



Research article

Spectroscopic characterization of humic and fulvic acids in soil aggregates, Brazil

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ABSTRACT

Agricultural management methods affect organic compounds in the soil. The aim of this study was to characterize humic and fulvic acids using infrared spectroscopy and nuclear magnetic resonance (NMR) in aggregates collected from areas under different crop and soil management systems. Soil samples were collected at depths of 0.00–0.10 m in a trial set up in 1989 with four management systems (no-till, no-till with chiseling every three years, disk harrowing and heavy disking) under two production systems (succession and rotation). In the laboratory, the soil was sieved and separated into two fractions: particle size of 2 mm or more, and less than 2 mm. From each of the samples an aliquot was extracted and the humic and fulvic acids purified for FTIR, UV-VIS and NMR-¹H analysis. The results obtained showed that the structural characterization of the humic and fulvic acid fractions were linked to organic matter left on the soil surface, especially where the agricultural system involved species diversity. Aggregates ≥ 2 mm produce higher NMR, UV-VIS and FTIR spectral magnitudes in aromatic and aliphatic structures than those < 2 mm. Aggregates collected from soil under no-till retained their aromatic and aliphatic chemical structures, resulting in higher spectral amplitude.

1. Introduction

Problems caused by agricultural management can lead to exaggerated responses, which can cause soil loss and degradation, nutrient leaching and loss of organic matter, which result productivity decline (Bispo et al., 2017).

Soil organic matter (SOM) is one of the agents responsible for stabilizing soil aggregates, supplying nutrients and maintaining soil micro-biological balance (Huang et al., 2010). SOM dynamics are driven by adding organic compounds, which are transformed as time progresses by a combination of chemical, physical and biological factors (Ver et al., 1999; Gude et al., 2012). These transformations occur as the organic matter decomposes, changing the size of the molecules, chemical composition, structure and functional groups, as well as the poly-electrolytic characteristics of the added material (Kononova, 1966; Stevenson, 1994; Loss et al., 2016).

In chemical terms, organic matter consists of three fractions of humic substances (HS): humin, fulvic acids and humic acids (Santos and Camargo, 1999). Each of these substances has a specific function in the

soil: for example, fulvic and humic acids play a role in transporting cations between exchange organic-mineral complexes and also affect cation-exchange capacity (CEC) of organic origin (Senesi et al., 1994; Janos, 2003; Benites et al., 2010).

The humic substances eventually form between 80 and 90% of all SOM. They consist of heterogeneous molecular compounds containing different functional groups (Chen et al., 2002). They are dark in color, with no defined property, hydrophilic and stable, and their constituents can vary as follows: 40–60% C; 30–50% O; 0–4% N; 2–4% H; 0–2% S (Moraes et al., 2011).

Humic substances interact with ions to form complexes of different stabilities and structural characteristics (Clemente et al., 2013). All these characteristics can indicate the soil management stage in agricultural areas. Some authors have used humic substances to indirectly evaluate soil management quality based on the degree of SOM humification (Canellas et al., 2004, 2007; Rosa et al., 2005).

SOM resulting from organic residues boosts carbon content, depending on the existing structures, generally with carboxyl and aromatic bonds, and there is a drop in carbon associated with

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polysaccharides (Zech et al., 1997; Canellas et al., 2007). Thus, humic fractions tend to increase particle cohesion and aggregate stability, and are associated with the distribution of aggregate particle sizes and conservation of carbon in the soil (Huang et al., 2010; Loss et al., 2016). Examining the spectral characteristics of separate fractions of organic matter can provide important information on how to improve soil quality (Oades et al., 1987; Rigobello et al., 2017).

The use of agricultural management with species diversity significantly increases the organic matter content, thus acting effectively on the relationship between soil aggregates. As consequence, it changes the soil chemical structure, and humic and fulvic acids increase as part of soil quality (Sarkhot et al., 2007).

Different management systems may affect the structural formation of humic and fulvic acids. This fact is the basis for the hypothesis that either the type of soil management and the aggregate particle size affect may the quality and spectra of humic substances. Thus, the aim of this study was to characterize humic and fulvic acids by means of infrared spectroscopy and nuclear magnetic resonance in aggregates collected from soils under different management and cropping systems.

2. Material and methods

2.1. Experimental area

Samples were collected in February, 2018, at location 23°11' S, 51°11' W (Brazil) in a dystroferic Red Latosol (Oxisol) area. The area was split up into fully randomized experimental units of 225 m² (7.5 m × 30 m), with four replicates per treatment. The experiment was divided in four agricultural management types (no-till; no-till chiseled every three years; disk harrowing; heavy disking) and two production systems (rotation and succession crops).

The following soil management systems were studied: No-Till (NT), in which seeds are sown in the waste of the previous crop by simply opening a narrow furrow; No-till, chiseled (NTC) with winter chiseling every 3 years using a chiseler with five tines spaced at 0.35 m, working to an average depth of 0.25 m; Disk Harrowing (DH), in which the soil is prepared every year before summer cropping to an average depth of 0.20 m, followed by leveling harrowing; Heavy Disking (HD) in which the soil is plowed to an average depth of 0.15 m followed by light harrowing prior to summer planting. Under the DH and HD systems, this procedure is also implemented prior to winter cropping. All soil management systems were assessed with crop rotation and soybean/wheat succession. Under NTC, the most recent chiseling operation had been carried out three years prior to the evaluation.

