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Artigo

Emprego de Técnicas Espectroscópicas para a Determinação do Grau de Humificação de Solos Sob a Adição de Cama de Aviário

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The Use of Spectroscopic Techniques to Determine the Degree of Humification in Soil Amended with Poultry Litter

Abstract: The adoption of management practices that promote fertility is essential to maintain the quality of agricultural soil. An example of a practice that has been used in order to increase the organic matter content of the soil and, consequently, soil quality, is the application of organic fertilizers. Therefore, this study evaluated the effects of poultry litter application on the degree of organic matter humification in an Oxisol under no-tillage, using spectroscopic techniques. The spectroscopic techniques used were laser induced fluorescence, ultraviolet-visible absorption and Fourier transformed infrared. The results obtained revealed that the use of poultry litter reduced organic matter humification in the superficial layers (0-2.5 and 2.5-5 cm) of the studied soil. Deeper layers probably did not suffer alterations due to the short time frame of the experiment.

Keywords: Spectroscopic techniques; Soil organic matter; degree of humification; Poultry litter.

Resumo

A adoção de práticas de manejo que promovam a manutenção da fertilidade é essencial para garantir a qualidade dos solos agrícolas. Um exemplo de prática que há muito vem sendo utilizada com a finalidade de elevar os teores de matéria orgânica do solo e, consequentemente, sua qualidade, é a adição de fertilizantes orgânicos. Neste sentido, o presente trabalho avaliou os efeitos da adição de cama de aviário sobre o grau de humificação da matéria orgânica de um Latossolo Vermelho cultivado sob plantio direto, por meio de técnicas espectroscópicas. As técnicas espectroscópicas utilizadas foram fluorescência induzida por laser, absorção de luz na região ultravioleta-visível e infravermelho com transformada de Fourier. Os resultados obtidos mostraram que a aplicação da cama de aviário diminuiu o grau de humificação da matéria orgânica das camadas superficiais do solo estudado (0-2.5 e 2.5-5 cm). As camadas mais profundas provavelmente não sofreram alterações em decorrência do curto tempo de experimento.

Palavras-chave: Técnicas espectroscópicas; Matéria orgânica do solo; Grau de humificação; Cama de aviário.

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Emprego de Técnicas Espectroscópicas para a Determinação do Grau de Humificação de Solos Sob a Adição de Cama de Aviário

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1. Introduction

The organic matter (OM) has a significant effect on several soil characteristics, such as cation exchange capability, water retention, microbial activity, structure, compaction and aeration.[1-3] For this reason, the maintenance of the soils agricultural productive capacity is directly related to the implementation of appropriate soil and crop residue management, so as to promote the accumulation of OM,[2,4] especially in tropical regions.

In tropical regions, the natural fertility of the soil is generally low and the application of organic and inorganic fertilizers has become a very important agricultural practice, as it improves soil quality and productivity.[5-8] Organic fertilizers are important for, among other characteristics, their high OM content,[7] representing an alternative for residue destination, when applied correctly.

Among organic fertilizers, poultry litter (a residue generated from poultry excreta mixed with wood shavings, in most cases, and disinfectant products), can be used in agriculture to improve soil fertility in grains production[9] and commercial crops[10] or pasture.[11]

Soil fertility is directly associated with OM, which, according to Stevenson (1994),[12] can be divided into two large fractions: the humic and the non-humic fractions. The humic fraction comprises the largest portion of the soil OM and it is characterized as a stable fraction with a relatively slower decomposition than the non-humic fraction.[12] According to Zech et al. (1997),[13] during the process of humification the main transformation that occurs is the transformation of macromorphologically identifiable matter into amorphous compounds. It has been related to the preferential oxidation of plant polysaccharides, the selective preservation of more recalcitrant organic compounds such as lignin and phenolic structures, and to the incorporation of organic compounds of microbial origin. Therefore, the humification process is closely related to OM decomposition and stabilization. Studies on the effect of management practices, such as the use of organic fertilizers, on soil OM quality using spectroscopic techniques, have been presented in the literature.[14-17] Techniques, such as the ones used in this study, consist of indirect measurements which reflect the structural changes that occur throughout the soil OM humification process. Therefore, they allow the measurement of degree of OM humification and are therefore, useful in its characterization.[18]

