Decomposition of maize straw in three European soils as revealed by DRIFT spectra of soil particle fractions

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Abstract

Diffuse Reflectance Infrared Fourier Transform (DRIFT) technique was used to investigate decomposition of maize straw residues in particle-size fractions of three European soils in a 1-year incubation experiment that simulated both incorporation and mulching practices. The aliphatic bands in the 2920–2860 cm⁻¹ regions were used to derive decomposition curves and mineralization rates of maize residues. Evaluation of soil organic matter changes by DRIFT in particle-size fractions depended on soil texture and soil aggregate stability. Decomposition could be followed over the full incubation period only in three size-fractions of the silty German soil because of its intermediate aggregate stability. DRIFT spectra were not useful in the least stable sandy Danish soil and in the most stable clayey Italian soil. Decomposition rates derived from DRIFT results were similar to those obtained by isotopic techniques. DRIFT spectroscopy may represent a rapid and accurate method to follow fresh organic matter degradation directly in soil matrix or particle-size fractions in some soils provided that adequate soil dispersion is obtained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: DRIFT spectroscopy; soil organic matter; decomposition; particle-sizes; fractionation; sonication

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1. Introduction

Maintenance of soil quality encompasses a better knowledge of soil organic matter dynamics and of effects of organic matter amendments on soil physical stability (Piccolo, 1996). The development of physical methods of soil fractionation has greatly improved the study of organic matter associated with different soil fractions (Stevenson and Elliot, 1989; Christensen, 1992; Piccolo, 1996). Soil fractionation into particle sizes or aggregates have shown the relation between structural stability and organic matter (Guggemberger et al., 1994) and the influence of soil texture on organic matter dynamics (Oades and Waters, 1991; Scott et al., 1996; Bosatta and Ågren, 1997).

Many investigations on soil organic matter turnover have been conducted by plant residues labelled by either radioactive $^{14}$C (Buyanosky et al., 1994) or stable $^{13}$C (Balesdent and Mariotti, 1996) isotopes and by following the rate of degradation through measurements of changes in isotopes content. Recent studies have suggested that infrared spectroscopy techniques such as Diffuse Reflectance Infrared Fourier Transform (DRIFT) and Multiple Internal Reflectance (MIR) can be successfully applied to investigate organic matter features and dynamics in soil (Cheshire et al., 1993; Skjemstad et al., 1993; Capriel et al., 1995; Capriel, 1997; Haberhauer et al., 1998). DRIFT spectroscopy seems particularly suitable because it allows an in situ, non-destructive, highly reproducible, rapid, and quantitative measure of organic matter features in the soil matrix (Capriel, 1997; Kaiser et al., 1997). In fact, DRIFT spectroscopy allows soil matrices to be analyzed without pressing them into pellets, thereby avoiding the common error of absorption IR spectrometry due to scattering (Bell et al., 1991), and gaining band intensity up to four times that obtained by pellet spectra when soil is mixed with finely powdered KBr (Piccolo and Conte, 1998).

The objective of this work was to verify the applicability of DRIFT spectroscopy in estimating the rate of mineralization and decomposition of maize straw residues in particle-size fractions of three European soils which were incubated in a 1-year incubation experiment in laboratory.

2. Materials and methods

2.1. Soils

Surface samples (0–20 cm) of three European agricultural soils along a North–South gradient were collected in September 1994, air-dried and sieved through a 2-mm sieve. Some physical and chemical properties of the soils studied are reported in Table 1. The soils were classified according to the FAO classification (1976). The Danish soil from Roskilde, Denmark (DK) is a Haplic...
Table 1

Some physical–chemical properties of the three European soils

<table>
<thead>
<tr>
<th></th>
<th>Haplic Luvisol DK</th>
<th>Haplic Luvisol DE</th>
<th>Eutric Regosol IT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (g kg⁻¹)</td>
<td>473</td>
<td>162</td>
<td>370</td>
</tr>
<tr>
<td>Silt (g kg⁻¹)</td>
<td>427</td>
<td>656</td>
<td>390</td>
</tr>
<tr>
<td>Clay (g kg⁻¹)</td>
<td>100</td>
<td>182</td>
<td>240</td>
</tr>
<tr>
<td>C org. (g kg⁻¹)</td>
<td>14</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>pH–H₂O</td>
<td>6.5</td>
<td>5.9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

*Clay minerals: C = chlorite; I = illite; H = halloysite; K = kaolinite; F = feldspar; A = allophane; ++ = predominant; + = present; = trace.