At the beginning of the trial, plots were sown with wheat and winter cover (white lupin or black oats) in April. Summer crops (soybean and maize) were sown in November.

2.2. Soil collection and characterization

Soil samples were collected at depths of 0.0–0.10 m, then air dried and sieved through a 2 mm mesh ready for chemical analysis and clay content evaluation, following the methods described in Pavan et al. (1992) and Claessen (1997) (Table 1). The following parameters were determined: potential acidity (H + Al) by SMP; Ca; Mg and Al extracted by 1N KCl and titrated with EDTA (Ethylenediamine tetraacetic acid) and NaOH; P and K by Melhich-1 extraction and spectrophotometry at 630 nm (P) and flame photometry (K); and carbon by oxidation with Cr₂O₇²⁻ and titration with FeSO₄. Clay content was determined in 20 g of fine oven dried soil using the pipette method with slow stirring (180 rpm) for 16 h and 1N NaOH as a chemical dispersant. After drying, the material was weighed and the following formula used: Clay (%) = ((Weight or mass of clay x 500) - 2).

2.3. Aggregate particle size

The aggregates were sieved through a 2 mm mesh to separate particles ≥2 and <2 mm.

2.3.1. Humic substance extraction and purification

The method used to extract the humic substances was as described in Giovanela et al. (2004) and Lamar et al. (2014), with some adaptations. Five grams of sampled material were washed in 0.145 mol l⁻¹ HCl for an hour with mechanical stirring in order to eliminate any minerals present. The suspension was then left for 24 h at 4 °C. The supernatant was separated by centrifuging at 5000 rpm for 20 min. The precipitate was washed in 0.113 mol l⁻¹ NaOH for 4 h under an inert atmosphere of N₂ and stirred constantly. The samples were then left for 24 h at 4 °C. The supernatant was separated from the precipitate by centrifuging. The alkaline extract was acidified by adding 6.034 mol l⁻¹ HCl to obtain a pH of approximately 1.203, and the humic (HA) and fulvic (FA) acids separated. The acids extracted were left for 24 h at 4 °C and then centrifuged.

The HA precipitate was washed in 0.141 mol l⁻¹ HCl/0.324 mol l⁻¹ HF (hydrofluoric acid) for 12 h with stirring. The suspension was washed in deionized water until the quantity of Cl⁻ dropped, as verified by 0.142 mol l⁻¹ AgNO₃. The humic acids were dissolved in 0.113 mol l⁻¹ NaOH and eluted using a column packed with Amberlite IRA 200 resin, and the extract frozen and then lyophilized.

The supernatant containing fulvic acids was eluted a number of times using Supelite XAD-8 resin, previously purified and acidified with 0.145 mol l⁻¹ HCl. The fulvic acids were adsorbed and the column washed with deionized water to eliminate any salts present and eluted in 0.113 mol l⁻¹ NaOH. The elutant was run several times through a column of Amberlite IRA 200. The concentrate was frozen and then lyophilized.

2.4. Characterization of samples the humic and fulvic acids

2.4.1. Fourier transform infrared Spectroscopy

The purified, lyophilized samples were prepared in tablets and compressed with KBr for analysis. The FTIR spectra at 400 to 4000 cm⁻¹ were obtained using a Bruker Vertex 70 FTIR spectrophotometer with Platinum ATR (attenuated total reflection) module. A resolution of 4 cm⁻¹ and 10 scans were used to obtain the 10 spectra, which were analyzed using Origin software (5.0, 2007).

2.4.2. ¹H nuclear magnetic resonance

Five hundred microliters of deuterium oxide (D₂O-99.9%, Sigma Aldrich®) were added to 100 mg of the purified, lyophilized sample. The spectra were obtained at the spectroscopy laboratory (SPEC) of the State University of Londrina using a Bruker Avance III spectrometer set to 400 MHz for ¹H, with 5 mm multinuclear probes. The zg30 program was used for ¹H, solvent suppression at 4.7 ppm with zgpr. Number of scans 64000 for ¹H.

2.4.3. UV/VIS Spectrophotometry

In the AJX-1600 spectrophotometer, two milligrams of purified sample were added to 10 ml 0.05 mol NaHCO₃ and the E₄/E₆ ratio determined by reading 465 and 665 nm absorbance in order to determine the degree of aromaticity.

3. Results and discussion

3.1. FTIR spectroscopy

The FTIR spectra for humic and fulvic acids extracted from aggregates of ≥2 mm or <2 mm are shown in Figures 1 and 2, and Table 2 gives

Table 1. Chemical properties and clay-content evaluated after 26 years of trials.

