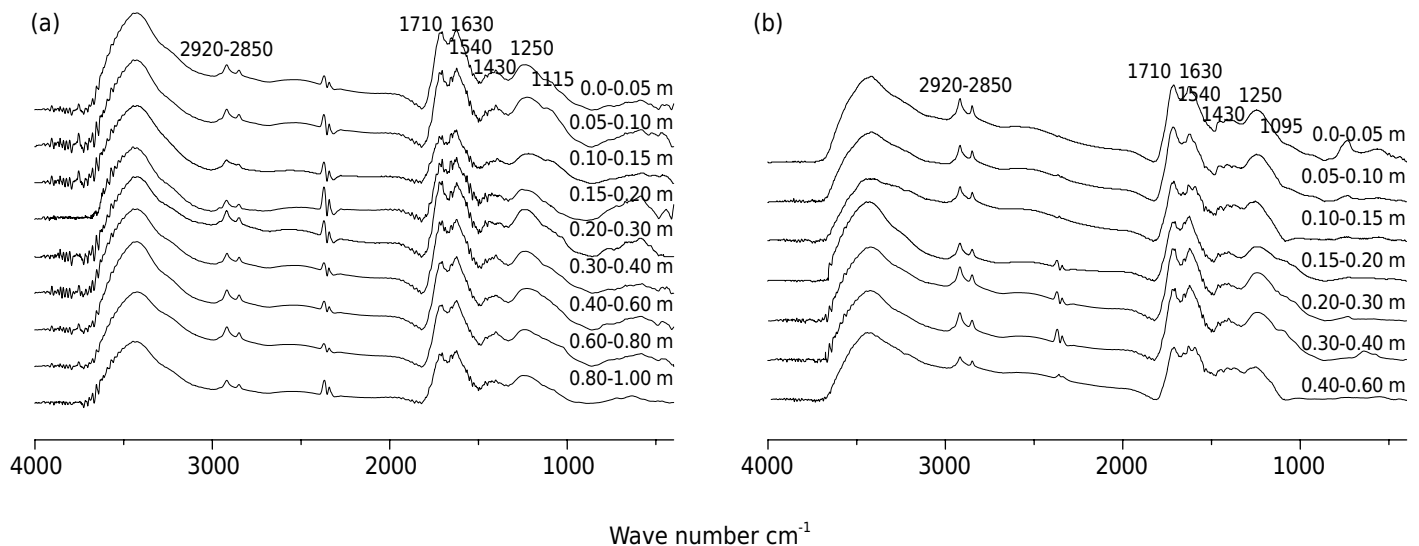
Figure 3. Fourier transform infrared spectroscopy (FTIR) spectra of (a) humic acids of a Fluvaquentic Humaquepts (FH) and (b) humin of Typic Haplosaprists (TS).

In OX, the HU fraction showed higher relative intensity (RI) in the aliphatic groups ($RI_{2950-2840}$) than the HA fraction, indicating the presence of more hydrophobic material. In addition, higher values of RI_{1075} were also observed, which shows carbohydrate-like structures (Table 3). This result suggests that the insolubility of the HU fraction in this profile is related to the hydrophobicity of the aliphatic groups. In contrast, a significant positive correlation was observed between the RI_{1075} variation and the Fed content ($R^2 = 0.97$ and $p<0.05$), suggesting that the labile and polar structures of HU are stabilized by organo-mineral interactions. The interaction between sugars and Fe and Al oxides has also been observed by other authors (Schöning et al., 2005; Hanke et al., 2015). In the same soil, HA showed higher RIs of the carboxylic (RI_{1710}) and aromatic (RI_{1630}) groups, as well as higher AI values (Table 3). This suggests that, although this fraction is more aromatic than HU, these aromatic groups are more functionalized by hydrophilic groups, permitting their extraction in alkaline medium.

