



## Characterization of soil organic matter from a sandy soil in relation to management practice using FT-IR spectroscopy

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### Abstract

Previous results from differently fertilized long-term field experiments on a sandy soil suggested that the chemical composition of soil organic matter (SOM) is affected by fertilization. The objective of this paper is to confirm this finding for a site with higher soil-clay contents. Four combinations of different fertilizer treatments at long-term field experiment located at a sandy loam were selected: liquid manure (LM), liquid manure+N (LM+N), straw+N (S+N) and mineral nitrogen only (N). Soil organic matter was extracted using sodium pyrophosphate solution at pH of 10 and hot water. The extracts were analyzed using Fourier-Transform infrared spectroscopy. The results indicate that the composition of SOM from the hot water extracts did not show significant differences while the sodium pyrophosphate extracted SOM is affected by the type of fertilization. Soil samples fertilized with LM+N and S+N show the highest intensity of the carboxyl band. This can be explained by the fact that the combination of S+N fertilization with green manure leads to an enrichment of carboxyl groups in SOM. Differences between the band intensities of the treatments for the SOM samples are, however, not as distinct as for the sandy soil samples. This is possibly a result of the higher clay content and lower age of the long-term experiment at the sandy loam site. The intensity of the carboxyl band of the SOM is correlated with the cation exchange capacity of the soil samples. The composition of SOM may, in addition to the SOM content, be used for studying quantitative effects of different management practices or even land use changes on soil properties.

### Introduction

The content and the chemical composition of the soil organic matter (SOM) depends on a large number of factors, such as soil texture, vegetation, land use, soil management, and climatic conditions (Jenkinson, 1988). While the soil texture can practically not be influenced by management practice, the SOM is mainly affected by the type of land use that determine the SOM turnover. In many agricultural soils changes in SOM content induced by management practices are difficult to detect since SOM content is changing relatively slowly and is small compared to the initial values or to the soil spatial variability (e.g., Powlson, 1996). The basic idea of establishing long term agricultural

field experiments (e.g., at Rothamsted (Jenkinson et al., 1994), at Askov (Christensen, 1996), at Bad Lauchstädt (Körschens and Müller, 1996)) is to study the effect of a constant management practice on the development of crop yield and soil properties.

For the 100-year-old experiment located at Bad Lauchstädt, Körschens and Müller (1996) found significant correlations between the management practice and crop yield as well as the soil properties of the Loess Chernozem such as organic carbon and total nitrogen ( $N_t$ ) content. In the 34-year-old field experiment located at a sandy site at Müncheberg, the SOM-content and the pH were found to be unaffected by the type of organic and mineral fertilization, although crop yields were significantly different (e.g., Rogasik et al., 1997). A detailed analysis of the SOM-composition (Ellerbrock et al., 1997) using Fourier-

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Transform infrared (FT-IR) spectroscopy showed that the content of the carboxyl- and hydroxyl-groups in the SOM pyrophosphate extracts was higher in the plots fertilized with cattle manure than in those that received straw+mineral nitrogen.

FT-IR spectroscopy has been widely used for the characterization of complex organic macromolecules (Stevenson, 1982). Several infrared absorption bands are characteristic for the molecular structure. The absorption intensity reflects the proportional amounts of functional groups. Van der Marel and Beutelspacher (1976) indicated that infrared spectra of humic acids from peat, coal, lignite, lignin from straw, black earth soils, podzol and Chernozem soils are relatively similar. However, there are differences in the absorption intensity and the wavenumber of absorption caused by slight differences in SOM composition. Changes in the proportion of functional groups during humification or composting were studied, for instance, by Inbar et al. (1989), Niemeyer et al. (1992), and Kögel-Knabner (1993). Hempfling et al. (1987) and Candler et al. (1989) found differences between two woodland soils using FT-IR spectroscopy. They hypothesized that during litter decomposition, humification, and soil podzolization the content of cellulose and lignin in SOM decreases, whereas hemicellulose and protein fractions remain unchanged. Celi et al. (1997) showed that the content of carboxyl groups of SOM can be determined by FT-IR spectroscopy.