Luvisol with a mean annual precipitation of 650 mm and a mean annual temperature of 8.4°C. The German soil is a Haplic Luvisol from near Munich, Germany (DE) with a mean annual precipitation of 833 mm and a mean annual temperature of 7.0°C. The Italian soil is an Eutric Regosol from Caserta, Italy (IT) with a mean annual precipitation of 415 mm and a mean annual temperature of 15.1°C. Soil mineralogy, soil texture (standard pipette analysis), C-organic and pH–H₂O were determined as described elsewhere (Page, 1982; Klute, 1986).

2.2. Soils incubation with maize straw

Harvested maize residues (leaves and stems) were air dried at 40°C, chopped and passed through a 2-cm sieve. The C content of the maize straw was 453 mg g⁻¹ dry matter (DM) whereas the total N content was 0.5 mg g⁻¹ DM. Soil samples were adjusted to 40% of the water-holding capacity (WHC, calculated from repacked air-dried soils). Rewetted soils were equilibrated by incubating for 14 days at 14°C and at constant moisture. The soil columns used for incubation were 7 cm high and 10 cm in diameter. Each column was filled with 700 g of rewetted soil (594, 586, and 586 g for DK, DE, and IT, respectively).

Three different treatments with three replications were established: (1) Control, no maize addition; (2) Incorporated, with maize straw mixed into the upper layer (0–7 cm); (3) Mulch, maize straw just placed on the soil surface. Amendments amounted to 10 g/100 cm² (10 t/ha) of maize straw residues corresponding to 6 ± 0.06 mg C g⁻¹ of soil. The incubation was carried out at 14°C and 40% WHC for 1 year maintaining moisture at field capacity by periodical additions of distilled water. Soil moisture was controlled by weight twice a week. Incubated soils were sampled for particle-size fractionation and subsequent infrared spectroscopy at the following times: \( t_0 \), at incubation start, \( t_2 = \) after 2 weeks, \( t_{16} = \) after 16 weeks, and \( t_{52} = \) after 52 weeks. After sampling the soils were stored at −20°C and thawed at 4°C 3 days before fractionation.
2.3. Particle size fractionation

The size fractionation is based on the method of Jocteur-Monrozier et al. (1991) and was conducted as described in detail by Stemmer et al. (1998). To minimize destruction of labile particulate organic matter, the soil water suspension was dispersed using low-energy sonication (0.2 kJ g\(^{-1}\) output energy). Briefly, moist samples equivalent to 35 g of air-dry weight, were placed in 150-ml plastic beaker with 100 ml of distilled water and carefully dispersed with a probe-type ultrasonic disaggregator (50 J s\(^{-1}\) for 120 s). Sieves were used to obtain larger particles, while centrifugation at 150 \(\times\) g and 3900 \(\times\) g yielded particle sizes of less than 63 and 2 \(\mu\)m, respectively. Particle size fractions were obtained in the following ranges: 2000–200 \(\mu\)m, coarse and medium sand (CS); 200–63 \(\mu\)m, fine sand (FS); 63–2 \(\mu\)m, silt (S); 2–0.1 \(\mu\)m, clay (C). Fraction < 0.1 \(\mu\)m consisted mainly of dissolved OM and was discarded. Fraction samples were freeze-dried and stored for subsequent analysis.

