Functional analysis of soil organic matter as affected by long-term manurial treatment

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Summary

The composition of soil organic matter (SOM) is influenced by land use and fertilization. We studied changes in the SOM in a long-term field experiment on a sandy Podzoluvisol. The control plot and four combinations of manurial treatments of the experiment were selected: one with mineral fertilizer only and three combinations of organic manure with mineral fertilizer: cattle manure + NPK, cattle manure + PK and straw + NPK. The SOM was extracted by sodium pyrophosphate solution (pH = 10) and hot water (100°C). The extracts were analysed by Fourier-Transform Infrared (FT-IR) spectroscopy and gel permeation chromatography (GPC). The FT-IR spectra from sodium pyrophosphate extracts indicate that composition of SOM is indeed influenced by different fertilization. The C=O band at $1710 \, cm^{-1}$ in the samples of the plots fertilized with cattle manure has the highest absorption intensity, whereas the material from the plot fertilized with straw + NPK has the least intense. The GPC analyses of the extracts showed that adding cattle manure + NPK increased the molecular size of SOM in comparison with the control plot. The analysis of hot-water extracts with FT-IR showed no significant differences in functional groups, but GPC chromatograms distinguished features in molecular size distribution. Fertilization with cattle manure increased the molecular size of the SOM in comparison with the control, but the differences in content of carboxylic groups and molecular weight were detected in sodium pyrophosphate extracts only.

Introduction

Long-term field-experiments have shown that soil organic matter (SOM) is influenced by management practices and especially by the addition of fertilizers and manures. The content of organic carbon in the soil is controlled by changes in management via the annual input of organic matter and the rate at which it decays (Jenkinson, 1988). These changes are not only quantitative; they also affect the quality of the SOM in terms of composition (Murray & Quirk, 1990). Composition means the nature, content and spatial arrangement of functional groups (e.g. carboxylic, phenolic) within the organic material and is correlated with sorption characteristics such as the cation exchange capacity (CEC) of SOM (Almendros, 1995; Gressel *et al.*, 1995).

Fourier-Transform Infrared (FT-IR) spectroscopy has been widely used for characterizing complex organic macromolecules (Stevenson, 1982). A variety of infrared bands are characteristic for molecular structure and functional groups. The content of carboxylic groups in

organic substances is correlated with CEC of these materials (Günzler & Böck, 1990). Changes of the proportion of functional groups during humification and composting were studied by Niemeyer *et al.* (1992) and Inbar *et al.* (1989). Ibarra (1989) showed that FT-IR spectra could be used to determine functional groups of humic acids in coal. Van der Marel & Beutelspacher (1976) found infrared spectra of humic acids from various origins to be similar but not identical. They thought that these variations were caused by slight differences in the acids' composition.

Hempfling *et al.* (1987) and Candler *et al.* (1989) found differences between two woodland soils with FT-IR. They stated that during decomposition of litter, humification and podzolization the content of cellulose and lignin decreases, whereas hemicellulose and protein fractions appear not to change. Their study was done on bulk samples.

Studies on SOM from the same soil type under different kinds of manurial practice by FT-IR should allow one to detect effects of manures on functional groups, and gel permeation chromatography should provide information on the molecular weight of the SOM. The former is correlated with CEC and the latter with mobility of the SOM. Changes in CEC and mobility

Table 1 Description of the selected experimental treatments (Smukalski & Rogasik, 1993)

| Treatment | N/P/K applied to growing crop[a] /kg ha^{-1} year^{-1} (1983–94) mineral + organic | | | |
	Winter wheat	Sugar beet	Spring barley	Potatoes
1 Control	0/0/0	0/0/0	0/0/0	0/0/0
2 NPK[b]	140/30/100	200/45/160	100/30/100	160/45/160
3 Cattle manure[c] + NPK	140/30/100	200/45/160	100/30/100	160/45/160
	+ 75/34/67	+ 75/34/67	+ 75/34/67	+ 75/34/67
4 Straw + NPK[d]	140/30/100	200/45/160	100/30/100	160/45/160
	+ 15/5/25	+ 15/5/25	+ 15/5/25	+ 15/5/25
5 Cattle manure + PK	0/30/100	0/45/160	0/30/100	0/45/160
	+ 75/34/67	+ 75/34/67	+ 75/34/67	+ 75/34/67

