SOIL MANAGEMENT PRACTICES: CHEMICAL AND SPECTROSCOPIC CHARACTERIZATION

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ABSTRACT - The aim of this study was to evaluate the possibility to apply chemical and spectroscopic analysis, coupled with chemometric tools, as a rapid method for soil characterization. Soil samples from different depths (0-10, 10-20 and 20-30 cm) and sites (fallow area for 5 years, area of no-tillage for 10 years and native forest) were applied in this study. Soil chemical characterization based on the concentration of macronutrients (P, K Ca, and Mg), micronutrients (Mn, Fe, Zn, and Cu), the level of aluminum, pH, organic matter (OM) and humification degree. For spectroscopic characterization, only the humic acid (HA) fraction was analyzed in the mid infrared spectrometer. Principal Components Analysis (PCA) and Hierarchical Clustering Analysis (HCA) showed clusters based on the management systems. These results support the application of chemometric toolls to evaluate the quality of soil providing a simple and rapid method for the soil science.
Key words: spectroscopy, chemometrics, soil management, PCA, HCA.

PRÁTICAS DE MANEJO DO SOLO: CARACTERIZAÇÃO QUÍMICA E ESPECTROSCÓPICA

RESUMO - O objetivo deste estudo foi avaliar a possibilidade de aplicar análises químicas e espectroscópicas, juntamente com ferramentas quimiométricas, como um método rápido para caracterização do solo. Para isso, amostras de solo de diferentes profundidades (0-10, 10-20 e 20-30 cm) e locais de tratamento (área em pousio de 5 anos, a área sob plantio direto por 10 anos e mata nativa) foram obtidas e analisadas. A caracterização química do solo baseou-se na concentração dos macro nutrientes (P, K Ca and Mg), micronutrientes (Mn, Fe, Zn and Cu), alumínio, pH, matéria orgânica (OM) e grau de humificação. Para caracterização espectral as amostras de solo foram analisadas por espectrometria de infravermelho médio. Resultados obtidos a partir da Análise de Componentes Principais (PCA, do inglês, *Principal Components Analysis*) e Análise Hierárquica de Agrupamentos (HCA, do inglês, *Hierarchical Clustering Analysis*) evidenciaram uma tendência de separação entre as amostras de acordo com o sistema de manejo. A partir destes resultados, conclui-se que o uso de ferramentas quimiométricas quando aplicado na avaliação da qualidade do solo pode fornecer um método simples e rápido para a ciência do solo.
Palavras-chave: espectroscopia, quimiometria, manejo do solo, PCA, HCA.

INTRODUCTION

Soil research needs a better understanding of all aspects of soil quality. In particular, the changes that result from different management systems. To evaluate the effects of land use and soil managements on soil quality, soil chemical attributes can be used as potential indicators, such as macro and micronutrients concentration, and organic matter (OM) (CHERUBIN et al., 2015).

Changes observed in the OM, might be a result of the management system adopted (ROSA et al., 2008; TIVET et al., 2013; MARTINS et al., 2011) and thus, detected through spectroscopic techniques. Among these, Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopies are useful techniques for characterizing the soil OM, since provide information about the OM structure (STEVENSON, 1994) and the

humification degree (DICK et al., 2008; SAAB; MARTIN- NETO, 2007; CHEN et al., 1977).

In addition to the spectroscopic techniques, chemical analysis can also contribute to studies about the effect of managements practices. Results published in the literature report that the chemical properties are influenced by tillage (CARNEIRO et al., 2009; SCHERER; NESI, 2009; SOUZA; ALVES, 2003).

However, chemical and spectroscopic analyses generate a great number of variables for each sample, which results in a large amount of information. The use of chemometric tools, that enable the comprehension of data without loss of relevant information, become necessary (SENA et al., 2002; HOPKE, 2003; SANTOS et al., 2010; MERLIN et al., 2015). In this context, the aim of this study was to evaluate and compare the chemical and

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spectroscopic characteristics of Cambissolo under different management systems. Chemometric toolls, as PCA and HCA were applied in order to obtain a global view of the data and provide a fast way to identify and quantify patterns among to the soil samples.

