



Effect of cover crop management on soil organic matter

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Abstract

Characterization of soil organic matter (SOM) is important for determining the overall quality of soils, and cover crop system may change SOM characteristics. The purpose of this study was to examine the effect of cover crops on the chemical and structural composition of SOM. We isolated humic substances (HS) from soils with the following cover crop treatments: (a) vetch (*Vicia villosa* Roth.)/rye (*Sesale cereale* L.), (b) rye alone, and (c) check (no cover crops) that were treated with various nitrogen (N) fertilizer rates. CPMAS-TOSS (cross-polarization magic-angle-spinning and total sideband suppression) ¹³C NMR results indicated that humic acids (HA) from soils under rye only were more aromatic and less aliphatic in character than the other two cover crop systems without fertilizer N treatment. Based on the DRIFT (diffuse reflectance Fourier transform infrared) spectra peak O/R ratios, the intensities of oxygen-containing functional groups to aliphatic and aromatic (referred to as recalcitrant) groups, the highest ratio was found in the HA from the vetch/rye system with fertilizer N. The lowest ratio occurred at the vetch/rye system without fertilizer N treatment. The O/R ratio of fulvic acids (FA) can be ranked as: vetch/rye without fertilizer > vetch/rye with fertilizer > no cover crop without fertilizer > rye alone (with or without fertilizer) soils. Both organic carbon (OC) and light fraction (LF) contents were higher in soils under cover crop treatments with and without fertilizer N than soils with no cover crop. These chemical and spectroscopic data show that cover crops had a profound influence on the SOM and LF characteristics.

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Abbreviations: ANOVA, analysis of variance; CPMAS-TOSS NMR, cross-polarization magic-angle-spinning total sideband suppression nuclear magnetic resonance; DRIFT, diffuse reflectance Fourier transform infrared spectroscopy; FA, fulvic acids; HA, humic acids; HS, humic substances; LF, light fraction; SOC, soil organic carbon; SOM, soil organic matter; TCN, total combustible nitrogen.

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1. Introduction

Soil organic matter (SOM) is a very reactive, ubiquitous component in soils. It is an important soil quality attribute, which influences the productivity and physical well-being of soils. Cover crops have been used to improve soil quality and reduce nonpoint sources of nutrient pollution, e.g., NO_3^- (Daliparthi et al., 1994). Thus, it is important from both an economic and environmental standpoint to determine how cover crop systems influence SOM characteristics and the biogeochemical cycling of carbon.

SOM contents and properties are a function of agricultural practices and the amounts and kinds of plant residues returned to the soil (Mann, 1985; Doran et al., 1987; Cheshire et al., 1990; Campbell et al., 1999; Ding et al., 2002). Based on data from long-term research plots of seven different locations (distributed in KY, MN, NE, OR, WV) in the USA, Doran (1980) reported that numbers of microbes, microbial biomass and potentially mineralizable N were greater for no-tillage than for conventional tillage in the 0–7.5 cm depth. However, these trends were generally reversed in the 7.5–15 cm depth, probably because conventional tillage moves some SOM to lower soil depths, which benefits microbial growth. Consequently, when the top 15 to 30 cm of soil under no-tillage is considered, often no net effect was observed (Doran, 1980; Angers et al., 1997). Wander and Traina (1996a) showed that SOM in crop rotation with cover crops was significantly higher than without cover crops. However, Lal et al. (1991) in a similar study reported no or minimal change of SOM content. The reason for not detecting any SOM change could be due to natural soil heterogeneity (Wander and Traina, 1996a).

In addition to SOM quantity, the quality (e.g., structure and composition) and distribution of individual fractions (e.g., humic acids, polysaccharides) can be important to the maintenance of soil fertility and structure. Monreal et al. (1995) observed a higher lignin dimer to lignin monomer ratio in continuous wheat rotation and this ratio decreased from large to small aggregate sizes, indicative of the change in the quality of SOM. Wander and Traina (1996b) used diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy to examine functional groups of SOM fractions and reported that the ratios of reactive to

recalcitrant fractions in HA best reflected overall SOM bioavailability. They also reported that the ratios in FA, LF and litter were useful in distinguishing temporal impacts of farming systems on SOM lability. They concluded that the characteristics and distribution of individual SOM fractions may provide a means for assessing management impacts on SOM quality that can be tied to soil productivity, and they specifically emphasized that further work is needed to determine how SOM composition changes with tillage and cropping practices.

DRIFT detects molecular vibrations and is useful for functional group analysis and for identification of molecular structures of SOM (Stevenson, 1994). But it cannot be used to quantify carbon contents of structural groups (e.g., aromatic-C). In contrast, ^{13}C NMR spectroscopy provides quantitative data for structural components (Mao et al., 2000). NMR has been successfully used to characterize SOM by many scientists (Wilson, 1987; Schnitzer et al., 1991; Preston, 1996). Thus, it would be advantageous to use both NMR and DRIFT to characterize SOM under different cover crop systems.

