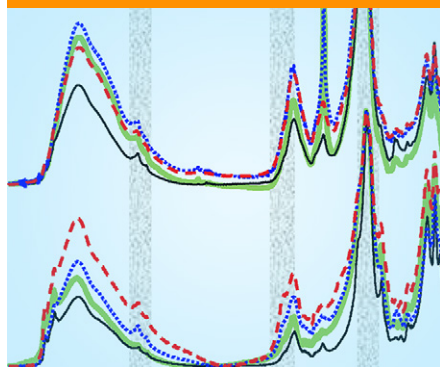## Original Research

Core Ideas
- Changes in soil OM composition found with FTIR could be related to sorption properties.
- CEC of pyrophosphate-soluble OM increased for long-term farmyard manure applications.
- CEC decreased for mineral N applications relative to unfertilized treatments.

Analyzing Management-Induced Dynamics of Soluble Organic Matter Composition in Soils from Long-Term Field Experiments

R.H. Ellerbrock* and H.H. Gerke

Soil organic matter (SOM) can be affected by adopted soil management options. However, it is unclear how mineral and organic fertilization could change the amount and composition of SOM. The objective of this study was to test the applicability of infrared spectroscopy for analyzing management-induced impacts on organic matter (OM) composition. Ap horizon samples were collected from the long term-field experiments at Bad Lauchstädt (loam), Groß Kreutz, and Müncheberg (both loamy sand) in plots fertilized with farmyard manure (FYM), farmyard manure plus mineral N (FYM + N), and mineral N only (N) and an unfertilized control plot. The SOM and hot-water-soluble and pyrophosphate-soluble (OM-PY) organic matter fractions were analyzed using Fourier-transform infrared (FTIR) spectroscopy. The OM composition was evaluated in terms of the ratio between absorption band intensities in FTIR. The soluble OM fractions of FYM had larger C=O/C−O−C ratios than the N and control treatments. While the cation exchange capacity (CEC) of OM-PY from FYM was larger, it was smaller for the N plots than the control at all sites. The results allowed identification of fertilization-induced long-term dynamics in (i) the OM composition and (ii) the CEC and the potential wettability of SOM and OM fractions. The OM-PY fraction could be used to identify and characterize the long-term changes in OM composition. For a more quantitative analysis, however, more replicate samples and a seasonal differentiation would be required to separate between shorter and longer term changes.

Agricultural soil and crop management practices (i.e., crop rotations, cultivation, and fertilization) can normally not change the texture of soil minerals; however, these practices can impact the soil organic matter (SOM) with respect to both content and composition (e.g., Kaiser et al., 2008). Agronomic effects on the long-term dynamics of soil properties have motivated the establishment of long-term field experiments on contrasting soils in many countries (e.g., Powlson, 1996; Lal et al., 1995). Depending on the soil type, organic matter (OM) has been assumed to consist of differently stable fractions (e.g., Wattel-Koekkoek et al., 2003; von Lützow et al., 2006). The hot water (OM-HW) extractable (Körschens et al., 1990) and the free-light OM fractions (e.g., Sohi et al., 2001; von Lützow et al., 2007) have been identified as easily decomposable. These fractions (OM-HW and free light) have been assumed to reflect more rapid changes in the OM composition than the more stable pyrophosphate-soluble (OM-PY) OM fraction (e.g., Ellerbrock and Kaiser, 2005).

The term OM composition has been frequently used (e.g., Ellerbrock et al., 1999b) to describe the type and the relative amount of functional groups in OM (e.g., carboxyl and hydroxyl groups). Spectroscopic techniques like nuclear magnetic resonance and Fourier-transform infrared (FTIR) spectroscopy allow determining the relative contents of the different functional groups (e.g., Stevenson, 1994). By using spectroscopic techniques,

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Niemeyer et al. (1992) and Gerzabek et al. (1997), among others, described changes in the proportions of functional groups during humification. The effects of fertilization on the content and the composition of soluble OM fractions of arable (top-) soils from long-term field experiments have already been reported (e.g., Ellerbrock et al., 1999b; Gerzabek et al., 2006; Tatzber et al., 2007). These previous studies analyzed mainly OM fractions of soils from plots of a single field experiment and neither considered the composition of the total SOM nor compared the OM composition of soils from different long-term field experiments. Data from the long-term field experiments at Bad Lauchstädt (Körschens, 1990) and Halle (Merbach et al., 1999) indicated that the composition of a sequentially extracted pyrophosphate-soluble OM fraction was affected by soil management and crop rotation (Kaiser et al., 2007). For the cold-water-soluble OM fraction (Ellerbrock and Kaiser, 2005), only negligibly small differences in the OM composition between differently fertilized soils were reported. Since the cold water extraction procedure has been criticized because of the relatively long (i.e., 12–24 h) extraction time, a more rapid (i.e., only 1 h) hot water extraction procedure was suggested by Körschens et al. (1990). Recently, von Lützow et al. (2007) used the OM-HW fraction for estimating the amount of labile SOM constituents. With respect to the composition of OM-HW fractions, Ellerbrock et al. (1999b) found only negligibly small differences in OM composition when comparing differently fertilized coarse-textured soils. Nevertheless, the long-term effects of fertilization on the composition of OM-HW of loamy soils remained unclear because of the highly dynamic nature of this relatively instable fraction.

The pyrophosphate-soluble OM fraction (OM-PY) was hypothesized to represent OM components involved in interactions with clay minerals and Fe oxides (e.g., Masiello et al., 2004; Kögel-Knabner et al., 2008). Thus, as a more stable fraction, OM-PY should reflect long-term changes better than OM-HW. However, the extraction of OM-PY was more difficult for loamy than for sandy soils because the above-mentioned interactions between OM and reactive soil minerals limited the extraction yields (e.g., Ellerbrock and Kaiser, 2005). For loamy soils, however, OM-PY yields were still larger than OM-HW yields (Ellerbrock et al., 1999a).