In FH, as observed in OX, the HA fraction is more aromatic, showing higher RI_{1710}, whereas the HU fraction is comparatively more aliphatic (Table 3). The RI of the C-O-alkyl groups of carbohydrate-like structures showed a linear correlation with the Feo content ($R^2 = 0.91$ and $p<0.05$), similar to the correlation between the Fed and RI_{1075} values observed in OX. This result indicates that these groups are protected from solubilization by interactions with low crystalline Fe oxides, which are abundant minerals in anoxic environments with a high SOM content. The interaction of C groups with Fe can occur even during the precipitation of amorphous phases, which may block preferential sites for the growth of crystalline planes (Henneberry et al., 2012).

In TS, the HU fraction is more aromatic than in HA and showed higher RI values of C-O-alkyl groups. As in FH, a positive correlation was observed between the Feo and RI of C-O-alkyl groups ($R^2 = 0.55$ and $p<0.05$). This suggests the occurrence of organo-mineral interactions that may preserve a higher carbohydrate content in this fraction. Thus, these results show that in all soils, the HU carbohydrates interact with the Fe oxides. These interactions occur with the crystalline oxides in the more weathered soil under the more oxidizing conditions of the top of the slope. In addition, in hydromorphic soils, this interaction is found between the carbohydrate-like structures and low crystalline minerals. This mechanism may be responsible for the preservation of highly biochemically labile compounds in soils. Furthermore, this organo-mineral interaction is an important preservation factor for organic C since the HU corresponds to excessive proportions of SOM. In FH, the HA showed a higher RI for aliphatic groups than the HU fraction, a trend

Table 3. Fourier transform infrared spectroscopy spectral relative intensities (RI) and aromatic index (AI) of soil organic matter fractions of soils in a toposequence under Araucaria moist forest in southern Brazil