The primary objective of this research was to evaluate the impact of cover crop systems on SOM in New England (USA), which was never investigated before. We chose to examine SOM fractions obtained using alkali extraction (HA and FA) and physical fractionation. The specific objectives are: (1) to determine structural and compositional changes of HS (HA and FA fractions) caused by cover crop systems using NMR and DRIFT, and (2) to evaluate the light fraction (LF) variability as affected by cover crop systems with or without fertilizer N treatment.

2. Materials and methods

2.1. Site description and sampling

Since 1990, cover crop experiments have been conducted in the Connecticut River Valley at the Massachusetts Agricultural Experiment Station Farm in South Deerfield, Massachusetts (USA). The soil in these plots is a fine sandy loam (coarse, mixed, mesic Fluventic Dystrudept) and low in SOM (~2%). Its upper 0.6 m is homogeneous, overlaying inclined layers of coarse and fine material to great depth. Three

cover crop treatments with four N rates (applied to corn after cover crop incorporation) were laid out in a complete factorial design (3 m×7.5 m plots) in four randomized blocks. Cover crop treatments and seeding rates were:

- (i) check (no cover crop)
- (ii) rye (125 kg/ha)
- (iii) hairy vetch+rye (46+65 kg/ha)

Fertilizer N rates were 0, 67, 135 and 202 kg N/ha using NH₄NO₃. Cover crops were seeded yearly on the same plots in early September and were cut using a flail mower at the end of May. Then the plots were rotor-tilled to a depth of 15 cm to incorporate cover crops into the soil for corn seedbed preparation. Corn was seeded in the first week of June and harvested in the last week of August. After harvest, corn stalks were also cut using a flail mower and disk-harrowed to a depth of 15 cm. In this work, we sampled only the plots with 0 and 202 kg N/ha. Samples were collected (early November, 1999) from the top (0–25 cm) soil using a 10×5 cm core sampler. In each plot, 15 cores were drawn and combined to form a plot composite. Soils were stored at 4 °C while in transit and maintained field moist until processed. Detailed soil sample information is listed in Table 1.

2.2. Density separation of light fraction (LF) material and humic substances (HS) extraction

The LF material from each soil sample was isolated using a modified density gradient method of Wander and Traina (1996a). Three sequential densitometric rinses were obtained by dispersing (1:1 w/v) 50 g soil in a NaBr solution (density 1.6 g/ml). The soil was shaken for 30 min and centrifuged at

Table 1
Soil samples from South Deerfield of Massachusetts

Sample number	Depth (cm)	Cover crops	Nitrogen rates (kg N ha ⁻¹)
VR1	0–25	Vetch/Rye	0
VR4	0–25	Vetch/Rye	202
RA1	0–25	Rye Alone	0
RA4	0–25	Rye Alone	202
C1	0–25	No Cover Crops	0
C4	0–25	No Cover Crops	202

Table 2

Organic carbon and total combustible nitrogen in the soil and light fraction under different cover crop systems

Sample number	OC (kg m ⁻³ soil)	TCN (kg m ⁻³ soil)	LF (kg m ⁻³ soil)	LF-OC%	LF-N%	C/N	Soil LF
VR1	15.1a ^a	1.75a	2.47a	25.4a	1.58a	8.6a	16.1b
RA1	14.1ab	1.61ab	2.46a	27.1a	1.31c	8.8a	20.7a
C1	11.4b	1.38b	2.23b	21.1b	1.40b	8.3a	15.0b
VR4	13.0b	1.55ab	4.12a	25.0a	1.43b	8.4a	17.5a
RA4	15.9a	1.71a	3.21b	26.3a	1.57a	9.3a	16.7a
C4	13.0b	1.48b	2.01c	23.5b	1.44b	8.8a	16.4a

Different letters within columns (e.g., OC or TCN) indicate that treatment means were significantly different at the 0.05 level. OC=organic carbon; TCN=total combustible nitrogen; LF=light fraction.

^a Statistical analysis was done for cover crop treatments within each fertilizer N level.

8000 rpm for 20 min. These rinses were then transferred into a 250 ml separatory funnel and allowed to settle overnight. The heavy SOM fraction, which settled to the bottom of the funnel, was removed and the LF material was filtered using a 0.45 µm polycarbonate membrane filter. The weight yield of light fraction was measured and the organic carbon and total combustible nitrogen content (for both LF and soil) were determined using a LECO-CN 2000 analyzer. The quantity of organic carbon (OC) determined from soil under different cover crop systems was calculated on a soil volume basis (associated with soil bulk density) (Table 2).

Soil samples were air-dried and passed through a 2 mm sieve before HS extraction. The extraction procedures followed the methods by Ding et al. (2002) for humic acids (HA) and Zalba and Quiroga (1999) for fulvic acids (FA).