MATERIAL AND METHODS
Study sites

Cambissolo Háplico Alumínico soil samples (EMBRAPA, 2013) from different depths (0-10, 10-20 and 20-30 cm) and management systems [fallow area for 5 years (FL), area under no-tillage for 10 years (NT) and native forest (NF)] were applied in this study. The composite samples were formed by sampling 12 points per management systems and depth, collected randomly. Samples were collected in Ponta Grossa, Paraná state, Brazil. The geographical coordinates of the sample areas were FL - 25°5'34.19" lat S, 50°15'2.44" long W, NT - 25°5'35.19" lat S, 50°15'4.61" long W and NF - 25°5'38.24" lat S, 50°15'17.35" long W, at altitudes of 841 m, 839 m, and 816 m, respectively.

The climate in the region has well defined thermal seasons, with the hottest month (February) averaging 21.2°C and the coldest month (July) with averages of 13.3°C (MAACK, 1981). The average of annual rainfall is 1542 mm, which is well distributed throughout the year, with a slight decrease occurring from April to August. The climate in the region was classified, according to the Köppen classification, as *Cfb* (Humid Subtropical Mesothermal).

Soil chemical characterization

The soil chemical characterization was evaluated according to the concentration of macronutrients (P, K Ca, and Mg), micronutrients (Mn, Fe, Zn, and Cu), the level of aluminum, pH, organic matter (OM) and humification degree. The analyses of macro and micro nutrients, the level of aluminum and pH were evaluated according to the methodology suggested by Pavan et al. (1992). The OM content was determined by wet oxidation in an acid dichromate solution according to the original Walkley-Black procedure described by Walkley (1947).

The humification degree was determined using two approaches. In the first one, the humification index was determined from the aromaticity degree (I_{1630}/I_{2920}), which is based on the ratio of the absorption intensity at 1630 cm^{-1} (corresponding to the aromatic groups) and 2920 cm^{-1} (corresponding to the aliphatic groups) (CHEFETZ et al., 1996). FTIR spectra were acquired in a Frontier spectrophotometer (Perkin Elmer, USA), equipped with a KBr beam splitter and DTGS detector. Spectra were collected in the KBr transmission mode (1.5 mg sample: 150 mg KBr) over a range of 4000-400 cm^{-1} by co-adding 64 scans at a resolution of 4 cm^{-1}. In the second approach, the humification index was determined using the ratio between the absorbance at 465 and 665 nm (E_4/E_6), as suggested by Chen et al. (1977). The analyses were performed using a UV-visible spectrophotometer model Lambda 40 (Perkin Elmer, USA).

Soil spectroscopic characterization

For soil spectroscopic characterization, only the humic acid (HA) fraction was analyzed. The HA fraction was extracted following the methodology suggested by the International Humic Substance Society (IHSS) (SWIFT, 1996).

Spectroscopic characterization of HA fraction was carried out using a Frontier spectrophotometer (Perkin Elmer, USA), using the same parameters applied in the determination of humification degree. UV-visible spectra of HA samples were acquired according to Chen et al. (1977) using a spectrophotometer model SP-22 (Bioespectro, Brazil).

Multivariate Analysis

Multivariate analyses were evaluated using Pirouette software (version 4.0, Infometrix Inc., Woodville, WA, USA). PCA and HCA models were developed in order to obtain a global view of the main variation in the data set. These models were performed using the results obtained by the soil chemical characterization (P, K Ca, Mg, Mn, Fe, Zn, Cu, Al, pH, OM, humification degree and humification index). Before the analysis, data were auto-scaled.

Results of the soil chemical characterization and the humification degree indexes are represented as mean ± standard deviation (SD). In order to evaluate the differences at a 95% confidence level, a factorial analysis of variance (ANOVA) was followed by Tukey's test using the Statistica 8.0 software (StatSoft, USA).