Laser induced fluorescence spectroscopy (LIFS), a spectroscopic technique that enables whole soil analysis without prior chemical treatment,[15,16,19-22] and ultraviolet-visible (UV-Vis) spectroscopy,[14,23-25] are usually used to determine the degree of OM humification. The Fourier transform infrared (FTIR) spectrometry technique provides information regarding the main classes of chemical compounds present in the OM structure, such as groups containing oxygen, carbohydrates, and proteins, and also the identification of mineral impurities,[12] it can also be used to estimate the aromaticity index.[14,17,26-28]

The current study highlights the importance of the structural characterization of OM from soils subjected to the application of organic fertilizers, providing relevant results for this agricultural practice, which is often employed in the studied area. Therefore, this study aims to evaluate, using spectroscopic techniques, the effects of poultry litter application on the degree of OM humification in an Oxisol under no-tillage.

2. Material and Methods

2.1. Experimental area

The experiment started in June 2011 at the Experimental Area of the Universidade Tecnológica Federal do Paraná (UTFPR), campus Pato Branco (26º10’31’’S; 52º41’21’’W). The studied soil was classified as a typical Oxisol.[29] In Brazilian terminology, the Oxisols are represented by the Latosol group which are characterized as deep (>3 m), well drained, red or yellow, clay-rich, structurally strong but nutrient-poor soils.[30] Soil samples were collected in the first year of the field experiment which was under a no-tillage system with the application of poultry litter.

2.2. Experiment and treatments

The experiments were performed in random blocks, subdivided into plots with four replicates. The main plots corresponded to four surface application times of poultry litter: 45, 30, 15 and 0 days before wheat was sown. In the sub-plots, increasing doses of poultry litter were applied: 0, 4.0, 8.0 and 12.0 Mg ha^{-1} (wet basis). Each plot had an area of 25 m^2.

The treatments under evaluation were: (T1) without poultry litter application on the seeding day and (T2) 45 days before seeding; and (T3) with the application of 12 Mg ha^{-1} poultry litter on the seeding day and (T4) 45 days before the seeding.

2.3. Sample collection and preparation

Samples were collected six months after the poultry litter application (December 2011), from the depths: 0-2.5; 2.5-5; 5-10 and 10-20 cm. The samples consisted of composite samples collected from two points using a spade. After collection, the soil samples were dried in an oven at 40 ^{O}C, ground in a knife mill and sieved through a 2 mm mesh sieve.

2.4. Chemical fractionation of humic substances

Humic acid (HA) extraction was based on the methodology proposed by the International Humic Substances Society (IHSS),[31] however, the process was interrupted after the application of 6 mol L^{-1} HCl in order to minimize the effects of successive solution applications.

2.5. Soil spectroscopic monitoring

2.5.1. LIFS

The soil samples were analyzed using the LIFS equipment belonging to EMBRAPA Instrumentação, São Carlos-SP. The analysis was carried out according to Milori et al. (2006).[16] Measurements were made in quadruplicate and the degree of humification (H_{LIF}) was determined using the ratio between the total fluorescence area (A_F) and the samples total carbon content (C_T), in g dm^{-3}, according to Equation (1).

$$H_{LIF} = \frac{A_F}{C_T} \qquad (1)$$

2.5.2. UV-Vis spectroscopy

The measurements of UV-Vis absorption were carried out according to Chen et al. (1977).[25] The analysis was carried out, in quadruplicate, using the HA samples, with absorbance intensity measurements at 465 and 665 nm using a Perkin Elmer Lambda 40 spectrophotometer belonging to the Central de Análises, of UTFPR, campus Pato Branco. After this, the degree of humification was determined from the calculation of the E_4/E_6 ratio, according to Equation (2).

