Soil organic matter quality of variously managed agricultural soil in the Czech Republic evaluated using DRIFT spectroscopy

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Abstract: This study focuses on the effect of agricultural soil management on soil organic matter (SOM) composition. The addition of manure and crop residues was tested under different pedoclimatic conditions. The quality of SOM was assessed using diffuse reflectance infrared spectroscopy. The following parameters were calculated from the spectra: sum of aliphatic bands (ΣAL), aromatic bands at wave numbers 1 620 and 1 520 cm^{-1} (AR$_{1620}$ and AR$_{1520}$), potential wettability (PWI), organic matter quality (OMQ), and decomposability (DI) indexes. The addition of manure or crop residues may not cause fundamental changes in the qualitative composition of SOM. Rather, pedoclimatic conditions determine which components are fixed in the soil on a long-term scale. A dominant effect of soil type was found in the distribution of all spectral parameters studied using main effect ANOVA. The main differences between the soil types concern the aromatic, oxygen and nitrogen groups contained in the SOM. Chernozems are soils with higher OMQ and DI, whereas Cambisols are soils with low OMQ and DI and the highest PWI. The stabilisation of SOM in soils can thus be based on the biochemical persistence of organic molecules, their specific affinity for minerals and the formation of aggregates that protect enclosed SOM.

Keywords: farmyard manure; fertilizing; infrared spectra; plant residues; soil types

In connection with climate change mitigation, more and more attention is focused on soil, especially soil organic matter (SOM) and its stabilization in soil. Often discussed topics are land use, soil tillage and also the use of organic fertilizers or amendments (e.g., Borůvka et al. 2022; Hendricks et al. 2022; Kochiieru et al. 2022). It is a well-known fact that SOM plays a key role in a number of soil properties, such as sorption characteristics or soil structure stability, thus influencing soil functions, typically hydrological or filtering, and its content also affects e.g., soil resistance to erosion (e.g., Brady & Weil 2008; Pavlů et al. 2021, 2022). The amount of organic matter in the soil is therefore a very important parameter, but the qualitative parameters of the organic matter, which also decide to some extent on its quantity, are almost more important (Cornu et al. 2023).

In the last two decades evaluation of SOM quality has undergone a significant transformation. Former

concept of humic substances (HS; fulvic/humic acids and humin) as stable recalcitrant macromolecules with high molecular weight (Stevenson 1994) was replaced by at least two parallel developing concepts. Piccolo (2002) reviewed that HS could be better described as a supramolecular association than being constituted by macromolecular polymers, as the traditional concept believed. Supramolecular associations could be interpreted as relatively small humic and chemically diverse organic molecules linked together by hydrogen bonds and hydrophobic interaction. The humification process does not therefore convey the increase of molecular mass of covalent macropolymers, but rather the progressive concentration of hydrophobic molecules which are expelled from the aqueous soil solution due to the thermodynamic hydrophobic effect (reduction of the solvatation energy of apolar molecules in water) and are no longer available to biodegradation. The process of concentration of humic hydrophobic molecules in the soil leads to the progressive accumulation of humus and to the formation of microaggregates whose hydrophobicity enhances the soil aggregates stability and the mean residence time of the soil organic carbon. This concept became the basis of the "Humeomics" approach to characterize natural humic molecules through a standard sequential fractionation without deliberately breaking C-C bonds and clarify their relations with ecosystems functions (Nebbioso & Piccolo 2012). Lehmann and Kleber (2015) describe SOM as continuum of organic compounds (polymers and monomers) of different size and degree of decomposition that interact with their environment, and it is these physicochemical interactions that protect some organic biomolecules from decomposition and enables their persistence in the soil (Schmidt et al. 2011).

Stabilization and long-term fixation of SOM in soil may thus be partially based on the rate and extent of microbial utilization of individual organic substances (von Lützow et al. 2006) or on stabilizing by the formation of mineral-associated organic matter and by the formation of aggregates (Schmidt et al. 2011; Angst et al. 2021). Furthermore, some biomolecules can be selectively preserved. Angst et al. (2021) in review state that, aromatic and aliphatic acids, such as lignin monomers, appear to be selectively retained on mineral surfaces in studies of mineral sorption of dissolved organic matter, polysaccharides and protein appear to be selectively preserved in organo-metallic complexes, and nitrogen-rich, microbial-derived biomolecules like amino sugars/acids appear to be selectively bound to mineral surfaces.

The qualitative parameters of soil organic matter can be determined variously by using different advanced analytical methods based on chemical or physical separation of SOM fractions, components, or molecules. Infrared spectroscopy in the near or mid infrared region of the spectrum belongs to indirect methods, and it can identify SOM composition without any chemical or physical extraction and separation from the soil. The mid-IR region is usually used to identify substances or specific functional groups of molecules. There are many variants of instrumentation for measuring IR spectra. It is different for solid, liquid, or gaseous samples. Diffuse reflection and attenuated total reflection (ATR), are most often used for soils, precisely for minimal sample pretreatment. In mixtures of substances such as soil, identification of individual molecules is difficult because the spectral bands of the organic and mineral components of the soil may overlap. Although mid-IR spectroscopy has its limits given the complexity of the soil, it detects the presence of important functional groups of SOM, and thus it can provide information about relative differences in SOM composition in different soil types and soil horizons (Pavlů et al. 2023) or for example in different land use (Thai et al. 2021).