2.4. Soil aggregate stability (SAS)

A soil aggregation stability index (SAS) was determined according to Murer et al. (1993). Four grams of air-dried soil aggregates (1–2 mm) were placed onto a sieve with a 0.165-mm mesh width and a 0.25-mm\(^2\) hole size and the sieve periodically immersed in distilled water for 5 min with a mechanical stroke length of 12.7 mm and a frequency of 42 cycles per minute. Aggregates remaining on the sieve were oven dried at 105\(^\circ\)C and weighed (A). These aggregates were then treated by a 0.1 M Na\(_4\)P\(_2\)O\(_7\) solution and sieved again. The sand fraction (> 0.25 mm) remaining on the sieve was oven dried and weighed (B). The soil aggregate stability index (SAS) was calculated as follows:

\[
\text{SAS} = \frac{[A(g) - B(g)]}{[4 - B(g)]} \times 100
\]

2.5. Drift spectroscopy

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of soil fractions were recorded with a Perkin Elmer 1720-X FT-IR spectrometer, equipped with a Perkin-Elmer Diffuse Reflectance accessory, accumulating up to 100 scans with a resolution of 4 cm\(^{-1}\). Before DRIFT analysis, freeze-dried samples were first thoroughly mixed to obtain a representative sample and then finely ground in a swinging mill and diluted with KBr powder (2.5/100, w/w) in a agate mortar. Three spectra from three different replicates were recorded for each fraction. The region between 3000 and 2800 cm\(^{-1}\) reveals the content of aliphatic groups without interference by other functional groups (Capriel et al., 1995; Capriel, 1997). The absorbance area of the 3000–2800 cm\(^{-1}\) region in
DRIFT spectra from maize-treated samples was hence integrated using a dedicated Perkin Elmer software (IRDM 1700). In order to evaluate only the contribution of maize residues, the integrated area of the same frequency interval (3000–2800 cm⁻¹) in spectra of control samples without maize-addition was subtracted from the area in spectra of samples incubated with maize at different times. The triplicate values of the area integrated over the 3000–2800 cm⁻¹ region were averaged (relative standard deviation was less than 6%) and used to construct decomposition curves of maize residues in treated soils by plotting peak areas versus weeks of incubation (Fig. 6).

3. Results and discussion

In order to verify the capability of DRIFT spectroscopy to follow in situ the changes of soil organic matter features with time, we applied DRIFT spectroscopy to soil particle-sizes fractionated by ultra-sonication. Input energy of sonication affects the separation intensity and nearly any possible distribution could be obtained by varying energy level (J) and sonication time (Gregorich et al., 1989). In the present experiment, low energy sonication (170 J g⁻¹) was used in order to reproduce the disturbing action of agricultural practices (ploughing), raindrop, and dry–wet cycles that cause breakdown of macroaggregates. Such fractionation procedure was found by Stemmer et al. (1998) to provide a feasible dispersion with preservation of the majority of microaggregate, thereby avoiding major redistribution of organic matter among particle sizes. Therefore, the particles obtained by low energy sonication represent a mixture of primary particle-size separates and aggregates.

The particle-size distribution obtained by sonication before and after incubation of soils with maize residues are shown in Table 2. Results indicate that particle-size fractionation was affected by the different textural composition of soils, whereas addition with maize straw had no significant effect on physical fractionation among different treatments. The Danish soil did not show any difference between the distribution of soil textural separates (Table 1) and that of sonicated fractions (Table 2). The highly sandy character of this soil did not allow stable interactions between particle size fractions at microaggregate level and thus a complete dispersion was obtained even by low energy sonication. Conversely, small but significant changes were found in particle-size distribution of both German soil and Italian soil. The higher microaggregate stability of these soils, consistent with their larger silt and clay content (Table 1), allowed interactions among soil particles and a more stable incorporation of finer fractions into coarser ones (Table 2).

DRIFT spectra of particle-sizes of the German soil incubated for 1 year with maize residues added by either mulching or incorporation, showed differences in IR bands according to the distribution of OC from maize over the different
size-particles (Fig. 1). In general, the Danish (Fig. 2) and German soils (Fig. 1) showed specific maize-derived bands in some if not all particle-sizes obtained after maize incubation, whereas DRIFT spectra of all particle-size fractions from Italian soil (Fig. 3) failed to reveal any specific maize band.