Fraction	Layer	$RI_{2950-2840}$	RI_{1710}	RI_{1630}	RI_{1540}	$RI_{1430-1360}$	RI_{1250}	RI_{1075}	AI
	m								
Humic Hapludox (OX)									
Humic acid	0.00-0.05	8.1	24.1	22.4	6.6	12.1	8.9	17.8	2.8
	0.05-0.10	7.2	25.2	23.2	6.2	13.2	9.2	15.8	3.2
	0.10-0.15	7.0	23.3	25.2	7.9	11.3	10.5	14.8	3.6
	0.15-0.20	6.2	22.3	29.2	7.1	10.8	10.1	14.3	4.7
	0.20-0.30	6.1	21.4	27.3	9.1	9.1	10.7	16.3	4.5
	0.30-0.40	6.4	23.4	29.1	8.1	8.6	8.3	16.1	4.5
	Mean	6.8	23.3	26.1	7.5	10.9	9.6	15.9	3.9
Humin	0.00-0.05	14.4	19.9	27.1	4.1	3.2	6.1	25.2	1.9
	0.05-0.10	14.6	22.3	22.1	4.8	3.7	6.4	26.1	1.5
	0.10-0.15	13.9	23.1	27.0	1.9	1.1	5.2	27.8	1.9
	0.15-0.20	15.1	18.4	25.1	3.1	3.1	5.1	30.1	1.7
	0.20-0.30	14.2	16.8	24.2	3.0	2.6	3.7	35.5	1.7
	0.30-0.40	13.8	11.7	24.7	2.1	2.3	6.5	38.9	1.8
	Mean	14.3	18.7	25	3.2	2.7	5.5	30.6	1.7
Fluvaquentic Humaquepts (FH)									
Humic acid	0.00-0.05	5.4	29.0	26.8	13.8	6.7	10.0	8.3	5.0
	0.05-0.10	5.2	25.2	23.8	13.3	7.8	13.3	11.4	4.5
	0.10-0.15	6.1	24.2	25.3	14.1	7.6	12.6	10.1	4.2
	0.15-0.20	5.0	28.3	27.9	16.4	7.3	11.0	4.1	5.5
	0.20-0.30	6.0	28.1	24.8	14.0	7.8	13.6	5.6	4.1
	0.30-0.40	5.2	28.2	28.2	14.6	7.5	11.7	4.7	5.5
	0.40-0.60	6.3	30.6	24.9	13.6	5.9	11.8	6.8	3.9
	0.60-0.80	7.4	27.6	26.9	13.6	8.3	9.6	6.6	3.6
	0.80-1.00	6.3	28.1	26.8	13.8	6.8	12.2	5.9	4.2
	Mean	5.9	27.7	26.1	14.1	7.3	11.8	7.0	4.5
Humin	0.00-0.05	7.3	22.0	29.9	13.6	7.9	10.5	8.7	4.1
	0.05-0.10	7.9	22.6	32.6	13.2	8.6	10.4	4.7	4.1
	0.10-0.15	8.2	22.4	30.6	14.7	8.8	9.4	5.9	3.7
	0.15-0.20	7.7	22.3	30.0	14.5	8.2	9.4	7.7	3.9
	0.20-0.30	8.7	19.7	30.7	14.7	7.8	9.2	9.2	3.5
	0.30-0.40	9.4	20.9	30.9	16.7	4.8	4.0	13.2	3.3
	0.40-0.60	8.9	22.2	27.1	14.4	7.2	6.6	13.7	3.1
	0.60-0.80	9.3	20.4	25.9	16.2	5.1	10.6	12.5	2.8
	0.80-1.00	11.2	23.5	31.3	12.0	7.8	8.9	5.2	2.8
	Mean	8.7	21.8	29.9	14.4	7.4	8.8	9.0	3.5
Typic Haplosaprists (TS)									
Humic acid	0.00-0.05	11.2	31.3	26.8	6.3	6.7	15.2	2.7	2.4
	0.05-0.10	10.0	32.9	26.4	6.0	7.0	15.2	2.5	2.7
	0.10-0.15	10.2	29.5	23.9	7.0	8.6	16.1	4.8	2.3
	0.15-0.20	8.9	28.4	28.4	8.9	6.5	11.9	7.0	3.2
	0.20-0.30	9.6	28.1	25.5	8.8	6.4	14.6	7.1	2.7
	0.30-0.40	5.0	28.5	27.3	9.7	7.5	13.3	8.6	5.4
	0.40-0.60	7.9	28.0	25.3	6.8	7.2	14.0	10.8	3.2
	Mean	9.0	29.5	26.2	7.6	7.1	14.3	6.2	3.1
Humin	0.00-0.05	7.9	19.2	25.4	11.0	10.1	10.6	15.8	3.2
	0.05-0.10	9.2	18.8	28.3	10.2	8.3	10.8	14.4	3.1
	0.10-0.15	7.7	24.7	24.1	11.1	8.1	10.7	13.6	3.1
	0.15-0.20	7.4	21.0	24.9	10.9	8.7	13.1	14.0	3.4
	0.20-0.30	8.9	21.9	24.7	10.9	8.5	12.1	13.0	2.8
	0.30-0.40	6.6	25.6	32.7	11.8	6.9	11.3	5.1	4.9
	0.40-0.60	8.1	20.4	30.1	14.5	8.6	8.6	9.7	3.7
	Mean	8.0	21.6	27.2	11.5	8.5	11.0	12.2	3.5

different from that observed in OX and FH. Additionally, HA has a high carboxyl group content (RI_{1710}) (Table 3). Although aliphatic compounds can show that HA is organized as a network of hydrophobic micelles (Piccolo et al., 2001), its functionalization by carboxylic groups allows solubilization in an alkaline medium.

The presence of carboxyls in HU supports the presence of organo-mineral interactions in this fraction. Generally, these groups are responsible for organic compound solubilization during SOM chemical fractionation. This is due to the acidic character and the high polarity of carboxyl structures. The preservation of carboxyls in an insoluble humic fraction is probably due to two main conditions: (i) the carboxyl groups are strongly bound to the minerals, mainly Fe and Al oxides and (ii) these groups are protected within hydrophobic micelles.

Iron and Al contents associated with SOM chemical fractions

The Fe content in the SOM chemical fractions decreased in the following order: $Fe_{(HSs)} > Fe_{(HCl)} > Fe_{(water)}$, with values of 1579, 320, and 58 mg kg^{-1}, respectively (Table 4). The same trend was observed for Al, which showed mean values of 11,088 mg kg^{-1} in HSs, 234 mg kg^{-1} in HCl extract, and 53 mg kg^{-1} in water extract (Table 5). Both the Fe and Al contents observed in the SOM fractions were generally higher than those observed in humic and non-hydromorphic soils of altitude in the state of Rio Grande do Sul (Sarante et al., 2011).