The results of Ellerbrock et al. (1997) indicated that differences in crop yields may be explained by variations in the hydrophilic character of the SOM. The hydrophilic character organic substances depends on the composition (type and amount) of functional groups, mainly carboxyl and hydroxyl-groups (Autorenkollektiv, 1984) and may affect, e.g., the soil water storage capacity of the plough horizon. Effects of different land use systems on the SOM-composition have also been reported by, e.g., Guggenberger et al. (1994) for a silty loam loess in a prealpine region. For a clay loam, Gerzabek et al. (1997), using FT-IR, found only for peat amendment some specific characteristics in the SOM-composition, while for plots with other treatments they could not observe any differences.

According to Stevenson (1985), the ratio between SOM and clay content is lower in a loamy than in a sandy soil. Thus, he expected that the effect of SOM on soil properties is smaller in a loamy than in a sandy soil. Soil properties, such as structure, water storage capacity, or CEC, are assumed to be more affected by

fertilization via changes in SOM in a sandy than in a loamy soil. Additionally, SOM can build complexes with clay minerals. SOM extraction from clayey soils is not as easy as from sandy soils, since the ability of soil to form stable organo mineral complexes (Stevenson, 1985) increases with the clay content.

The approach of analyzing the chemical composition of SOM for studying the effects of agricultural management seems to be applicable to very sandy soils only. In this study, we want to know whether differences in SOM composition due to fertilization could be observed also at sites with a somewhat higher clay content. A long-term field experiment on a sandy loam with climatic conditions comparable to Müncheberg site is located at Dedelow (Kühn, 1996). However, this experiment is younger than that in Müncheberg, and liquid manure was used as organic fertilizer instead of cattle manure. The second question is to investigate if the combination of mineral fertilizer+liquid manure/+straw+green manure lead to long-term changes in SOM-composition which are comparable to change induced by application of mineral fertilizer+cattle manure at the loamy sand.

## Materials and methods

### *Long-term field experiments*

The Dedelow experimental site was established in 1976 by the former Research Centre of Soil Fertility, Müncheberg, Germany, to study effects of different fertilizer combinations on grain yield and soil properties. A detailed description of the field experiments at Dedelow can be found in Kühn (1996). The village of Dedelow is located approximately 150 km north of Berlin near the city of Prenzlau. The soil is an Orthic Luvisol, classified as a sandy loam according to US soil taxonomy (average contents of 570g sand, 340 g silt, and 90 g clay per kg topsoil). The soil is not influenced by groundwater. The mean annual precipitation at Dedelow is 520 mm. The mean annual temperature is 7.9 °C. The experiment comprises 16 manurial treatments in all, with four replications for each. The soil is conventionally tilled by ploughing each autumn. Crop rotation is corn, pea, oil flax, and summer barley. The seedbed for the barley is prepared in autumn and for the other crops in spring. Table 1 gives the mean annual input rates of organic matter (excluding stubble and roots) and nitrogen fertilizer. Organic fertilizer is applied every four years in spring before planting corn.

*Table 1.* Annual average input rates of dry organic matter (DOS), nitrogen in the organic ( $N_{org}$ ) and mineral ( $N_{min}$ ) fertilizer applied to the treatments at Müncheberg and Dedelow ( $\text{kg ha}^{-1}$ ). In the Müncheberg experiment (Ellerbrock et al. 1997) cattle manure (CM) wheat straw ( $S^*+N$ ) was used instead of liquid manure (LM) and wheat straw+green manure ( $S+N$ )

| Dedelow |      |           |           | Müncheberg |      |           |           |
|---------|------|-----------|-----------|------------|------|-----------|-----------|
| Plots   | DOS  | $N_{org}$ | $N_{min}$ | Plots      | DOS  | $N_{org}$ | $N_{min}$ |
| LM      | 1000 | 50        | 30        | CM         | 1380 | 75        | 0         |
| LM+N    | 1000 | 50        | 110       | CM+N       | 1440 | 75        | 140       |
| S+N     | 830  | 0         | 110       | $S^*+N$    | 940  | 15        | 140       |
| N       | 0    | 0         | 110       | N          | 0    | 0         | 140       |

For the present study four of the fertilizer treatments were selected as follows: (1) liquid manure with low mineral nitrogen (LM), (2) liquid manure with high mineral nitrogen (LM+N), (3) wheat straw mixed with mustard as green manure with high mineral nitrogen ( $S+N$ ), (4) high mineral nitrogen, only (N).

Soil samples were taken from 0–25 cm depth using an auger, with eight replications from each plot of the treatments and mixed. The soil samples were air dried and sieved up to pass 2 mm.

