

Distribution of total and clay-associated organic matter in profiles of arable loamy sand Spodosol

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Abstract

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Stabilisation of soil organic matter (SOM) in clay particles is important when the effect of management practices on organic carbon sequestration is being assessed. The objective of the present study was to quantify the differences in total SOM content in bulk soils and clay particles along four soil profiles under perennial grass-red clover and vetch-oat mixtures with and without farmyard manure (FYM) amendment. The results have shown that the highest accumulation of total SOM in bulk soil was observed in top horizons of soils amended with FYM for both crops. The total SOM content in bulk soil decreased down the soil profile but on average it was higher in the FYM-amended soils. Primary minerals (quartz, feldspar), as compared to phyllosilicates (micas and chlorite), dominated in clay-sized fractions of soils. The highest clay-associated SOM content was also determined in the topsoil horizons. A more pronounced effect of FYM on the content of clay-associated SOM was observed in the topsoil under vetch-oat mixture. The clay-associated SOM content decreased with soil depth and negatively correlated to abundance of micas ($r = -0.50$ to -0.99).

Keywords

crops, farmyard manure, soil profile, total and clay-associated organic matter

Introduction

Maintenance of required levels of soil organic matter (SOM) content is one of the integral aims of soil management practices applied for achieving sustainable soil quality. Labile organic substances are considered to be functionally important agents in carbon biochemical cycling, turnover of nutrients and water-stable aggregates in soils (CAMBARDELLA and ELLIOTT, 1992; BALASHOV and BUCHKINA, 2011; TOBIAŠOVÁ, 2011). However the efficiency of any management practice in arable soils is mainly quantified in terms of sustainable crop yields and accumulation and protection of inert humic substances (humic and fulvic acids, humins) of SOM. These components of SOM, apart from nonhumic aliphatic and alkyl carbon compounds, are mainly associated with silt- and clay-sized fractions of soils and therefore are stronger protected against the

microbial-induced decomposition (KÖGEL-KNABNER et al., 2008) as silt and clay particles show high affinity to adsorption of more oxidized organic substances on mineral surfaces (VON LÜTZOW et al., 2008). A high SOM dynamics in coarse-textured soils can be induced by fast changes in the content of easily decomposable particulate organic matter associated with sand-sized fractions (CAMBARDELLA and ELLIOTT, 1992). In the fine-textured soils the dynamics in SOM content is mainly related to the accumulation and loss of stable, humified SOM in silt- and clay-sized fractions (GALANTINI et al., 2004). Each soil demonstrates a different capacity of saturation by SOM within soil mineral matrix. HASSINK (1997) reported that while the total SOM content in sandy grassland soils was higher than that in arable soils, there were no differences in clay- and silt-associated SOM content, i.e. the total SOM content in these particles could have reached its maximum. The

results of this research also showed that dominant clay minerals did not affect the relationships between the SOM content in the soil size fractions of $<20\ \mu\text{m}$ and the amount of these soil size fractions. Therefore application of different rates of farmyard manure (FYM) can result in different contents of total SOM and its labile components in bulk soils but may not lead to any differences in the SOM content in silt and clay particles if they have a low saturation capacity. According to BALDOCK and SKJEMSTAD (2000), the mineralogy of clay particles exerts its control over protection of SOM through its effects on the type and density of active sites capable of adsorbing organic materials. The results of WISEMAN and PÜTTMANN (2006) noted that the SOM content significantly correlated with kaolinite and illite, but did not demonstrate any significant correlations with smectite content in Antrosol, Vertisol and Gleysol Chernozem.

The objective of the present study was to quantify the differences in total SOM content in bulk soil and clay particles within four soil profiles under mixture of perennial grass and red clover, and vetch-oat mixture with and without application of FYM.

Material and methods

Soil sampling was carried out at the experimental station of the Agrophysical Research Institute in the St. Petersburg region of Russia ($59^{\circ}34'N$, $30^{\circ}08'E$) in May of 2011. In the studied region average annual air temperatures reached $+5.2$, $+5.7$, $+6.2$, $+5.0$, $+4.8$ and $+6.0\ ^{\circ}\text{C}$ in 2006, 2007, 2008, 2009, 2010 and 2011, respectively. Average air temperatures during the growing seasons (May–September) of the same years were equal to: $+14.8$, $+14.4$, $+12.9$, $+14.1$, $+16.2$ and $+15.6\ ^{\circ}\text{C}$, respectively. During the growing season of 2011 average daily air temperature ranged from $+1.9$ to $+26.8\ ^{\circ}\text{C}$.