The Fe content in water and HCl extract is related to Fe in association with low molecular weight hydrophilic organic compounds. Fe levels in both extracts were more similar to each other than to $Fe_{(HSs)}$, and showed a random variation at depth (Table 4). The $Fe_{(HCl)}$/Feo ratio ranged from 0.01 to 0.05, indicating that only a small fraction of the Fe extracted by ammonium oxalate in an acidic medium (pH = 3) can be derived from the Fe associated with the organic compounds of the SOM fractions.

The Al content determined in the water extract also varied randomly at depth - from 12 to 139 mg kg^{-1} (Table 5). Al content in HCl extract was significantly higher in TS (mean 576 mg kg^{-1}) than in OX (76 mg kg^{-1}) and FH (50 mg kg^{-1}) (Table 5). In OX, the $(Al_{(water)} + Al_{(HCl)})$/(Al exchangeable) ratio ranged from 0.10 to 0.96 and decreased with depth (Table 6). This supports the idea that, on the surface, the exchangeable Al is associated with the non-humic fractions and, at depth, the Al is in its ionic form, mainly interacting with the reactive sites of the mineral surface. This is because this extraction method (0.1 mol L^{-1} HCl solution) extracts the low molecular weight organic compounds that are associated with Al and measured by atomic absorption. In FH, this ratio ranged from 0.10 to 0.63, and was lower at depth than near the surface (Table 6). In contrast, in TS, all these ratio values were high, indicating that almost all of the Al considered exchangeable is actually associated with the most labile SOM compounds. The formation of SOM-Fe and SOM-Al complexes in solution can substantially increase the stability of the SOM-labile fraction (Heckman et al., 2013) and corroborate the high C contents observed in the humic and histic horizons.

The Fe content in the humic substances extract is mainly associated with the HA fraction, which can be observed by the higher values of the $Fe_{(HA)}/Fe_{(HSs)}$ ratio than the $Fe_{(FA)}/Fe_{(HSs)}$ ratio (Table 6). For the Al, a contrary trend was observed, since this ion is more associated with the FA fraction, even after extract purification with DAX-8 resin (Table 5). Similar results were observed by Sarante et al. (2011), who verified a higher molar Al/Fe ratio in FA than in HA, confirming the higher affinity of Al for the FA organic ligands. The higher affinity of Fe and Al for these humic fractions may be due to differences in their chemical composition. Al is considered a hard Lewis acid and has a higher affinity for interacting with hard Lewis bases, such as carboxylic groups, which are more abundant in the FA structures (Sparks, 1995). The interaction between Fe and SOM groups, for its part, is mainly due to phenolic hydroxyls and aliphatic compounds, since these interactions are more hydrophobic. In addition, these interactions can occur through the peripheral

Table 4. Iron in water extract [Fe$_{(water)}$], Fe in HCl extract [Fe$_{(HCl)}$], Fe in NaOH extract [Fe$_{(HSs)}$], Fe associated with HA [Fe$_{(HA)}$], and Fe in FA extract [Fe$_{(FA)}$] contents of soils in a toposequence under Araucaria moist forest in southern Brazil