#### *Chemical analyses and spectroscopy*

Organic carbon content ( $C_{org}$ ) was analyzed by elemental analysis (LECO, CNS 2000) as carbon dioxide by infrared detection after dry combustion according to DIN ISO 10694 (1994) in two replicates. Measurement error was  $\pm 0.5\%$ . The cation exchange capacity was determined according to DIN 19684 part 8 (1977) using 5 g soil. CEC was measured as exchangeable barium ions by atomic absorption spectroscopy (Perkin Ellmer type 1100B). The results obtained from the soil samples were corrected using data from blank solutions. The measurement error was  $\pm 5 \text{ mmol kg}^{-1}$  (mmol singular positive charged ions).

SOM of soil samples was extracted in two different ways:

1. Sodium pyrophosphate (Ellerbrock, 1997): 10 g soil were mixed with  $0.1 \text{ dm}^3$  of  $0.1 \text{ M Na}_4\text{P}_2\text{O}_7$  and shaken for 6 hours at room temperature (Hayes, 1985). The solid residue was separated by centrifugation. The remaining solution was adjusted with 1 M HCl towards a pH value of 2, to precipitate SOM. After 12 h the precipitation was complete and the aqueous mixture was again centrifuged. The precipitate was washed with distilled

water until it was free of chloride, then it was freeze dried.

2. Hot water extraction was chosen assuming that it represents the easily decomposable part of SOM. Ten g of the soil were mixed with  $0.1 \text{ dm}^3$  of distilled water and heated under reflux for one hour according to Körschens et al. (1990). The solid residue was separated by centrifugation. Removal of ions was done by dialysis, then the solution was freeze dried.

FT-IR spectra were obtained using a BioRad<sup>®</sup>, FTS 135. KBr-technique (2 mg sample/150 mg KBr) (Capriel et al., 1992; Celi et al., 1997) was used to measure absorption spectra of soil organic matter extracts. All spectra were obtained using a resolution of  $1 \text{ cm}^{-1}$  (wavenumber) and equal measurement conditions ( $3900\text{--}450 \text{ cm}^{-1}$ , 16 scans, scans means 16 repetitions of a single FT-IR measurement). All spectra were corrected to reduce the effects of mineral contents, using the subtraction method (BioRad, 1996a) as follows: spectra of the soil mineral part (organic matter was destroyed with peroxide) were prepared under the same measurement conditions. Subtraction of the mineral spectra from the extraction spectra was done with BioRad<sup>®</sup> software Win-IR Foundation<sup>®</sup> (BioRad, 1996b).

#### **Results and discussion**

The organic carbon content in the four different fertilizer treatments varies between 7.8 and  $8.1 \text{ g kg}^{-1}$  (Table 2). In accordance with our findings at Müncheberg (Ellerbrock et al., 1997), but in contrast to results from other field experiments, the treatment differences were not significant at Dedelow. Eich et al. (1982) found for a loam that fertilization with cattle

Table 2. Cation exchange capacity (CEC) [mmol kg<sup>-1</sup>], pH, total N (N<sub>t</sub>) and organic C content (C<sub>org</sub>) [g kg<sup>-1</sup>] of the soils of the different fertilized plots at Müncheberg and Dedelow site. In the Müncheberg experiment (Ellerbrock et al. 1997) cattle manure (CM) wheat straw (S\*+N) was used instead of liquid manure (LM) and wheat straw+green manure (S+N)

| Dedelow |                     |                  |                |      | Müncheberg |                     |                  |                |      |
|---------|---------------------|------------------|----------------|------|------------|---------------------|------------------|----------------|------|
| Plots   | pH <sub>CaCl2</sub> | C <sub>org</sub> | N <sub>t</sub> | CEC  | Plots      | pH <sub>CaCl2</sub> | C <sub>org</sub> | N <sub>t</sub> | CEC  |
| LM      | 6.53                | 7.9              | 0.7            | 53.3 | LM         | —                   | 4.6              | —              | 31.5 |
| LM+N    | 6.46                | 8.1              | 0.7            | 54.8 | LM+N       | 6.0                 | 4.9              | 0.58           | 35.6 |
| S+N     | 6.64                | 7.8              | 0.7            | 66.7 | S*+N       | 6.0                 | 5.2              | 0.51           | 34.0 |
| N       | 6.62                | 7.8              | 0.7            | 53.4 | N          | 6.1                 | 4.7              | 0.48           | 32.0 |

manure+N increases the organic carbon content more than fertilization with N, only. We hypothesize that because of the higher sand content at Dedelow, stronger mineralization prevents an increase in C<sub>org</sub> content at this site compared to the loamy site Eich studied.