This study aims to evaluate soil organic matter quality using diffuse reflectance infrared spectroscopy with Fourier transformation (DRIFT) to find differences among long-term on-farm trials with various fertilizing level and type established by the Central Institute for Supervising and Testing in Agriculture at ten experimental sites with various soil-climatic conditions in the Czech Republic. The effort was primarily to verify the effect of additions of manure and incorporation of crop residues (straw and beet tops), as measures often mentioned in connection with the storage of carbon in the agricultural soils, on qualitative parameters of soil organic matter. Crop residues (especially straw) can be understood as a source of mainly aliphatic components (cellulose), while manure as a source of a greater amount of aromatic and nitrogenous components. This is also the main hypothesis of this research, i.e., that during the long-term supply of the mentioned fertilizers, not only the content of SOM will change, but also the qualitative composition of SOM will be affected.

MATERIAL AND METHODS

Study sites. Long-term on-farm trials have been established within the years 1993 and 2000 by the Central Institute for Supervising and Testing in Agriculture at ten experimental sites with various soil-climatic conditions in the Czech Republic (Klement et al. 2012; Hynšt at al. 2022). Selected characteristics of the experimental sites are given in Table 1.

The same crops in the same order were planted at all experimental sites except for locations with the lowest altitude. At the sites of Lednice, Pusté Jakartice and Věrovany, beet was grown instead of potato. Six crops were rotated in the following order: pea, canola, winter wheat, spring barley, beet/potato, and again spring barley. Six treatments were studied: unfertilized treatment (control), mineral fertilization (NPK), application of farmyard manure (FYM), a combination of farmyard manure and mineral fertilization (FYM+NPK), incorporation of crop residues (ST/BT – straw/beet tops) and a combination of crop residues incorporation and mineral fertilization (ST/BT+NPK). The incorporation of cereal and canola straw (ST) was accompanied by the application of 40 and 20 kg N/ha, respectively. Each treatment had four replicates. More details are presented by Sedlář et al. (2023).

Soil analyses. Soil samples were collected from topsoil (up to 30 cm) after spring barley harvest (the second one in the trail). Samples were air-dried and sieved through a 2-mm sieve. The total organic carbon content (Ctot) in soil was determined from about 50 mg of soil by the dry combustion method at 960 °C with a CHNS Vario MACRO cube analyser (Elementar, Langenselbold, Germany). Each treatment was repeated three times during the soil analysis.

Part of the sieved samples was ground to analytical fineness to measure the infrared spectra. Infrared spectra were measured using the diffuse reflection technique and instrument Nicolet iS10 (Thermo Fisher Scientific Inc., USA). The spectral range was $4\,000$–$400\ cm^{-1}$. Before the measurement, the samples were not diluted with KBr or otherwise modified. The gold mirror was used as a background reference. The 64 scans with a resolution of $4\ cm^{-1}$ and spectra conversion to Kubelka–Munk units were applied. OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., USA) was used for spectra analysis. Well-definable bands of soil components functional groups were determined in the spectra and their reflectance converted to Kubelka–Munk units was measured and used for following calculations.

Figure 1 shows the average DRIFT spectra of soils in all studied sites. Most of the spectral bands of both mineral and organic soil components can be found in all soil types. The exception are the bands of carbonates (around $2\,515$ and $1\,450\ cm^{-1}$) which are slightly visible in the several individual spectra. The spectra were normalized with the reflectance (converted to Kubelka-Munk units) of the bands at $810\ cm^{-1}$ for mutual comparability of individual peaks (Pavlů et al. 2023). In the following text se-

Table 1. Study sites description (values of Ctot, Ntot, and pH are related to the control plot, i.e., they are not affected by fertilization or additions of organic matter)

Site name	Site abbreviation	Soil type*	Altitude (m)	AAP (mm/year)	AAT (°C)	Ctot	Ntot	pH$_{CaCl_2}$
						(%)		
Lednice	LED	Chernozem	172	461	9.6	1.5	0.15	6.8
Věrovany	VER	Chernozem	207	502	8.7	1.4	0.15	6.6
Chrastava	CHT	Luvisol	345	738	8.0	1.3	0.13	5.4
Jaroměřice	JAR	Luvisol	425	488	8.2	1.1	0.12	5.6
Hradec n. S.	HRA	Luvisol	460	616	7.4	0.8	0.09	6.0
Staňkov	STV	Luvisol	370	549	8.3	1.3	0.13	5.9
P. Jakartice	PJA	Retisol	290	584	8.3	1.0	0.11	6.1
Vysoká	VYS	Retisol	595	611	7.1	1.4	0.15	5.3
Horažďovice	HOR	Cambisol	472	585	7.8	1.1	0.12	5.5
Lípa	LIP	Cambisol	505	594	7.5	1.4	0.13	5.8

AAP – average annual precipitation; AAT – average annual temperature; Ctot – total organic carbon content; Ntot – total nitrogen content; *based on IUSS Working Group WRB (2022) simplified for sorting purposes

lected heights of normalized bands are named ΣAL in the case of two aliphatic bands sum (in the range 2 950–2 820 cm^{-1}) and AR$_{1620}$ or AR$_{1520}$ in the case of bands including vibration of aromatics around 1 620 and 1 520 cm^{-1}, respectively. Next quantitative information describing soil organic matter quality was computed from spectra as follows indexes: potential wettability index (PWI), organic matter quality index (OMQ), and decomposability index (DI).