The effectiveness of OM to interact with soil minerals was found to depend on the presence of carboxyl and carbonyl (C=O) groups within the OM (Aquino et al., 2007). The C=O groups in organic molecules are important for sorption of reactive solutes in the soil (e.g., Senesi et al., 2001). The absorption bands indicative for C=O groups are indicators for the cation exchange capacity (CEC) of the OM fractions (Celi et al., 1997). A nearly linear relation between FTIR data and the CEC of OM fractions was found by Kaiser et al. (2008) for the ratio between C=O and C–O–C groups (i.e., part of polysaccharides) (C=O/C–O–C ratios) in FTIR spectra of sequentially extracted OM-PY (i.e., the pyrophosphate extraction was performed on the same sample after the water extraction step). It was unclear if OM-PY could reflect long-term fertilizer effects on the dynamics of OM composition and changes in the CEC also for a nonsequential extraction procedure.

The studies above hypothesized that (i) fertilization-induced short-term OM dynamics were reflected more in the composition of OM-HW than in that of OM-PY or SOM, (ii) the content and composition of OM-HW and OM-PY were more affected by the kind and the amount of fertilizers and better detectable in coarser than in finer textured soils, and (iii) the intensity of C=O bands in FTIR spectra of the OM-PY fraction reflected most of the CEC of the OM-PY and more the long-term changes in OM composition due to fertilization. The objective of this study was to test the applicability of infrared spectroscopy for analyzing dynamic changes in OM composition that result from long-term fertilization and to identify OM fractions that reflect such effects. To describe the long-term dynamics of SOM properties, CEC and FTIR data of SOM and soluble OM fractions were compared. Data from mixed samples from long-term field experiments with sandy and loamy soils were used.

Materials and Methods
Long-Term Field Experiments
Soil samples were from the following four long-term field experiments in Germany. The experiment in Bad Lauchstädt (BL) located 10 km west of the city of Halle (Table 1) was established

Table 1. Information on long-term field experiments at Bad Lauchstädt (BL), Groß Kreutz M4 (GK1), Groß Kreutz P60 (GK2), and Müncheberg (MB): year of establishment (Start), annual mean precipitation (Prec.), annual mean temperature (Temp.), soil type (FAO, 1990), and the clay, silt, and sand contents as well as the pH range determined in 0.1 $mol\ L^{-1}$ $CaCl_2$ solution (soil/solution = 1:5) for the soils.

Site	Start	Location	Prec.†	Temp.†	Soil type (FAO, 1990)	Clay† $<2\,\mu m$	Silt† $63–2\,\mu m$	Sand† $>63\,\mu m$	pH
			mm yr^{-1}	°C			——— g kg^{-1} ———		
BL†	1902	52°81′18.3″, 57°0′5.9″	490	8.6	Haplic Chernozem	211	677	212	5.3–6.8
GK1	1967	52°22′47.2″, 12°45′45.0″	532	8.9	Albic Luvisol, Luvisol Arenosol	50	220	730	5.0–6.5
GK2	1959	52°22′47.2″, 12°45′45.0″	532	8.9		50	220	730	5.5–6.3
MB†	1963	52°31′0.1″, 14°7′18.9″	527	8.2	Podzoluvisol to Arenosol	50	210	740	5.4–5.9

† From Körschens (1990).

in 1902; the soil was a Haplic Chernozem (FAO, 1990) from loess. The experiment in Müncheberg (MB) located about 50 km east of the city of Berlin was established in 1963 on loamy sands from glacial till (i.e., mainly Haplic Luvisols; FAO, 1990). The two experiments in Groß Kreutz (GK) located 20 km west of the city of Potsdam (Table 1) were established in 1967 (GK1) and 1959 (GK2) on coarse-textured sediments (i.e., Albic Luvisols/Luvic Arenosols; FAO, 1990) from glacial outwash sands. The crop rotations were winter wheat (*Triticum aestivum* L.), sugarbeet (*Beta vulgaris* L.), summer barley (*Hordeum vulgare* L.), and potato (*Solanum tuberosum* L.) for GK1 and maize (*Zea mays* L.), winter rye (*Secale cereale* L.), and winter rye for GK2 since 1996 (Table 2). From 1959 to 1978, the crop rotation of the GK2 experiment was potato, oat (*Avena sativa* L.), and winter rye; from 1979 to 1993 it was potato, pea (*Pisum sativum* L.), and winter rye; and from 1990 to 1995 it was potato, winter rye, and winter rye. The crop rotation of the experiments at BL and MB was the same as the rotation at GK1.

All experiments were originally established to study the effects of different fertilizer combinations on grain yield and plant nutrition (e.g., Körschens, 1990) and were continuously cultivated since establishment. The seedbed for the crops was prepared in autumn for barley and in spring for the other crops. Plowing depth at all sites was between 25 and 20 cm. Table 2 gives the mean annual application rates of mineral N fertilizer and OM in the form of farmyard manure. Organic fertilizer was applied every second year in spring at BL, MB, and GK1 and every third year at GK2 before planting sugarbeet, potato, or maize, respectively. More details on the soil and crop management were provided by Körschens (1990) and Zimmer et al. (2005).

Four treatments were selected: control, unfertilized plots; only mineral N; farmyard manure (FYM; cattle) without mineral N (except for MB); and FYM + N, cattle manure plus mineral N. Sampling was performed in August 1997 (BL) after summer barley,

in July 1998 (GK1) after winter wheat, in July 1998 (GK2) within a maize crop, and in April 1999 (MB) after harvest of winter wheat, representing 95 (BL), 31 (GK1), 39 (GK2), and 35 (MB) yr of continuous different fertilization treatments. Note that the plots at GK2 received FYM in spring before planting of maize, while GK1 received the FYM in the year before the soil sampling. Soil samples were obtained from each of the eight (MB), four (GK), and two (BL) replicate plots of the same crop rotation and fertilization trial. The soil samples were collected from the 0- to 25-cm depth in eight replicates along a diagonal across each plot using an auger. The auger samples from each replicate plot were combined into a single composite sample of 1- to 1.5-kg soil mass per site and fertilizer treatment. The composite samples were mixed, air dried, and sieved to pass 2 mm. While focusing first on the principle usefulness of the approach to study fertilization effects on the dynamics of OM composition, only a composite sample per fertilizer treatment was used considering the unequal number of replicate plots per site (i.e., 2, 4, and 8) and assuming that the soil spatial heterogeneity was included in the composite samples such that fertilizer effects instead of soil heterogeneity could be studied.