Layer	Fe(water)	Fe(HCl)	Fe(HSs)	Fe(HA)	Fe(FA)
m	mg kg^{-1}				
Humic Hapludox (OX)					
0.00-0.05	24 ±2	211 ±11	1109 ±42	735 ±28	374 ±12
0.05-0.10	39 ±4	107 ±5	1089 ±35	711 ±21	378 ±16
0.10-0.15	22 ±2	113 ±0	901 ±33	705 ±33	197 ±18
0.15-0.20	17 ±2	148 ±13	757 ±12	498 ±17	259 ±18
0.20-0.30	18 ±2	98 ±8	549 ±18	454 ±13	95 ±7
0.30-0.40	22 ±3	123 ±9	535 ±12	401 ±14	134 ±6
Mean	24	117	823	584	239
Fluvaquentic Humaquepts (FH)					
0.00-0.05	41 ±3	396 ±21	952 ±38	743 ±31	209 ±17
0.05-0.10	59 ±5	332 ±17	1231 ±51	898 ±44	333 ±11
0.10-0.15	51 ±3	381 ±14	1838 ±72	1376 ±41	461 ±29
0.15-0.20	102 ±7	331 ±19	1236 ±39	866 ±27	370 ±9
0.20-0.30	113 ±4	297 ±6	1952 ±36	1502 ±22	450 ±10
0.30-0.40	143 ±6	336 ±8	1239 ±38	822 ±27	417 ±18
0.40-0.60	52 ±2	572 ±27	1509 ±54	1106 ±42	403 ±14
0.60-0.80	166 ±8	632 ±24	918 ±12	690 ±31	228 ±7
0.80-1.00	40 ±3	269 ±12	1446 ±27	1037 ±33	410 ±19
Mean	85	394	1369	1005	364
Typic Haplosaprists (TS)					
0.00-0.05	37 ±2	511 ±22	1381 ±29	990 ±18	391 ±7
0.05-0.10	81 ±6	542 ±27	1571 ±32	1122 ±29	449 ±21
0.10-0.15	83 ±3	576 ±13	3440 ±67	2743 ±58	697 ±20
0.15-0.20	67 ±6	474 ±19	3892 ±49	2989 ±41	903 ±30
0.20-0.30	98 ±2	302 ±11	3766 ±37	2876 ±26	890 ±21
0.30-0.40	51 ±5	401 ±14	2652 ±32	1610 ±49	1042 ±31
0.40-0.60	39 ±4	334 ±8	1109 ±28	912 ±31	196 ±16
Mean	65	449	2544	1892	652

Table 5. Aluminum in water extract [Al$_{(water)}$], Al in HCl extract [Al$_{(HCl)}$], exchangeable Al^{3+} (Al$_e$), Al in NaOH extract [Al$_{(HSs)}$], Al associated with HA [Al$_{(HA)}$], Al in FA extract [Al$_{(FA)}$], and Al in FA extract after purification with DAX-8 resin [Al$_{(PFA)}$] contents of soils in a toposequence under Araucaria moist forest in southern Brazil