The PWI was evaluated according to the adsorption band of the alkyl C-H groups – A (2 950–2 820 cm^{-1}), indicating the relative hydrophobicity, and adsorption band of the C=O groups – B (1 740–1 698 and

1 640–1 600 cm^{-1}), which is ascribed to hydrophilicity. Aromatic rings (whose bands are in the range 1 640–1 600 cm^{-1}), generally assumed to indicate hydrophobic groups, can show hydrophilic properties if they are conjugated with C=O groups (Ellerbrock et al. 2005; Leue et al. 2010). PWI was calculated as a ratio by summing up the intensity of the C-H and C=O groups (PWI = A/B) (Ellerbrock et al. 2005). The higher index value indicated the lower wettability of the soil.

The ratio of the band around 1 640–1 600 cm^{-1} and the aliphatic band (around 2 930 cm^{-1}) was used as an indicator describing OMQ which is applicable for noncarbonates and carbonates soil (Pavlů et al. 2023) because selected bands do not overlap even in carbonate soils and identify important components of SOM. Based on this index, the relative proportion of aliphatic, aromatic, or C=O-containing groups of SOM was evaluated.

Ratio of band 1 640–1 600 cm^{-1} and band around 1 520 cm^{-1} was used as an indicator of the DI of organic matter depending on the content of its nitrogenous components (Haberhauer et al. 1998). The use of this index is limited in soils with a higher carbonate content, where the peak in the spectral band around 1 520 cm^{-1} can be covered by a broad and intensive carbonates band. However, none of the tested samples contained such an amount of carbonates that would limit the use of this index.

Statistical analysis. One-way and main-effect analyses of variance were performed using STATISTICA software (Ver. 13.5.0.17) (TIBCO Software Inc., USA).

RESULTS

The results show that, just as the experimental sites differ in pedoclimatic and basic chemical characteristics (Table 1), the spectral parameters describing the qualitative parameters of SOM are also different (Table 2).

More illustrative is a visualization of selected relationships in Figure 2. It is evident that the Ctot content has no relation to the quality of the organic matter (OMQ) in individual localities. It is obvious, that there are some differences among soil types. Chernozems are soils with higher Ctot and with higher OMQ and DI. Cambisols are contrary soils with low values of OMQ and DI. Interesting is that the highest OMQ was found in Luvisol site with the lowest Ctot.
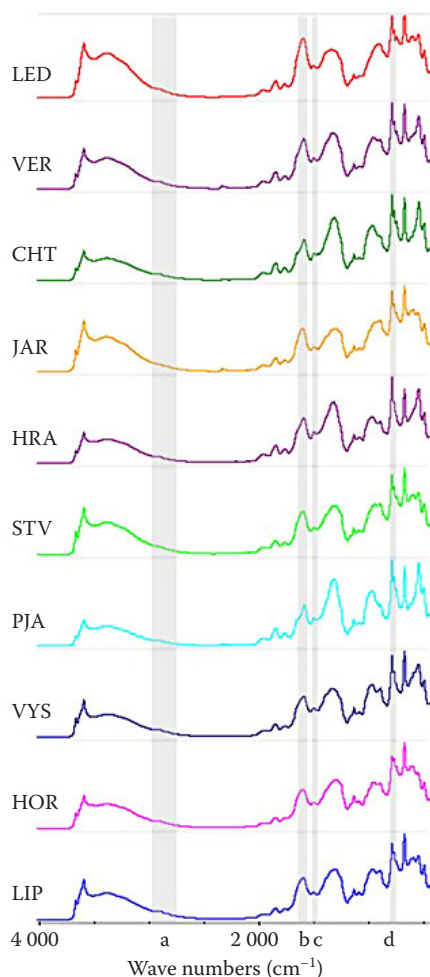

Figure 1. Average DRIFT spectra (*n* = 24, Kubelka-Munk units) of soils in studied sites with highlighting bands using for SOM quality evaluation

a – aliphatic bands in range 2 950–2 820 cm^{-1}; b – band of aromatics and C=O vibrations in range 1 640–1 600 cm^{-1}; c – band of aromatics and amid vibrations around 1 520 cm^{-1}; d – quartz band at 810 cm^{-1}; for the site name abbreviations see Table 1

Table 2. Average ($n = 24$) spectral parameters of soil computed for each study site and results of one-way ANOVA (95% LSD)