Soil Analyses

Soil organic C content (SOC) was calculated as the difference between the total C and the CO_3–C. The CO_3–C content of the soil samples was determined after application of H_3PO_4 by gas-chromatographic analysis of CO_2 evolution (International Organization for Standardization, 1997). The content of total C in the soil samples was determined in duplicate by elemental analysis (CNS 2000, Leco Ltd.) as CO_2 via infrared detection after dry combustion at 1250°C (International Organization for Standardization, 1996). The detection limits were 0.1 g kg^{-1} for SOC. The CEC of the soil samples was determined using 5 g of soil (air dried and sieved) with the percolation technique according to the International Organization for Standardization (1977). The CEC was measured as exchangeable Ba^{2+} ions using an atomic absorption spectrometer (1100B, PerkinElmer). The Ba concentrations of the samples were corrected by using data from blank solutions. The measurement error was ±0.5 cmol$_c$ kg^{-1}. The CEC of the OM-PY fractions was determined using 0.1 g of OM-PY mixed with 4.9 g of quartz sand (Leinweber et al., 1993), using the above percolation technique.

The soil samples were extracted (Ellerbrock et al., 1999b) as follows. For the OM-HW fraction, 10 g of soil was mixed with 100 cm^3 of distilled water and heated under reflux (100°C) for 1 h (Körschens et al., 1990). The solid residue was separated by centrifugation and subsequent membrane filtration (0.45 μm, Nytran,

Table 2. Information on continuous cultivation of the long-term field experiments at Bad Lauchstädt (BL), Groß Kreutz M4 (GK1), Groß Kreutz P60 (GK2), and Müncheberg (MB): Crop rotation and fertilization with farmyard manure (FYM) (dry matter) and mineral fertilizer (N) according to Körschens (1990). Numbers in bold in the FYM + N column indicate the amount of N from the FYM.

Site	Crop rotation†	Fertilization	Units	Control	N–P–K	FYM	FYM + N
BL	TA, BV, HV, ST	FYM	dt ha^{-1} yr^{-1}	0	0	37.5	37.5
		N	kg ha^{-1} yr^{-1}	0	155	75	**75** + 155
GK1	TA, BV, HV, ST	FYM	dt ha^{-1} yr^{-1}	0	0	50	50
		N	kg ha^{-1} yr^{-1}	0	200	100	**100** + 200
GK2	SM, SC, SC (since 1996)	FYM	dt ha^{-1} yr^{-1}	0	0	42	21
		N	kg ha^{-1} yr^{-1}	0	105	83	**41** + 125
MB	TA, BV, HV, ST	FYM	dt ha^{-1} yr^{-1}	0	0	-	32
		N	kg ha^{-1} yr^{-1}	0	150	-	**64** + 150

† TA, winter wheat (*Triticum aestivum* L.); BV, sugarbeet (*Beta vulgaris* L.); HV, summer barley (*Hordeum vulgare* L.); ST, potato (*Solanum tuberosum* L.); PS, pea used for forage (*Pisum sativum* L.); SC, winter rye (*Secale cereale* L.).

Schleicher&Schüll). The ions were removed from the solution by dialysis before the solution was freeze-dried. For the OM-PY fraction, 10 g of soil was mixed with 100 cm^3 of 0.1 mol L^{-1} Na$_4$P$_2$O$_7$ solution (i.e., 0.1 mol of Na$_4$P$_2$O$_7$ was mixed with water to obtain a solution with a volume of 1 dm^3) and shaken for 6 h at room temperature (Hayes, 1985). The solid residue was separated by centrifugation. The remaining solution was adjusted with 1 mol L^{-1} HCl solution (i.e., 1 mol of HCl was mixed with water to obtain a solution with a volume of 1 dm^3) to pH 2 to precipitate the OM. After 12 h (i.e., precipitation completed), the mixture was centrifuged and the precipitate was washed free of salt with distilled water and freeze-dried. Each extraction was done using two replicate samples. The results of these laboratory replicates were very close, and averaged values were used.

The KBr technique was applied by using 0.5 mg of either the finely ground soil, the OM-HW, or the OM-PY fractions mixed with 80 mg of KBr (Celi et al., 1997; Ellerbrock et al., 1999b) to obtain transmission FTIR spectra measured with a BioRad FTS 135 (BioRad Corp.). For all spectra, identical measurement conditions were used (i.e., a wave number [WN] resolution of 1 cm^{-1}, between WN 4000–400 cm^{-1}, and 16 scans). The spectra were smoothed (boxcar moving average algorithm, factor 25) and corrected for baseline shifts using WIN-IR Pro 3.4 software (Digilab). The C−H bands in transmission FTIR were identified at WN 2920 and 2880 cm^{-1} (Capriel, 1997). At the peak maxima, the band heights were measured as the vertical distance from a local baseline (Ellerbrock et al., 2009). The heights of absorption bands in the regions from WN 1720 to 1700 cm^{-1} (groups with C=O double bonds of ketones, carboxylic acids, or amides) and from WN 1625 to 1600 cm^{-1} (groups with C=O double bonds of carboxylate anions and aromatic groups) (c.f., Senesi et al., 2003) were measured as the height from the total baseline. The sum was denoted as the height of the C=O bands using WIN-IR Pro 3.4 . The spectra of all samples were normalized for the band at WN 1000 cm^{-1}, which was used as a measure of the content of C−O−C groups within the OM. However, in the FTIR spectra of the soil samples, the signal at about 1010 cm^{-1} is mainly (about 95% of the time) caused by Si−O−Si groups from soil mineral components, while in the FTIR spectra of OM-PY and OM-HW the signal at about 1010 cm^{-1} is mainly caused by C−O−C bands within polysaccharides. The C=O/C−O−C and C−H/C=O ratios were calculated from the values of the absorption band heights as described above (and not from the areas) for each individual spectrum (Kaiser et al., 2008).

For the statistical analysis of differences in site properties (e.g., clay content), the fertilizer combinations were assumed to represent the replicates for each site. The spectral data (C−H/C=O ratios) obtained by transmission FTIR were tested for outliers using the Nalimov test, and the differences of the mean C−H/C=O ratios between soils were compared with a Student's *t*-test (Kaiser and Gottschalk, 1977).