$$E_4/E_6\text{ratio} = \frac{\text{Absorbance Intensity at 465 nm}}{\text{Absorbance Intensity at 665 nm}} \qquad (2)$$

2.5.3. FTIR spectroscopy

In order to obtain the FTIR spectra, HA samples were compacted into 1:100 KBr pellets (1.5 mg sample for each 150 mg KBr) and analyzed according to the methodology described by Stevenson (1994).[12] Measurements were made in duplicate using a Perkin Elmer FT-IR Frontier spectrometer belonging to the Central de Análises, from UTFPR, campus Pato Branco. Absorption bands were attributed according to Rosa et al. (2008),[14] Santos et al. (2010),[21] Potes et al. (2010),[26] Dick et al. (2008),[28] Castellano et al. (2010),[32] Canellas et al. (2001),[33] González-Pérez et al. (2008).[34] The degree of humification was evaluated using the aromaticity index (I_{1630}/I_{2920}), which consists of the absorption intensity at 1630 cm^{-1} (corresponding to the aromatic groups) divided by the absorption intensity at 2920

cm^{-1} (corresponding to the aliphatic groups) (Equation (3)), as described by Cheftez et al. (1996).[35] The values of the intensities were obtained using the equipment`s software, after base line adjustment.

$$I_{1630}/I_{2920} = \frac{\text{Absoption intensity at 1630 cm}^{-1}}{\text{Absorption intensity at 2920 cm}^{-1}} \qquad (3)$$

2.6. Statistical treatment

The linear correlation determination between the humification indices (H_{LIF}, E_4/E_6 and I_{1630}/I_{2920}) was carried out using the Origin Lab. 8.0 software. The FTIR results were analyzed statistically using the principal component analysis (PCA) using the Pirouette 4.0 software. Pre-processing of the data was carried out by mean-centered and second derivative transformation.

3. Results and Discussion

Table 1 presents the H_{LIF}, E_4/E_6 ratio and I_{1630}/I_{2920} results.

H_{LIF} values presented variation from 721 ± 23 to 1155 ± 37 (Table 1). In the literature, wide variations for this index can be found in a number of different studies,[15,19-22] and can be attributed to a number of different factors. Soil properties are defined by their parent material[36] and also the different management systems employed, all of which can alter the soils physical, chemical and biological properties.[1,37] Therefore, direct comparison is not suitable when the samples do not belong to the same type of soil.

The lowest H_{LIF} values observed were for the surface layer (0-2.5 cm) of the soils treated with poultry litter (T3 and T4). This result suggests that the application of residue to the soil, regardless of the time, promoted changes to the soil OM structural characteristics, reducing its H_{LIF}. This result is also evidence that the OM supplied by the poultry litter had a low degree of decomposition, showing a similarity to other organic residues frequently applied to the soil, such as sludge,[21] different types of manure (chicken, swine, quail and cattle) and commercial compost.[38]

When analyzing H_{LIF} variation through the soil profile, it was observed that the poultry litter treatments (T3 and T4) presented a proportional relation between the increase in depth and H_{LIF} (Table 1). This result may suggest that the accumulation of OM at the soil surface, which comes from the deposition of vegetable remains from the no-tillage system, had a lower effect on the soil OM structural characteristics compared with the effects of poultry litter application.

The lower influence of no-tillage on the OM characteristics in the soil superficial layers might also result from the short time frame of the field experiment, which was only one year. In general, studies about effect of management systems have demonstrated that changes in OM content were slow, therefore, a relatively long experiment period is necessary to observe relevant changes.[39] According to data from Rosa et al. (2008),[14] a no-tillage system tends to preserve soil total organic carbon content and causes the occurrence of humic substance with a lower degree of decomposition in the surface layer (0-2.5 cm).