Layer	Al(water)	Al(HCl)	Al$_e$	Al(HSs)	Al(HA)	Al(FA)	Al(PFA)
m	mg kg^{-1}						
Humic Hapludox (OX)							
0.00-0.05	41 ±6	71 ±4	117 ±5	4585 ±111	795 ±32	3790 ±97	2390 ±132
0.05-0.10	25 ±4	96 ±4	238 ±7	4745 ±132	1124 ±74	3621 ±92	2132 ±156
0.10-0.15	27 ±3	111 ±8	351 ±7	3984 ±91	1194 ±71	2789 ±76	2157 ±201
0.15-0.20	32 ±3	80 ±4	374 ±18	4111 ±78	634 ±32	3478 ±62	2429 ±234
0.20-0.30	34 ±3	58 ±4	459 ±26	3232 ±39	430 ±17	2801 ±33	1512 ±98
0.30-0.40	12 ±1	41 ±2	518 ±24	2728 ±47	608 ±27	2120 ±34	1388 ±49
Mean	29	76	343	3898	798	3100	2001
Fluvaquentic Humaquepts (FH)							
0.00-0.05	15 ±2	48 ±6	99 ±11	6860 ±122	2070 ±82	4790 ±97	2622 ±117
0.05-0.10	24 ±3	45 ±2	367 ±22	8123 ±234	1912 ±118	6212 ±174	3437 ±239
0.10-0.15	26 ±3	49 ±7	583 ±47	15602 ±278	4115 ±177	11487 ±213	7288 ±402
0.15-0.20	54 ±9	46 ±4	567 ±24	8083 ±97	2206 ±66	5877 ±75	4111 ±265
0.20-0.30	64 ±7	48 ±3	689 ±22	11417 ±202	3019 ±151	8398 ±173	5874 ±272
0.30-0.40	80 ±5	47 ±5	662 ±22	9505 ±134	2394 ±223	7111 ±169	5342 ±67
0.40-0.60	21 ±2	46 ±5	202 ±11	10111 ±132	2129 ±109	7982 ±117	7211 ±302
0.60-0.80	51 ±4	78 ±7	340 ±31	8456 ±307	1907 ±142	6549 ±221	3890 ±144
0.80-1.00	21 ±2	47 ±3	719 ±52	11832 ±402	2289 ±88	9543 ±247	6701 ±38
Mean	40	50	470	9999	2449	7550	5164
Typic Haplosaprists (TS)							
0.00-0.05	62 ±6	653 ±21	720 ±12	12439 ±128	1766 ±81	10673 ±103	4322 ±81
0.05-0.10	88 ±6	612 ±31	713 ±19	17563 ±244	2686 ±178	14877 ±192	6987 ±327
0.10-0.15	77 ±7	493 ±16	649 ±14	23983 ±502	3762 ±211	20221 ±323	9890 ±166
0.15-0.20	102 ±5	587 ±27	649 ±41	27777 ±387	2653 ±143	25123 ±298	12444 ±532
0.20-0.30	139 ±7	556 ±30	649 ±21	24347 ±202	2900 ±54	21447 ±181	8321 ±340
0.30-0.40	82 ±4	342 ±21	517 ±34	15632 ±144	5810 ±303	9822 ±241	6202 ±77
0.40-0.60	77 ±5	789 ±61	875 ±46	13827 ±137	3916 ±76	9911 ±118	7089 ±103
Mean	90	576	682	19367	3356	16011	7894

Table 6. Relation between Fe, Al, and C contents, determined in different chemical and mineralogical compartments of soils in a toposequence under Araucaria moist forest in southern Brazil