2.3. Diffuse reflectance Fourier transform infrared (DRIFT) analysis

DRIFT was performed in an Infrared Spectrophotometer (Midac series M 2010) with a DRIFT accessory (Spectros Instruments). All SOM fractions were powdered with a sapphire mortar and pestle and stored over P₂O₅ in a drying box. Three-milligram solid samples were mixed with KBr to a total weight per sample of 100 mg, and then, ground with an agate mortar and pestle (Wander and Traina, 1996b). The milled sample was immediately transferred to a

sample holder, its surface was smoothed with a microscope glass slide. Before analysis, the diffuse reflectance cell containing the samples was flushed with nitrogen gas to eliminate interference from carbon dioxide and moisture. A small jar (20 ml) containing anhydrous $\text{Mg}(\text{ClO}_4)_2$ was placed inside the sample compartment to further reduce atmospheric moisture.

To obtain DRIFT data, 100 scans were collected at a resolution of 16 cm^{-1} and spectra, as well as numerical values for major peaks' wavenumbers and intensities, were recorded. The background consisted of powdered KBr was scanned under the same environmental conditions as the sample–KBr mixtures. Absorption spectra were converted to a Kubelka–Munk function using Grams/32 software package (Galactic Corporation). Peak assignments and intensity (by height) ratio calculation were done following the methods of Baes and Bloom (1989), Niemeyer et al. (1992), Wander and Traina (1996b), and Ding et al. (2002).

2.4. Solid-state ^{13}C NMR spectroscopy

CP-TOSS (cross-polarization and total sideband suppression) was used to obtain all ^{13}C NMR spectra. Samples were run at 75 MHz (^{13}C) in a Bruker MSL-300 spectrometer. HA (one composite sample from each treatment, a total of 6, see Table 1) was packed in a 7-mm-diameter zirconia rotor with a Kel-F cap. The spinning speed was 4.5 kHz. A ^1H 90° pulse was followed by a contact time (t_{cp}) of 500 μs , and then a TOSS sequence was used to remove sidebands (Schmidt-Rohr and Spiess, 1994; Mao et al., 2000). The 90° pulse length was 3.4 μs and the 180° pulse was 6.4 μs . The recycle delay was 1 s with the number of scans about 4096. The details are reported elsewhere (Mao et al., 2000).

2.5. Statistical analyses

All data presented were the mean of the measurements from the four replicate plots of each treatment, except for solid-state ^{13}C NMR data because of the high cost per sample and low availability of the instrument where a composite sample from each treatment was used. Preliminary NMR measurements with one HA showed minimal

variations, which was consistent with the results of an extensive NMR study conducted in our laboratory (Mao et al., 2000). A two-way analysis of variance (ANOVA) was used to analyze cover crop system and nitrogen fertilization effects on SOM. Cover crop system and nitrogen rate were the experimental factors. SigmaStat software (SPSS, Richmond, CA) was used for each test at a 0.05 level of significance.

3. Results

3.1. Yields of organic carbon and light fraction materials

With no fertilizer N treatment, the OC content was the highest in the vetch/rye system and lowest in the soil without cover crop (Table 2). However, with nitrogen fertilizer, OC in vetch/rye appeared to decrease (from 15.1 to 13.0 kg m^{-3}). After 10 years field experiment, OC differences were significant between the cover crop systems (both vetch/rye and rye alone) and no cover crop systems with or without fertilizer treatments. The OC content was significantly affected by the fertilizer N applications. Total combustible nitrogen (TCN) showed the similar trend for all three different cover crop systems with or without fertilizer. The C/N ratios of the soil were not significantly affected by cover crop and fertilizer treatments.

Cover crop treatments also significantly influenced LF content (Table 2). Again, without fertilizer N treatment, LF with cover crop was significantly higher than with no cover crops. With fertilizer treatment, the highest LF content was in the vetch/rye plots, followed by rye alone, and the soil without cover crop had a significantly lower LF pool than the other two. The amount of OC in LF varied between 21% and 27%. In both with or without fertilizer N treatments, the LF-OC% was higher in rye alone than vetch/rye. However, LF-OC% was significantly lower in the soil without cover crops than with cover crops. Compared to the whole soil, the C/N ratios of the LF were distinctly higher. Without fertilizer treatment, the highest C/N ratio of LF appeared in rye alone system, significantly higher than other two treatments.