Another parameter we used to evaluate the degree of soil OM humification was the E_4/E_6 ratio. In contrast to the H_{LIF}, the E_4/E_6 ratio reduced with the increase of degree of humification,[12] an increase in the E_4/E_6 ratio could indicate a low degree of condensation of aromatic rings and the presence of aliphatic structures[40] or even the presence of molecules with a lower molecular weight.[25]

Table 1. Humification indices H_{LIF}, E_4/E_6 and I_{1630}/I_{2920} obtained for the studied Oxisol, with and without the application of poultry litter, on the day of wheat sowing and 45 days before the wheat sowing

Sample	Depth (cm)	Treatment	Time of application	H_{LIF}*	E_4/E_6**	I_{1630}/I_{2920}*
T1 0-2.5	0-2.5	Without poultry litter appplication	On the day of sowing	995 ± 23	1.63 ± 0.04	0.82 ± 0.02
T1 2.5-5	2.5-5	Without poultry litter appplication	On the day of sowing	933 ± 38	1.04 ± 0.03	0.84 ± 0.04
T1 5-10	5-10	Without poultry litter appplication	On the day of sowing	948 ± 14	0.66 ± 0.04	0.87 ± 0.09
T1 10-20	10-20	Without poultry litter appplication	On the day of sowing	993 ± 12	0.626 ± 0.006	0.82 ± 0.02
T3 0-2.5	0-2.5	With poultry litter appplication	On the day of sowing	721 ± 23	0.594 ± 0.004	0.83 ± 0.04
T3 2.5-5	2.5-5	With poultry litter appplication	On the day of sowing	816 ± 10	1.210 ± 0.007	0.87 ± 0.02
T3 5-10	5-10	With poultry litter appplication	On the day of sowing	953 ± 17	0.88 ± 0.03	0.83 ± 0.02
T3 10-20	10-20	With poultry litter appplication	On the day of sowing	997 ± 10	0.64 ± 0.07	0.84 ± 0.02
T2 0-2.5	0-2.5	Without poultry litter appplication	45 days before sowing	874 ± 38	0.62 ± 0.05	0.901 ± 0.001
T2 2.5-5	2.5-5	Without poultry litter appplication	45 days before sowing	979 ± 21	0.65 ± 0.12	0.84 ± 0.02
T2 5-10	5-10	Without poultry litter appplication	45 days before sowing	883 ± 30	0.62 ± 0.07	0.82 ± 0.02
T2 10-20	10-20	Without poultry litter appplication	45 days before sowing	1155 ± 37	0.705 ± 0.002	0.819 ± 0.001
T4 0-2.5	0-2.5	With poultry litter appplication	45 days before sowing	778 ± 4	0.680 ± 0.009	0.8 ± 0.1
T4 2.5-5	2.5-5	With poultry litter appplication	45 days before sowing	838 ± 27	0.70 ± 0.09	0.82 ± 0.04
T4 5-10	5-10	With poultry litter appplication	45 days before sowing	1039 ± 76	0.81 ± 0.12	0.83 ± 0.04
T4 10-20	10-20	With poultry litter appplication	45 days before sowing	1075 ± 23	0.81 ± 0.04	0.85 ± 0.02

*H_{LIF} ± Standard Deviation and I_{1630}/I_{2920} ± Standard Deviation; ** E_4/E_6 ± Standard Error.

The E_4/E_6 ratio values varied from 0.594 ± 0.004 to 1.63 ± 0.04 (Table 1), and differed from previous studies.[14,23,24,41] A comparison between different studies was not proposed due to the differences between the types of soil and management systems in each study, as these characteristics appear to interfere significantly with soil OM properties.

The UV-Vis absorption results showed that the E_4/E_6 ratio did not show any relation with depth (Table 1). A similar result was observed by Miranda et al. (2007).[41] Table 1 also reveals that there was an increase in the E_4/E_6 ratio because of the poultry litter applied to the soil, except for T1 0-2.5 cm. This result reinforces the idea that the residue presents low degree of decomposition, indicating that the OM of the soils submitted to residue application, both 45 days before sowing and on the day of sowing, showed a lower degree of humification than the OM of the soils without this application. However, according to Saab and Martin-Neto (2007),[24] the UV-Vis absorption data should be carefully considered, as it has limitations.