Results

The SOC contents of topsoil samples from soils with a larger sand content (MB and GK) were smaller than those of the loamy BL soil (Fig. 1a). Smaller SOC contents (Table 3) corresponded with the smaller clay contents at MB and GK (Table 1). The largest SOC contents were found for the FYM + N and FYM fertilized soils and the smallest for the unfertilized control plots (Table 3). However, for the sandy soils, the differences in the SOC content among fertilizer treatments were smaller than for the loamy soil (BL).

For both loamy and sandy soils, the CEC increased with the SOC content (Fig. 1b). However, the CEC (Table 3) of the loamy soils was five to six times larger than that of the sandy soils because of the clay content (Table 1). The CEC values increased in the sequence control = N < FYM < FYM + N for BL and GK1; for GK2 it was control < N < FYM + N < FYM; and for MB it was control = N < FYM + N (Table 3). For the MB site, however, such differences in the CEC of the soil among the fertilizer treatments were smaller than the measurement error of the CEC analysis (±0.5 cmol$_c$ kg^{-1}). For the loamy soil, the CEC of the OM-PY was 10 times larger than the CEC of the original soil samples; for the sandy soils, the CEC of the OM-PY was about 20 times larger than
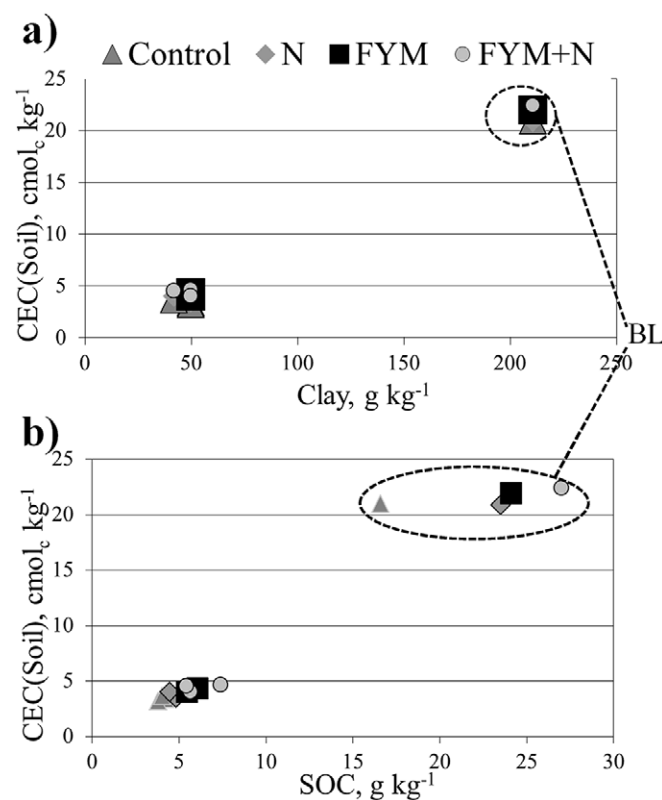

Fig. 1. The cation exchange capacity of the soil [CEC(Soil)] vs. (a) the clay content (Clay) and (b) the soil organic C content (SOC) for samples from the N fertilizer, farmyard manure (FYM), FYM + N, and control plots of the long-term field experiments at Bad Lauchstädt (BL), Groß Kreutz (GK1, GK2), and Müncheberg (MB).

that of the soil (Table 3). Differences in the CEC values among the fertilization treatments were larger for OM-PY than for the soil and most pronounced for OM-PY from the sandy soils.

All FTIR spectra (Fig. 2) showed a similar general scheme, with seven main absorption bands at the following wave numbers (WN):

1. WN 3700–2700 cm^{-1}: This adsorption band indicated O–H stretching vibrations of functional groups included in alcohols, phenols, and water molecules. Its broadness was generally attributed to hydrogen bonding (MacCarthy and Rice, 1985). Note, that these bands could strongly be influenced by the water content.

2. WN 2922–2926 cm^{-1}: This adsorption band was attributed to asymmetric and symmetric vibrations of aliphatic C–H bonds (e.g., in methyl and methylene groups) and usually superimposed as a shoulder of the broad O–H band (1) (e.g., Ellerbrock et al., 2005).

3. WN 1698–1701 cm^{-1}: This adsorption band was attributed to stretching vibration of the C=O bonds (e.g., in carboxylic acids, cyclic and acyclic aldehydes, and ketones) (van der Marel and Beutelspacher, 1976).

4. WN 1600–1613 cm^{-1}: This adsorption band was assigned to stretching vibrations of aromatic C–C bonds conjugated with C=O or COO– bonds or both that are part of functional groups within unsaturated ketones or amides (MacCarthy and Rice, 1985).

5. WN 1540 cm^{-1}: This adsorption band was assigned to stretching vibrations of C=C double bonds.

6. WN 1400 cm^{-1}: This adsorption band was assigned to C=O and O–H bonds in carboxylic and carbonylic groups (Senesi et al., 2003).

7. WN 1010–960 cm^{-1}: This adsorption band was assigned to Si–O–Si within silicates (Bertaux et al., 1998) and C–O–C bonds within polysaccharides.

The FTIR spectra of the soils (Fig. 2a–2d, top) showed the most intense absorption band at a WN of about 1010 cm^{-1}, mostly indicative of soil minerals (Bertaux et al., 1998) since the SOC content of the soil was <3% (Table 3) and absorption bands in this region were also assigned to Si–O–Si groups. The spectra of the soil samples differed in the intensities of the C–H and C=O absorption bands.

The intensity of the C=O absorption bands in the FTIR spectra of the soil samples (Fig. 2a–2d, top) were much smaller than those in the spectra of the OM-HW (Fig. 2a–2d, center) or OM-PY fractions (Fig. 2a–2d, bottom). The FTIR of the OM-HW fractions from the FYM + N fertilized soils had the highest intensity of the C=O band (Fig. 2a–2d, bottom) and the largest C=O/C–O–C

Table 3. Mean annual input rates of farmyard manure dry matter (FYM) and N (Körschens et al., 1990) as well as the soil organic C (SOC) contents and the cation exchange capacity (CEC) of the soils [CEC(Soil)] and pyrophosphate-soluble organic matter [CEC(PY)] from the differently fertilized soils at Bad Lauchstädt (BL), Groß Kreutz (GK1 and GK2), and Müncheberg (MB) sites.