Depth	Mgmt.	Clay	C	H + Al	pH	Ca	Al	Mg	P	K
0.00–0.10 m	HD	786	12.0	4.87	4.76	4.15	0.08	1.85	22.8	0.65
	DH	780	11.7	5.46	4.64	3.92	0.07	1.49	17.3	0.56
	NTC	742	12.1	5.58	4.73	4.11	0.10	1.85	37.9	0.74
	NT	710	16.6	4.22	5.26	5.36	0.01	2.56	38.5	0.94

Depth in m. pH determined by CaCl_2 ; H + Al determined by SMP; Ca, Mg and Al extracted by KCl; P and K extracted by Mehlich-1; C extracted by $\text{K}_2\text{Cr}_2\text{O}_7$; and clay determined by the slow stirring method. H + Al; Ca; Mg; Al; K in Cmolc dm^{-3} ; P in mg dm^{-3} ; C in g kg^{-1} ; Clay in g kg^{-1} . Mgmt.: Management; HD: heavy disking; DH: disk harrowing; NTC: no-till chiseled; NT: no-till.

absorption bands for each component according to [Stevenson \(1994\)](#); [González Pérez et al. \(2004\)](#) and [Moraes et al. \(2011\)](#). The spectra of the main chemical structures (OH stretch; C=O; C=C aromatic; C-H and polysaccharides) are similar (Figures 1 and 2). This is due to the complex composition of humic and fulvic acids and the diversity of kinds of organic matter from which they are formed ([Moraes et al., 2011](#)).

Wavelengths in the $3700\text{--}3620\text{ cm}^{-1}$ band denote the appearance of OH, alcohols and free phenols, which can be seen for all treatments in humic acids (Figure 1), but in lower incidence in fulvic acids (Figure 2). These bands can denote impurities associated with minerals or water, or show the complexity of the chains in humic acids ([Stevenson, 1994](#)) resulting from the kind of management system applied, and humic acids are more recalcitrant than fulvic acids.

In all humic and fulvic acid spectra, there are wide bands between 3400 and 3200 cm^{-1} , indicating COOH stretch on H bridges. The strength of intra-molecular bonds is related to stretching and widening: the greater the width the higher the number of bridges and the more acid the material ([Oliveira Dias et al., 2009](#)).

In the humic acid fractions (HAF) of aggregates $\geq 2\text{ mm}$ (Figure 1) under no-till with crop rotation and fulvic acid fractions (FAF) in the no-till chiseled there was a greater intensity, and under disk harrowing with

succession a lower intensity of peaks in FAF, which could be correlated with the management systems and cropping in the area. [Dobbss et al. \(2009\)](#) observed intense bands in HA than in FA, corroborating the spectra found in this study. These authors also state that narrow bands denote a low degree of humic substance association.

For all treatments, aromatic characters were observed (mainly in humic acids) in the 1580 cm^{-1} region. This aromatic region indicates less labile structures in humic acids, in contrast to fulvic acids extracted from aggregates $\geq 2\text{ mm}$, where these bands were not found, showing that these compounds were not predominant. In fulvic acids extracted from aggregates $< 2\text{ mm}$, and humic acids extracted from aggregates $<$ and $\geq 2\text{ mm}$, the carbon is retained in the soil, even under the effects of waste decomposition in more intense management systems and the presence of biological activity. Working on isolated soil humic acids, alginates, lignites, organic compounds and commercial chemicals, [Pospíšilová et al. \(2015\)](#) found similar values and stated that the characteristics of humic acids are linked to soil type and origin from management, as well as the kind of organic matter input and this organic matter is degraded. Exposure to enzymatic attack increases humification, therefore more molecular structures can be observed in humic acids (Figures 1 and 2). Biological activity is essential for chemically degrading organic matter