Figures 1a, 1b, 1c and 1d show the FTIR spectra corresponding to the HA samples at depths of 0-2.5; 2.5-5; 5-10 and 10-20 cm, respectively.

The absorption at 3694 cm^{-1}, observed for all spectra, might be attributed to O–H or N–H vibrations.[32,33] The band with maximum intensity at approximately 3400 cm^{-1} corresponds to the O–H stretching vibration of hydrogen linked to O–H groups and, possibly, to N–H groups.[14,21,26,28,33,34] The presence of a discrete shoulder at the 2509 cm^{-1} region does not match with studies found in the literature. The peak at 1630 cm^{-1} is characteristic of the presence of COO^- groups, with contributions from the aromatic C=C vibrations.[26,28,34,40] The very weak bands around 1450 cm^{-1} are due to C–H deformation of $-CH_2$ and $-CH_3$ groups.[14] The absorption at 1100 cm^{-1} might be attributed to COO^- groups linked to metallic cations.[33] The peak at 1040 cm^{-1} corresponds to C–O stretching of polysaccharides.[14,26,28,33,34] Absorptions in the region between 1010 and 470 cm^{-1} are related to the presence of mineral impurities in the samples.[32,33] However, from the spectra interpretation, it was not possible to observe the presence of signs around 2919 and 2850 cm^{-1}, which are characteristic of the occurrence of C–H stretching of aliphatic groups and observed in most HA spectra.[14,26,34]

Figure 1 shows that HA spectra presented similar peaks and bands, so, it was not possible to say for sure whether the spectra presented a statistically significant difference. Therefore, were used statistical tools aimed at grouping the samples.

Samples were divided into two groups for statistical treatment. The first group had eight samples (corresponding to T1 and T3) and the second one comprised the samples corresponding to T2 and T4. Figure 2 shows the PCA scores graphs obtained for the HA samples submitted to treatments (a) T1 and T3 and (b) T2 and T4, at depths of 0-2.5; 2.5-5.0; 5.0-10 and 10-20 cm, at the 3700 to 2400 cm^{-1} and 1800 to 1400 cm^{-1} absorption regions.