IR absorbances in the regions around 2920 and 1730 cm\(^{-1}\), respectively attributed to the C–H stretchings of CH and CH\(_2\) groups and to C=O stretchings in carboxyl groups (Piccolo and Conte, 1998), can be used to follow maize decomposition during incubation (Fig. 1). These bands were visible in DRIFT spectra of maize-incorporated samples of German soil only in the CS fraction after 2 weeks of incubation (\(t_2\)), whereas both CS and FS fractions were able to show the same bands when maize had been mulched (Fig. 1). No bands in the regions around 2920 and 1730 cm\(^{-1}\) were detectable in DRIFT spectra of the remaining particle-size fractions (silt-sized and clay-sized) of the German soil for either mulched or incorporated samples and for any incubation period. Conversely, IR bands relative to the added maize were visible in DRIFT spectra of all particle-size fractions of the Danish soil at time \(t_2\), in either incorporated or mulched samples (Fig. 2). However, in the further time course of incubation, no more maize bands were shown in DRIFT spectra of any particle-size fractions of the Danish soil.

The different DRIFT responses observed for the soil particle-size fractions may be related to differences in soil texture (Table 1) and soil aggregate stability.
Fig. 1. DRIFT spectra of maize straw and particle-size fractions of German Haplic Luvisol under different treatments (Coarse sand incorporated (CS inc.); Coarse sand mulched (CS mulch); Fine sand mulched (FS mulch)) 2 weeks after incubation onset ($t_2$).

(Table 3). The Danish soil was found to be the most sandy and least clayey soil whereas the German soil was the highest in silt and the Italian soil the richest in clay (Table 1). As suggested by the data obtained by ultra-sonication dispersion (Table 2), the different aggregate stability of soils and consequently the different incorporation of maize residues may be attributed to differences in soil texture. The relationship between soil aggregate stability and particle-size dispersion by sonication is well established (Christensen, 1986; Kemper et al., 1987; Piccolo, 1996). Table 3 shows that the lowest stability was, in fact, exhibited by the sandy Danish soil whereas stability increased significantly passing from the silty German soil to the clayey Italian soil. Moreover, Table 3 indicates that maize incorporation stabilized all soils more than mulch treatment. The latter was even
found to somewhat decrease stability as compared to control. It is, hence, plausible that soil incubation has resulted in a different distribution of OC derived from maize over size-particles according to soil texture and stability, thereby providing different DRIFT spectra for the different size-fractions of the amended soils.

It has been also recognized that textural composition affects SOM dynamics since it is related to aggregate formation and stability, and, consequently, to organic matter accumulation (Borchers and Perry, 1992; Hassink, 1992). In particular, silt-sized fractions have been shown to control storage and stabilization of C from plant residues into stable aggregates (Aita et al., 1997; Angers et al., 1997). In fact, slaking-resistant aggregates in silty soils appear to be enriched and stabilized by recently deposited organic matter (Puget et al., 1995; Angers and Giroux, 1996). Christensen (1986) found that straw incorporation
increased organic matter content preferentially in silt-sized separates, and improved aggregation was closely correlated to silt and clay content in loamy-sand soils, whereas no effect of straw incorporation was noted in sandy clay-loam soils.

In this experiment of maize incubation, the presence of stable microaggregates in German and Italian soils (Table 2) may be the reason for more extensive interactions between soil particles and the OC derived from maize straw residues. The large content of silt-sized particles in aggregates of the silty-loam German soil (Tables 1 and 2) could have favored incorporation of OC from
Table 3
Soil aggregate stability (%) of different samples after incubation ($t_{12}$)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Haplic Luvisol DK</th>
<th>Haplic Luvisol DE</th>
<th>Eutric Regosol IT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>22.8$^b$</td>
<td>36.6$^a$</td>
<td>64.4$^a$</td>
</tr>
<tr>
<td>Mulch</td>
<td>18.2$^a$</td>
<td>37.0$^a$</td>
<td>62.7$^a$</td>
</tr>
<tr>
<td>Incorporated</td>
<td>25.0$^c$</td>
<td>47.9$^b$</td>
<td>67.6$^b$</td>
</tr>
<tr>
<td>mean</td>
<td>22.0$^a$</td>
<td>40.5$^b$</td>
<td>64.9$^C$</td>
</tr>
</tbody>
</table>