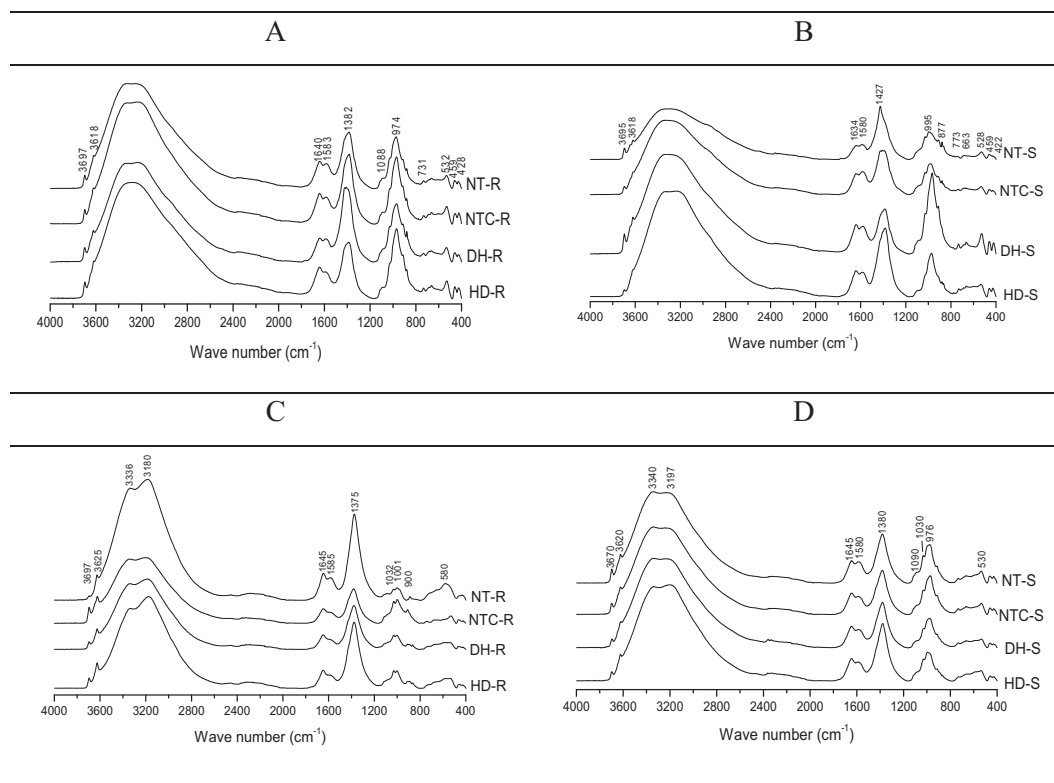


Figure 1. Wave numbers in the middle infrared with Fourier Transforms (FTIR) of fractions of humic acids for the following treatments: NT- No-till; NTC - No-till, chiseled; DH - Disk harrowing; HD - Heavy disking; R - crop rotation; S - crop succession. (A) humic acid fractions (HAF) extracted from aggregates $< 2\text{ mm}$ under crop rotation; (B) HAF extracted from aggregates $< 2\text{ mm}$ under crop succession; (C) HAF extracted from aggregates $\geq 2\text{ mm}$ under crop rotation; (D) HAF extracted from aggregates $\geq 2\text{ mm}$ under crop succession.

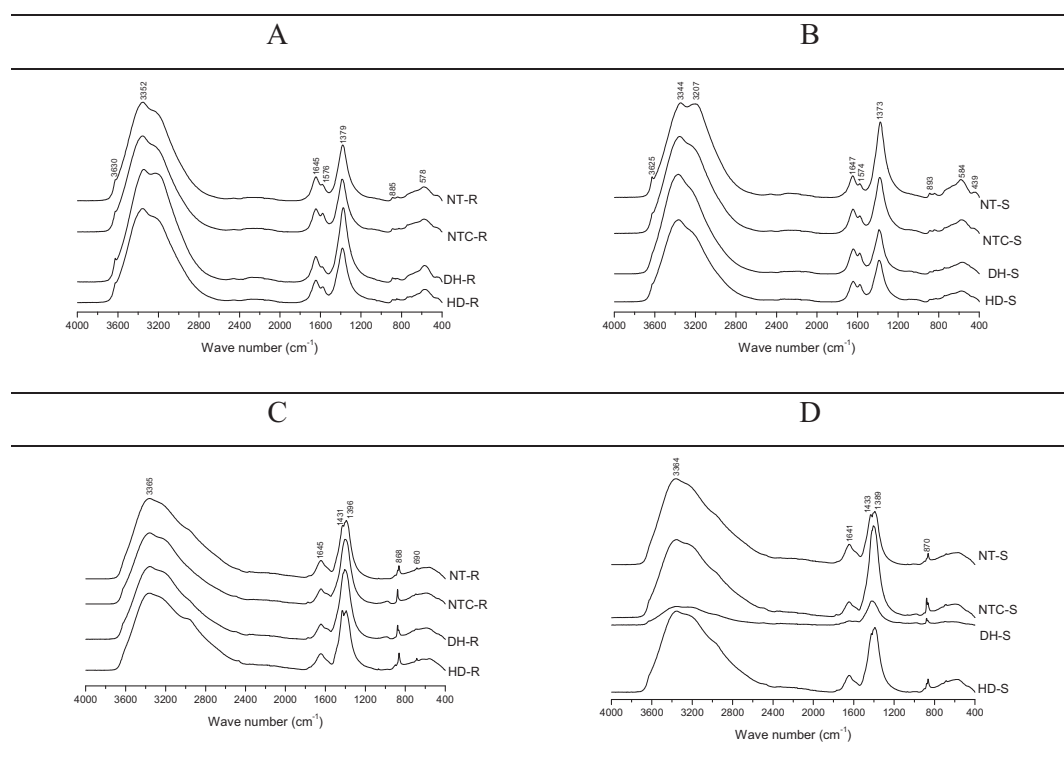


Figure 2. Wave numbers in the middle infrared with Fourier Transforms (FTIR) of fractions of fulvic acids for the following treatments: NT- No-till; NTC - No-till, chiseled; DH - Disk harrowing; HD - Heavy disking; R - crop rotation; S - crop succession. (A) Fulvic acid fractions (FAF) extracted from aggregates < 2mm under crop rotation; (B) FAF extracted from aggregates < 2mm under crop succession; (C) FAF extracted from aggregates ≥ 2 mm under crop rotation; (D) FAF extracted from aggregates ≥ 2 mm under crop succession.

Table 2. Proposed attributions for wavelengths (cm^{-1}) of FTIR spectra.