Site	Fertilizer†	FYM	N	SOC	CEC(Soil)	CEC(PY)
		t ha^{-1} yr^{-1}	kg ha^{-1} yr^{-1}	g kg^{-1}	—— cmol$_c$ kg^{-1} ——	
BL	control	0	0	16.6	21.0	220.6
	N	0	155	23.5	20.9	203.9
	FYM	3.75	75	24.1	21.9	242.8
	FYM + N	3.75	*75+155*	27.0	22.4	229.4
GK1	control			4.2	3.4	100.8
	N	0	200	4.9	3.6	99.8
	FYM	5.0	100	5.5	4.0	123.8
	FYM + N	5.0	*100+200*	7.4	4.6	143.1
GK2	control	0	0	3.8	3.2	95.8
	N	0	105	4.8	3.5	80.8
	FYM	4.15	83	6.1	4.3	127.4
	FYM + N	2.05	*41+125*	5.7	4.0	97.6
MB	control	0	0	4.0	3.7	129.2
	N	0	150	4.5	4.0	114.7
	FYM + N	3.2	*64 +150*	5.5	4.5	139.4

† FYM was applied at BL, GK1, and MB every second year at twice the annual rate before sugarbeet or potato and at GK2 every third year at three times the annual rate before maize. The doses of FYM were applied of the basis of the annual values given in Table 1.

ratios (Table 4) for BL, GK1, and MB; for GK2, the FYM-fertilized soil had the highest intensity of the C=O band and the largest C=O/C–O–C ratio. The differentiation in the C=O/C–O–C ratios according to the kind of fertilization was much stronger for the OM-HW fractions (0.287–0.921) than the soil (0.231–0.343) or OM-PY (0.357–0.687) (Table 4). For the loamy soils, the C=O/C–O–C ratios of the OM-HW fractions were about 10 to 20% smaller than for the sandy soils (Table 4). For GK2, the C=O/C–O–C ratio of the OM-HW fraction from the mineral N treatment was smaller than that from the control.

As for OM-HW, the C=O/C–O–C ratio for OM-PY differed among the fertilization treatments, but the differences between the unfertilized and N plots were relatively small for soils from all sites (Table 4) except MB. The C=O/C–O–C ratios of the OM-PY from FYM plots were larger than those of the OM-PY from the unfertilized control plots, which was most pronounced for the sandy soils. Especially large was the difference between the control and FYM plots for the OM-PY from GK2. Assuming the differently fertilized soils from the same site to be replicate samples, the C=O/C–O–C ratios in the OM of the samples from the four long-term field experiments were compared. The *t*-test indicated that the mean values of the C=O/C–O–C ratio of the OM-HW from the loamy soil was significantly smaller at the 95% level than
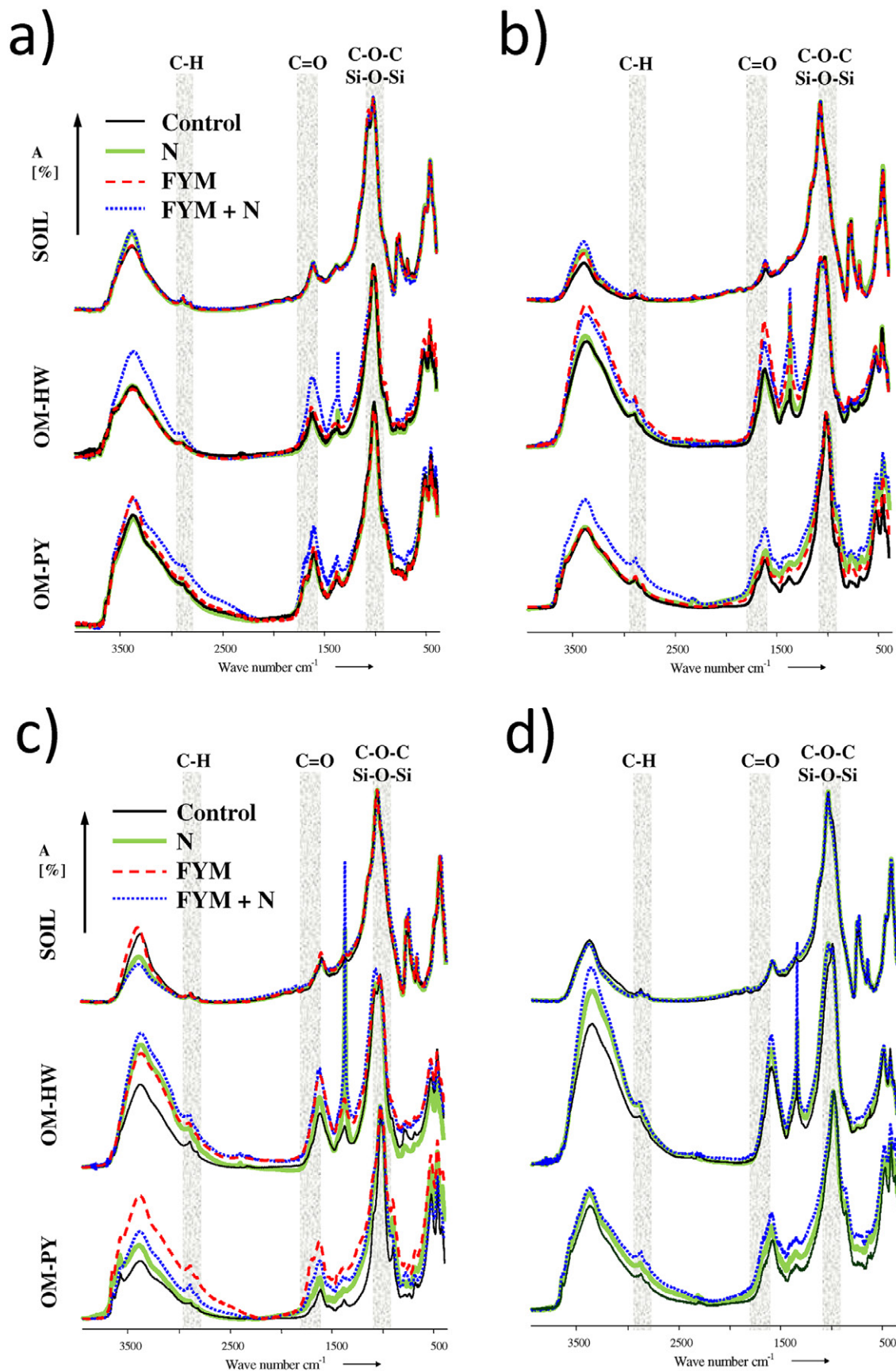
Fig. 2. Fourier-transform infrared spectra of the soil (top) and the water-soluble (OM-HW, center) and pyrophosphate-soluble (OM-PY, bottom) organic matter fractions of samples from the N fertilizer, farmyard manure (FYM), FYM + N, and control plots of the long-term field experiments at (a) Bad Lauchstädt, (b) Groß Kreutz 1, (c) Groß Kreutz 2, and (d) Müncheberg.