Annual precipitation was equal to: 959; 914; 1,269; 1,356; 1,026 and 1,263 mm in 2006, 2007, 2008, 2009, 2010 and 2011, while during the growing seasons of these years amount of precipitation reached: 456, 555, 627, 778, 634 and 784 mm, respectively.

The soil was typical for the studied arable area: loamy sand Spodosol. Parent material of the soil was presented by quaternary sand, gravel and clay deposits in ground moraines. A distribution of sand-, loam- and clay-sized fractions in genetic horizons of the loamy sand Spodosol is shown in Fig. 1.

The field experiment was established in 2003 on 1.5 ha plot. The plot was divided into three 0.5 ha ($50 \times 100\text{m}$) sub-plots. The first sub-plot did not receive any FYM. The second sub-plot received, in total, $300\ \text{t ha}^{-1}$ of FYM ($80\ \text{t ha}^{-1}$ in 2003, $80\ \text{t ha}^{-1}$ in 2004, $60\ \text{t ha}^{-1}$ in 2005 and $80\ \text{t ha}^{-1}$ in 2009) and the third sub-plot received, in total, $700\ \text{t ha}^{-1}$ of FYM ($160\ \text{t ha}^{-1}$ in 2003,

$320\ \text{t ha}^{-1}$ in 2004, $60\ \text{t ha}^{-1}$ in 2005 and $160\ \text{t ha}^{-1}$ in 2009). In order to establish two crop rotations, each of the three sub-plots was divided into two parts in 2006. Then each part was divided into nine parallel lines representing mineral fertilizer treatments. In the end, each sub-plot part included 3 replicates without mineral fertilizers, 3 replicates with medium rate of mineral fertilizers and 3 replicates with high rate of mineral fertilizers (OLENCZENKO et al., 2012). There were two crop rotations grown in the experiment. The first one consisted of: white cabbage (*Brassica oleracea* L.), carrot (*Daucus carota* L.), beetroot (*Beta vulgaris* L.), spring barley (*Hordeum vulgare* L.) with undersown mixture of perennial grass and red clover (*Phleum pratense* L. and *Trifolium pratense* L.), mixture of perennial grass and red clover (*Phleum pratense* L. and *Trifolium pratense* L.) of first and second year. The second crop rotation included: spring barley (*Hordeum vulgare* L.) with undersown mixture of perennial grass and red clover (*Phleum pratense* L. and *Trifolium pratense* L.), mixture of perennial grass and red clover (*Phleum pratense* L. and *Trifolium pratense* L.) of first and second year, winter rye (*Secale cereale* L.), potato (*Solanum tuberosum* L.), vetch-oat mixture (*Vicia sativa* L. and *Avena sativa* L.).

Soil sampling was carried out in the last year of the two crop rotations and only on the sub-plots without FYM (“no FYM”) and the sub-plots with the highest FYM rate ($700\ \text{t ha}^{-1}$; “FYM”). Four soil profiles were dug in the centers of the lines without mineral fertilizer incorporation. Statistically it would be more reasonable to have more soil profiles but we had to work under very strict conditions not allowing us to destroy significant part of the whole field experiment. Totally, twenty-three composite soil samples were taken from the soil profiles. One composite soil sample consisted of twelve sub-samples collected from a particular soil horizon around a soil profile. All composite soil samples were air-dried and passed through 1-mm or 2-mm sieve. All the analyses were conducted in three replicates and mean values are being used in the discussion.

A pipette method was used to determine amounts of sand ($1,000\text{--}10\ \mu\text{m}$), silt ($10\text{--}1\ \mu\text{m}$) and clay ($<1\ \mu\text{m}$) particles in the soil samples (RASTVOROVA, 1983). Besides, clay particles ($<1\ \mu\text{m}$) were subsequently extracted from soil samples by sedimentation and electrophoresis methods. A 24-h sedimentation of soil samples in water was performed in 1-litre glass columns according to the pipette method (RASTVOROVA, 1983). Before the sedimentation, soil samples were subjected to ultrasonic dispersion in water for 15 min at 315 W using the Branson 450 digital ultrasonic sonifer equipped with a tapped disruptor horn (13 mm in diameter). After the sedimentation, clay particles-water suspension ($500\ \text{cm}^3$ in volume) was placed into a work cell of electrophoresis device equipped with a Cu-anode and a Pb-cathode (MOISEEV et al., 2012). Electrophoretic extraction of