3.2. Solid-state ^{13}C NMR spectra

Although CP-TOSS spectra cannot be used for absolute quantitation, they could be compared in this study because all of the HA samples were run under the same conditions and from the same type of soil. Functional group assignments were reported elsewhere (Stevenson, 1994; Preston, 1996). The six soil HA NMR spectra were quite similar in peak position and intensity (Fig. 1). They exhibited several distinct peaks in the aliphatic (0–108 ppm), aromatic (108–162 ppm) and carboxyl (162–190 ppm) regions. The peak at 31–33 ppm is long alkyl chains (CH_2)_n. The aromatic region contains a large peak at about 131 ppm. This resonance signal is assigned to ring carbons in which the ring is not substituted by strong electron

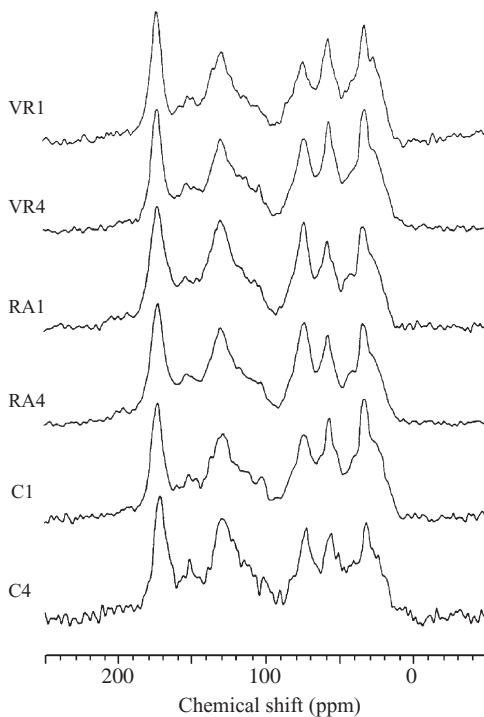


Fig. 1. Solid-state ^{13}C NMR spectra of six humic acids extracted from soil under different cover crop systems (VR1, vetch/rye with no fertilizer; VR4, vetch/rye with fertilizer N; RA1, rye alone with no fertilizer; RA4, rye alone with fertilizer N; C1, no cover crop, no fertilizer; C4, no cover crop with fertilizer N). Functional groups are assigned for carbon types: alkyl (0–50 ppm), carbohydrate (50–108 ppm), aromatic (108–145 ppm), phenolic (145–162 ppm), and carboxyl/ester carbon (162–220 ppm).

donors such as oxygen and nitrogen (Schnitzer and Preston, 1986). Alkyl benzenes are typical components which can yield such resonance. Therefore, it appeared that in the HA, a large proportion of the aromatic carbon was not substituted by oxygen and nitrogen. The small peak at approximately 155 ppm is the presence of oxygen- and nitrogen-substituted aromatic-C groups (phenolic OH or aromatic NH_2). The large peak near 175 ppm is due to carboxyl groups associated with carboxylic acids, amides, and esters.

The six HA spectra displayed little difference that can be described in terms of presence or absence of specific peaks (Fig. 1). There were, however, some differences in relative signal intensity. Carbon distribution in aliphatic groups (0–108 ppm) was showed in Fig. 2A. An examination of the data showed that HA from rye alone system differed from the other HA in aliphatic region and the carbon content of the rye alone plot in this region was the lowest without fertilizer treatment. The aliphatic-C of the vetch/rye without fertilizers was 55.3%, and 48.9% for rye alone without fertilizers (Fig. 2A). The alkyl region (0–50 ppm) showed the similar trend as for the aliphatic region (Fig. 2B). With or without fertilizer N treatment, the alkyl carbon changes were minimal for both vetch/rye and rye alone systems. The alkyl carbon content was higher in control (no cover crop system) without fertilizer than with fertilizer. It should be noted that these were simple comparisons without statistical analysis.

The phenolic-C (145–162 ppm) of HA for rye alone systems with or without fertilizers N was slightly higher than that of vetch/rye cover systems (data not shown). We found that phenolic-C was higher in the no cover crop system with fertilizer than without fertilizer N treatment. The HA extracted from rye alone system, compared with vetch/rye systems with or without fertilizers, was relatively enriched in aromatic-C (108–145 ppm) (Fig. 2C). The HA aromatic-C for no cover crop treatments, was greater with fertilizer N than without fertilizer N treatment.

The aromaticity (expressed in terms of aromatic-C as a percentage of the aliphatic+aromatic) of HA was higher in rye alone system with or without fertilizer N than vetch/rye treatments (Fig. 2D). Furthermore, the HA aromaticity of both vetch/rye and rye alone systems was greater in the plots without fertilizer N