Site	Soil	ΣAL	AR_{1620}	AR_{1520}	PWI	OMQ	DI
LED	Chernozem	0.371[ab]	0.980[a]	0.566[bc]	0.015[f]	4.670[b]	1.732[a]
VER	Chernozem	0.354[cd]	0.895[c]	0.582[b]	0.013[gh]	4.563[c]	1.541[c]
CHT	Luvisol	0.313[e]	0.727[e]	0.507[de]	0.022[d]	4.225[d]	1.434[d]
JAR	Luvisol	0.355[bcd]	0.751[de]	0.465[f]	0.012[h]	3.792[e]	1.618[b]
HRA	Luvisol	0.348[d]	0.937[b]	0.668[a]	0.014[fg]	4.862[a]	1.404[f]
STV	Luvisol	0.370[abc]	0.759[de]	0.500[e]	0.017[e]	3.682[f]	1.522[c]
PJA	Retisol	0.306[e]	0.747[e]	0.538[cd]	0.017[e]	4.483[c]	1.391[f]
VYS	Retisol	0.380[a]	0.787[d]	0.586[b]	0.030[b]	3.758[ef]	1.345[g]
HOR	Cambisol	0.338[d]	0.656[f]	0.467[f]	0.025[c]	3.528[g]	1.406[ef]
LIP	Cambisol	0.387[a]	0.731[e]	0.512[de]	0.038[a]	3.406[h]	1.428[de]

ΣAL – normalized aliphatic bands sum; AR_{1620} and AR_{1520} – normalized bands including vibration of aromatics in 1 620 and 1 520 cm^{-1}, respectively; PWI – potential wettability index; OMQ – organic matter quality index; DI – decomposability index; for the site name abbreviations see Table 1

On the basis of the above-mentioned differences main effect analysis of variance was performed (Table 3). The effect of fertilizing treatment and soil type was tested. A dominant effect of soil type was found in the distribution of all studied soil parameters. Treatment has an effect on Ctot distribution only. It was proved that farmyard manure application (FYM and FYM+NPK treatments) increases Ctot content in the soil.

The differences in SOM spectral parameters among soil types are presented in Figure 3. Normalised

heights of spectral bands show, that for example Chernozems and Cambisols do not differ in aliphatic components contents, but a significant difference was found in the case of aromatics and C=O vibrations band in the range 1 640–1 600 cm^{-1} and of aromatics and amid vibrations band around 1 520 cm^{-1}. This is then significantly reflected in the OMQ, PWI and DI in detail (discussed below).

The results of the analysis of variance did not change even in the case of merging the variants of the experiment into groups, namely without the
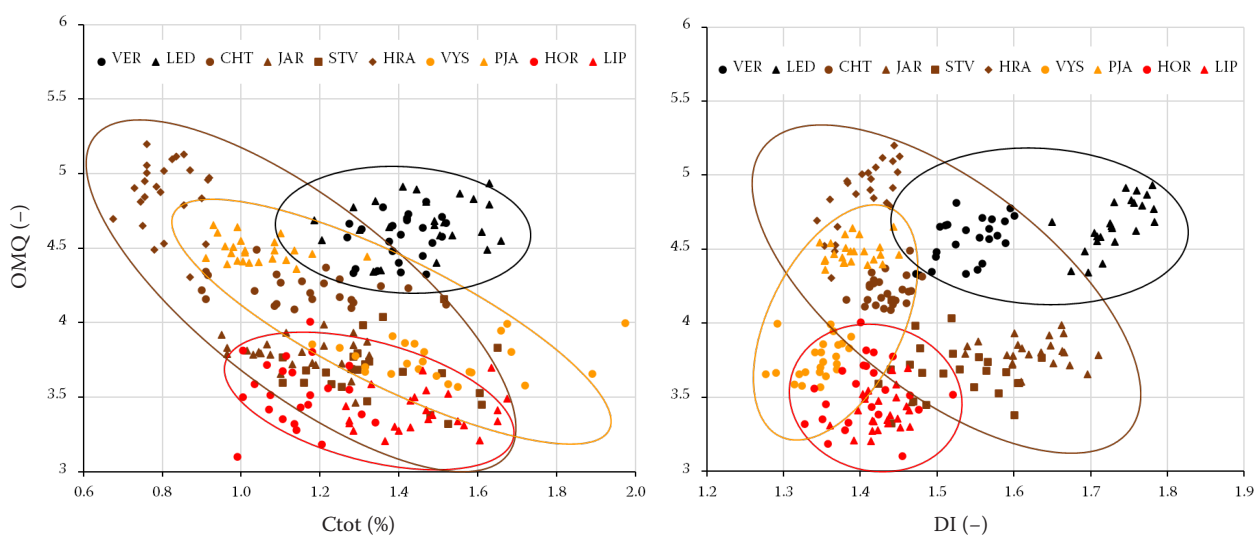

Figure 2. Relationships among total organic carbon content (Ctot) and indexes describing organic matter quality (OMQ) and decomposability (DI) in experimental sites
Red – Cambisol sites; brown – Luvisol sites; yellow – Retisol sites; black – Chernozem sites; for the site name abbreviations see Table 1

Table 3. Results of main effect ANOVA (95% LSD)