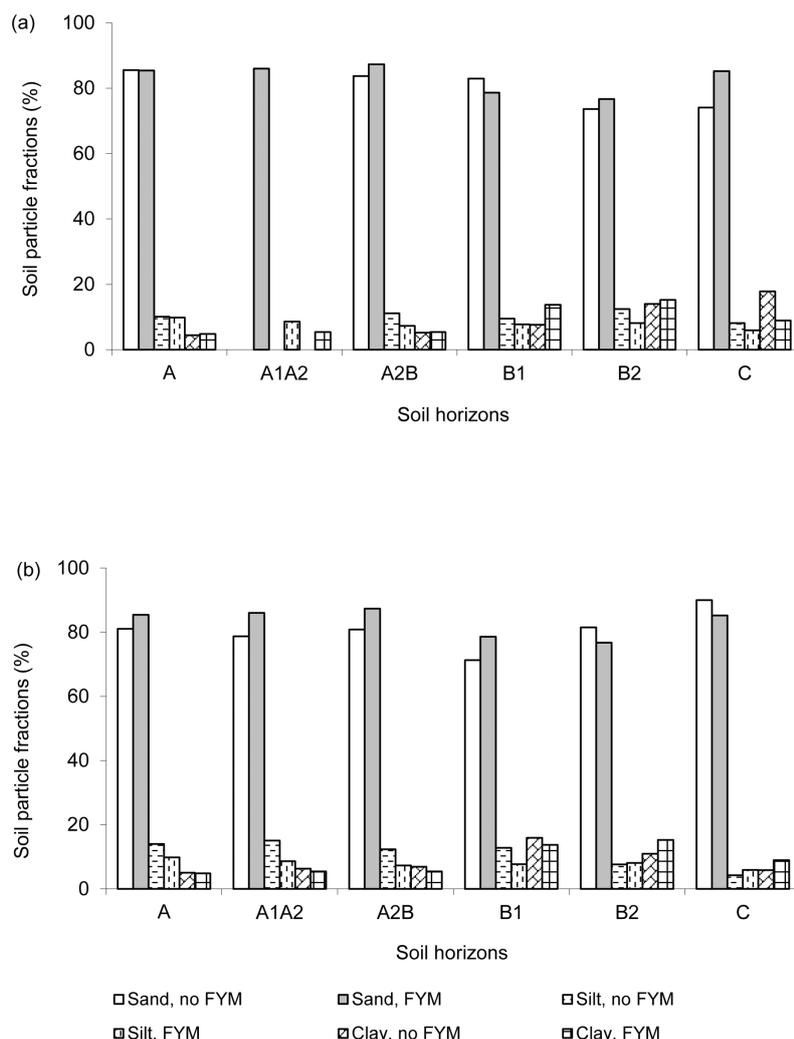


Fig. 1. Distribution of amount of sand, silt and clay size fractions in the profiles of loamy sand Spodosol in the first (a) and second (b) crop rotation on the no FYM and FYM sub-plots.

clay particles was performed at voltage of 320 V, current of 0.25 A and temperature of 20–24 °C and did not exceed 18 min. Then the clay particles were carefully detached from the anode and dried in an oven at temperature of 35–40 °C. The mineral composition of the clay particles was assessed using X-ray diffraction (XRD) analysis of oriented samples using DRON-3 X-ray diffractometer with Cu K α tube (30 kV, 30 mA). Samples were scanned from 3° to 40°. Quartz, potassium feldspar and plagioclase were identified by the reflections at 0.424, 0.324 and 0.318 nm, respectively. Dioctahedral (muscovite), trioctahedral (biotite) and interlayer deficient (illite) micas were recognized by the reflections at 0.50, 1.00 and 1.08 nm, respectively. Chlorite was identified at the 1.41 nm reflection. Standard reference tables were used for interpretation of the XRD results (FRANK-KAMENETZKY, 1983).

The total SOM content in the soil samples (later called as bulk soil) and clay-associated SOM content were measured by the Tjurin method of acid dichromate

digestion (RASTVOROVA et al., 1995). Soil pH values were measured by a pH-meter at 1 : 2.5 ratio of soil to 1 N KCl solution (RASTVOROVA et al., 1995). Amounts of exchangeable P₂O₅ and K₂O in soil samples were determined by a KIRSANOV method modified by CINAO using 0.2M HCl solution for the extraction as well as photoelectric colorimeter and flame photometer for their quantitative determination (GOST SSSR, 1991).

In the first crop rotation, the agrochemical properties of the FYM and no FYM soil under perennial grass and red clover mixture of second year were measured only in the topsoil (A horizon, 0–23 cm). The FYM and no FYM topsoils were respectively, characterized by: pH (KCl) – 6.1 \pm 0.1 and 5.3 \pm 0.1; exchangeable P₂O₅ – 668 \pm 18 and 217 \pm 10 mg kg⁻¹ soil; exchangeable K₂O – 290 \pm 12 and 120 \pm 6 mg kg⁻¹ soil (OLENCZENKO et al., 2012).