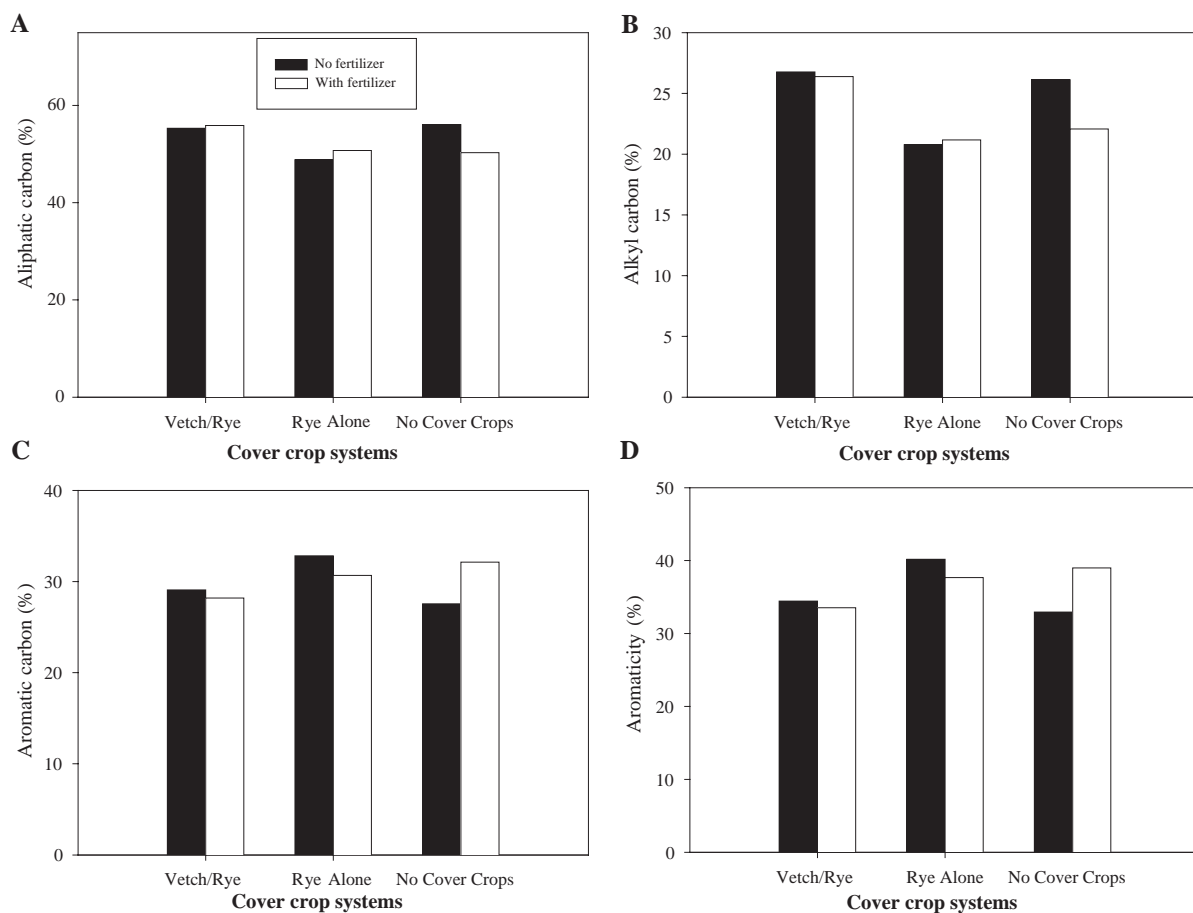


Fig. 2. Solid-state ^{13}C NMR integration data under different cover crop systems: (A) aliphatic-C (0–108 ppm); (B) alkyl-C (0–50 ppm); (C) aromatic-C (108–162 ppm); (D) aromaticity (108–162 ppm)/(0–162 ppm).

treatment than that with fertilizer. The reverse trend was true for no cover crop systems.

3.3. DRIFT spectroscopy of HA and FA

Wavenumbers and assignments for peaks in DRIFT were the same as in IR and FTIR spectroscopy (Baes and Bloom, 1989; Niemeyer et al., 1992; Ding et al., 2002). All peaks in our HA and FA were similar to the typical HA and FA spectra, respectively as reported in the literature. Representative HA and FA spectra from each treatment were presented in Figs. 3 and 4, respectively. In general, the spectral resolution was significantly improved compared with previously published spectra using dispersive or FTIR spectrophotometers (Baes and Bloom, 1989).

The peaks at 1715 to 1730 cm^{-1} (mostly COOH groups), at 1620 cm^{-1} (mostly aromatic-C), and at 1200 cm^{-1} (mostly OH or COOH) were distinct and sharp in all our spectra.

The HA exhibited the most distinct COOH bands in both 1720 and 1200 cm^{-1} regions (Fig. 3). The high intensity of these bands was a typical characteristic of HA, and their presence reflected the high solubility and acidity. The signal between 3000 to 3700 cm^{-1} was of low intensity and appeared in regions of little importance to humic material (Niemeyer et al., 1992).