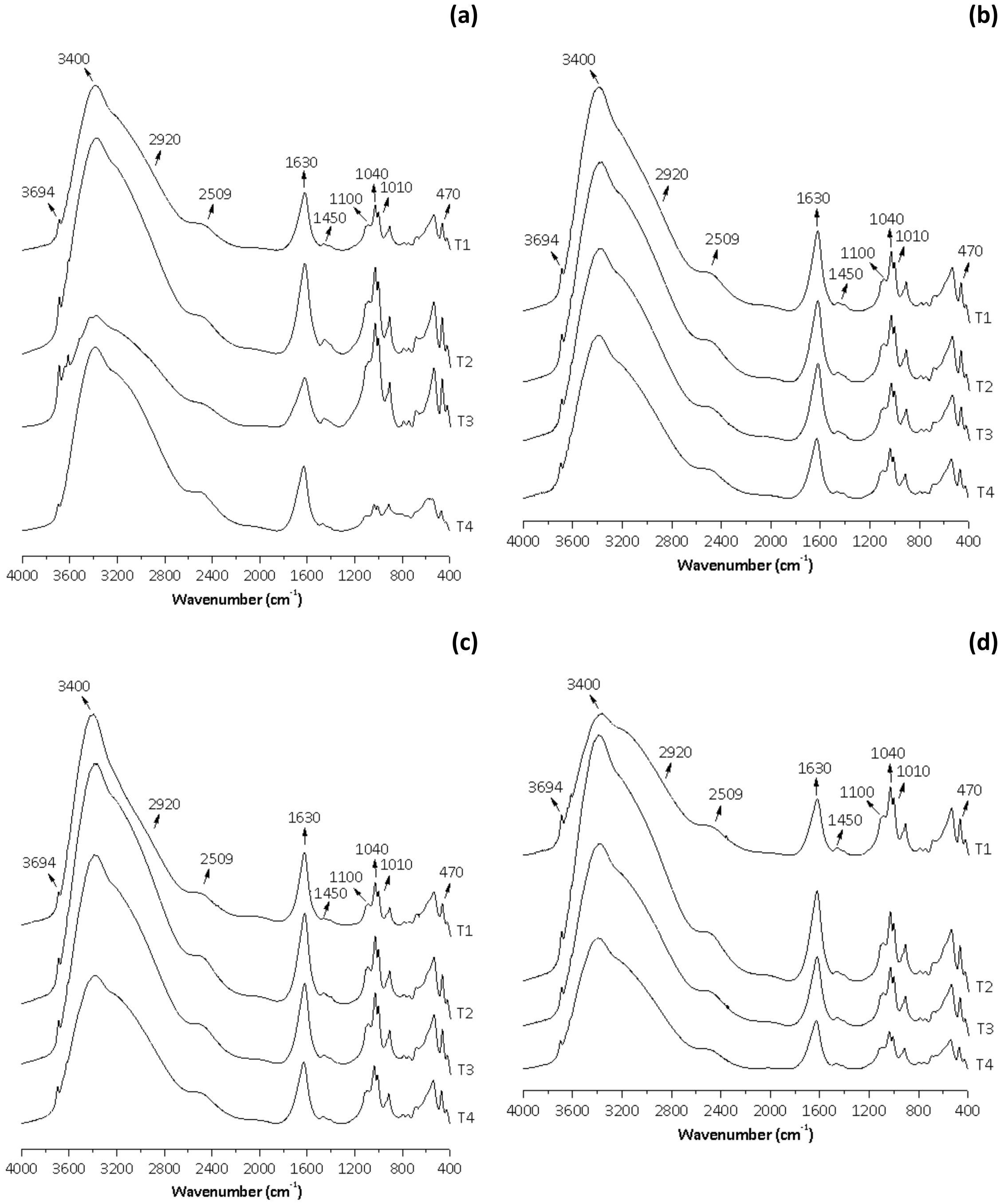

Figure 1. FTIR spectra of humic acid samples extracted from soils under the treatments: no application of poultry litter (T1) on the day of seeding and (T2) 45 days before seeding; with the application of 12 Mg ha^{-1} of poultry litter (T3) on the day of seeding and (T4) 45 days before seeding; collected at depths of: (a) 0-2.5; (b) 2.5-5; (c) 5.0-10 and (d) 10-20 cm