the mean C=O/C–O–C ratios of the OM-HW from the sandy soils. For the C=O/C–O–C ratios of the OM-HW, the differences between GK1 and GK2 samples and between GK2 and MB were not significant at the 95% level. For the OM-PY fraction, the C=O/C–O–C ratios from MB were larger than those from BL or GK2 at the 95% level, while the differences between GK1 and GK2 and between BL and GK1 or GK2 were not significant at the 95% level.

For the FYM plots, the CEC of the OM-PY (Table 3) was related to the C=O/C–O–C ratios (Table 4); however, the relationship (not shown) was not as linear as that described by Kaiser et al. (2008) for a sequentially extracted OM(PY) fraction. The OM-PY fraction in this study could have still included water-soluble OM components. Such water-soluble OM components were included in the FTIR, however not in the CEC, because these water-soluble components were probably washed out during the first step of the CEC analysis. Note that the solubility of OM in BaCl solution increased with the C=O group content. Thus, the CEC determined by percolation was related to a smaller number of C=O groups than the number present in the original OM-PY fraction that was analyzed with FTIR spectroscopy.

◆ Discussion

In the following, the usefulness of FTIR and soluble OM fractions for the identification of fertilizer effects on the composition of SOM and soluble OM fractions and their CEC are discussed.

Soil Organic Carbon vs. Cation Exchange Capacity

The larger differences in SOC contents for BL compared with GK and MB (Fig. 1a) could be explained by differences in the clay contents (Table 1), which is also reflected in the CEC values (Table 3). For the soil samples from all four experiments, the CEC values of the fertilized plots tended to be generally larger than those of the control (Fig. 3a). The relative increase in CEC between 0 and 10% for the N plots and 5 to 45% for the FYM plots pointed toward a more positive effect on the CEC of the soil of FYM applications. This effect was more pronounced for the sandy soils at MB and GK than for the loamy soil (BL).

Composition of Hot-Water-Extractable and Pyrophosphate-Extractable Organic Matter

The significantly smaller C=O/C–O–C ratio in the OM-HW fraction from the loamy soil than the sandy soils (Table 4) could be explained by interactions between C=O groups in the OM and soil minerals (Aquino et al., 2007). The hot water solubility of C=O-rich OM fractions decreased with clay content because of larger interactions between the OM and soil minerals—mainly

Table 4. The ratios between the C=O and C–O–C intensity bands (C=O/C–O–C) and between C–H and C=O bands (C–H/C=O) determined from Fourier-transform infrared spectra of the soil and hot-water-soluble (HW) and pyrophosphate-soluble (PY) organic matter (OM) fractions from the differently fertilized soils at Bad Lauchstädt (BL), Groß Kreutz (GK1 and GK2), and Müncheberg (MB) sites. For both OM fractions a soil/liquid ratio of 1:10 was used.

Site	Fertilizer†	C=O/C–O–C			C–H/C=O		
		Soil	OM-HW	OM-PY	Soil	OM-HW	OM-PY
BL		*	*	*	*	*	*
	control	0.311	0.287	0.414	0.175	0.058	0.051
	N	0.324	0.312	0.458	0.131	0.072	0.084
	FYM	0.304	0.451	0.417	0.189	0.075	0.057
	FYM + N	0.326	0.548	0.481	0.180	0.070	0.057
GK1		*	*		*	*	*
	control	0.324	0.409	0.477	0.125	0.162	0.176
	N	0.306	0.536	0.353	0.112	0.121	0.121
	FYM	0.343	0.676	0.629	0.145	0.085	0.100
	FYM + N	0.290	0.710	0.500	0.128	0.097	0.117
GK2		*	*	**	*		*
	control	0.231	0.588	0.393	0.086	0.102	0.204
	N	0.275	0.574	0.475	0.110	0.103	0.119
	FYM	0.288	0.921	0.687	0.120	0.063	0.138
	FYM + N	0.267	0.848	0.448	0.143	0.095	0.160
MB			*	**			
	control	0.290	0.676	0.452	0.172	0.083	0.108
	N	0.294	0.774	0.621	0.173	0.072	0.097
	FYM + N	0.293	0.890	0.615	0.139	0.071	0.147

* Significant differences between sites at the 0.05 level.
** Significant differences between sites at the 0.01 level.
† Application of FYM at BL, GK1, and MB every second year at two times the annual rate before sugarbeet or potato and at GK2 every third year at three times the annual rate before maize. The doses of FYM were applied on the basis of the annual values given in Table 1.

because the reactive mineral surface areas increased with the clay-sized particles content. Thus, the sodium pyrophosphate preferably extracted C=O-rich OM, while hot water extracted mainly OM with a smaller amount of C=O groups. For BL, the missing increase in the C=O/C–O–C ratio of the OM-PY for FYM compared with the control (Table 4) could be explained by the relatively high clay content (Table 1) that limited the extraction of OM rich in C=O groups.