In the second crop rotation, the agrochemical characteristics of the FYM and no FYM soil under vetch-oat mixture were measured in 2011 not only in the topsoils

but also in the lower soil horizons. For the topsoils values of soil pH, contents of exchangeable P_2O_5 and K_2O were equal to: 6.3 ± 0.1 and 5.3 ± 0.1 , 515 ± 11 and $237 \pm 15 \text{ mg kg}^{-1}$ soil, 275 ± 5 and $89 \pm 4 \text{ mg kg}^{-1}$ soil, respectively, for the FYM and no FYM soil (OLENCZENKO et al., 2012). According to VITKOVSKAYA et al. (2014), the agrochemical characteristics in the underlying soil horizons varied in the ranges of: 4.1 ± 0.1 to 6.0 ± 0.1 and 3.9 ± 0.1 to 5.4 ± 0.1 (pH), 108 ± 4 to 553 ± 11 and 122 ± 3 to $295 \pm 11 \text{ mg kg}^{-1}$ soil (exchangeable P_2O_5), 81 ± 4 to 221 ± 11 and 19 ± 1 to $120 \pm 5 \text{ mg kg}^{-1}$ soil (exchangeable K_2O), respectively, for the FYM and no FYM soils.

Strength of the relationships between the sets of selected soil parameters in each soil profile was assessed with Spearman's rank correlation coefficients (Table 1) as the studied parameters were related by non-linear, monotonic functions.

A significance of effects of two independent factors (soil horizon, FYM amendment) on the means of the selected soil data sets was estimated by two-way analysis of variance (ANOVA) without repetitions at $p \leq 0.05$ (Table 2).

Results

The high-rate application of FYM resulted in higher contents of exchangeable P_2O_5 and K_2O in the amended topsoil layers under both crop rotations. If the two soil profiles of the second crop rotation were assessed together, the results of two-way analysis of variance showed that FYM amendment significantly ($p < 0.05$) affected only a content of exchangeable K_2O in the whole soil profile (Table 2). Soil horizons showed an insignificant influence only on the profile distributions of exchangeable P_2O_5 and K_2O content.

Our results demonstrated that the FYM incorporation had caused an increase in total SOM content in bulk soil in the topsoil layers (Fig. 2).

For the first crop rotation the highest total SOM content in the bulk soil of the no FYM sub-plot was observed in the topsoil. In the 22–32 cm layer (A2B horizon) it was 15.3 times lower with a slight increase in other underlying layers. In the soil of the FYM sub-plot the total SOM content in bulk soil in the 0–23 cm layer (A horizon) was also high but did not differ from that in the 23–33 cm layer (A1A2 horizon), declined

Table 1. Results of Spearman's rank correlations between parameters: soil organic matter content in bulk soil (SOMbs), clay-associated organic matter content (SOMcl), clay content (Cl), intensities of reflection of primary minerals (Pm) and micas (Mc) in a loamy sand Spodosol in the first and second crop rotation on the no FYM and FYM sub-plots

| Crop rotation No., FYM amendment | First rotation, no FYM | | First rotation, FYM | | Second rotation, no FYM | | First rotation, FYM | |
|-------------------------------------|---------------------------|----------|---------------------|----------|----------------------------|----------|---------------------|----------|
| | <i>r</i> | <i>p</i> | <i>r</i> | <i>p</i> | <i>r</i> | <i>p</i> | <i>r</i> | <i>p</i> |
| SOMbs vs. SOMcl | 0.45 | 0.19 | 0.08 | 0.80 | 0.66 | 0.16 | 0.71 | 0.11 |
| SOMcl vs. Pm | 0.40 | 0.50 | -0.09 | 0.87 | -0.37 | 0.47 | 0.14 | 0.79 |
| Mc vs. Pm | -0.70 | 0.19 | -0.09 | 0.87 | 0.37 | 0.47 | -0.14 | 0.79 |
| Mc vs. Cl | 0.90 | 0.04* | 0.58 | 0.23 | 0.84 | 0.04* | 0.76 | 0.08 |
| Pm vs. Cl | -0.90 | 0.04* | -0.03 | 0.95 | 0.06 | 0.91 | -0.58 | 0.23 |

Significant differences at * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$.