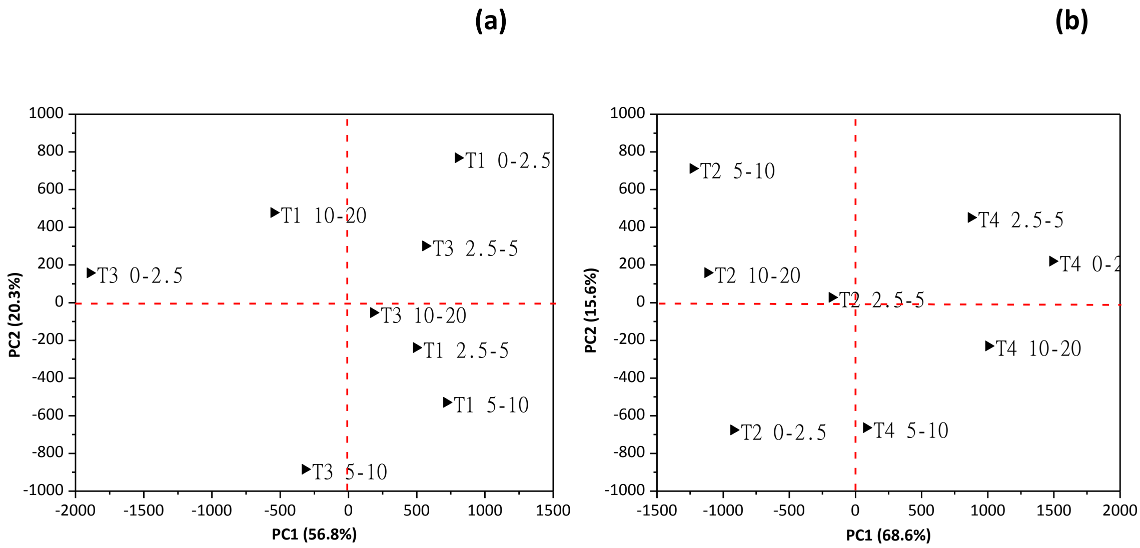

Figure 2. PC1 versus PC2 scores graphs obtained from HA FTIR spectral data (at the intervals 3720 to 2400 cm^{-1} and 1800 to 1400 cm^{-1}) corresponding to treatments (a) T1 and T3 and (b) T2 and T4

The PCA analysis between T1 and T3 (Figure 2a) and between T2 and T4 (Figure 2b) showed that, with two main components, it was possible to describe 77.1 and 84.2% of the data variability, respectively. In Figure 2a it was not possible to observe the grouping of samples submitted to the same treatment, suggesting that there was no separation between T1 and T3. On the other hand, the separation did occur in Figure 2b, when the treatments compared were T2 and T4. This result indicates that, according to the FTIR spectroscopic evaluation, the soil OM structural characteristics of T2 and T4 presented differences resulting from the poultry litter application 45 days before sowing.

From the FTIR results, it was possible to determine the aromaticity index, I_{1630}/I_{2920}. According to Rosa et al. (2008).[14] This index refers to the degree of HA condensation/saturation, that is, the relation between the vibration intensity of C=O and C=C groups with the intensity of C–H groups. The I_{1630}/I_{2920} calculation has been used as an indication of the degree of humification of HA samples extracted from soils[14,26,28,42] and vermicomposts.[27] The values were around 0.8 ± 0.1 and 0.901 ± 0.001 (Table 1), which is similar to the values found in the literature,[14,26,28] in which the variation observed was 0.57 to 2.8.

The sample collected from the 0-2.5 cm layer of T4 presented the lowest value for this index when compared to all other samples (Table 1). This result suggests that there was a higher proportion of aliphatic groups and might be indication of a lower degree of humification. In application, for T4, the I_{1630}/I_{2920} presented a gradual increase with depth. Potes et al. (2010)[26] and Dick et al. (2005)[43] pointed out that the soil OM aromatic character is expected to increase with the depth due to the effect of dilution at the soil surface because of the presence of residue and also the translocation of aromatic compounds through the profile. Moreover, for T4 there was an effect of poultry litter application, which presented characteristics that were very distinct from those of the soil. For the remaining treatments this gradient was not observed, suggesting that the application of poultry litter, 45 days before sowing, promoted higher levels of transformations in the soil OM structure when compared to the poultry litter application on the day of the sowing in T3. It may also be inferred that the dilution effect, resulting from the presence of residue[26,43] did not result in any significant variation of the OM characteristics, probably due to the short time frame of the experiment (T1 and T2). However, it is important to highlight that the band at 2920 cm^{-1} was not clearly seen in the spectra, which might result in the under or overestimation of the calculations.

The correlation graphs , from all the sampled data (depths and treatments), showed that the H_{LIF}, E_4/E_6 and I_{1630}/I_{2920} indices were not related to each other, as r^2 values were 0.009; 0.000 and 0.002, for H_{LIF} versus E_4/E_6; I_{1630}/I_{2920} versus E_4/E_6 and I_{1630}/I_{2920} versus H_{LIF}, respectively.