Assignment of the OH stretching band to phenolic OH rather than an aliphatic alcoholic OH was supported by the C–OH stretching band centered about 1250 cm^{-1} which was characteristic of oxygen

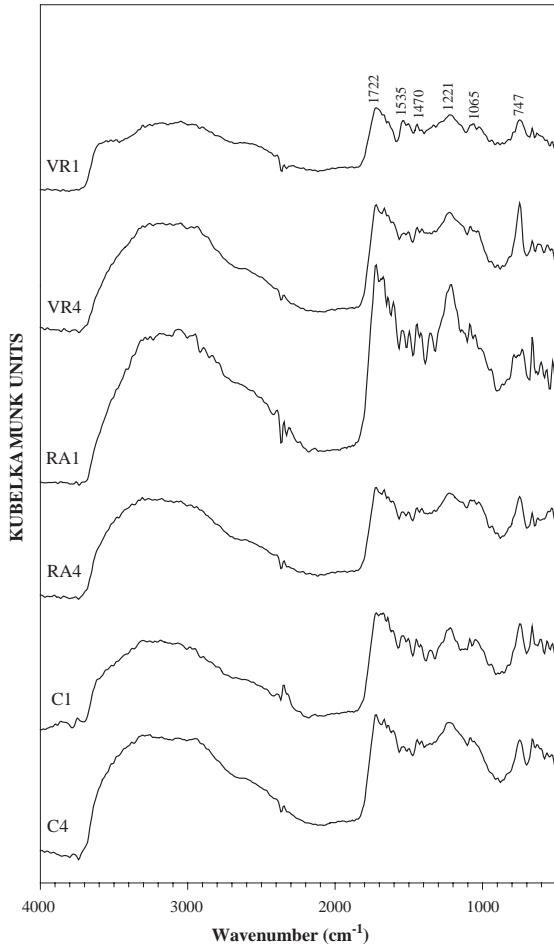


Fig. 3. DRIFT spectra of six humic acids extracted from soil under different cover crop systems (VR1, vetch/rye with no fertilizer; VR4, vetch/rye with fertilizer N; RA1, rye alone with no fertilizer; RA4, rye alone with fertilizer N; C1, no cover crop, no fertilizer; C4, no cover crop with fertilizer N).

on an aromatic ring. The center of the band was much more apparent in the HA compared to the FA spectra. The C–OH stretching vibration of phenolic OH occurred at frequencies above 1200 cm^{-1} . Aliphatic alcohols were indicated by a broad and intense C–OH stretching band at lower frequencies ($1015\text{--}1150\text{ cm}^{-1}$) (Conley, 1972).

All DRIFT spectra of each fraction were similar in their basic peaks. For example, the DRIFT spectra of FA fractions from all treatments had the same functional groups (Fig. 4). It was a common practice to draw conclusions on factors affecting SOM composition by spectral peak positions and intensity changes.

However, this method does not often provide the kind of detailed information required to ascertain cover crop management effect on SOM. Therefore, detailed insight on the reactivity of HA and FA was provided by calculation of O/R ratios, which were the intensities of oxygen-containing functional groups vs. aliphatic and aromatic (referred to as recalcitrant) groups (Niemeyer et al., 1992; Wander and Traina, 1996b). The reactivity of SOM was related with organic oxygen because it was present in all major functional groups, e.g., carboxyl, phenolic, hydroxyl, alcohol, and carbonyl and could be associated with

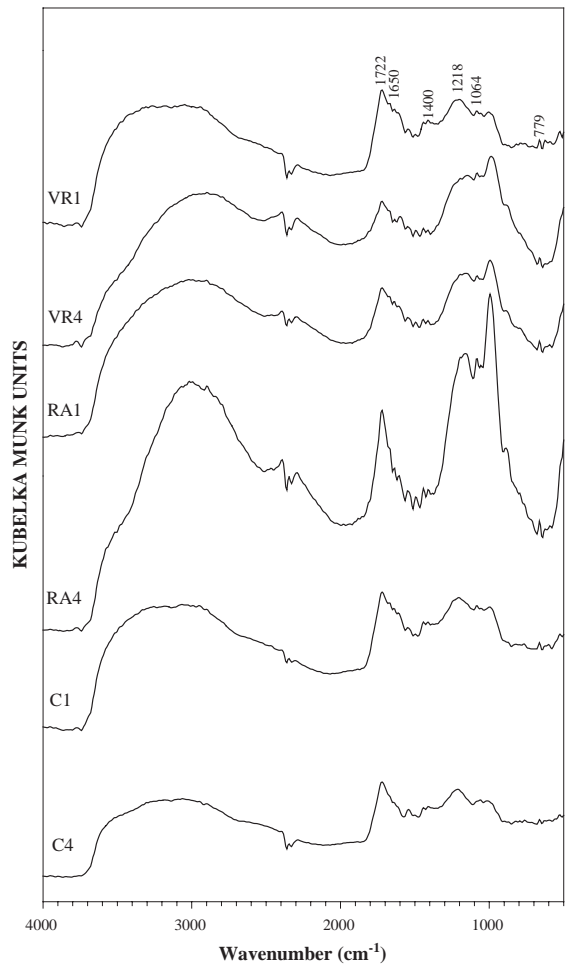


Fig. 4. DRIFT spectra of six fulvic acids extracted from soil under different cover crop systems (VR1, vetch/rye with no fertilizer; VR4, vetch/rye with fertilizer N; RA1, rye alone with no fertilizer; RA4, rye alone with fertilizer N; C1, no cover crop, no fertilizer; C4, no cover crop with fertilizer N).