The stronger dependency of the OM-HW than the OM-PY composition (Table 4) on the kind of fertilization found for GK2 than for GK1 confirmed the hypotheses that OM-HW and OM-PY reflected different short- and long-term effects of fertilization on OM dynamics. Note that the plots at GK2 received FYM in spring shortly before the sampling, while GK1 received the FYM in the year before. The OM-HW from the FYM-fertilized soils at GK2 should therefore reflect mostly the properties of the FYM. The results in Table 4 confirmed that
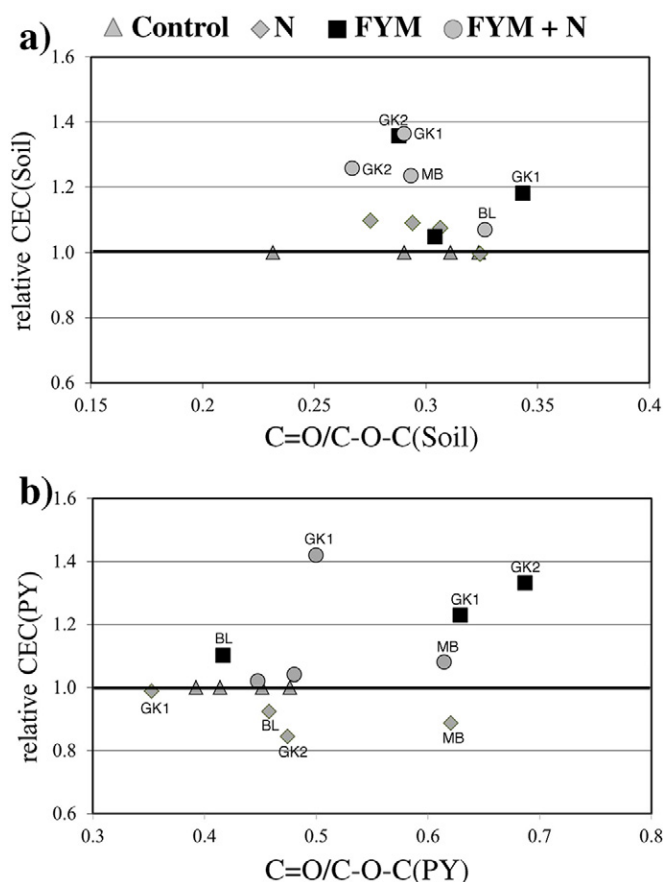
Fig. 3. The cation exchange capacity (CEC) of the N fertilizer, farmyard manure (FYM), and FYM + N plots relative to that of the control vs. the C=O/C−O−C band ratio in Fourier-transform spectra for (a) the soil [relative CEC(Soil) vs. C=O/C−O−C(Soil)] and (b) the pyrophosphate-soluble organic matter fraction [relative CEC(PY) vs. C=O/C−O−C(PY)] of samples from long-term field experiments at Bad Lauchstädt (BL), Groß Kreutz (GK1 and GK2), and Müncheberg (MB).

for GK2 this expected stronger (short-term) effect of FYM fertilization was observed more strongly in the OM-HW fraction and less in the OM-PY fraction. However, for the composition of OM-PY and the OM of the soil, the differences caused by the FYM application were smaller between GK1 and GK2, indicating that OM-PY fractions were less dynamic than OM-HW and more reflective of longer term effects. Although the OM-HW fraction could more easily be analyzed, it could contain artifacts formed by thermal denaturation of proteins, among other components. Artifacts in the OM-HW fraction would limit the possibility of identifying shorter or longer term effects of fertilizer treatments on OM composition, as discussed by von Lützow et al. (2007).

Cation Exchange Capacities of Soil Organic Matter and Pyrophosphate-Extractable Organic Matter

The CEC values of the OM-PY fraction (80.8–242.8 cmol$_c$ kg^{-1}; Table 3) were on the same order of magnitude as those found

previously for sequentially extracted OM-PY fractions (86–354 cmol$_c$ kg^{-1}; soils from BL, Halle, Rotthalmünster; Kaiser et al., 2008); and for the fertilizer treatments, similar differences in the CEC of the soil and that of the OM-PY fraction were reported. The similarity indicated a long-term fertilization effect on the CEC of the OM-PY. The ratios between CEC(PY) and CEC(Soil) of 23 to 31 for BL observed here were larger than those of 1 to 18 reported by Kaiser et al. (2008) for the sequentially extracted OM-PY because of the contribution of the water-soluble components still present in the OM-PY fraction analyzed in this study, among other differences in the experimental conditions.

The CEC of the OM-PY relative to the unfertilized control [relative CEC(PY)] was >1 for FYM plots and <1 for mineral N plots (Fig. 3b). For FYM, the CEC of the OM-PY was about 5 to 35% larger than that of the unfertilized soil (Fig. 3b). This increase is on the same order of magnitude as that of FYM for the soil CEC (Fig. 3a). For the mineral N plots, the CEC of the OM-PY was up to 18% smaller than the CEC of the unfertilized control. Note that the CEC could not be determined for OM-HW with standard methods. The N and FYM + N fertilization appeared to result in somewhat similar effects on the composition of SOM (Fig. 3a) and OM-PY, the latter excepting GK1.

Cation Exchange Capacity vs. Carbon–Oxygen Double-Bond Groups of Pyrophosphate-Extractable Organic Matter

The hypothesis that long-term mineral and organic fertilization changed the OM composition was tested by comparing the relative intensity of C=O bands in the FTIR spectra of the OM-PY fraction with the relative CEC of this fraction (Fig. 3b). For all soils, the C=O/C−O−C ratios and the CEC values of the OM-PY were highest for FYM; and the CEC of the OM-PY generally increased with C=O/C−O−C ratios depending on fertilization (Table 2) and soils (Table 1). However, the relationship between the C=O/C−O−C of OM-PY (Table 4) and the CEC of OM-PY (Table 3) was not as linear as previously reported (Kaiser et al., 2008). In contrast to the absolute values (Table 3), the relative values of the CEC of OM-PY (i.e., relative to the values of the unfertilized control treatment) suggested an increase with C=O/C−O−C ratios for FYM and a decrease for the pure mineral N fertilization (Fig. 3b). And for all sandy soils, the FYM plots had a relatively larger increase in the CEC of the OM-PY than the FYM treatment on the loamy soil. This could be explained by the lower OM-PY extraction yields for loamy soils (e.g., Ellerbrock and Kaiser, 2005), which also reflected a stronger interaction between C=O groups and soil minerals (Aquino et al., 2007). This stronger interaction could have led to a selection of OM-PY in the extracted fraction that was depleted in C=O groups. The results indicate that the C=O/C−O−C ratio in the FTIR spectra of OM-PY could be a possible indicator of long-term fertilization induced changes in OM composition.