Wavelength cm^{-1}	Proposed attribution
3700–3620	Free OH stretch
3400–3200	OH stretch, inter- and intra-molecular N-H, amine NH and phenol OH
1660–1630	Amide C=O stretch; quinone C=O and/or C=O bonded to H in paired ketones; C=C aromatic
1600–1580	C = C aromatic group stretching
~1430	Stretching of methyl and methylene C-H bonds
1400–1380	Aliphatic C-H stretch
<1000	C-O stretches; aromatic C-H corresponding to polysaccharides and carbohydrates

Stevenson (1994); González Péres et al. (2004) and Moraes et al. (2011).

(Silva et al., 2014). Thus, chemical forms are more marked in the aromatic region.

Low-intensity bands were observed at 1645 cm^{-1} , corresponding to C=O stretches in carboxyl groups. This wavelength was found under all treatments. However, comparing bands at shorter wavelengths, it can be seen that, irrespective of the treatment, humic acids contain more C=O, -COO-, ketone and polysaccharide group molecules, due to the amount of peaks present.

In the fulvic acid fraction extracted from aggregates < 2 mm, there were neither N-H stretch bands nor C=N stretch at 1430 cm^{-1} . However, these bands were observed in aggregates ≥ 2 mm, and could indicate the presence of methyl and methylene groups. The solubility of fulvic acids could have affected absorption in these bands (fulvic acids are less soluble and easier to remove), indicating the presence of lignin at this amplitude, therefore eliminating the amplitude of 1430 cm^{-1} . With aggregates breakdown and soil drying, exposing organic compounds, decomposition increases in the aerobic environment and the

humification rate, causing bands of lower peaks for some treatments (DiDonato et al., 2016).

Bands related to aliphatic C-H stretching were observed in the 1380 cm^{-1} band, with high intensity of fulvic acids extracted from aggregates < and ≥ 2 mm for all the treatments evaluated, except DH-S for aggregates ≥ 2 mm, in which there was a low incidence. This low incidence could be linked to the breakup of the aggregates and exposure of organic matter to the environment, preventing reads in the spectrum. Working with humic substances in soil under degraded pasture, Santana et al. (2011) observed the same wavelength, but at lower intensity, showing that degradation influences wavelength. The use no-till and rotation crops have positive effect in C-H stretching in fulvic and humic acids fractions.

For humic acids extracted from aggregates ≥ 2 mm under crop succession and extracted from aggregates < 2 mm under crop succession and rotation, there were specific peaks at wavelengths below 1000 cm^{-1} , corresponding to CO stretching in polysaccharides, and aromatic or out-of-plane C-H. However, for fulvic acids there were few of these peaks

under both treatments (Figure 2). Since fulvic acid fractions are less stable, they show peaks at low incidence in the region below 1000 cm^{-1} in aggregates both larger and smaller than 2 mm, obtained under the crop rotation and succession conditions evaluated.

Vibrations between $1090\text{--}995\text{ cm}^{-1}$ could also be due to aluminosilicate impurities (Si-O stretch) (Madejová and Komadel, 2001) that, during the extraction process, were not completely removed from the humic acids (Pernet-Coudrier et al., 2011). In this case, ascribing these bands to aluminosilicate impurities is based on several factors, including the additional presence of bands at 890 cm^{-1} (AlAlOH stretch) and 530 cm^{-1} (Al-O-Si stretch) (Rodríguez et al., 2016).

3.2. ^1H nuclear magnetic resonance

Differences in the spectral intensities were observed in line with the diversity and activity of the soil management systems (Figures 3 and 4). Peaks were interpreted based on Rumjanek (2005), Khan et al. (2006) and Rodríguez et al. (2016). The region close to 5 ppm, corresponding to D_2O . Although there are similarities in the chemical structures shown by the spectra, peak magnitudes do vary.

Figure 3 shows more aliphatic structure than aromatic in humic acids fractions, with peak distribution between 0 and 4 ppm. Methyl ($\text{CH}_3\text{-R}$) and methylene ($\text{R-CH}_2\text{-R}$) were observed for all treatments, but with greater intensity under NT and NTC with crop rotation and succession (Figure 3). Clement et al. (2013) point out that these structures are typical of molecules which have high and low molecular weight and form part of the polymer lipids, cutin and suberin.

The same structure ($\text{CH}_3\text{-R}$) was found in the HAF extracted from aggregates $<2\text{ mm}$, but with lower intensity under NTC-R, NTC-S, DH-R and HD-R. The soil under NT, however, showed the highest intensities for aliphatic chains (0–4 ppm) (Figure 4). This result indicates that the diversity of species grown on the land boosts the presence of polysaccharides from the cell walls, formed by chains of polysaccharides, proteins and phenolic compounds, which can be very resistant to decomposition. The fraction of humic acids extracted from aggregates $\geq 2\text{ mm}$, resulted in higher intensities of aliphatic and aromatic chains. This aggregate particle size could help conserve intra and inter-aggregate organic material, preventing its rapid decomposition. It could, therefore, be indicative of structural changes in systems in which the aggregates are broken down during soil preparation and in which agricultural systems like rotation are used, and the quality of the material depends on recalcitrant organic matter. Khan et al. (2006) found similarity between ^1H spectra for all areas incubated with *Oryza sativa*, *Quercus dendata* and *Cryptomeria japonica*.