RESULTS AND DISCUSSION
Soil chemical characterization

As can be seen in Table 1, most of the chemical parameters analyzed in soil samples varied according to both soil management systems and depths. Veloso et al. (1992) found that Brazilian soils are generally acidic, with high amount of Al and Mn, low concentration of P, Ca and Mg, as shown by the results obtained for the NF soil samples.

P concentration ranged from 0.7 (soil from FL system) to 7.7 (soil from NT system) mg dm^{-3} in the soil samples of different management systems (Table 1). The highest concentration of P was observed in the soil under NT system and could be associated with the addition of phosphate fertilizers (SANTOS et al., 2008; FALLEIRO et al., 2003; OLIVEIRA et al., 2004; RHEINHEIMER; ANGHINONI, 2001). P concentration also varied for soil samples collected from different depths: samples from the 0-10 cm layer exhibited higher concentration than those obtained from the 20-30 cm layer. This behavior could be associated with three factors: (1) the presence of crop and root residues on the soil surface, that is typical of the systems under study; (2) the fact that the soil is not revolved in the NT, NF and FL; and (3) the addition of phosphate fertilizers in the NT area (SANTOS et al., 2008; FALLEIRO et al., 2003; OLIVEIRA et al., 2004; RHEINHEIMER; ANGHINONI, 2001).

On the other hand, K concentration did not vary significantly among management systems and depth ($p \leq 0.05$) (Table 1). Ca and Mg concentrations ranged from 0.4 (soil from NF) to 6.2 (soil from NT system) $cmol_c$ dm^{-3} and from 0.2 (soil from NF) to 3.0 (soil from NT system) $cmol_c$ dm^{-3} (Table 1). The higher concentration of these macronutrients in soils under the NT system is probably due to the addition of fertilizers in this system. Among to the soil samples from different depths, the higher concentration of Ca and Mg were obtained for samples from 0-10 cm layer, as could be seen for P concentration.

The higher concentration of Al was found for the soil under the NF management system (6.5 $cmol_c$ dm^{-3}), which could be associated with the physical-chemical characteristics of the soil, as reported by Jakelaitis et al. (2008). Soil samples collected from NF also showed higher concentrations of Mn (62 mg dm^{-3}), Fe (149 mg dm^{-3}) and lower pH (3.7) (Table 1).

The correlation between Al element and pH showed that soils with high Al concentration are acid (PRIMO et al., 2011; FALLEIRO et al., 2003; SORATTO; CRUSCIOL, 2008). Pavan (1983) reported that Al is found in acid soils, with a pH lower than 5.5. Among the soils analyzed, the higher acidity was observed in the NF soil which also had the highest concentration of Al.

Zn concentration ranged from 0.6 (soil from NF) to 1.3 (soil from NT system) mg dm^{-3} for soil samples from different management systems. Soils from NT system also showed higher concentration of Cu (7.4 mg dm^{-3}) (Table 1). Overall, the chemical analysis demonstrated that the NT system was able to maintain larger quantities of important macro (P, Ca and Mg) and micronutrients (Zn and Cu), and low quantities of the toxic element (Al), allowing a pH between 4.3 and 5.3.

Comparing the management systems and depth, OM concentration did not vary significantly ($p \leq 0.05$) (Table 1). OM characterization is important because it provides information about the decomposition degree of humification. As can be seen in Table 1, the highest aromaticity index (I_{1630}/I_{2920}) was obtained for NF (20-30 cm) soil sample. According to Dick et al. (2008) and Rosa et al. (2008), this index expresses the relation between the aromatic groups and the aliphatic ones. Conversely, the humification degree obtained by the E_4/E_6 was lower for the soil collected in the 0-10 cm depth, indicating a greater humification degree in the soil surface layer. For FL and NF systems, it was observed a pattern of increase of E_4/E_6 ratio with the increase of depth.