[a] Crop rotation: Winter wheat, sugar beet, spring barley, potatoes.
[b] NPK: Mineral fertilizer N, nitrogen; K, potassium; P, phosphorus.
[c] FYM: Cattle manure (3.2 t dry matter ha^{-1} year^{-1}).
[d] Straw: Cereal (wheat) straw (2 t dry matter ha^{-1} year^{-1}).

of SOM due to manuring might be used to predict effects on soil properties.

Materials and methods

A long-term experiment was established in 1963 by the former Centre of Soil Fertility at Muencheberg, Germany, ≈ 50 km east of Berlin (Smukalski & Rogasik, 1993). The soil is a loamy sand with deep groundwater table. It is a Podzoluvisol to Arenosol according to the FAO Guidelines (FAO, 1990). Mean annual precipitation is 527 mm, with 314 mm during the main growing season (April to September). Mean annual temperature is 8.2°C. The experiment comprises 21 manurial treatments in all, with eight replications for each treatment, and each plot is 6.0 m × 5.0 m. The cropping system is a conventional tillage with ploughing each autumn (Table 1). The seedbed was prepared in autumn for the cereals and in spring for the other crops. Table 1 presents the annual input of mineral nitrogen, phosphorus and potassium applied to the growing crop. Four of the treatments and the control plot were chosen for the present study as follows.
1 Control.
2 Mineral fertilizer (NPK = nitrogen, phosphorus and potassium) only.
3 Cattle manure with mineral fertilizer (cattle manure + NPK).
4 Cereal straw (wheat) with mineral fertilizer (straw + NPK).
5 Cattle manure with mineral fertilizer (cattle manure + PK) (without mineral nitrogen since 1982).

The topsoil (0–25 cm depth) has average contents of 50 g clay kg^{-1}, 210 g silt kg^{-1} and 740 g sand kg^{-1} soil. Organic carbon content varies between 4.3 and 5.2 g C kg^{-1} (Table 2). Soil samples were taken at 0–25 cm depth with eight replications from each plot of the treatments and mixed. The soil samples were air-dried and sieved to pass 2 mm.

Analytical methods

Organic carbon content and cation exchange capacity. Organic carbon content of the soil samples was analysed by elemental analysis (LECO) as carbon dioxide by infrared detection after dry combustion in two replicates. The results are given in Table 2. The measurement error was ± 0.5%.

Cation exchange capacity (Table 2) was determined according to DIN (1977), with 5 g soil and measured as exchangeable barium ions by atomic absorption spectroscopy. The results obtained were corrected by data from blank solutions. The measurement error was ± 5 mmol kg^{-1} (mmol singular positive charged ions).

Gel permeation chromatography. Gel permeation chromatography (GPC) was done with equipment from Bischof and AQUA-OH columns from Macherey & Nagel. The technique separates substances according to their molecular sizes (MS). An eluent has to be used which avoids interactions between the sample solution and the column surface (Town & Powell, 1992; Clapp *et al.*, 1993; Piccolo *et al.*, 1996). We chose a mixture of a 0.1 M solution of sodium citrate in water with methanol (1:1) containing 0.01% sodium dodecylsulphate with a pH of 7 as eluent. The quality of separation was tested by sodium polystyrol sulphate standards from Knauer: these are of high molecular size (1 000 000–3000 Da), aromatic and soluble in water. The injection volume was 0.5 µl, the flow rate was 0.5 ml min^{-1}, and the detection wavelength was 280 nm. The SOM extracts, obtained by either sodium pyrophosphate

Table 2 Organic carbon content and cation exchange capacity of the soil

Treatment	Average	
	C_{org}[a] /g kg^{-1}	CEC[b] /mmol$_c$ kg^{-1}
1 Control	4.3	32.5
2 NPK	4.7	32.0
3 Cattle manure + NPK	4.9	35.6
4 Straw + NPK	5.2	34.0
5 Cattle manure + PK	4.6	31.5

[a] C_{org}, organic carbon content; measurement error 0.5 g kg^{-1}.
[b] CEC, cation exchange capacity; measurement error 5 mmol$_c$ kg^{-1}.

or hot water, were dissolved in the eluent, filtered through a 0.45-μm membrane filter and injected. Parallel different salt solutions were injected to prove if such ions as K^+, Mg^{2+} and SO_4^{2-} and PO_4^{3-} disturb the GPC of SOM. We found that the corresponding cations and anions need twice the time to pass the GPC column as SOM does.