Table 2. Changes in soil properties in response to effects of soil horizon layout and FYM amendment

| Factor | Parameters | | | | | | | |
|---------------|--------------------------------------|--------------------------------|--------------|---------------------|-------|----------|----------|--------|
| | Total SOM content in bulk soil | Clay-associated SOM content | Clay content | Primary minerals | Micas | Chlorite | P_2O_5 | K_2O |
| Horizon | 0.02* | 0.001*** | 0.01** | 0.68 | 0.04* | 0.44 | 0.11 | 0.17 |
| Layout | | | | | | | | |
| Fertilization | 0.20 | 0.24 | 0.70 | 0.75 | 0.52 | 0.03* | 0.20 | 0.04* |

Significant differences at * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$, two-way ANOVA.

by 2.8 times only in the 33–50 cm layer (A2B horizon). However the amounts of clay- and silt-sized fractions in these horizons did not differ from those in the A and A1A2 horizon (Fig. 1). Our results also showed a higher total SOM content in bulk soil in the illuvial B1 horizons than in the podzolic A2B ones only in the profile on the no FYM sub-plot. There were higher values of total SOM content in the bulk soil in B2 and C horizons than in the B1 horizon (Fig. 2).

On average, the total SOM content in bulk soil within the soil profile was higher on the FYM sub-plot than on the no FYM sub-plot. In the second crop rotation, the total SOM content in bulk soil showed the similar values in the 0–23 cm (A horizon) layers of the FYM and no FYM sub-plots. In the 22–33 cm layers (A1A2 horizons) the values slightly increased in the no FYM soil and slightly declined in the FYM soil.

There was the substantial decrease in total SOM content in bulk soil in the A2B horizons on both sub-

plots. In other three underlying layers the total SOM content in bulk soil, on average, showed slightly higher values in the FYM soil.

The clay-associated SOM content was higher in the upper 50 cm part of the soil profiles (Figs 2 and 3). In contrast to the total SOM content in bulk soil, the FYM amendment has resulted in little differences in the clay-associated SOM contents in the 0–23 cm layers (A horizon) (Fig. 3). The content of clay-associated SOM in the FYM soil in the first crop rotation slightly increased in the 22–33 cm layer (A1A2 horizon). However, the difference was much higher in the FYM soil in the second crop rotation. The clay-associated SOM content in the topsoil layers was on average higher in the second than in the first crop rotation. A drastic decrease in the clay-associated SOM content was observed in the A2B horizons of all the profiles. In the underlying soil horizons (depths of 48–168 cm) the clay-associated SOM content showed much lower val-

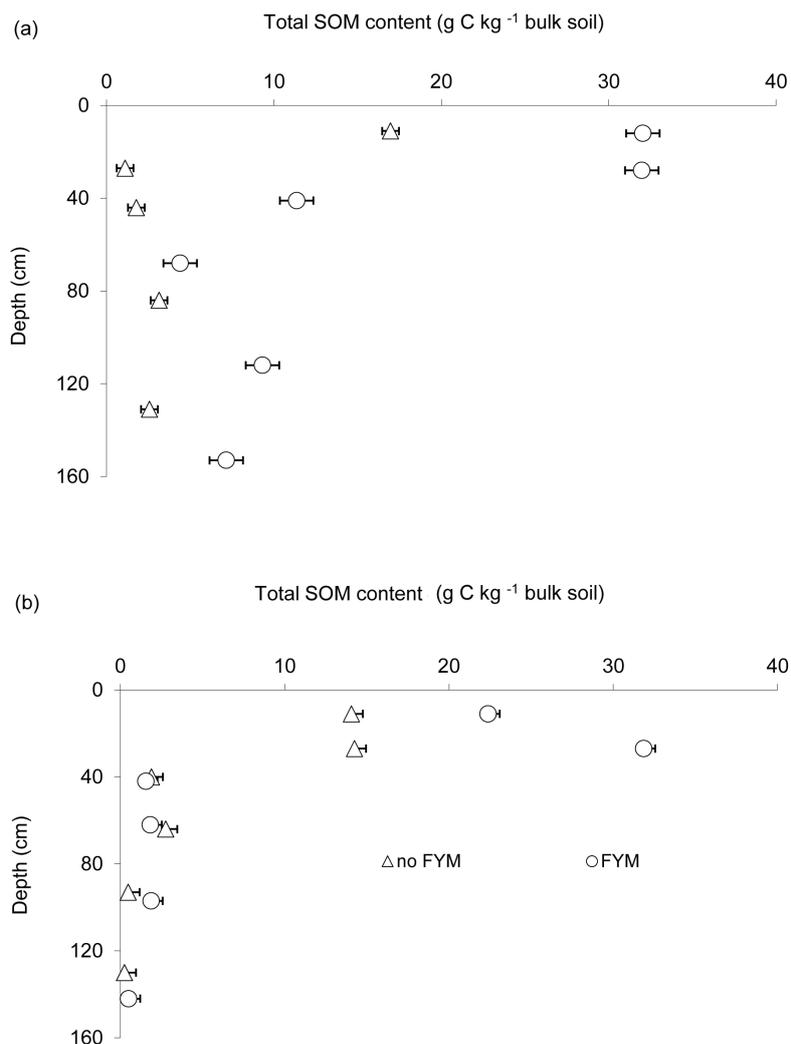


Fig. 2. Distribution of total SOM content in bulk soil in the profiles of loamy sand Spodosol in the first (a) and second (b) crop rotation on the no FYM and FYM sub-plots (horizontal bars are standard deviations at $p \leq 0.05$).