In the literature, the humification degree based on I_{1630}/I_{2920} and E_4/E_6 indexes has been widely reported (DICK et al., 2006; SAAB; MARTIN-NETO, 2007). According to Dick et al. (2006), the I_{1630}/I_{2920} showed significant correlation with ^{13}C nuclear magnetic resonance (^{13}C NMR) data.

**Soil spectroscopic characterization**

Figure 1 shows the FTIR spectra of HA extracted from soil samples of 0-10 cm depth, under FL, NT and NF management systems. The spectra show a prominent absorption band centered at 3390 cm^{-1}, which could be associated with the strong O−H stretching vibrations of kaolinite and OM. The band at 1625 cm^{-1} may be related to the stretching of the C=C double bonds found in both aromatic and alkene organic compounds (POTES et al., 2010; DICK et al., 2008) or the COO^- group in metal carboxylate (SANTOS et al., 2010; GONZÁLEZ-PÉREZ et al., 2008).

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TABLE 1 - Concentration of macronutrients, micronutrients and OM, the level of the toxic element (Al), the pH, and the humification degree data (I_{1630}/I_{2920} and E_4/E_6 ratios) obtained for soil samples under different management systems: fallow area for 5 years (FL), area under no-tillage for 10 years (NT) and native forest (NF).

Management system	Depth (cm)	K* ←	Ca* (cmolc dm⁻³)	Mg*	Al* →	Mn* ←	P*	Fe* (mg dm⁻³)	Zn*	Cu* →	pH* (CaCl₂)	OM* (g dm⁻³)	I_{1630}/I_{2920}*	E_4/E_6**
FL	0-10	$0.1^a\pm0.0$	$3.5^{abc}\pm0.0$	$2.2^{abc}\pm0.3$	$0.1^b\pm0.0$	$21^{bc}\pm7$	$1.0^{cd}\pm0.5$	$103^a\pm32$	$0.9^{ab}\pm0.1$	$5.4^b\pm0.4$	$4.7^b\pm0.1$	$52^a\pm1$	$0.83^{bc}\pm0.03$	3.13 ± 0.02
FL	10-20	$0.1^a\pm0.0$	$2.2^{abc}\pm0.2$	$1.7^{bcd}\pm0.2$	$0.5^b\pm0.1$	$12^c\pm2$	$0.7^d\pm0.0$	$103^a\pm2$	$0.7^{ab}\pm0.0$	$5.5^{ab}\pm0.2$	$4.3^c\pm0.1$	$43^a\pm2$	$0.88^{abc}\pm0.01$	5.25 ± 0.02
FL	20-30	$0.1^a\pm0.0$	$1.2^{bc}\pm0.0$	$0.8^{de}\pm0.0$	$2.0^b\pm0.0$	$4^c\pm0$	$0.7^d\pm0.0$	$85^a\pm0$	$0.8^{ab}\pm0.0$	$5.5^{ab}\pm0.0$	$4.2^c\pm0.0$	$43^a\pm0$	$0.94^{abc}\pm0.03$	10.67 ± 0.02
NT	0-10	$0.2^a\pm0.1$	$6.2^a\pm0.8$	$3.0^a\pm0.7$	$0.0^b\pm0.0$	$27^{abc}\pm3$	$7.7^a\pm0.6$	$63^a\pm24$	$1.2^{ab}\pm0.2$	$6.1^{ab}\pm1.0$	$5.3^a\pm0.0$	$52^a\pm9$	$0.76^c\pm0.02$	2.73 ± 0.03
NT	10-20	$0.1^a\pm0.1$	$4.6^{ab}\pm2.9$	$1.2^{cde}\pm0.2$	$0.5^b\pm0.0$	$7^c\pm2$	$1.0^{bc}\pm0.5$	$50^a\pm9$	$0.7^{ab}\pm0.2$	$5.3^b\pm0.7$	$4.3^c\pm0.1$	$39^a\pm4$	$1.08^{ab}\pm0.09$	8.38 ± 0.03
NT	20-30	$0.2^a\pm0.1$	$5.0^{ab}\pm0.2$	$2.6^{ab}\pm0.2$	$0.0^b\pm0.0$	$25^{abc}\pm14$	$4.6^b\pm1.0$	$63^a\pm3$	$1.3^a\pm0.3$	$7.4^a\pm0.4$	$5.0^{ab}\pm0.1$	$46^a\pm5$	$0.76^c\pm0.02$	3.25 ± 0.04
NF	0-10	$0.2^a\pm0.1$	$0.4^c\pm0.0$	$0.5^e\pm0.2$	$6.5^a\pm1.5$	$62^a\pm21$	$2.8^{bc}\pm0.6$	$149^a\pm46$	$0.9^{ab}\pm0.1$	$1.5^c\pm0.2$	$3.7^d\pm0.1$	$50^a\pm9$	$1.07^{ab}\pm0.02$	4.33 ± 0.02
NF	10-20	$0.2^a\pm0.1$	$0.4^c\pm0.1$	$0.2^e\pm0.2$	$6.5^a\pm1.7$	$54^{ab}\pm8$	$2.5^{bcd}\pm0.2$	$114^a\pm58$	$0.6^b\pm0.1$	$0.7^c\pm0.3$	$3.7^d\pm0.1$	$54^a\pm2$	$0.97^{abc}\pm0.07$	9.67 ± 0.02
NF	20-30	$0.1^a\pm0.1$	$0.5^c\pm0.2$	$0.2^e\pm0.1$	$6.2^a\pm1.5$	$41^{abc}\pm10$	$1.0^{bc}\pm0.5$	$69^a\pm10$	$0.7^{ab}\pm0.2$	$0.6^c\pm0.1$	$3.8^d\pm0.1$	$42^a\pm0$	$1.11^a\pm0.14$	12.67 ± 0.03