Fertilization and Potential Wettability of Organic Matter and Its Fractions

Not only the presence and amount of sorption sites for cations but also the three-dimensional arrangement of C=O groups (Stevenson, 1994; Coles and Yong, 2006) and the wettability of the surfaces are preconditions for "effective" sorption capacity and exchange between OM and cations in the soil solution. With respect to OM wettability, the FTIR analyses allowed the determination of potential wettability in terms of the C–H/C=O ratio (Ellerbrock et al., 2005). For the unfertilized control, a two to four times smaller C–H/C=O ratio in the OM(PY) from BL than GK1, GK2, and MB (Table 4) indicated the largest potential wettability for OM-PY from the loamy BL soil. The BL plots had also the largest CEC(PY) values (Table 3). The relatively larger potential wettability (i.e., smaller C–H/C=O ratios) together with the larger CEC of the OM-PY for BL indicated the highest effective sorption capacity of the OM from this soil. Despite the lower potential wettability of the OM-PY fraction, the long-term FYM fertilization led to an increase in the CEC of the OM-PY compared with that of the control. In contrast, for the N-fertilized soils, the relative CEC decreased (Fig. 4b). The results indicate that both ratios, C–H/C=O and C=O/C–O–C, obtained with FTIR spectroscopy qualitatively reproduced fertilization-induced long-term changes in the OM composition.

Applicability of Methods

These preliminary results indicated that long-term fertilization effects were reflected mostly in changes in the composition of the OM-HW and OM-PY fractions. Such differences in OM composition could be analyzed by using FTIR spectroscopy. We assumed that the CEC of the OM-PY was related to the composition of this OM fraction. The composition of the OM-HW seemed to reflect—as expected—mostly short-term effects, while the composition of the OM-PY could be used to estimate the long-term effects. In this study, only the general applicability of the methods for the study of dynamics in OM composition and not the quantitative differences were the focus. However, for the identification of significant differences, a strategy that considers a randomized sampling of replicate plots at each experimental site is needed. Additionally, it will become necessary to separately analyze seasonal and longer term changes in the OM composition.

◦ Conclusions

The composition of the OM-HW and OM-PY fractions was identified to reflect shorter and longer term changes due to crop and soil management options. These soluble OM fractions seemed to reflect the dynamics of the OM composition better than the SOM in total. The combination of FTIR spectroscopy with CEC analysis determined on the OM fractions allowed an additional differentiation of the OM dynamics between the fertilization treatments and soils.
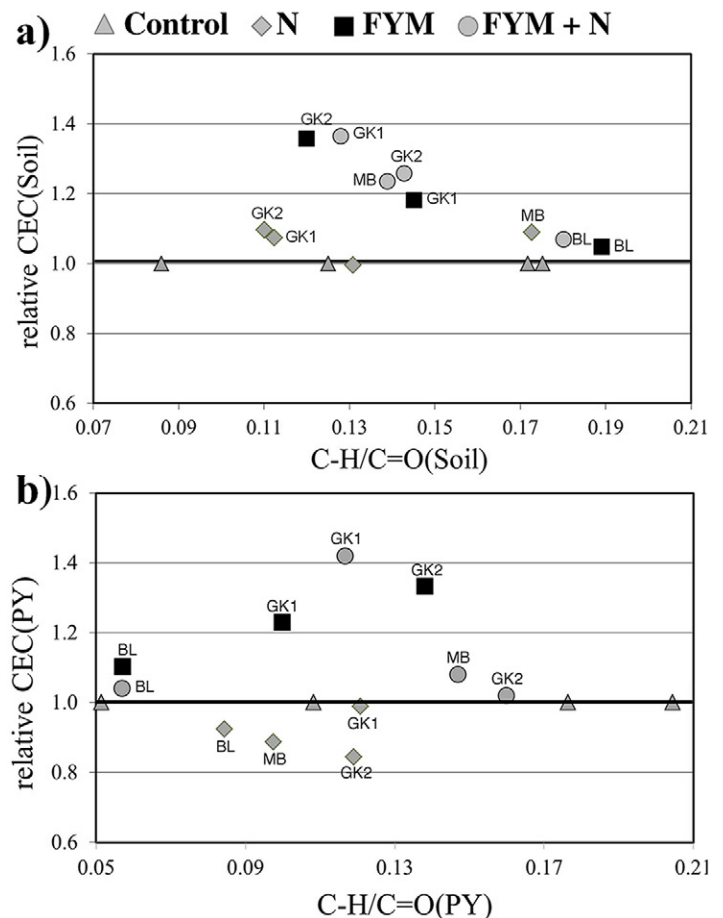

Fig. 4. The cation exchange capacity (CEC) of the N fertilizer, farmyard manure (FYM), and FYM + N plots relative to that of the control vs. the C–H/C=O band ratio in Fourier-transform spectra for (a) the soil [relative CEC(Soil) vs. C–H/C=O(Soil)] and (b) the pyrophosphate-soluble organic matter fraction [relative CEC(PY) vs. C–H/C=O(PY)] of samples from long-term field experiments at Bad Lauchstädt (BL), Groß Kreutz (GK1 and GK2), and Müncheberg (MB).

The results confirmed that the composition and the CEC of the OM-PY were affected more strongly by long-term fertilization than the composition and the CEC of the SOM. The mineral N application reduced the relative CEC of the OM-PY, while the FYM application resulted in a long-term increase. The results suggest that a better understanding of the dynamics of SOM quality requires the analysis of SOM and OM fractions in addition to the analysis of the SOM content. The OM-PY fraction was most sensitive and could be used to identify and characterize the long-term changes in the OM composition. The results also demonstrate that the composition of OM modified the CEC and the potential wettability of the SOM and OM fractions. This study focused on exploring the possibilities of the FTIR analysis of the OM composition. A more quantitative analysis of long-term differences in OM composition among treatments would require more replicate samples, probably additional soils, and a seasonal differentiation to separate between shorter and longer term changes. However, this was beyond the scope of the present study.

Acknowledgments

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