Layer	$Fe_{(HCl)}/Feo$	$Fe_{(HA)}/Fe_{(HSs)}$	$Fe_{(FA)}/Fe_{(HSs)}$	$C_{(water)}/Fe_{(water)}$	$C_{(HCl)}/Fe_{(HCl)}$	$C_{(HA)}/Fe_{(HA)}$	$C_{(FA)}/Fe_{(FA)}$	$(Al_{(HCl)}+Al_{(water)})/Al_t$	$Al_{(HA)}/Al_{(HSs)}$	$Al_{(FA)}/Al_{(HSs)}$	$Al_{(PFA)}/Al_{(HSs)}$	$C_{(water)}/Al_{(water)}$	$C_{(HCl)}/Al_{(HCl)}$	$C_{(HA)}/Al_{(HA)}$	$C_{(FA)}/Al_{(FA)}$
m	—————————— mol mol^{-1} ——————————								—————————— mol mol^{-1} ——————————						
Humic Hapludox (OX)															
0.00-0.05	0.03	0.66	0.34	0.18	0.03	0.03	0.08	0.96	0.17	0.83	0.52	0.05	0.04	0.03	0.01
0.05-0.10	0.02	0.65	0.35	0	0.05	0.03	0.07	0.51	0.24	0.76	0.45	0	0.03	0.02	0
0.10-0.15	0.03	0.78	0.22	0	0.05	0.04	0.05	0.39	0.30	0.70	0.54	0	0.02	0.02	0
0.15-0.20	0.05	0.66	0.34	0.05	0.03	0.03	0.09	0.30	0.15	0.85	0.59	0.01	0.03	0.03	0
0.20-0.30	0.03	0.83	0.17	0	0.04	0.04	0.05	0.20	0.13	0.87	0.47	0	0.03	0.03	0
0.30-0.40	0.04	0.75	0.25	0.06	0.02	0.02	0.02	0.10	0.22	0.78	0.51	0.05	0.03	0.01	0.01
Mean	0.03	0.72	0.28	0.05	0.04	0.03	0.06	0.41	0.20	0.80	0.51	0.02	0.03	0.02	0.01
Fluvaquentic Humaquepts (FH)															
0.00-0.05	0.01	0.78	0.22	0.61	0.04	0.28	0.11	0.63	0.3	0.70	0.38	0.84	0.15	0.02	0.01
0.05-0.10	0.01	0.73	0.27	0.35	0.03	0.19	0.17	0.19	0.24	0.76	0.42	0.42	0.10	0.04	0
0.10-0.15	0.01	0.75	0.25	0.35	0.02	0.02	0.08	0.13	0.26	0.74	0.47	0.33	0.09	0.01	0.01
0.15-0.20	0.01	0.70	0.30	0.51	0.03	0.01	0.08	0.18	0.27	0.73	0.51	0.46	0.09	0.02	0.01
0.20-0.30	0.01	0.77	0.23	0.41	0.04	0.06	0.06	0.16	0.26	0.74	0.51	0.34	0.12	0.02	0
0.30-0.40	0.01	0.66	0.34	0.43	0.04	0.10	0.24	0.19	0.25	0.75	0.56	0.37	0.15	0.04	0
0.40-0.60	0.00	0.73	0.27	0.34	0.01	0.09	0.17	0.34	0.21	0.79	0.71	0.40	0.09	0.04	0
0.60-0.80	0.02	0.75	0.25	0.32	0.03	0.08	0.24	0.38	0.23	0.77	0.46	0.50	0.12	0.04	0
0.80-1.00	0.01	0.72	0.28	0.38	0.06	0.02	0.18	0.10	0.19	0.81	0.57	0.35	0.16	0.04	0
Mean	0.01	0.73	0.27	0.41	0.03	0.09	0.15	0.25	0.25	0.75	0.52	0.45	0.12	0.03	0
Typic Haplosaprists (TS)															
0.00-0.05	0.01	0.72	0.28	0.06	0.02	0.14	0.38	0.99	0.14	0.86	0.35	0.02	0.01	0.10	0.01
0.05-0.10	0.02	0.71	0.29	0.03	0	0.13	0.17	0.98	0.15	0.85	0.40	0.01	0	0.03	0
0.10-0.15	0.02	0.80	0.2	0.09	0	0.19	0.14	0.88	0.16	0.84	0.41	0.05	0	0.05	0
0.15-0.20	0.02	0.77	0.23	0.03	0	0.13	0.13	1.06	0.10	0.90	0.45	0.01	0	0.07	0
0.20-0.30	0.04	0.76	0.24	0.05	0.02	0.11	0.13	1.07	0.12	0.88	0.34	0.02	0.01	0.06	0
0.30-0.40	0.02	0.61	0.39	0.06	0.01	0.09	0.23	0.82	0.37	0.63	0.40	0.02	0	0.03	0
0.40-0.60	0.01	0.82	0.18	0.12	0.02	0.08	0.27	0.99	0.28	0.72	0.51	0.03	0	0.03	0
Mean	0.02	0.74	0.26	0.06	0.01	0.12	0.21	0.97	0.19	0.81	0.41	0.02	0	0.05	0

$Fe_{(HCl)}/Feo$: mass ratio between Fe extracted by HCl solucion (0.1 mol L^{-1}) and low crystallinity Fe oxide contents, extracted with ammonium oxalate (0.2 mol L^{-1}, pH 3.0); $Fe_{(HA)}/Fe_{(HSs)}$: mass ratio between Fe in the humic acid fraction and Fe in the soluble humic substances; $Fe_{(FA)}/Fe_{(HSs)}$: mass ratio between Fe in the fulvic acid fraction and Fe in the soluble humic substances; $C_{(water)}/Fe_{(water)}$: mass ratio between C and Fe in the water extract; $C_{(HCl)}/Fe_{(HCl)}$: mass ratio between C and Fe in the HCl extract; $C_{(HA)}/Fe_{(HA)}$: mass ratio between C and Fe in the humic acid fraction; $C_{(FA)}/Fe_{(FA)}$: mass ratio between C and Fe in the fulvic acid fraction; $(Al_{(HCl)} + Al_{(water)})/Al_t$: mass ratio between the sum of Al in water and HCl extracts by the exchangeable Al; $Al_{(HA)}/Al_{(HSs)}$: mass ratio between Al in the humic acid fraction and Al in the soluble humic substances; $Al_{(FA)}/Al_{(HSs)}$: mass ratio between Al in the fulvic acid fraction and Al in the soluble humic substances; $Al_{(PFA)}/Al_{(HSs)}$: mass ratio between Al in the purified fulvic acid fraction and Al in the soluble humic substances; $C_{(water)}/Al_{(water)}$: mass ratio between C and Al in the water extract; $C_{(HCl)}/Al_{(HCl)}$: mass ratio between C and Al in the HCl extract; $C_{(HA)}/Al_{(HA)}$: mass ratio between C and Al in the humic acid fraction; $C_{(FA)}/Al_{(FA)}$: mass ratio between C and Al in the fulvic acid fraction.