	Ctot	PWI	OMQ	DI	ΣAL	AR$_{1520}$	AR$_{1620}$
Soil (*F*/*P*)	27.42***	107.0***	75.24***	101.9***	3.98**	12.14***	62.88***
Treatment (*F*/*P*)	7.07***	0.665	0.115	0.449	0.935	0.891	0.894
Cher. (*n* = 48)	1.433[a]	0.014[d]	4.617[a]	1.636[a]	0.363[a]	0.574[a]	0.938[a]
Luvi. (*n* = 96)	1.117[c]	0.016[c]	4.140[b]	1.495[b]	0.347[b]	0.535[b]	0.793[b]
Reti. (*n* = 48)	1.274[b]	0.023[b]	4.120[b]	1.368[d]	0.343[b]	0.562[a]	0.767[b]
Cambi. (*n* = 48)	1.306[b]	0.031[a]	3.467[c]	1.417[c]	0.363[a]	0.489[c]	0.693[c]
CON (40)	1.207[b]	0.019[a]	4.113[a]	1.496[a]	0.349[ab]	0.531[a]	0.792[ab]
NPK (40)	1.232[b]	0.020[a]	4.099[a]	1.482[a]	0.354[ab]	0.542[a]	0.801[ab]
FYM (40)	1.323[a]	0.021[a]	4.117[a]	1.484[a]	0.351[ab]	0.539[a]	0.797[ab]
FYM+NPK (40)	1.381[a]	0.021[a]	4.083[a]	1.471[a]	0.363[a]	0.559[a]	0.818[a]
ST/BT (40)	1.145[b]	0.020[a]	4.106[a]	1.484[a]	0.350[ab]	0.538[a]	0.796[ab]
ST/BT+NPK (40)	1.210[b]	0.021[a]	4.064[a]	1.477[a]	0.346[b]	0.527[a]	0.777[b]

Ctot – total organic carbon content; PWI– potential wettability index; OMQ– organic matter quality index; DI– decomposability index; ΣAL– normalized aliphatic bands sum; AR$_{1620/1520}$ – normalized bands including vibration of aromatics in 1 620 and 1 520 cm^{-1}; CON – control; NPK – mineral fertilization; FYM – farmyard manure; ST/BT – incorporation of crop residues of straw/beet tops; results of *F*-test with *P*-values of significance (red) and average values with letters describing significant difference (red) between groups of soil or fertilizing

addition of organic matter (CON and NPK), with the addition of manure (FYM and FYP+NPK) and with the addition of post-harvest crop residues (ST/BT and ST/BT+NPK); data not shown. Soil type was still the dominant sorting criterion, and the variant of management played a role only in the distribution of Ctot, where a higher content was found in the group with the addition of manure.

Several significant differences between the above-mentioned groups were only detected using one-way ANOVA separately computed for individual locations (Table 4). Most often, the group fertilized with manure is shown to be different from either the other two groups or from the group without the addition of organic matter. The addition of organic matter somewhere led to an increase in the
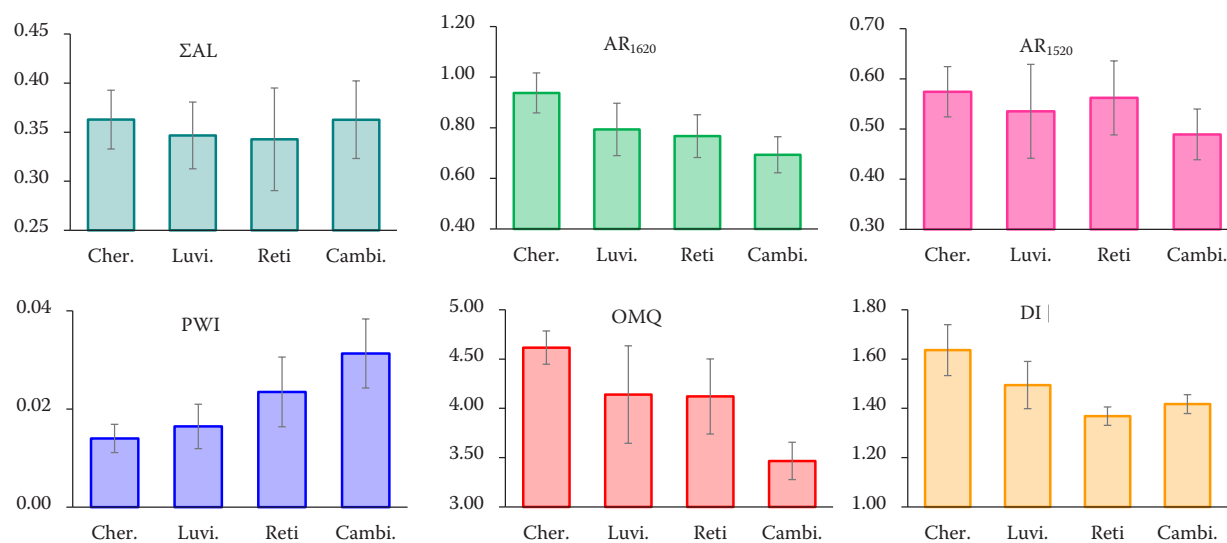

Figure 3. Spectral parameters (mean values; standard deviation as error bar) in studied soil types
ΣAL– normalized aliphatic bands sum; AR$_{1620/1520}$ – normalized bands including vibration of aromatics in 1 620 and 1 520 cm^{-1}, respectively; PWI– potential wettability index; OMQ– organic matter quality index; DI– decomposability index

Table 4. Results of one-way ANOVA (95% LSD)

