

# Humic Substances of Spodic Horizons in the Coastal Plain of São Paulo State

J.M. Lopes, P. Vidal-Torrado, P. Buurman, and P.B. Camargo

**Abstract** The most common soils that occurred in environments generically called restinga are podzols that are characterized by the presence of spodic horizon (Bh or Bhm). There are few scientific studies related to the genesis of these soils in tropical regions, and there are few detailed studies assessing the chemical characteristics and composition of organic matter (OM) present in these soils, as well their relations with time. The cities Cananéia and Bertioga were selected for this research due to the presence of different sedimentary units and remaining vegetation. The characterization of humic acids (HA) was realized using spectroscopic techniques like Fourier transform infrared spectroscopy (FTIR) and fluorescence. Samples were extracted from different podzol horizons in order to achieve more details about the OM present in these soils and relate the results to the stability of carbon and the mean residence time (MRT) of OM. The main hypothesis tested was that the profiles where the OM has less MRT would have the highest contents of more recalcitrant compounds. In this context, the main results related to the objectives were as follows: The older profiles were those with the highest concentrations of more recalcitrant compounds, especially in the subsurface horizons (Bh and Bhm). This inference may indicate that with transcurrent time, OM tends to undergo changes in its composition and become recalcitrant.

**Keywords** Coastal plain • Humic substances • Mean residence time • Podzol • Soil organic matter • Spodic horizons

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## Introduction

The organic matter (OM) plays a fundamental role in the podzol formation process, consisting of humic substances (HS) that are products of oxidative degradation and subsequent humification of OM (Stevenson 1994). The HS are organic substances chemically complex, amorphous, generally dark, hydrophilic, acidic, or partially aromatic (Schnitzer 1982) and composed by compounds that have a wide variety of functional groups (carboxylic, hydroxyl, phenolic, carbonyl, etc.). Part of the HS present in the Bh and Bhm horizons comes from the superficial OM decomposition, and some authors have suggested that the mean residence time (MRT) estimated by  $^{14}\text{C}$  and, consequently, the stability of OM in the soil increase with depth (Paul et al. 1997).

The study of SH is possible using spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) (González-Pérez et al. 2008), which permits the study of the structure of HS. Another technique widely used is the fluorescence, by which it is possible to estimate the humification degree (Milori et al. 2002), allowing the elucidation of different aspects of reactivity and chemical structure of OM.