In the humic acid fraction (HAF) from aggregates $<2\text{ mm}$, the spectra obtained were similar for all treatments (Figure 4). NT-R, NT-S and of the spectra for DH-S and HD-S showed similar magnitudes; the same was true of NTC-R; NTC-S; DH-R and HD-R. Working with organic soils, Enev et al. (2014) observed the presence of aliphatic and aromatic structure in soils with organic compounds. This corroborates the values in Table 3, especially for NT in which the crop waste is left on the soil surface. Tadini et al. (2015) report that the cell walls contain cutin and suberin, resistant aliphatic biopolymers that are derived from lignin, cellulose and hemicellulose, and affect the ^1H NMR spectra, mainly in no-till.

Table 3 shows the E_4/E_6 ratio for absorbance between 465 and 665 nm that defines the degree of aromaticity in humic substances. According to Rumjanek (2005), the higher the E_4/E_6 ratio, the higher the degree of aromaticity. The values in Table 4 corroborate with the spectrometry results. The degree of aromaticity is dependent on the humification of humic substances and represented by a low E_4/E_6 ratio, showing that little humified residue is present (Saab and Martin-Neto, 2007).

Rigobello et al. (2017) reported that the E_4/E_6 ratio is influenced by molecule size, environmental pH, levels of oxygen, carbon and carboxyl groups, and the age of the humic material. This affects the formation of humic substances, which, according to Stevenson (1994), occurs through three mechanisms: a) microbiological activity releases nitrogenated compounds that react with lignins; b) oxidation of polyphenolic compounds to form quinones that are condensates in reactions with aminated compounds, and c) reduction of sugars that react with aminated compounds and change into macropolymers of dark in color and with high molecular mass. Microorganisms play a fundamental role in forming the structures of HAF and FAF, releasing compounds and enzymes, in addition to degrading lignin, which binds the chains (Silva et al., 2014).

The different E_4/E_6 ratios and spectra observed according to aggregate particle size could be related to the quantity of organic matter incorporated into the soil, such as lignins, carbohydrates, lipids, polysaccharides, etc. These compounds are degraded and form complexes such as lignin-carbohydrate that is amphiphilic and has a tendency to form aggregates, especially mycelial aggregates (Canellas et al., 2007).

Another point to be considered is that the E_4/E_6 ratio is related to aggregate aromatic condensation and the content of phenol and benzene-carboxyl groups (Rubenacker et al., 2012). A low E_4/E_6 ratio suggests that humic substance particles are large with high molecular masses and degrees of humification (Traversa et al., 2014) but it depends on the type of organic matter to be inserted into the agricultural system. The degree of humification could have affected the fulvic acid fraction (FAF), whereas the humic acid fraction contains highly humified organic compounds that are resistant to degradation, and therefore tend to persist for longer. Thus, management systems like NT directly influence the