*Values are expressed as mean ± SD (*n=2; **n=4). Mean values with different letters, in the same column, are significantly different ($p \leq 0.05$).

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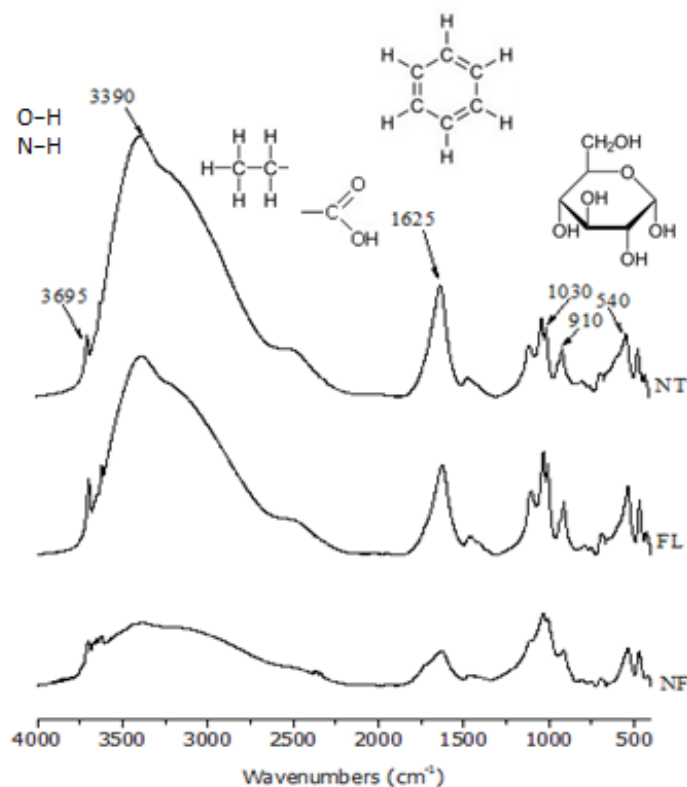
FIGURE 1 - FTIR spectra of HA extracted from soil samples collected on 0-10 cm depth, under the following management systems: fallow area for 5 years (FL), area under no-tillage for 10 years (NT) and native forest (NF).

