DRIFTS and near infrared spectroscopy analysis of fresh and decomposed cattle manure

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Introduction

When animal manures are applied in excess, groundwater as well as air quality may be degraded. The nitrogen (N) supplying capacity of manures has been measured traditionally using laboratory incubations. Incubations, however, may be biased due to the artificial environmental conditions, and also may take days or weeks to produce results.

Mid infrared and near infrared (NIR) spectroscopy have been used to measure quantitative and qualitative attributes of agricultural materials such as soils and plant tissues. Because of it's quick and non-destructive qualities, infrared spectroscopic techniques could be used as a basis for a more practical analysis of manure fertilizer quality [1 - 4]. In our laboratory, we have shown how Fourier-transformed mid infrared spectroscopy (DRIFTS) can be used to characterize changes in manure as it decomposes during laboratory incubation [5]. However, data from field-based studies is needed to determine if the laboratory results can be replicated under field conditions. Further, it will be useful to determine if NIR spectroscopy, besides DRIFTS, is sensitive to changes in manure during decomposition.

The objective of this research was to analyze manure at different stages of decomposition in the field. Both DRIFTS and NIR spectroscopy were used to analyze the manure and the techniques compared for their ability to discern between the manures.

Materials and methods

We carried out a nine week field incubation of manure in order to perform spectroscopic measurements at different stages of manure decomposition. The experiment was performed in nine sites that varied in soil carbon and moisture content. Dairy manure and dairy heifer manure were evaluated. Manure application was equivalent to 100 kg N ha^{-1}. Fresh manure was placed in the soil inside mesh bags, which allowed for the retrieval and analysis of decomposed manure. The manure bags were buried in the soil at a depth of 2.5 cm on day 1 of the trial. The manure was sampled periodically thereafter for spectroscopic analysis. Samplings were carried out after zero, one, four, and nine weeks of decomposition. There were three replicates per treatment combination.

Ground and lyophilized samples were scanned undiluted with KBr in the mid-infrared region from 4,000 to 400 cm^{-1} (2,500 – 25,000 nm) on a DIGILAB FTS 7000 spectrometer fitted with a diffuse reflectance accessory (AutoDIFF™, Pike Technologies, Madison, WI, USA) using KBr as a background reference. Samples were also scanned in a rotating sample cup at the visible and near infrared wavelengths (400 – 2,498 nm) using a scanning monochromator (Model 6500, Foss–NIRSystems, Silver Spring, MD, USA) equipped with Si (400 – 1,098 nm) and PbS (1,100 – 2,498 nm) detectors. Principal components analysis was carried out using the PRINCOMP procedure of SAS version 8.02 (Cary , North Carolina, U.S.A.).

Results and discussion

Figure 1 contrasts the DRIFTS spectra of the fresh dairy manure and manure that has been decomposing for nine weeks. Data for the dairy heifer manure were similar to that of the dairy manure. Bands associated with carboxylic acids (3,000 cm^{-1}) and C-H bonds (2,870 cm^{-1}) declined during manure decomposition. In general, absorbance at wavenumbers above 1,700 cm^{-1} increased during decomposition. This included bands associated with proteins (1,653 cm^{-1}), lignin (1,510 cm^{-1}), and primary amines (1,340 cm^{-1}). The changes at the carboxylic acid, C-H bond, protein, lignin, and primary amine-specific bands agree with a previous study where manures were incubated under controlled laboratory conditions [5]. The changes in absorbance at specific bands suggested a scenario where fatty acids were degraded by microbes during decomposition, while proteins were concentrated in the manure through preferential degradation of C-rich compounds by the soil microbes.

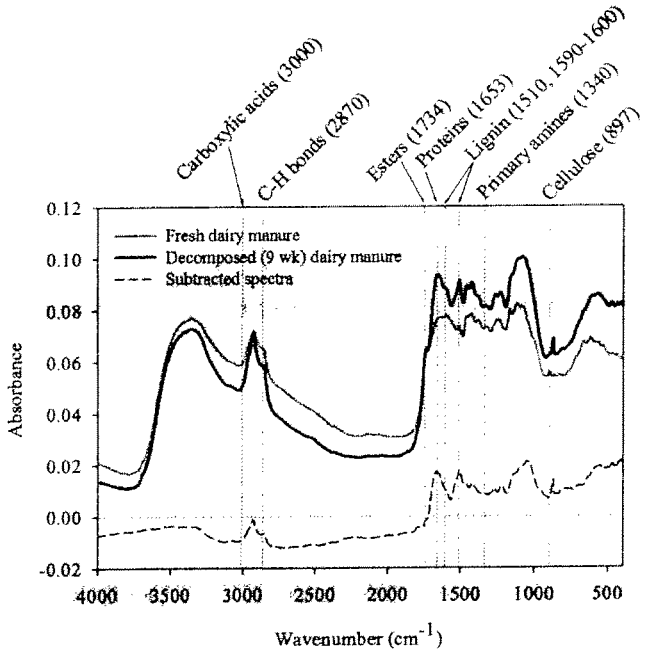

Figure 1. Average DRIFTS spectra for three scans of fresh dairy manure and manure recovered from the field after nine weeks of decomposition at one site. The dashed line represents the subtracted spectra and is shown to indicate the magnitude and direction of the change in the spectra during decomposition.