carboxyls present in the larger alkyl chains. Both these structures are more abundant in HA (Dobbs et al., 2009). The higher affinity of Fe for HA and Al for FA is supported by the observed values for the C/Fe and C/Al molar ratios in humic fractions, with the C/Fe ratio lower in HA and the C/Al ratio lower in FA (Table 6).

For humic fractions (HA and FA) and non-humic fractions (water and HCl), the values observed for $C_{(water)}/Al_{(water)}$, $C_{(HCl)}/Al_{(HCl)}$, $C_{(FA)}/Al_{(FA)}$, and $C_{(HA)}/Al_{(HA)}$ ratios were low and similar to each other, suggesting that the affinity of these fractions with Al is similar (Table 6). The exception to this trend was observed for the $C_{(water)}/Al_{(water)}$ and $C_{(HCl)}/Al_{(HCl)}$ ratios in FH, which exhibited higher values, ranging from 0.33 to 0.84 and 0.09 to 0.16 mol mol^{-1}, respectively (Table 6). This result indicates that in FH, Al has more affinity for the

organic ligands that are present in the humic substance structures than the ligands of water-soluble compounds of the non-humic fractions.

The humic and non-humic fractions had a similar C/Fe molar ratio in OX, suggesting that under oxidizing and more weathered conditions, the SOM fractions have a similar affinity for that metal (Table 6). In FH, lower values of this ratio were observed in HCl extract and in HA. However, in TS, the SOM non-humic fractions had lower values for the C/Fe molar ratio. The processes of Fe reduction in the hydromorphic floodplain, as well as the low pH values observed in this profile, may increase Fe availability in solution in ionic form. The ionic Fe in solution can form complexes and associations with more labile hydrophilic compounds, such as organic acids of low molecular weight, carbohydrates, and amino sugars.

The high Fe and Al contents measured in the humic and non-humic fractions highlight the importance of SOM as an environmental filter in C-rich environments due to the capacity of SOM in interacting with metals. These interactions, especially those that occur with the hydrophilic and lower molecular weight compounds, may be responsible for the SOM mobilization in the profile that contributes to C enrichment in the subsurface, as well as C stabilization.

CONCLUSIONS

Organic C enrichment in the toposequence increased from the most oxidizing positions to the floodplain. The differences observed in the SOM content and its chemical composition were defined by the differences in the soil water regime.

The Iraí conservation area has a large reserve of C and N, which can be used as a physiographic reference for the ecological-economic zoning of this region. The amount of C stored in the subsurface represents approximately 70 % of the total. Thus, conservation of the soils of the floodplain and lower third of the slope is essential for the C stocks at depth since drainage or use for other activities could imply a progressive decline in SOM content.

The carbohydrate-like structures of the HU fraction were protected from solubilization in acid/alkaline medium by interaction with the higher crystalline Fe oxides in the Oxisol. In addition, in the hydromorphic soils, the carbohydrate-like structures are associated with low crystalline Fe oxides. The organo-mineral interactions may represent an important mechanism for conservation of organic compounds in these soils.

Soluble humic substances showed the highest contents of co-extracted Fe and Al, and their compartments have different affinities for Fe and Al. Thus, Fe is preferentially associated with HA, whereas Al showed higher affinity for FA.

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