The cation exchange capacity of the soil samples varies between 53.3 and 66.7 mmol kg<sup>-1</sup> (Table 2). The soil fertilized with straw+N results in the highest and the one fertilized with LM in the lowest CEC. Although, no significant differences in organic carbon and clay content were found, the difference (13.4 mmol kg<sup>-1</sup>) in CEC is significant. The fact that a higher content of carboxyl groups in SOM — which are accessible for cation sorption reactions — will result in a higher cation exchange capacity (Günzler and Böck, 1990) may serve as a possible explanation.

Figure 1 shows the FT-IR spectra of the sodium pyrophosphate extracts of the different fertilized soils. The wavenumber indicates the kind of functional groups which are due to absorption. Absorption bands are located at:

- 3500–3200 cm<sup>-1</sup> due to hydroxyl groups (alcohols, phenols, water molecules),
- 2922–2926 cm<sup>-1</sup> due to CH<sub>3</sub>, CH<sub>2</sub>, and CH groups of alkyls,
- 1701–1698 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> due to carboxyls and carbonyl groups,
- 1600–1613 cm<sup>-1</sup> due to aromatic C=C bonds conjugated with C=O bonds of unsaturated ketones or amides, and
- 1010 and 960 cm<sup>-1</sup> due to C-O vibration of ether groups.

The intensity of absorption bands depends on the amount of absorbing functional groups. That means that a high absorption indicates a high content of the corresponding functional group whereas a low ab-

sorption band indicates a low content of this group (Günzler and Böck, 1990).

The spectrum for the SOM extracted with sodium pyrophosphate from the plot fertilized with liquid manure (Figure 1 LM) is comparable to the one Niemeier et al. (1992) prepared from pure manure compost. Comparison of the FT-IR spectra (Figure 1) shows that the intensity of the bands at 1710 cm<sup>-1</sup> and 1690 cm<sup>-1</sup> increases in the sequence: LM > S+N > N > LM+N. Due to this sequence it can be concluded that fertilization with liquid manure results in the highest content of carboxylic groups. This is comparable to the findings at Müncheberg experiment for the cattle manure fertilization.

In contrast to the Müncheberg experiment (Ellerbrock et al., 1997), the SOM of the straw+N fertilized plot has not the lowest absorption intensity. A possible explanation is that straw fertilization at Dedelow was combined with green manure, which was not the case at Müncheberg. Green manure is a rapidly decomposable material and straw input increases the air content in soil. Consequently, it may be possible that straw+N+green manure may result in a high carboxyl content in a similar way as cattle manure at Müncheberg. On the other hand, the farmyard manure is different at Dedelow compared to Müncheberg: Liquid manure contains not as much solid organic material as cattle manure and the mineralization is faster. This may be an explanation of the observed effect that liquid manure leads to a lower content of carboxylic groups at Dedelow.

According to the high absorption intensity at 1710 cm<sup>-1</sup> and 1690 cm<sup>-1</sup> we expect relatively high CEC values for the SOM of the samples from the LM and S+N plot. The correspondence between absorption intensity and CEC, however, could only be confirmed for the plot fertilized with S+N (Figure 1