Different letters in columns indicate significance at the 0.05 probability level ($n = 3$). Different capital letters in rows indicate significance at the 0.05 probability level ($n = 3$).

Maize straw into microaggregates by allowing a more stable aggregation of coarser size fractions with partially decomposed residues. This mechanism of physical aggregation of soil particles has been indicated as an important process of organic matter accumulation in soil (Oades and Waters, 1991; Golchin et al., 1994). The same process may have determined interactions between maize residues and particle-size fractions in the Italian clay–loam soil. In this soil, however, the higher clay content provides a greater resistance of coarser aggregates against physical disruption. In fact, the low ultrasonication energy used in this study was least capable to disrupt the Italian soil, whereas more extensive was the disruption of aggregation in the less stable German and Danish soils.

Such different interactions between particle sizes and maize residues may explain the results obtained by DRIFT analysis of particle-size fractions of soils. The spectra of different fractions from the Italian soil (Fig. 3) showed that, while maize aliphatic components were only slightly visible in the 3000–2920 cm$^{-1}$ region, each particle-size was dominated by a high clay content. This was revealed by the shape and intensity of the 1630 cm$^{-1}$ band that can be attributed to O–H bending of water molecules in hydration layers of soil phyllosilicates (Mendelovici et al., 1995). This band is in fact similar to that recorded by DRIFT for a model Na-Montmorillonite (Fig. 3). It is hence likely that the tight protection exerted on maize degradation products by clayey components prevented their detection by DRIFT in all particle-sizes of the Italian soil. This is because DRIFT spectroscopy is a technique based on surface reflection and would reveal only organic matter present at the surface of soil particles.

Conversely, surface reflection of DRIFT was capable to show IR bands of maize residues in the coarser fractions of German and Danish soils. Again, this may be attributed to the lower content in textural clay of these soils and to their relative lower stability to sonication. Particle-size fractions of these soils should have allowed exposure of inner surfaces to IR radiation. IR bands of maize residues or its degradation products were visible even in the silt- and clay-sized particles of the Danish soil because its lowest aggregate stability produced the
most extensive disaggregation by ultrasonication and allowed DRIFT analysis of exposed surfaces.

This interpretation of our DRIFT results is supported by Stemmer et al. (1999) who followed, in the same soil samples, the distribution of maize-derived $^{13}$C-isotope among particle-sizes by isotopic dilution techniques. They showed that $^{13}$C accumulated in the coarser-size fractions of all soils within a short incubation time ($t_2$) but it was equally distributed, regardless of soil type, in all particle-size fractions after a longer incubation. Moreover, they reported that

![Fig. 4. DRIFT spectra of CS fraction from mulched sample of the German Haplic Luvisol: changes in the 3000–2700 cm$^{-1}$ region with incubation time ($t_2 = 2$ weeks, $t_{16} = 16$ weeks, $t_{52} = 52$ weeks).](image-url)
organic matter from maize was more decomposed and protected within soil inorganic compounds when mixed into the soil than when mulched on the soil surface.

Though we found that DRIFT spectroscopy can be applied to monitor organic matter dynamics depending on soil aggregate stability, we have used the decrease of IR spectral bands in some of the soil particle-size fractions to evaluate mineralization and decomposition of maize residues with incubation time. For the German soil, the region around 2860–2920 cm$^{-1}$ decreased steadily with incubation time in the CS fraction for the incorporation treatment.