Table 3
Ratios of selected peak heights from DRIFT spectra of humic acids
(Wander and Traina, 1996b)

Samples	HA O/R ratio ^a	FA O/R ratio ^b
VR1	0.57b ^c	4.31a
RA1	0.69ab	1.09c
C1	1.00a	2.31b
VR4	1.18a	2.65a
RA4	0.84b	0.93b
C4	0.85b	1.05b

Different letters within the column indicate that treatment means were significantly different at the 0.05 level.

^a HA O/R ratio was generated from HA DRIFT spectrum and calculated at $(1727+1650+1160+1127+1050)/(2950+2924+2850+1530+1509+1457+1420+779)$.

^b FA O/R ratio was generated from FA DRIFT spectrum and calculated at $(1850+1650+1400+1080+560)/(3340+2924+1535+1457)$.

^c Statistical analysis was done for cover crop treatments within each fertilizer N level, not between the two fertilizer levels.

SOM binding characteristics. The impact of cover crop system on spectral composition was summarized in the peak ratio (i.e., O/R ratios) Table 3.

With fertilizer N, the HA fraction isolated from the vetch/rye plots had the highest O/R ratio; significantly different from rye alone and no cover crop systems, but there was no difference between the latter two (Table 3). The relatively high O/R ratios may indicate that SOM in the vetch/rye plots was more active (chemically and biologically). Without fertilizer N, the O/R ratio was the highest with no cover crop, followed by rye alone and vetch/rye treatments. In contrast to HA O/R ratios, the FA O/R ratio was greater in the vetch/rye without fertilizer than with the fertilizer (Table 3). Furthermore, the ratios from the vetch/rye treatment were significantly higher than rye alone treatment regardless of N level. The O/R ratios of FA did not differ much between the rye alone and no cover crop system with fertilizer.

4. Discussion

Cover crops have long been recognized to play an important role in sustainable agriculture due to their functions in preventing soil erosion, improving soil productivity, contributing nutrients to succeeding crops, and suppressing weeds. However, the relationship between SOM characteristics and cover crop

management practices is not well understood. Although the mechanisms affecting the sequestration of organic matter in soil are complex (Doran et al., 1987; Campbell et al., 1991, 1999), it is clear that the different types of plant residues do not contribute to the same extent to humus formation and that intrinsic biodegradability is a key factor related to the microbial activity (Campbell et al., 1991).

Quantitative changes in SOM were associated with accumulation of C and N in the vetch/rye and rye alone systems (Table 2). This condition was obviously due to the lack of incorporation of plant residue into the soil under the no cover crop system, and was consistent with other reports (Campbell et al., 1999). With fertilizer N treatment, the highest OC and TCN contents appeared under the rye alone rather than the vetch/rye system. This means that fertilizer had a significant influence on rye biomass input but had little, if any, effect on vetch biomass production. A field study by Torbert et al. (1996) on a Norfolk loamy sand soil in east-central Alabama showed that N fertilization increased biomass production for rye, whereas very little increase was observed for the clovers owing to nitrogen fixation. They also reported that the biomass production of rye had a linear relation with the amount of nitrogen fertilizer applied.

The LF material consists largely of plant residues in varying stages of decomposition and varies in physical size. The LF has been used as an indicator of changes in labile organic matter as affected by tillage, crop rotation, and environmental factors (Campbell et al., 1999). In other words, characterizing the size of the active pool, as well as its C and N contents, may show changes due to management practice more rapidly than measuring changes in the magnitude of the whole SOM pool (Monreal et al., 1995; Wander et al., 1994). Large variation in LF contents (Table 2) implies that the cover crop system with different fertilizer N rates had significantly influenced (at or <0.05 level) the percentage of SOC isolated as LF material. Significant differences in the LF distribution with fertilizer N supported the notion that the two cover crops may hold different organic matter pool sizes. Vetch has a larger readily decomposable pool, while the rye may have a larger recalcitrant pool, which was confirmed by our ¹³C NMR data that HA from rye alone had more aromatic-C than vetch/rye systems (Fig. 2C). Furthermore, HA O/R ratios from

DRIFT spectra indicated that there was a significant difference between vetch/rye and rye alone treatments (Table 3), demonstrating that SOM from vetch/rye treatments was more active than from rye alone with fertilizer N application. Thus, DRIFT and ^{13}C NMR can be used as complementary methods for the characterization of HS.