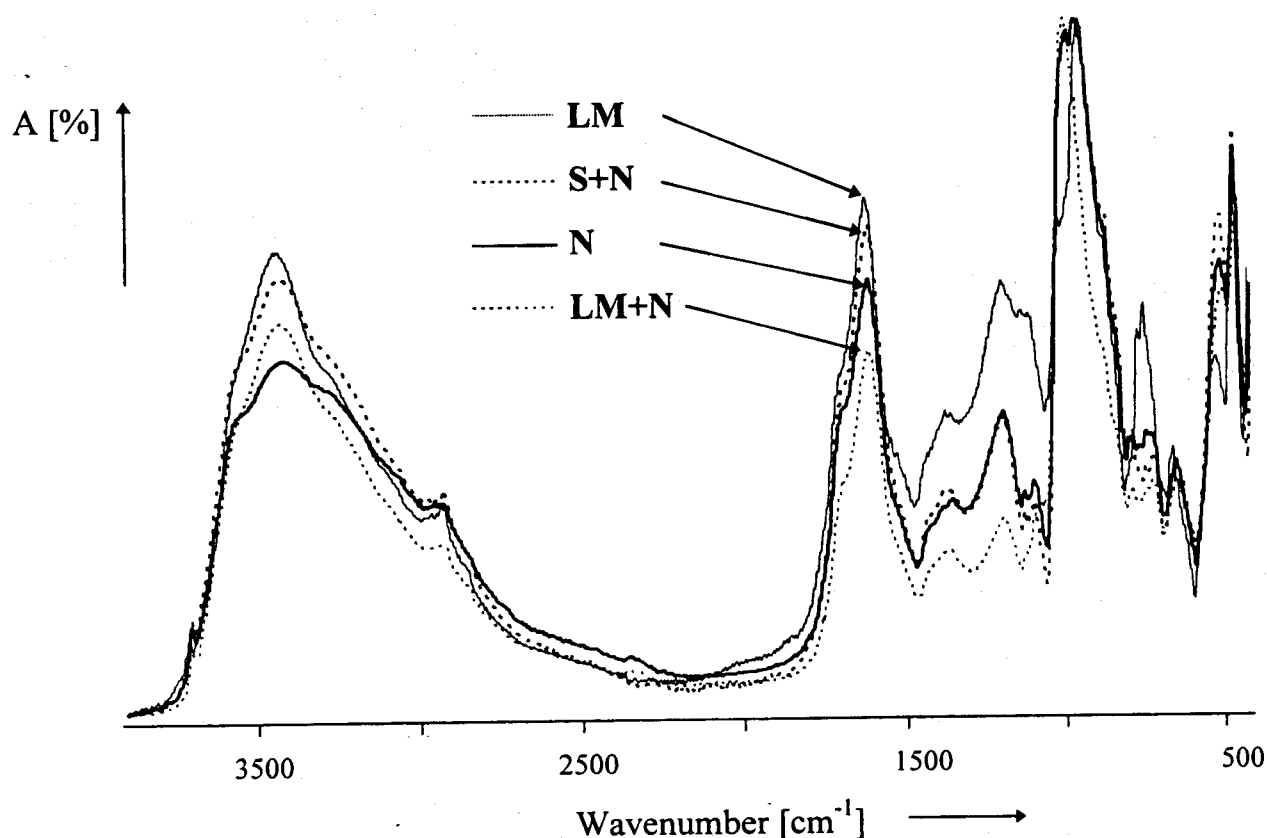


Figure 1. FT-IR spectra of sodium pyrophosphate extracts of the Dedelow plots LM, LM+N, S+N and N.

S+N and Table 1). On one hand, the accessibility of the C=O groups may be different for both samples depending on the three dimensional structure of SOM which cannot be detected using FT-IR spectroscopy. On the other hand, the spectra were obtained using extracts of on the SOM and therefore they are only partially representative for the CEC of the SOM.

The differences in FT-IR spectra of the sodium pyrophosphate extracts from the sandy loam samples (Figure 1) are not as distinct as for the loamy sand samples (Ellerbrock et al., 1997). A possible explanation is that the higher clay and silt content stabilizes SOM in the sandy loam (Dedelow). Especially the CEC active part of SOM is able to interact with clay mineral particles (Jasmund and Lagaly, 1993) building up organo mineral complexes using polyvalent cations as bridges. This stabilization is the cause that fertilization needs a longer time to affect SOM composition in the sandy loam. A second effect is that it is more difficult to isolate SOM from soils with higher clay contents.

The FT-IR spectra from SOM extracted with hot water (Figure 2) did not show distinct differences

between the different fertilized plots. This is in accordance to the findings corresponding sandy soil samples from Müncheberg experiment (Ellerbrock, 1997). Compared to hot water, the SOM extraction by sodium pyrophosphate seems to be more effective in characterizing SOM composition. This can be explained by the fact that the pyrophosphate anion is an complexing agent (Greenwood and Earnshaw, 1984). It complexes the polyvalent cations which are the binding bridges between SOM and clay minerals in the organo mineral complexes. If these binding bridges are complexed, than SOM normally fixed in organo mineral bindings becomes soluble. Hot water extraction is not able to do so, because a complexing agent is missing.

## Conclusions

The characterization of SOM by FT-IR spectra shows that the composition of SOM from a sandy loam was affected by the type of fertilization. Comparing the long-term field experiments from Dedelow and

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