ues except for that in the C horizon on the FYM soil in the first crop rotation. Spearman's rank correlation coefficients between the clay-associated SOM content and total SOM content in bulk soil within the whole soil profiles were positive but insignificant in the first crop rotation on the no FYM and FYM sub-plot, as well as in the second crop rotation on both sub-plots (Table 1). The results of two-way analysis of variance demonstrated that soil horizons significantly and FYM amendment insignificantly affected the clay-associated SOM contents in the second crop rotation (Table 1).

All the soil profiles demonstrated a uniform distribution of sand-sized fraction (Fig. 1). There were only trends in a decrease of silt-sized fraction amounts and in an increase of clay-sized fraction amounts with increasing depth. Among the soil minerals associated with the clay-sized fraction, only the abundance of micas showed positive Spearman's rank correlations with clay content in the soil profiles on the no FYM and FYM sub-plots in the first crop rotation, as well as on the no FYM and FYM sub-plots in the second crop rotation

(Table 1). Results of the two-way analysis of variance demonstrated that soil horizons significantly affected the distribution of clay-sized fraction and micas abundance in the second crop rotation (Table 2).

Primary minerals including quartz, potassium feldspar and plagioclase have dominated in the assemblage of soil minerals in the studied soil profiles (Table 3).

There was not any clear distribution of primary minerals within the four soil profiles. Two-way analysis of variance showed insignificant effects of soil horizons and FYM amendment on the abundance of primary minerals in the second crop rotation (Table 2).

In contrast to the profile distribution of primary minerals, the abundance of micas in soil profiles increased with the depth (Table 3). There were negative Spearman's rank correlations between the intensities' reflection of micas and the clay-associated SOM content in all the soil profiles (Table 1). The results of two-way analysis of variance showed that soil horizons significantly and FYM amendment insignificantly affected the abundance of micas in the soil profiles of the second

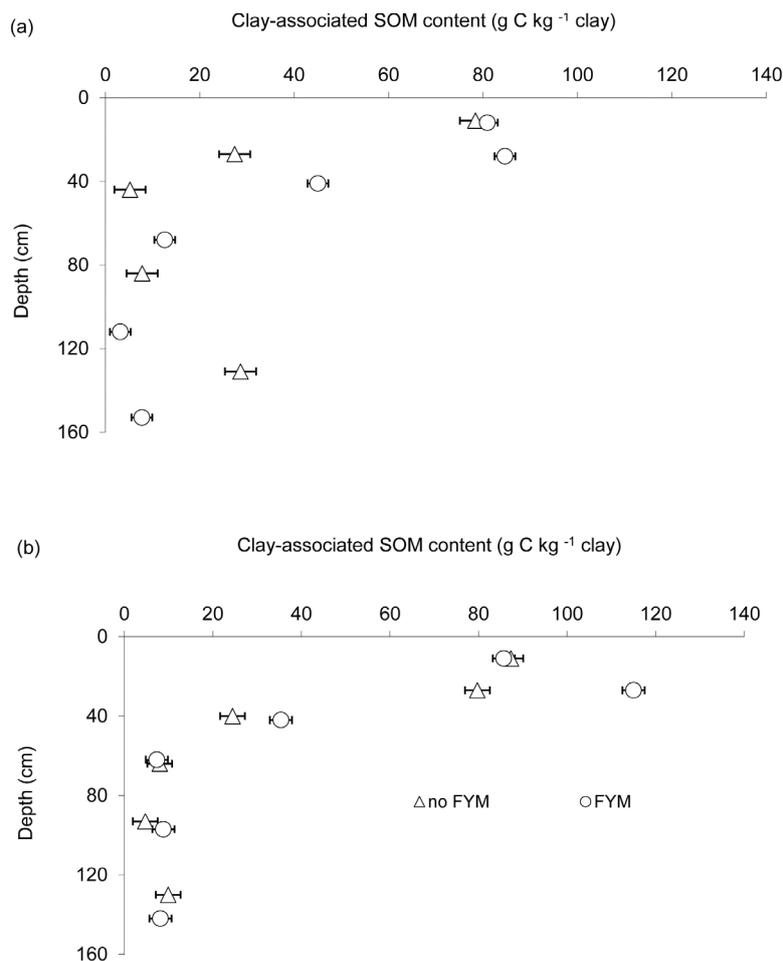


Fig. 3. Distribution of clay-associated SOM content in the profiles of loamy sand Spodosol in the first (a) and second (b) crop rotation on the no FYM and FYM sub-plots (horizontal bars are standard deviations at $p \leq 0.05$).