Principal component analysis of the DRIFTS spectra showed that fresh and decomposing manures tended to group separately (Figure 2). While the fresh manures clustered separately from the week nine decomposed manures along component one, the separation between intermediate sampling times was not clear. Multivariate analysis of the DRIFTS data was in agreement with a previous laboratory based study carried out in our laboratory [5], suggesting that the response patterns shown here were typical for this type of manure under different environment conditions.

The NIR spectra of the fresh dairy manure was different from that of the decomposed manure of nine weeks (Figure 3). The absorbance at wavelengths above 1,312 nm declined during decomposition, while absorbance at wavelengths below 1,312 nm increased during decomposition. These changes in the spectra were reflected in the principal component analysis of the NIR spectroscopy data, which showed a chronological separation between fresh manure and decomposed

manure (Figure 4). Unlike the DRIFTS data, the NIR spectroscopy data was able to clearly separate fresh manure from the decomposing manure sampled at the different times.

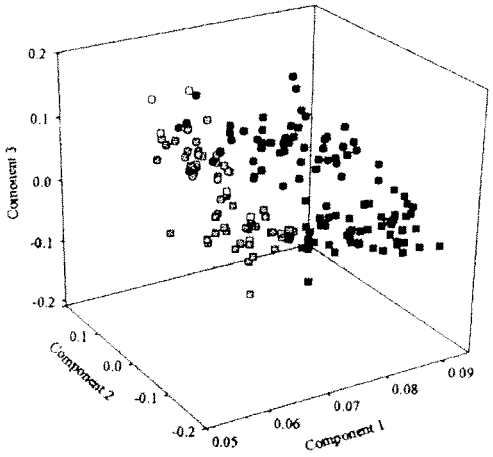

Figure 2. Principal components analysis of the DRIFTS spectra. Both the dairy manure (circles) and the dairy heifer manure (squares) are included. White symbols = fresh manure; light gray symbols = one week decomposition, dark gray symbols = four weeks decomposition; black symbols = nine weeks decomposition.

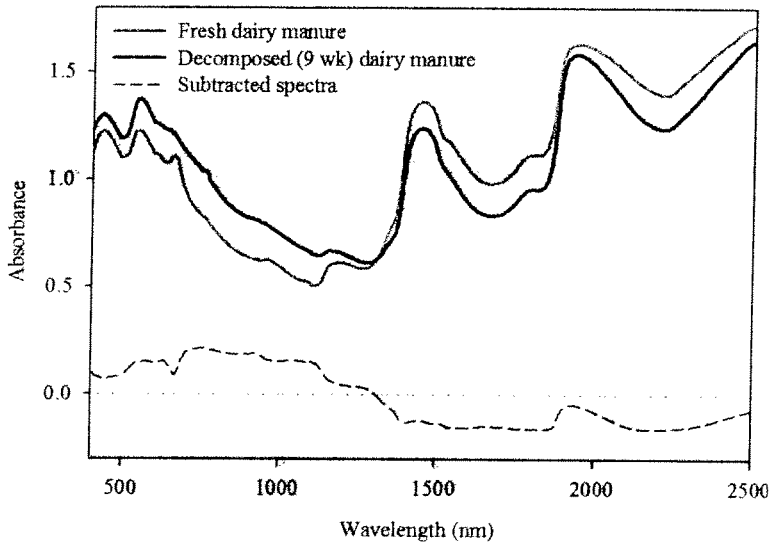

Figure 3. Average NIR spectroscopy spectra for three scans of fresh dairy manure and the manure recovered from the field after nine weeks of decomposition at one site. The dashed line represents the subtracted spectra and is shown to indicate the magnitude and the direction of the change in the spectra during decomposition.

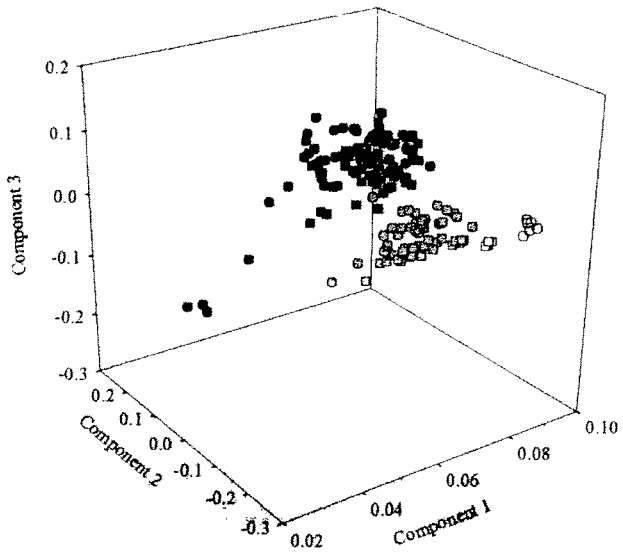

Figure 4. Principal components analysis of the NIR spectra. Both the dairy manure (circles) and the dairy heifer manure (squares) are included. White symbols = fresh manure; light gray symbols = one week decomposition, dark gray symbols = four weeks decomposition; black symbols = nine weeks decomposition.

Conclusions

We have shown that both DRIFTS and NIR spectroscopy are sensitive to compositional changes in manure. NIR spectroscopy seems to be better at resolving the early stages of decomposition relative to DRIFTS. The next step will be to ascertain which of the particular wavelengths identified here will be useful to predict important practical aspects of manure management. Of particular importance will be to predict the fertilizer value of manure, which is otherwise not easily determined by simple chemical assays.

References

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