## Materials and Methods

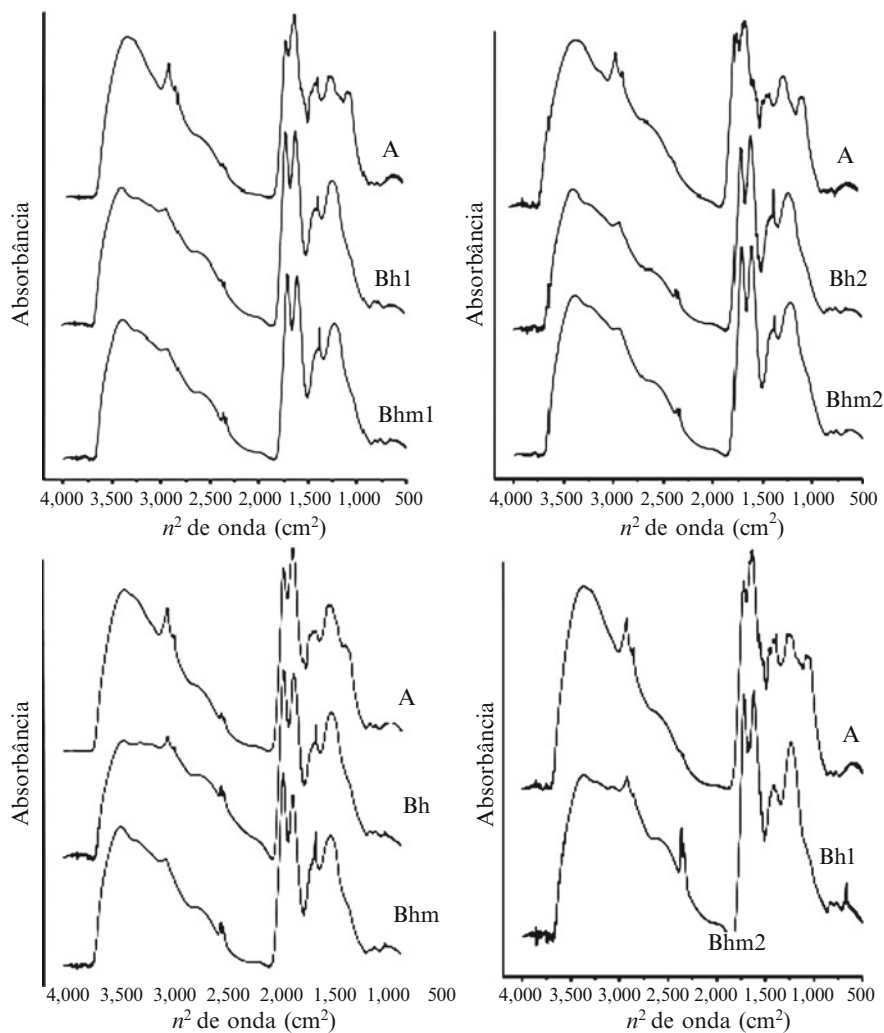
The profiles called P03, P10, and P30 are located in Cananéia, and the profile P04 in Bertioga. FTIR measurements were performed using methods well established in the literature (Stevenson 1994) using tablets with 1 mg of SH and 100-mg KBr. For preparation of the tablets, samples were ground with KBr, packed in a mold, and pressed. The spectra were obtained using 16 scans in the range  $4,000\text{--}400\text{ cm}^{-1}$ , with spectral resolution of  $4\text{ cm}^{-1}$  and a range of  $1\text{ cm}^{-1}$ .

For fluorescence analysis, the HA extracted from the soil profiles were dissolved in  $\text{NaHCO}_3$  solution  $0.05\text{ mol L}^{-1}$ . The spectra were obtained according to the methodology proposed by Milori et al. (2002).

For the dating of the soil source material (coastal sediments) by thermoluminescence (TL), the samples were collected with the aid of black PVC pipe inserted horizontally to the ground surface.

## Results and Discussion

The FTIR spectra of HA extracted from different horizons (A, Bh, and Bhm) from the profiles P03, P04, P10, and P30 are shown in Fig. 1. It is possible to observe that the spectra of HA extracted from different soil profiles show similarities. There are



**Fig. 1** FTIR spectra of HA extracted from the surface horizons (A) and subsurfaces (Bh and Bhm) from P03, P10, P30, and P04 profiles, respectively

no significant structural and chemical variations between samples in HA, but it is possible to observe changes in the intensities between the groups in each profile.

In the spectra of all profiles, it can be observed that samples of the soil surface have an absorption band between  $1,170$  and  $950\text{ cm}^{-1}$ , the same being absent in the spectra obtained for the subsurface layers Bhm and Bh. This band is assigned to CO stretching of polysaccharides. This result is related to higher content of OM decomposed or even by the presence of microbial activity. It is well known that microorganisms produce polysaccharides during the decomposition of OM (Stevenson 1994). Another region of the spectrum that can be observed only for

the samples of the soil surface is between 1,660 and 1,630  $\text{cm}^{-1}$ , which is attributed to stretching of C=O from amide, which can usually be associated with proteins.

In the spectral region between 3,400 and 3,300  $\text{cm}^{-1}$ , the absorption due to stretching of the H-bond to OH and NH is stronger in samples from the superficial horizons, and the lower intensity is observed for Bh horizons. Another variation in intensity is observed in the region between 2,940 and 2,900  $\text{cm}^{-1}$ , which is assigned to CH stretching of aliphatic groups, being observed as a greater intensity of this band in the soil surface, showing a higher concentration of aliphatic.