Fourier-Transform Infrared spectroscopy. The FT-IR measurements were made with a BioRad® FTS 135. We used the KBr technique (2 mg sample in 150 mg KBr) (Capriel *et al*., 1992; Celi *et al*., 1997) to obtain absorption spectra of SOM extracts (range of wave number 3900–400 cm^{-1}). All spectra were obtained under the same resolution (1 cm^{-1}) and measurement conditions.

As the FT-IR spectra show a certain mineral content, all spectra were corrected mathematically by a subtraction method as follows. Spectra of the mineral part of the soil were prepared under the same conditions. We did the subtraction of the mineral spectra from the extraction spectra with the BioRad® software Win-IR Foundation®. We preferred this procedure because the alternative treatment of SOM with HF–HCl produces artefacts.

Extraction methods

To minimize alteration of SOM during extraction the mixed samples were extracted in two ways as follows.
1 *Sodium pyrophosphate*: Ten grams of soil was mixed with 0.1 dm^3 of 0.1 M $Na_4P_2O_7$ and shaken for 6 h at room temperature (by the method of Hayes, 1985). The solid residue was separated by centrifuging. The remaining solution was adjusted with 1 M HCl to pH 2, to precipitate the SOM. After 12 h the precipitation was completed and the mixture centrifuged. The precipitate was washed free of salt with distilled water and freeze-dried.
2 *Hot water*: We chose hot water for our second extraction method, assuming that it represents the easily decomposable

part of SOM (Körschens *et al*., 1990). Ten grams of soil was mixed with 0.1 dm^{-3} distilled water. The mixture was heated under reflux (100°C) for 1 h as described by Körschens *et al*. (1990). The solid residue was separated by centrifuging. We removed ions by dialysis (pore size of the membrane smaller than 0.2 μm), then the solution was freeze-dried.

Results and discussion

The organic carbon content of the soils in the different plots varies around 4.7 g kg^{-1} (Table 2). We concluded that different fertilizer treatments in this experiment had not caused detectable differences in the organic matter content of the soil. This finding contrasts with results from other field experiments. For example, fertilizing with a combination of organic and mineral fertilizer caused an increase in soil organic carbon content at the static fertilization experiment at Bad Lauchstädt (Körschens, 1996).

The CEC of the soil varies between 31.5 and 35.6 mmol kg^{-1} (Table 2). The differences between the soil in the different plots were not larger than the measurement error. It seems that fertilization had not changed the CEC. This and the fact that there was no detectable change in the organic matter content due to fertilization might be because the experiment is only 34 years old.

Gel permeation chromatograms

Figure 1(a–f) presents the gel permeation chromatograms of the sodium pyrophosphate and hot-water extracts for the control and treatment number 3 and number 5. The absorption intensities are 10–12 mV for all samples. The chromatograms show peaks, which indicate molecules of different sizes. The peaks at short retention time are caused by SOM with larger molecules, whereas those of longer retention time are due to SOM with smaller molecules.

The gel permeation chromatograms of the sodium pyrophosphate extracts of the selected plots (Figure 1a–c) are different. The chromatograms from cattle manure + NPK (Figure 1b) show two broad overlapping peaks. The one for the control (Figure 1a) also shows two overlapping peaks: the first is intense, whereas the second one appears only as a shoulder of the first. Additionally the centre of the peaks from the control is shifted to smaller molecules, and the molecular size distribution has a smaller range. The GPC of cattle manure + PK (Figure 1c) shows a broad single peak with a somewhat lower retention time than cattle manure + NPK. This indicates that the content of the SOM with small molecules is less in this sample. We concluded that cattle manure produced SOM with larger molecules than that in the control.