Quartz showed two peaks around ~1120 cm^{-1} and ~1030 cm^{-1}, which are related to the stretching of Si-O-C and Si–O–Si, respectively (SANTOS et al., 2010; CASTELLANO et al., 2010; POTES et al., 2010; DICK et al., 2008). The region between 900 and 500 cm^{-1} included several weak peaks that may be attributed to other carbonated elements (such as Mg^{2+}, Li^+, K^+ and Na^+). The main spectral differences among the soils under the different management systems were the absorption intensities at 3600-2900, 1625 and 1200-900 cm^{-1}, which were associated with changes in the soil composition, especially the OM characteristics.

Multivariate analysis

In order to obtain a better view of the results, a PCA and HCA analysis were evaluated. Figure 2a and 2b shows de PCA score plot and loading, respectively. PC1, which explained 51.1% of the variation in the data, clearly discriminated the samples according to management system. Soil samples from the NF were grouped at one end of PC1, whereas samples under the NT management system were grouped at the other end (Figure 2a). PC2, which explained 25.7% of the variation in the data, showed a tendency to discriminate the soil samples based on collection depth (Figure 2a). A group composed by FL (10-20), FL (20-30) and NF (20-30) soil samples were also observed in the PCA score plot (Figure 2a), indicating chemical similarity among to the samples.
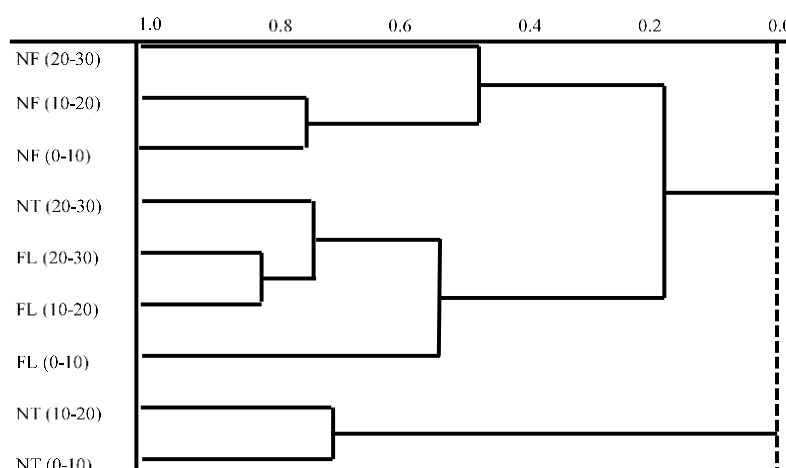
(a)