Fig. 5. DRIFT spectra of FS fraction from mulched sample of the German Haplic Luvisol: changes in the 3000–2700 cm$^{-1}$ region with incubation time ($t_2 = 2$ weeks, $t_{16} = 16$ weeks, $t_{52} = 52$ weeks).
and in both CS and FS fractions for the mulch treatment. The decrease of the bands at 2860 and 2920 cm\(^{-1}\) with incubation time in the mulch treatment of the German soil is shown in Fig. 4 for the CS fraction and in Fig. 5 for the FS fraction. The bands of aliphatic groups at around 2920 cm\(^{-1}\) have been already used to quantitatively evaluate the fate of organic matter added to soil (Capriel et al., 1995; Capriel, 1997).

The areas between 3000 and 2800 cm\(^{-1}\) from the spectra of Figs. 4 and 5, as well as those from the spectra of CS fractions of incorporated samples of the German soil (not shown), were used to derive curves of maize straw decomposition with time (Fig. 6). From the regression equations of the curves, the decomposition rates \(k\), weeks\(^{-1}\) for maize residues in each size-fraction were obtained. Similar results were found by Stemmer et al. (1999) by applying isotopic techniques. They also reported small but noticeable differences among treatments. In fact, a faster decomposition of maize residues in incorporated samples than in mulched samples is suggested by both a higher decomposition rates \(k = 0.130\) in the CS fraction from the maize-incorporation treatment (Fig. 6) and the disappearance, already at \(t_2\), of the DRIFT bands of maize in the FS fraction from incorporated samples (not shown).

Values of decomposition rates obtained by DRIFT were compared to mineralization rates obtained in similar studies on SOM dynamics by using either \(^{14}\)C-labelled (Parton et al., 1987; Jenkinson and Rayner 1977) or \(^{13}\)C-labelled (Aita et al., 1997) straw material (Table 4). Our DRIFT-derived data are not

![Fig. 6. Decomposition curves of maize residues in particle-size fractions obtained from incorporated (CS: ---○---) and mulched (CS: ---□---; FS: ···△···) samples of the German Haplic Luvisol.](image)
Table 4
Comparison between SOM mineralization rates, \( (k = \text{weeks}^{-1}) \) reported in literature and those obtained by DRIFT spectroscopy

<table>
<thead>
<tr>
<th>DRIFT</th>
<th>Century(^a)</th>
<th>Rothamstead(^b)</th>
<th>(^{13}\text{C})-labelling(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS inc: 0.130</td>
<td>Labile SOM: 0.140</td>
<td>Decomposable plant</td>
<td>CS fraction: 0.090</td>
</tr>
<tr>
<td>CS mulch: 0.090</td>
<td>Soil litter: 0.094</td>
<td>material: 0.094</td>
<td>0.090</td>
</tr>
<tr>
<td>FS mulch: 0.085</td>
<td>Surface litter: 0.076</td>
<td>0.080</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Parton et al., 1987.
\(^b\)Jenkinson and Rayner, 1977.
\(^c\)Aita et al., 1997.

Distinctly different from those of these previous studies. This indicates that the DRIFT technique may have the potential to be used to follow the dynamics of fresh organic matter in soils, provided that either poorly aggregated soils are investigated or optimum sonication energies are applied to uncover the inner surfaces of soil particle-size fractions where the degradation products of the decomposed organic matter may reside.

4. Conclusion

Our results indicate that DRIFT spectroscopy may be applied as a rapid and useful method to follow fresh organic matter decomposition directly in soil matrix or particle-size fractions. This method was found to produce results similar to those obtained by isotopic studies. Our results indicate that application of DRIFT analysis to follow organic matter dynamics depends on soil texture and aggregate stability. In fact, soil textural composition influences incorporation of plant residues in particle-size fractions and, hence, the capacity of a surface reflectance spectroscopy such as DRIFT to detect organic matter features at the surface of soil particles. Further investigations on the relation between sonication energy and visibility of infrared bands are needed as a basis for a more general applicability of the proposed method.

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Descriptive text for the table and further discussion about the results and implications of the study, particularly the comparison between the DRIFT technique and previous studies.
References