Therefore, samples were separated according to treatment to determine the correlation between spectroscopic technique indices. In Table 2, r^2 values for each treatment are shown, taking into consideration the correlation between H_{LIF} versus E_4/E_6; H_{LIF} versus I_{1630}/I_{2920} and E_4/E_6 versus I_{1630}/I_{2920}.

Table 2. Correlation between indices: H_{LIF}, E_4/E_6 and I_{1630}/I_{2920}, for all treatments

Treatment	H_{LIF} versus E_4/E_6	H_{LIF} versus I_{1630}/I_{2920}	E_4/E_6 versus I_{1630}/I_{2920}
T1	$r^2 = 0.088$	$r^2 = 0.54$	$r^2 = 0.22$
T2	$r^2 = 0.70$	$r^2 = 0.28$	$r^2 = 0.15$
T3	$r^2 = 0.0018$	$r^2 = 0.018$	$r^2 = 0.67$
T4	$r^2 = 0.99$	$r^2 = 0.85$	$r^2 = 0.76$

It was observed that the indices calculated for the samples submitted to T1 did not show a correlation, as the r^2 values were very low (0.088, 0.54 and 0.22 for H_{LIF} versus E_4/E_6; H_{LIF} versus I_{1630}/I_{2920} and E_4/E_6 versus I_{1630}/I_{2920}, respectively). The lowest r^2 value observed for the relationship between H_{LIF} and E_4/E_6 indices might be the result of the distinct behavior observed for the degree of humification, through the profile, according to these indices. While the E_4/E_6 ratio showed a tendency for increasing degree of humification with increasing depth, H_{LIF} did not present linear behavior.

The results for the T3 samples showed little or no correlation between indices (Table 2). This result is probably because, in this treatment, the H_{LIF} index was the only one that increased gradually through the profile, indicating an increase in the degree of humification. No linear variation was observed for the E_4/E_6 ratio in relation to depth. The I_{1630}/I_{2920} index did not show significant variation between samples.

The evaluation of the results for T2 samples showed a reasonable correlation between the H_{LIF} and E_4/E_6, with an $r^2 = 0.70$.

The highest r^2 values were observed for the indices for the T4 samples (Table 2). This result is probably because in T4 all indices presented a gradual and increasing variation with depth (Table 1). However, the increasing variation of the E_4/E_6 ratio indicates a reduction in the degree of humification with depth, in contrast with the other indices.

In general, the low correlation between techniques might result, among other factors, from the already mentioned limitations of each technique. These results reinforce the importance of using data sets obtained from several spectroscopic techniques to infer significantly about the structural characteristics of soil OM amended with poultry litter.

4. Conclusions

From the H_{LIF}, E_4/E_6 and I_{1630}/I_{2920} indices, obtained through spectroscopic techniques, LIFS, UV-Vis absorption and FTIR, respectively, it was possible to detect the effects of poultry litter application on the OM characteristics of an Oxisol under no-tillage system.

H_{LIF} revealed a reduction in the degree of humification of the superficial layers (0-2.5 and 2.5-5 cm) as a result of poultry litter application at both application times. This indicates that the residue has a low degree of humification and, therefore, interferes significantly with the soil OM structural characteristics. The same was not observed for deeper layers, probably due to the short time frame of the experiment, which did not allow the residue to be incorporate into the soil.

From the E_4/E_6 ratio, it was observed that the soil OM submitted to the application of residue 45 days before sowing and on the day of sowing, had a lower degree of humification than the soil OM without the application of residue, except for the application of residue on the day of sowing in the 0-2.5 cm layer. This result reinforces the idea that the residue has a low degree of decomposition.

It was possible to observe significant variations in soil OM characteristics from the I_{1630}/I_{2920} data only when comparing T2 and T4 at the 0-2.5 cm layer, revealing a reduction in the degree of humification with the application of residue.

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