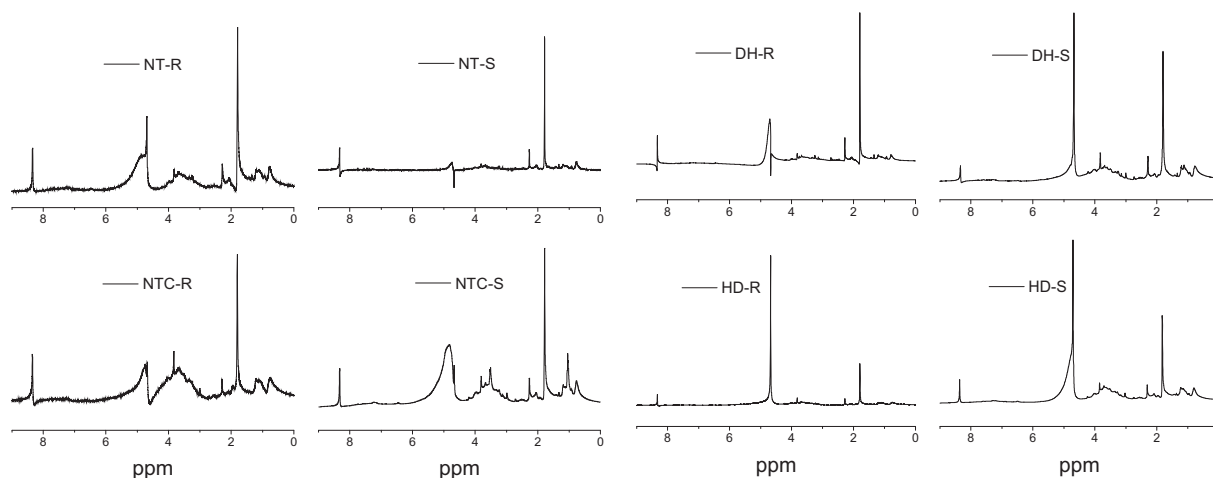
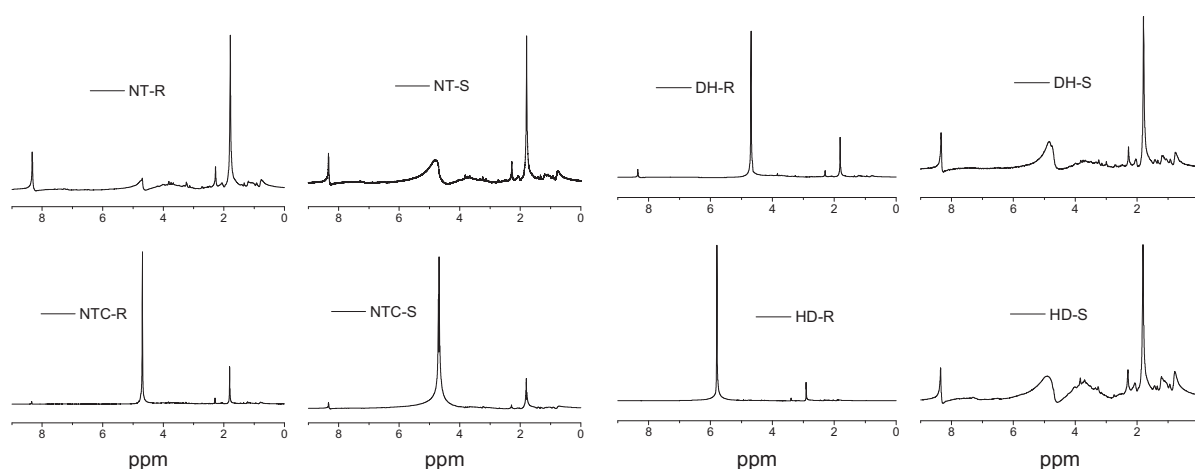
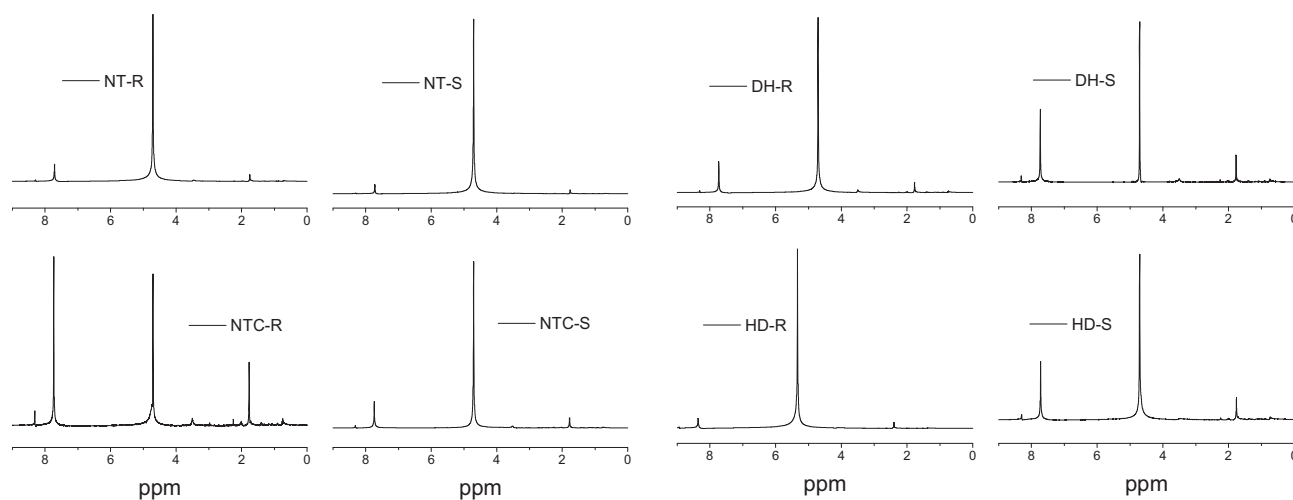


Figure 3. ^1H NMR spectra for humic acid fractions extracted from aggregates $\geq 2\text{ mm}$ under different management systems. NT: no-till; NTC: no-till, chiseled; DH: disk harrowing; HD: heavy disking; R: rotation; S: succession.

Table 3. Ratio of E_{465} to E_{665} , (E_4/E_6) obtained by UV/VIS spectrophotometry for different management systems in humic and fulvic acid fractions extracted from aggregates $<$ and ≥ 2 mm.

System	E_4/E_6 ratio			
	HAF		FAF	
	≥ 2 mm	< 2 mm	≥ 2 mm	< 2 mm
NT-R	7.0	15.3	9.9	6.8
NT-S	4.3	15.0	11.2	6.0
NTC-R	8.5	42.0	7.7	7.1
NTC-S	4.6	29.0	9.2	15.3
DH-R	11.4	19.0	5.3	9.5
DH-S	8.7	13.3	6.3	14.6
HD-R	18.0	17.3	14.3	5.6
HD-S	11.7	11.6	14.0	5.9

NT: no-till; NTC: no-till, chiseled; DH: disk harrowing; HD: heavy disking; R: rotation; S: succession.