Site Soil type	group	Ctot	PWI	OMQ	DI	ΣAL	AR$_{1520}$	AR$_{1620}$
LED Cher.	WA	1.48[b]	0.0133[b]	4.70[a]	1.74[a]	0.368[a]	0.562[a]	0.977[a]
	MA	1.61[a]	0.0153[ab]	4.71[a]	1.74[a]	0.371[a]	0.568[a]	0.987[a]
	RA	1.30[c]	0.0170[a]	4.60[a]	1.72[a]	0.375[a]	0.569[a]	0.976[a]
VER Cher.	WA	1.44a	0.0131[a]	4.55[a]	1.53[a]	0.357[a]	0.591[a]	0.899[a]
	MA	1.45[a]	0.0124[a]	4.59[a]	1.55[a]	0.344[a]	0.567[a]	0.876[a]
	RA	1.32[b]	0.0130[a]	4.55[a]	1.55[a]	0.362[a]	0.589[a]	0.912[a]
CHT Luvi.	WA	1.19[a]	0.0210[a]	4.29[a]	1.43[a]	0.309[a]	0.508[a]	0.727[a]
	MA	1.25[a]	0.0221[a]	4.19[a]	1.43[a]	0.317[a]	0.511[a]	0.730[a]
	RA	1.04[b]	0.0226[a]	4.20[a]	1.44[a]	0.313[a]	0.503[a]	0.724[a]
JAR Luvi.	WA	1.12[b]	0.0110[a]	3.72[a]	1.64[a]	0.349[a]	0.443[a]	0.724[a]
	MA	1.27[a]	0.0135[a]	3.81[a]	1.62[a]	0.359[a]	0.472[a]	0.762[a]
	RA	1.05[b]	0.0120[a]	3.84[a]	1.60[a]	0.358[a]	0.480[a]	0.768[a]
HRA Luvi.	WA	0.78[b]	0.0141[a]	4.94[a]	1.41[a]	0.350[a]	0.678[a]	0.958[a]
	MA	0.88[a]	0.0144[a]	4.85[a]	1.41[a]	0.344[a]	0.655[a]	0.922[a]
	RA	0.78[b]	0.0144[a]	4.80[a]	1.39[a]	0.351[a]	0.672[a]	0.932[a]
STV Luvi.	WA	1.28[b]	0.0168[ab]	3.74[a]	1.51[a]	0.378[a]	0.521[a]	0.786[a]
	MA	1.54[a]	0.0193[a]	3.63[a]	1.52[a]	0.377[a]	0.505[a]	0.762[a]
	RA	1.23[b]	0.0163[b]	3.68[a]	1.54[a]	0.356[a]	0.475[a]	0.729[a]
PJA Reti.	WA	1.05[a]	0.0169[a]	4.47[a]	1.40[a]	0.295[b]	0.514[b]	0.720[b]
	MA	1.11[a]	0.0181[a]	4.44[a]	1.37[a]	0.335[a]	0.591[a]	0.809[a]
	RA	0.96[b]	0.0161[a]	4.54[a]	1.40[a]	0.287[b]	0.510[b]	0.712[b]
VYS Reti.	WA	1.36[b]	0.0275[b]	3.75[a]	1.37[a]	0.364[b]	0.552[b]	0.753[b]
	MA	1.72[a]	0.0313[a]	3.78[a]	1.33[b]	0.402[a]	0.631[a]	0.835[a]
	RA	1.44[b]	0.0310[a]	3.75[a]	1.35[ab]	0.374[ab]	0.575[b]	0.772[ab]
HOR Cambi.	WA	1.08[b]	0.0261[a]	3.47[b]	1.43[a]	0.348[a]	0.463[a]	0.664[a]
	MA	1.16[b]	0.0240[a]	3.63[a]	1.40[b]	0.334[a]	0.478[a]	0.666[a]
	RA	1.20[a]	0.0244[a]	3.48[ab]	1.39[b]	0.333[a]	0.459[a]	0.637[a]
LIP Cambi.	WA	1.41[b]	0.0383[a]	3.44[a]	1.42[a]	0.399[a]	0.533[a]	0.760[a]
	MA	1.53[a]	0.0379[a]	3.37[a]	1.43[a]	0.390[a]	0.512[a]	0.729[a]
	RA	1.45[ab]	0.0373[a]	3.41[a]	1.44[a]	0.373[a]	0.491[a]	0.704[a]

Ctot – total organic carbon content; PWI– potential wettability index; OMQ– organic matter quality index; DI– decomposability index; ΣAL– normalized aliphatic bands sum; AR$_{1620/1520}$ – normalized bands including vibration of aromatics in 1 620 and 1 520 cm^{-1}; WA – without the addition of organic matter, MA – with the addition of manure and RA – with the addition of crop residues; letters describing significant difference (red) between treatment groups

value of PWI elsewhere OMQ or a decrease in the value of DI. In some cases, it only reflected a higher amount of Ctot by higher contents of all studied components of organic matter.

DISCUSSION

It is clear from the results that the long-term addition of farmyard manure or post-harvest crop residues to the soil in a system with a six-year sowing cycle, may not cause fundamental changes in the qualitative composition of SOM. Added organic material is decomposed and pedoclimatic conditions will rather decide which components will be fixed in the soil on the long-term scale.