Other results were observed on GPCs of hot-water extracts (Figure 1d–f). For cattle manure + PK there was only a single peak at low molecular weight, whereas the GPC of the control shows two separate peaks. The signal
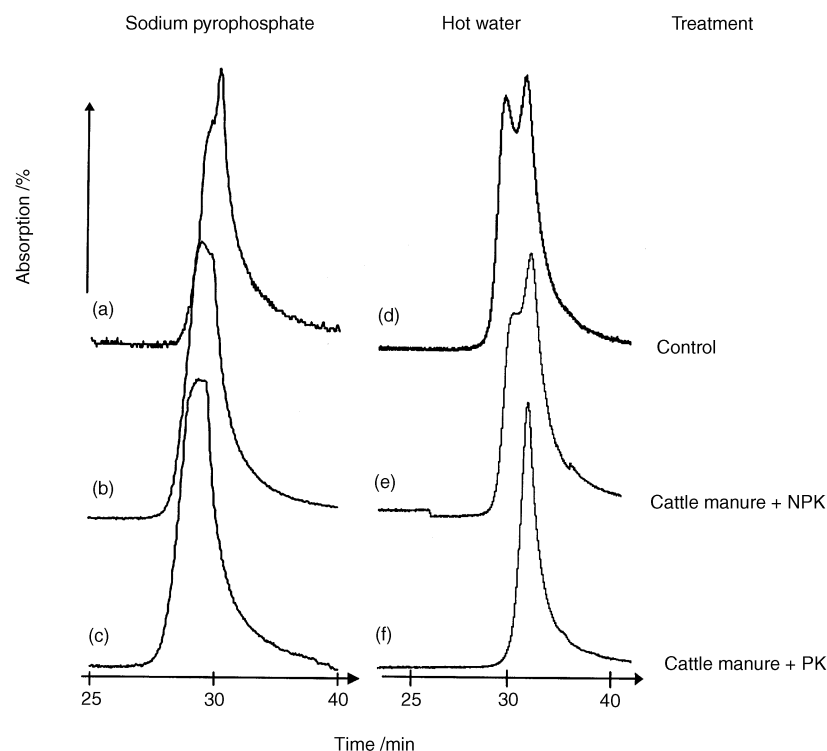
Figure 1 Gel permeation chromatograms of sodium pyrophosphate and hot-water extracts from soil of plots control, cattle manure + NPK, and cattle manure + PK. Absorption is at $\lambda = 280$ nm.

for the larger molecules decreases strongly in the GPC of cattle manure + PK, and we could not detect it. Cattle manure + NPK shows a combination of two peaks: the first (large molecules) appears as a shoulder on the more intense peak (smaller molecules). The effect of cattle manure + NPK is not as great as the one of cattle manure + PK. The molecules decrease in size in the sequence control plot < cattle manure + NPK < cattle manure + PK.

Fourier-Transform Infrared spectra

The FT-IR spectra of sodium pyrophosphate extracts of soil samples from different plots illustrate an overall scheme, as follows. The bands between 400 and 800 cm^{-1} and at 1100 cm^{-1} wave number result mainly from inorganic components (clay minerals such as kaolinite, and quartz) which could not be completely eliminated during purification. To eliminate corresponding bands of the mineral phases we corrected the spectra by mathematical subtraction. A spectrum of the mineral phases from the sample was subtracted from the spectra of the corresponding sodium pyrophosphate extract. The resulting spectra are shown in Figure 2 and Figure 3. Absorption bands are located at the following positions.

1 3500–3200 cm^{-1} due to O–H stretching vibrations (included in alcohols, phenols and water molecules). Its broadness is generally attributed to hydrogen bonding (MacCarthy & Rice,

1985). These bands are strongly influenced by water content. This has to be considered in interpretation.

2 2922–2926 cm^{-1} attributed to asymmetric and symmetric vibrations of aliphatic C–H bonds (methyl, methylene groups). These bands are usually superimposed as a shoulder of the broad O–H band.