(b)
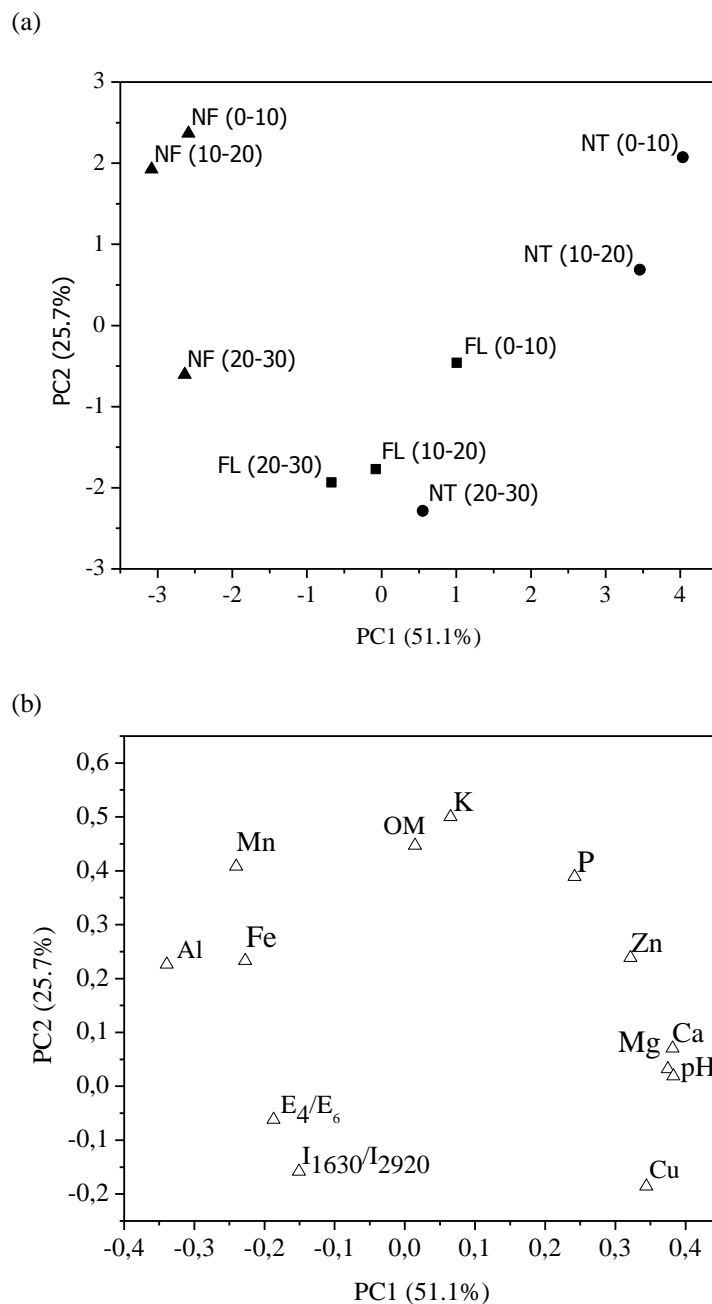
FIGURE 2 - (a) PCA scores plot (PC1 x PC2) illustrating the clusters formed by the soil samples under different management systems: fallow area for 5 years (FL, ■), area under no-tillage for 10 years (NT, ●) and native forest (NF, ▲) and (b) the respective loadings plot (Δ).

PCA loading plot (Figure 2b) reveals that the soil samples from NF could be characterized by higher concentrations of Mn, Fe and Al and lower concentration of Ca, Cu and Mg. Conversely, the soil samples under NT (0-10 and 10-20 cm) could be characterized higher concentrations of Ca, P, Mg and Zn and lower concentrations of Al and Fe. In addition, the loading graphic indicated that the samples NF (20-30) and FL (20-30) were characterized by higher humification degree

(E_4/E_6 ratio). These conclusions were in agreement with the results shown in Table 1.

Similar results were observed in the HCA model (Figure 3). The dendrogram showed mainly three groups composed by: (1) the soil samples from NF, (2) the soil samples under FL system and the soil samples under NT system at 20-30 cm depth and (3) the soil samples under NT system at 0-10 and 10-20 cm depths.

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FIGURE 3 - Dendrograms obtained by HCA for the soil samples under different management systems: fallow area for 5 years (FL), area under no-tillage for 10 years (NT) and native forest (NF).

CONCLUSION

The land use, NT and FL, affect significantly the Cambissolo chemical characteristics. The Al, Ca, Mg and Cu concentrations and pH enable to differentiate the NF from the NT and FL systems. No significant differences were found in K, Fe and OM content. The highest aromaticity index (I_{1630}/I_{2920}) was obtained for NF (20-30 cm) soil sample, indicating that this sample has a greater humification degree. On the other hand, the effects of land use of soil could be verified by UV-visible spectroscopic.

Finally, PCA and HCA facilitated the interpretation of soil data, allowing an easy visualization of the similarities and differences among to the samples and the relations between the variables.

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