Table 3. Profile distribution of intensities of reflections of primary and phyllosilicate minerals in clay fraction (<1 µm) of a loamy sand Spodosol in the first and second crop rotation on the no FYM and FYM sub-plots (mean value ± standard deviation)

| Treatment, horizon | Depth (cm) | Primary minerals (impulse s ⁻¹) | Micas | Chlorite |
|------------------------------|------------|---|-------------|----------|
| First crop rotation, no FYM | | | | |
| A | 0–22 | 3,307 ± 166 | 155 ± 8 | 152 ± 7 |
| A2B | 22–32 | 3,149 ± 226 | 133 ± 15 | 172 ± 12 |
| B1 | 32–57 | 1,823 ± 120 | 185 ± 13 | 0 |
| B2 | 57–112 | 2,865 ± 212 | 1,009 ± 55 | 287 ± 22 |
| C | 112–150 | 1,623 ± 107 | 898 ± 59 | 0 |
| First crop rotation, FYM | | | | |
| A | 0–23 | 3,028 ± 241 | 0 | 0 |
| A1A2 | 23–33 | 2,926 ± 210 | 665 ± 46 | 142 ± 12 |
| A2B | 33–50 | 2,945 ± 214 | 890 ± 79 | 0 |
| B1 | 50–85 | 1,955 ± 152 | 868 ± 69 | 158 ± 8 |
| B2 | 85–138 | 3,168 ± 255 | 1,275 ± 92 | 217 ± 15 |
| C | 138–168 | 2,891 ± 213 | 1,489 ± 110 | 135 ± 12 |
| Second crop rotation, no FYM | | | | |
| A | 0–22 | 1,928 ± 213 | 143 ± 12 | 205 ± 15 |
| A1A2 | 22–31 | 2,968 ± 233 | 158 ± 12 | 182 ± 17 |
| A2B | 31–48 | 2,007 ± 159 | 1,000 ± 81 | 192 ± 18 |
| B1 | 48–79 | 2,900 ± 234 | 1,330 ± 105 | 182 ± 19 |
| B2 | 79–106 | 2,920 ± 239 | 1,593 ± 124 | 215 ± 16 |
| C | 138–168 | 3,353 ± 261 | 1,216 ± 95 | 203 ± 16 |
| Second crop rotation, FYM | | | | |
| A | 0–22 | 3,143 ± 235 | 190 ± 14 | 0 |
| A1A2 | 22–33 | 2,915 ± 233 | 1,013 ± 81 | 0 |
| A2B | 33–50 | 3,133 ± 235 | 995 ± 81 | 138 ± 11 |
| B1 | 50–75 | 2,855 ± 235 | 1,022 ± 83 | 165 ± 13 |
| B2 | 75–120 | 1,545 ± 127 | 1,424 ± 113 | 163 ± 12 |
| C | 120–165 | 3,283 ± 242 | 1,497 ± 177 | 153 ± 11 |

crop rotation (Table 2). Chlorite had the lowest abundance and did not show any distinct differences in the profile distribution on all the sub-plots (Table 3).

Discussion

The application of FYM at the total rate of 700t ha⁻¹ expectedly resulted in the improvement of topsoil quality (A horizons) of loamy sand Spodosol in terms of its increased soil pH, contents of exchangeable P₂O₅ and K₂O. The favorable changes in the soil quality indicators contributed to increasing soil productivity. OLENCZENKO et al. (2012) reported that in 2011 yields

of perennial grass and red clover mixture of second year reached 11.6t ha⁻¹ and 13.2t ha⁻¹ on the no FYM and FYM sub-plots. The yield of vetch-oat mixture was also higher on the FYM sub-plot (25.7t ha⁻¹) than on the no FYM sub-plot (19.8t ha⁻¹) in 2011.

Maintenance of integrity of the whole soil profiles is also one of the crucial aims of sustainable management practices. Soil inherent mineral and organic properties are key agents in maintaining sustainability of the whole soil profile. Our results showed that the whole soil profile of the no FYM sub-plot in the first crop rotation was shorter than other three soil profiles because of absence of transient A1A2 horizon, probably, due to a disturbance by moldboard ploughing. Therefore we

had to perform joint statistical analyses of distributions of selected soil parameters only in two whole soil profiles in the second crop rotation.