3 1698–1701 cm^{-1} stretching vibration of the C=O group (carboxylic acids, cyclic and acyclic aldehydes and ketones (van der Marel & Beutelspacher, 1976)).

4 1600–1613 cm^{-1} assigned to stretching vibrations of aromatic C=C double bonds conjugated with C=O or COO^{-} bonds or both, i.e. of unsaturated ketones or amides (MacCarthy & Rice, 1985).

5 1540 cm^{-1} due to stretching vibrations of C=C double bonds.

6 1400 cm^{-1} due to carboxylic and carbonylic groups.

7 1081 cm^{-1} due to C–O vibration of C–O–C groups of cellulose, for example.

The intensity of the absorption bands depends on the amount of absorbing groups (Günzler & Böck, 1990). The most intense band at 1081 cm^{-1} (used as an internal standard) facilitates a comparison. With a decrease of the relation between the absorption intensity of the bands at 1700 cm^{-1} and 1081 cm^{-1} the amount of C=O groups relative to the amount of C–O group also decreases. All the following statements concerning the content of functional groups are applied to this relation.
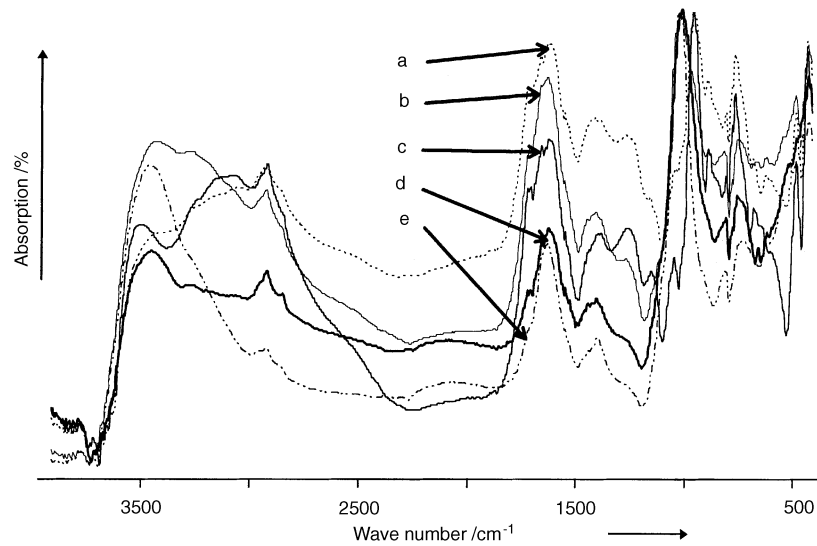
Figure 2 FT-IR spectra of sodium pyrophosphate extracts of soil from treatments (a) cattle manure +PK, (b) cattle manure +NPK, (c) control, (d) straw +NPK, and (e) NPK after correction with the mineral phase.
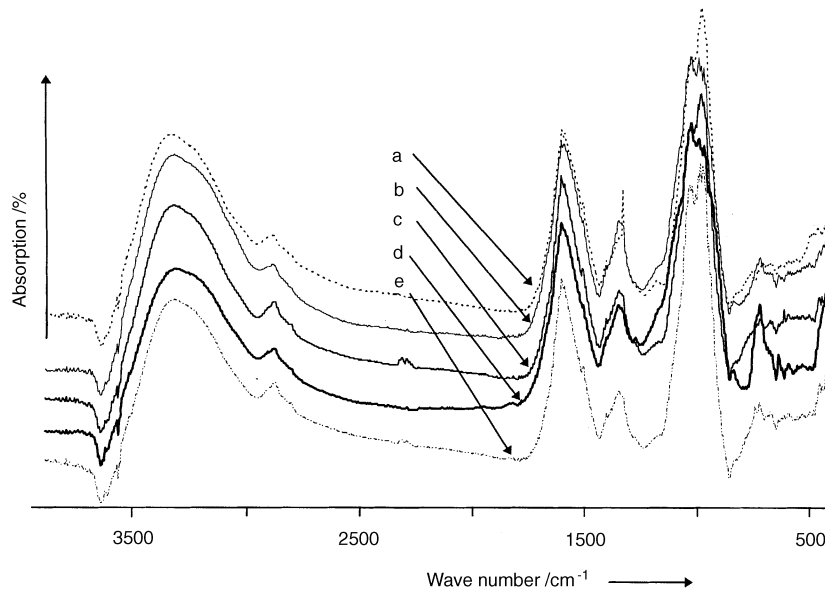