Another variation in depth may be observed in the spectral region between 1,725 and 1,720  $\text{cm}^{-1}$  in which the absorption is due to stretching C=O of COOH, being observed a greater intensity in the subsurface horizons. A reverse trend can be observed in the region of the spectrum between 1,280 and 1,200  $\text{cm}^{-1}$ , in which absorption may be due to CO stretching of aryl ethers and/or phenolic. The greater intensity of this band occurs in the spectra of samples from subsurface horizons, showing a higher concentration of phenolic compounds in depth. The intensities of the band assigned to aliphatic CH stretching region of the spectrum between 1,460 and 1,450  $\text{cm}^{-1}$  showed a slight increase for the samples of surface horizons, with almost imperceptible difference in intensity of this band for the samples of Bh and Bhm horizons.

In general, the results suggest an increasing degree of humification of OM in depth, as evidenced by the presence of more condensed compounds in the subsurface layers and the highest concentration of aliphatic compounds and the presence of polysaccharides in the surface horizons.

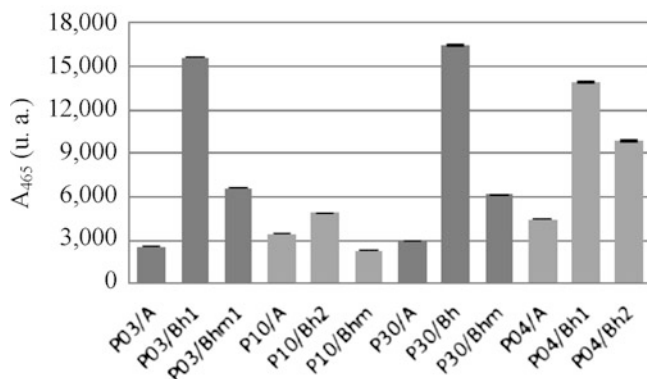
The results of fluorescence showed that the greatest degree of HA humification was obtained for the Bh horizons of the profiles P03 and P30 in relation to the profiles P10 and P04. The lower degree of humification was determined in HA from the surface horizons of all profiles. The degree of humification is related to the presence of compounds with more complex structures such as aromatic compounds.

Looking at Fig. 2, the samples that have higher rates of humification are the ones with the higher content of more recalcitrant compounds. Some studies suggest good correlations between the humification rate obtained by fluorescence spectroscopy and other techniques to achieve results directly or indirectly related to the stage of humification of OM evaluated (Milori et al. 2002).

The results obtained by fluorescence showed that the same trend of humification was maintained for the different horizons of the different profiles. Comparison between the profiles showed the same results obtained by FTIR. The P30 is the profile that has the highest rates of humification in relation to others (Table 1).

By evaluating the results of fluorescence and comparisons made with the results of FTIR and dating, it was possible to establish a positive relationship between the transcurrent time and humification of the HS. Considering only the MRT of OM, it was possible to conclude that the older the profile, the more stable the OM present in it.

Further investigation about the stability of OM and its comparisons with other factors that influence this process should be made, since there is a need for greater understanding in the concentrations of OM as well its preservation in soil.



**Fig. 2** Index  $A_{465}$  obtained from fluorescence spectra of HA extracted from *P03*, *P10*, *P30*, and *P04* profiles, according to Milori et al. (2002)

**Table 1** Age of the sediment by TL

Sample	Depth (cm)	Age of material TL <sup>a</sup> (years)	TRM (years B.P.) <sup>b</sup>
P03 Bhm1	120–142	131.500 ± 15.100	9.600
P10 Bhm	117–150	41.200 ± 3.400	4.260
P30 Bhm	58–105	271.000 ± 85.300	18.500

<sup>a</sup>TL Termoluminescência

<sup>b</sup>B.P. Before Present

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