The decomposition and mineralization kinetics are determined by residue and soil characteristics. Residue characteristics include N content, C chemistry, particle size, and quantity added (Lal et al., 1991). Important soil characteristics include soil texture, pH, aeration, and for low nutrient residues, soil nutrient status. After determining dry matter losses of cover crop residues during decomposition in the field of Massachusetts, Liu (1997) reported that hairy vetch had a significantly faster rate of decomposition than rye. High decomposition rates in the vetch system was an indicator of the rapid decay of carbohydrates, protein, and other low C/N ratio compounds. Low decay rates in rye systems were representative of slow decomposition of recalcitrant materials such as lignin, which was consistent with our NMR data that aromatic-C of HA in rye alone with or without fertilizers was higher than in vetch/rye cover. Plant residues with high N content showed high decomposition rates and nutrient release (Liu, 1997). The negative effect of polyphenols on decomposition of organic matter and nutrient release was reported by Vallis and Jones (1973). Negative correlations were also observed between decomposition rate constants and C/N ratio, percent lignin and polyphenol content of plant residues (Tian et al., 1995). With further humification, HA from rye systems may become more aromatic.

Agricultural tillage and crop management practices of soils contribute to a reduction in C/N ratio. For instance, mean C/N ratio is 13:1 in agricultural soils whereas that of virgin soils is approximately 20:1 (Stevenson, 1994). The relatively high C/N ratio in LF (Table 2) of the rye alone system without fertilizer may suggest that this soil has the lowest inherent N supply potential. This result may suggest that soil N availability was the main limitation for non-legumes. With fertilizer treatment, N content in LF of the rye system was the highest, indicating that N fertilization might contribute to a larger increase in total N uptake for rye than for other two systems. However, without

fertilizer N application, the N content of vetch/rye plot in LF was significantly higher than the rye alone plots. It is consistent with the results obtained by Torbert et al. (1996). Legumes utilize both soil N and atmospheric N gas in meeting their N requirements. If the soil does not have enough N they can fix N to meet their requirements. They further reported that total N content of rye had a direct linear relation with N application. The total N content of clover plant was not affected by fertilizer N application. However, the proportion of N in the plant from N gas fixation was reduced by application of N fertilizer.

Our results suggested that HA from rye alone system may contain more structures inherited from tannins and lignins than vetch/rye treatment because tannins and lignins are the main contributors in the aromatic and phenolic regions (Preston, 1996). Another distinguishing feature of the intensity distribution was that fertilization was associated with a small decrease of aliphatic-C and increase of aromatic-C content within no cover crop treatments (Figs. 2A and C). One possible explanation was that the use of fertilizer N may enhance the decomposition and polymerization processes of SOM.

FA has relatively low molecular weights and higher oxygen contents, and as a result is more polar than HA (Stevenson, 1994; Wander and Traina, 1996b). The O/R ratios from both vetch/rye treatments were significantly higher than rye alone treatments. This may imply that FA fractions from vetch/rye system are more biologically active than from rye alone system. As the O/R ratios of FA were not much different between the rye alone and no cover crop system with fertilizer N treatment, the FA fraction may undergo similar changes for these two management systems by chemical oxidation and/or microbial process.

Soil minerals and SOM are the major components for sorption of organic chemicals including pesticides, but crop management would not change much the percentage and chemistry of soil minerals as did for SOM. It has been reported that sorption increases with elevated levels of SOM, which can reduce leaching potential. In addition, SOM structure and chemistry can change the sorption of organic chemicals by soils. Nanny and Maza (2001) observed that the percent aromaticity of the HA and FA and the solution pH influenced the extent of noncovalent interactions with monoaromatic compounds. Therefore, the changes of

the quantity and quality of SOM by cover crop systems may potentially alter sorption behavior, mobility, and biological activity of pesticides in soils.

5. Conclusions

Organic carbon was higher in soils under both vetch/rye and rye alone management systems than under no cover crop. This was due to low input of plant residues into the soil under no cover crop system. Yields of LF material under different cover crop systems were strongly dependent on the fertilizer N rates. For no N fertilizer treatments, LF content changes were minimal. However, with fertilizer N application, the LF content changes were substantial under different cover crop systems. All DRIFT spectra of each fraction were similar, but cover crop systems and fertilizer N rates changed the O/R ratios of HA and FA. The CP-TOSS ^{13}C NMR data showed that there were no major differences among the 6 HA spectra in terms of the number and position of peaks. However, by calculating aliphatic- and aromatic-C contents, the HA extracted from rye alone was more aromatic and less aliphatic than HA extracted from vetch/rye, indicative of the impact of the cover crop systems on the structure and composition of humic substances. Further research is needed to illustrate how these SOM changes (composition and structure) are related to soil property, productivity, and pesticide sorption.

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