Figure 3 FT-IR spectra of hot-water extracts of soil from treatments (a) cattle manure +PK, (b) cattle manure +NPK, (c) control, (d) straw +NPK, and (e) NPK after correction with the mineral phase.

The FT-IR spectra of the sodium pyrophosphate extracts of the soils (Figure 2a–e) show differences depending on the fertilizer treatments. The bands at $1710 \, \mathrm{cm^{-1}}$ and $1690 \, \mathrm{cm^{-1}}$ are most informative. Fertilization with cattle manure results in the greatest intensity of these bands. The intensity increases in the sequence straw +NPK ≤ NPK < control plot < cattle manure +NPK < cattle manure +PK. The same can be observed for the absorption bands at $1402–1411 \, \mathrm{cm^{-1}}$. Consequently the SOM from plot 3 and 5 (Figure 2d,e, respectively) contains the largest content of carboxylic groups. The SOM from plot 4 (Figure 2c) fertilized with straw and mineral nitrogen contains the least. We

did not expect this sequence. As the difference in fertilization is most extreme between the control plot and the fertilized ones, we expect the greatest difference between the control and the fertilized treatments. But we found that the difference between cattle manure +NPK and control plot was less than the difference between cattle manure +NPK and straw +NPK. Although both treatments combine an organic manure and an inorganic fertilizer they produce SOM of different composition. This can be explained by the kind of organic matter added either in the manure or the straw. Straw contains much cellulose (hardly decomposable), whereas cattle manure originally

contains compounds with more carboxyl groups. Therefore the SOM can be enriched in the corresponding components, resulting in different FT-IR spectra.

Additional differences can be seen in the bands at 3500–3200 cm^{-1}. Organic matter from the straw + NPK treatment shows the least intensity in this band. This SOM contains less hydroxylic groups than the others. The band at 2922–2926 cm^{-1} (which appears as a shoulder of the band at 3500–3200 cm^{-1}) shows that the content of CH$_2$ groups depends on fertilizer treatment too: its content is greatest for cattle manure + PK. The sequence is cattle manure + PK = control plot > cattle manure + NPK > straw + NPK > NPK.

In contrast to GPC, FT-IR spectra of hot-water extracts (Figure 3a–e) show no significant differences. It seems that these extracts contain the same functional groups with similar portions, but different molecular size. The sodium pyrophosphate solution probably isolates a part of the SOM not isolated by hot water. Polyvalent cations are responsible for maintaining SOM in an insoluble state in many soils (Greenwood & Earnshaw, 1984). Pyrophosphate anions (in sodium pyrophosphate solution) remove these cations from SOM by building complexes, resulting in solubilization of SOM which can be extracted. This is not possible in hot water, because a complexing agent is missing. Consequently hot water and sodium pyrophosphate extract chemically different soil organic matter.

Conclusions

Our results have demonstrated that the total amount of soil organic matter did not discriminate between different manurial practices over 34 years. Fourier-Transform Infrared spectroscopy, however, showed that there were distinct differences in the properties of the functional groups. It seems that the organic material extracted by sodium pyrophosphate represents the fraction of SOM most affected by adding manure. Adding cattle manure increased the carboxylic content of the SOM, whereas application of straw resulted in the least content of this functional group. With GPC we found that molecular size distribution of the SOM extracted was also influenced by fertilization: cattle manure produced SOM with larger molecules than that in the control.

Results from FT-IR and GPC investigations on hot-water extracts show that fertilization affected the molecular weight only. From this we conclude that manuring influences the SOM in different ways. It affects the composition and molecular size in SOM extractable by sodium pyrophosphate, but the part extractable by hot water is influenced in molecular size only.

Acknowledgements

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