The uniform distribution of sand-sized fraction in the soil profile was induced by composition of its parent material, which was presented by quaternary sand, gravel and clay deposits in ground moraines. Therefore the content of clay-associated fraction was higher in a bottom part than in an upper part of the soil profile. In contrast to primary minerals, the abundance of micas increased with increasing soil depth on all the sub-plots (Table 1). These results supported data of scientists showing, firstly, that trioctahedral and dioctahedral micas were more sensitive to anthropogenic disturbing impacts than primary minerals and, secondly, that an increase in amount of micas with increasing soil depth could be induced by their downward migration (CHIZHIKOVA, 2005).

Primary minerals, as compared to phyllosilicates, have lower specific surface area, saturation capacity, and surface reactivity. The application of FYM contributes to an input of aliphatic compounds (polysaccharides, lignin, fatty acids, lipids etc.) into topsoil layers (EUSTERHUES et al., 2003; ŠIMON, 2005). The association of the aliphatic organic compounds with surfaces of primary minerals is induced by H-bonding and ligand exchange (VON LÜTZOW et al., 2008). In the topsoil the highest abundance of primary minerals could induce the accumulation of the greatest amounts of clay-associated aliphatic moieties originated from FYM (KÖGEL-KNABNER et al., 2008). Our results showed that FYM amendment contributed to the increase of total SOM content in bulk soil and did not affect the clay-associated SOM content in the topsoil that supported the data of HASSINK (1997).

The association of phyllosilicates with SOM becomes stronger with increasing degree of SOM humification as a result of dominant ligand exchange reactions producing strong bonds between singly coordinated carboxyl groups at the edges of phyllosilicates and carboxyl and phenolic groups of the organic matter (JONES and SINGH, 2014). The results of our studies demonstrated that the profile distribution of total SOM in bulk soil and clay-associated SOM had positive but insignificant Spearman's rank correlations in all the soil profiles. The micas abundance increased with increasing soil depth, but had negative Spearman's rank correlations with contents of clay-associated SOM in all the soil profiles (Table 1). We assume that micas did not play a key role in the association with the clay-associated organic compounds, which, in the profiles of the studied light-textured soil, could be mainly presented by those with a low degree of humification. Our data supported the results of WISEMAN and PÜTTMANN (2006) that chlorite had played a little role in binding SOM in the soil profiles.

Primary minerals in clay particles were probably main agents in the accumulation of clay-associated

SOM in the studied soil profiles. KIEM et al. (2000) reported that unmanured arable soils had higher proportions of aromatic (alkyl) carbon and lower proportions of O/N-alkyl carbon than the FYM-amended soils. Our results demonstrated that the management of loamy sand Spodosol on the FYM sub-plots did not necessarily lead to significant changes in SOM humification in the topsoil horizons and whole soil profiles in two crop rotations. Negative Spearman's rank correlation coefficients ($r = -0.50$ to -0.99) between the clay-associated SOM content and micas abundance probably supported the opinion that the clay-associated SOM had the low degree of humification and affinity to adsorption on micas surface (JONES and SINGH, 2014). The low degree of SOM humification could be induced by fast turnover of easily decomposable particulate organic matter associated with sand-sized fractions (CAMBARDELLA and ELLIOTT, 1992). The profile distribution of the total SOM in bulk soil and clay-associated SOM reflected inherent processes in the loamy sand Spodosol which had a leaching water regime and were subjected to strong weather and management impacts. Our data showed that (1) the podzolization process could induce a translocation of dissolved low molecular organo-mineral complexes from the A2B to illuvial B horizons, and, (2) there was a difficulty in maintaining a favorable content of SOM with the high degree of its humification in the top horizons at a long-term scale even by application of high rate of FYM.

Conclusions

The results of our study showed that the highest accumulation of total SOM in bulk soil was observed in the top horizons (A and A1A2) of FYM soils in two crop rotations with perennial grass-red clover and vetch-oat mixtures. The total SOM content in bulk soil drastically decreased in subsoil horizons (A2B, B1, B2, C), but on average was also higher in the FYM soil in both crop rotations.

The highest clay-associated SOM content was also determined in the topsoil horizons. A greater effect of FYM on the content of clay-associated SOM was observed in the topsoil under vetch-oat mixture. The clay-associated SOM content decreased down the soil profile and negatively ($r = -0.50$ to -0.99) correlated to the abundance of micas.

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