We can present this statement on considerably different soil types. Chernozems are soils typical for their very dark colour, high base saturation, high

animal activity, a moderate to high content of organic matter, and loamy texture of chernic horizon (IUSS Working Group WRB 2014, 2022). Older literary sources referred to these soils as soils with a high proportion of humic acids rich in aromatic components and a lower content of fulvic acids containing a larger amount of aliphatic components (Němeček et al. 1990; Stevenson 1994; Sposito 2008). Spectral analysis confirms the highest content of aromatic components in Chernozem's SOM, which is evident from the values of the normalized heights of the spectral bands at 1 620 and 1 520 cm^{-1} (AR$_{1520}$, AR$_{1620}$). The content of aliphatic components (ΣAL) differs from Luvisols and Retisols but does not differ from Cambisol. The mutual ratio of aromatic and aliphatic components (OMQ) then shows the highest values precisely in Chernozems. High OMQ indicates that organic matter with the lowest proportion of aliphatic components (e.g., polysaccharides, proteins, aliphatic organic acids, etc.) occurs there. Aromatic substances are generally considered to be hydrophobic groups and their ability to protect hydrophilic components of organic matter from relatively rapid decomposition by forming supramolecular structures is known (Piccolo 2002; Piccolo et al. 2004). SOM richer in aromatic, alkyl, and carboxyl groups, but containing lower amounts of hetero-alkyl groups can be considered as more humified and chemically mature. Conversely, a lower number of aromatic groups and a higher percentage of O, N-alkyl C, predominantly in carbohydrate and polypeptide structures, represents a lower degree of humification and chemical maturity (Maryganova et al. 2010). This is also evidenced by the highest DI values in the Chernozems, which means a lowest proportion of nitrogenous groups (1 520 cm^{-1}) compared with C=O containing groups (1 620 cm^{-1}), i.e. by Cotrufo et al. (2013) a lower attractivity for microorganisms and thus lower level of decomposability of organic substances. From this point of view, SOM in Chernozems can be characterized as stable and relatively recalcitrant and resistant to decomposition. OMQ index can point to the mobility or stability of SOM through aliphatic/aromatic components' affinity for soil minerals and water. Aromatic compounds are less mobile because of their hydrophobic character which leads to the formation of stable microaggregates and selective retention on mineral surfaces, therefore, they are likely retained in the soil (Piccolo 2002; Feng et al. 2005; Bi et al. 2013). Based on the above, it can be assumed that in Jaroměřice site (JAR, Luvisol area), where the lowest Ctot content and the highest OMQ were found, they are these aromatic compounds that resist decomposition and form the main part of SOM.

On the other hand, Cambisols are characterized by slight or moderate weathering of parent material and by the cambic horizon usually showing higher Fe oxide and/or clay contents than the underlying layer. Cambisols with high base saturation in the temperate zone are among the most productive soils on earth. More acid Cambisols, although less fertile, are used for mixed arable farming and as grazing and forest land (IUSS Working Group WRB 2014, 2022). Studied Cambisol localities appertain to more acid one. It is clear from the results that these soils have the lowest OMQ and DI is lower than in Chernozem. Similar results were found in the other Chernozem and Cambisol regions in the Czech Republic (Pavlů et al. 2023). Although the difference of Chernozems and Cambisols in carbon content is significant, it is not generally valid (in studied Chernozem Ctot vary from 1.30% to 1.61% and in one of Cambisol site (LIP) from 1.41% to 1.53%). This along with low OMQ and DI shows that the composition of organic matter itself, its aromaticity, or the content of nitrogenous components are not the only factors influencing SOM stabilization. The presence of iron oxides can play an important role here. Polysaccharides and proteins are selectively preserved in organo-metallic complexes (Nierop et al. 2005; Tonneijck et al. 2010). Other studies show that nitrogen-rich, microbial-derived biomolecules like amino sugars/acids are also selectively bound to mineral surfaces (e.g., Kopittke et al. 2018). Interactions between molecules of SOM and mineral surfaces that form stronger (e.g., via ligand exchange) or weaker bonds (e.g., via Van der Waals forces) increase the protection of that SOM against decomposition (von Lützow et al. 2006). Moreover, SOM is stabilized not only by the formation of mineral-associated organic matter, but also by the retention inside the stable aggregates and the positive effect of iron forms on aggregate stability in Cambisols was found by Pavlů et al. (2022). The highest values of PWI in Cambisol indicated the lowest wettability of the soil, which ensures, among other things, higher stability of soil aggregates (Thai et al. 2022) and thus protection of the soil SOM contained in them. Enclosed and physically protected soil carbon within soil aggregates contributes to its long-term fixation in the soil (Schmidt et al. 2011; Vancampenhout et al. 2012).