**Figure 4.** ^1H NMR spectra for humic acid fractions extracted from aggregates < 2 mm under different management systems. NT: no-till; NTC: no-till, chiseled; DH: disk harrowing; HD: heavy disking; R: rotation; S: succession.**Figure 5.** ^1H NMR spectra for fulvic acid fractions extracted from aggregates ≥ 2 mm under different management systems.

various structural compounds. The length of the trial and the diversity of the species grown could be another factor that influenced the structures, with lower impact on humic acids and higher on fulvic acids.

Fulvic acid fractions were similar (Figures 5 and 6). Under NTC-R, DH-S and HD-S, they were chemically more aromatic, corroborating

the values in Table 3, with peaks between 7 and 9 ppm. E_4/E_6 ratios and magnitudes are related to the formation process and the structural chain, since fulvic acids are more soluble and tend to be rapidly degraded.

The ^1H NMR spectra for fulvic acids extracted from aggregates < 2 mm were very similar under NT-R and S; NTC-R and S; DH-R and HD-R.

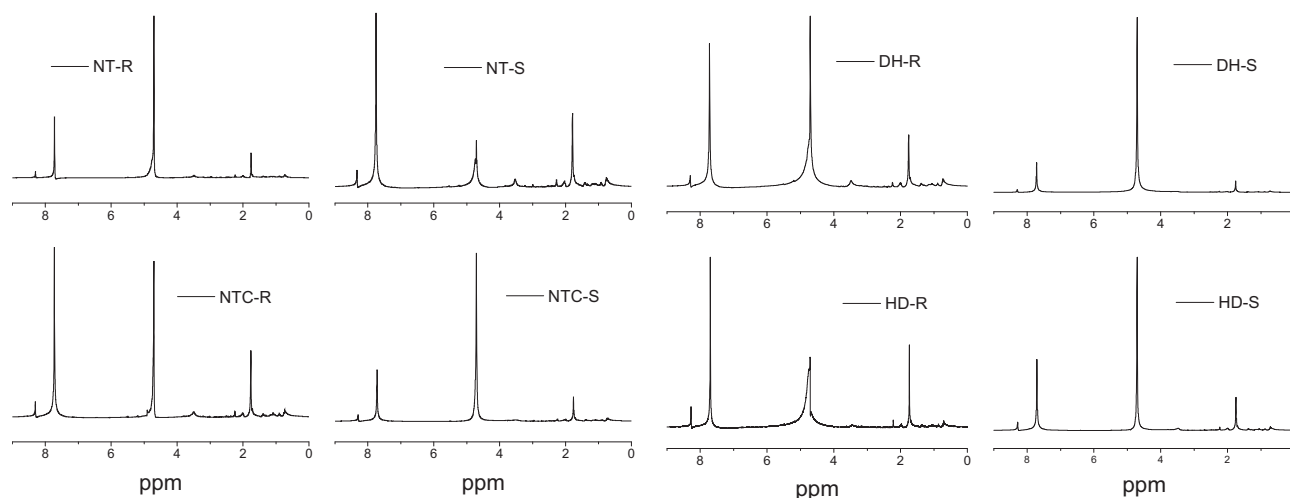


Figure 6. ^1H NMR spectra for fulvic acid fractions extracted from aggregates <2 mm under different management systems.

The influence of various rotated crops and their decomposition is clearly visible, since the magnitudes of spectra are between 7 and 9 ppm, showing the aromatic nature of the structures. These spectral magnitudes correlate with the values in Table 3.

In the light of the silviculture work carried out by Moraes et al. (2011), a number of hypotheses can be considered regarding the formation of aliphatic and aromatic structures. Under no-tillage systems, the organic matter cycle tends to be constant throughout a given period, favoring the formation of labile C chains in the fulvic and humic acid fractions. Therefore, the aromatic nature of the fulvic acids could be related to exposure of the material to microbial attack due to the disruptions of the soil, boosting oxidation of the organic matter and forming more labile organic structures.

According to González-Péres et al. (2008), some chemical structures, such as aromaticity, could be related to the fresh organic matter or the slow process of decomposition on superficial horizons. However, for aliphatic structures, increments of lignin directly influence these structures.

Ikeya et al. (2015) reported that humic substances, especially the humic acid fraction, are a mixture of many molecules that can vary according to the origin, age and degree of humification. It is difficult to establish a structural parameter for humic substances in view of environmental influences.

4. Conclusion

No-till soil management systems produced aliphatic chemical structure and the no-till method maintained the stability of the chemical structures in the soil and increased the magnitude and amplitude of the ^1H NMR and FTIR spectra.

Aggregates ≥ 2 mm conserved more organic matter, therefore contain a greater diversity of chemical compounds.

Both humic fractions presented aliphatic and aromatic character but with greater representativeness in humic acids and aggregates ≥ 2 mm. The diversity of the crop species grown in the trial area influenced the structure of HAF and FAF, especially in the presence of open-chain structures, helping to increase the magnitude of spectral peaks.

Declarations

Author contribution statement

W. Machado: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

J. C. Franchini: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data.

M. Guimarães: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

J. Tavares Filho: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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