If we focus more on the effect of adding different quality organic matter, we can start from a microbial-centric concept (e.g., Cotrufo et al. 2013). The base of this concept is the high quality of organic substrates is indicated by lower carbon-to-nutrient ratios and lower concentrations of recalcitrant compounds. Accordingly, the higher the quality, the higher the microbial substrate use efficiency, and the higher the build-up of microbial biomass, whose residues eventually interact with the soil mineral phase to form aggregates and mineral-associated organic matter. In our case, this could correspond to higher Ctot values for the variant fertilized with manure. However, almost no differences were found in the qualitative parameters of the soil organic matter composition. There are also studies that describe the preferential fixation of plant biomolecules in the soil (Castellano et al. 2015; Angst et al. 2017; Van der Voort et al. 2017) which then become part of the stable SOM component. In principle, this should distinguish the variant with the addition of crop residues from the others. However, the effect of the addition of crop residues was demonstrated only at one of the Chernozem locations, where it increased the PWI compared to the control variant. A similar result was found when organic mulches, including straw, were used (Thai et al. 2022).

Sedlář et al. (2023) tested the same sample set by different methods based on the isolation of humic and fulvic acids with a solution of sodium pyrophosphate in a mixture with sodium hydroxide. Their research brought results that in some cases are valid more generally, not only for selected localities as in our case. The combination of farmyard manure with mineral fertilising resulted in the change of qualitative SOM parameters (higher humification index, humification rate, humic acid carbon content and fulvic acid carbon content compared to variant with only mineral fertilizing) and the addition of crop residues similarly as in our research did not bring any change in terms of soil organic matter quality.

CONCLUSION

It can be concluded that, in the long term, soil type (i.e., the set of climatic, geological, and geographical conditions) plays an important role in the stabilization and conservation of organic matter in the soil. The addition of certain forms of organic matter, such as manure, can increase the total organic matter content but does not significantly determine the chemical

composition (visible in DRIFT spectra of soils) of retained organic matter. Organic matter of Chernozems maintains a high proportion of aromatics even with different treatments, and in contrast, the proportion of aliphatic components remains high in all treatments of acid Cambisols. However, it cannot be ruled out that some more advanced or specific analytical methods (e.g., solid-state NMR in case of soil sample analysis without extraction standard or sequential fractionation without deliberately breaking C-C bonds) would not reveal certain differences in SOM quality between the studied variants of the experiment.

REFERENCES

Angst G., Mueller K.E., Kögel-Knabner I., Freeman K.H., Mueller C.W. (2017): Aggregation controls the stability of lignin and lipids in clay-sized particulate and mineral associated organic matter. Biogeochemistry, 132: 307–324.

Angst G., Mueller K.E., Nierop K.G.J., Simpson M.J. (2021): Plant- or microbial-derived? A review on the molecular composition of stabilized soil organic matter. Soil Biology and Biochemistry, 156: 108189.

Bi R., Lu Q., Yuan T., Zhou S., Yuan Y., Cai Y. (2013): Electrochemical and spectroscopic characteristics of dissolved organic matter in a forest soil profile. Research Journal of Environmental Sciences, 25: 2093–2101.

Borůvka L., Penížek V., Zádorová T., Pavlů L., Kodešová R., Kozák J., Janků J. (2022): Soil priorities for the Czech Republic. Geoderma Regional, 29: e00525.

Brady N.C., Weil R.R. (2008): The Nature and Properties of Soils. New Jersey, Pearson Prentice Hall.

Castellano M.J., Mueller K.E., Olk D.C., Sawyer J.E., Six J. (2015): Integrating plant litter quality, soil organic matter stabilization, and the carbon saturation concept. Global Change Biology, 21: 3200–3209.

Cornu S., Keesstra S., Bispo A., Fantappie M., van Egmond F., Smreczak B., Wawer R., Pavlů L., Sobocká J., Bakacsi Z., Farkas-Iványi K., Molnár S., Moller A., Madenoglu S., Feiziene D., Oorts K., Schneide F., Gonçalves M., Mano R., Garland G., Skalský R., O'Sullivan L.M., Kasparinskis R., Chenu C. (2023): National soil data in EU countries, where are we? European Journal of Soil Science, 74: e13398.

Cotrufo M.F., Wallenstein M.D., Boot C.M., Denef K., Paul E. (2013): The Microbial Efficiency-Matrix Stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: Do labile plant inputs form stable soil organic matter? Global Change Biology, 19: 988–995.

Ellerbrock R.H., Gerke H.H., Bachmann J., Goebel M.-O. (2005): Composition of organic matter fractions for explaining wettability of three forest soils. Soil Science Society of America Journal, 69: 57–66.

Feng X., Simpson A.J., Simpson M.J. (2005): Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. Organic Geochemistry, 36: 1553–1566.

Haberhauer G., Rafferty B., Strebl F., Gerzabek M.H. (1998): Comparison of the composition of forest soil litter derived from three different sites at various decompositional stages using FTIR spectroscopy. Geoderma, 83: 331–342.

Hendricks S., Zechmeister-Boltenstern S., Kandeler E., Sanden T., Diaz-Pines E., Schnecker J., Alber O., Miloczki J., Spiegel H. (2022): Agricultural management affects active carbon and nitrogen mineralisation potential in soils. Journal of Plant Nutrition and Soil Science, 185: 513–528.

Hynšt J., Jančíková S., Komprsová I., Prchalová R., Smatanová M. (2022): Fifty Years of Long-Term Field Experiments in ÚKZÚZ and Sixty Years of Agrochemical Testing of Agricultural soils in the Czech Republic. Brno, ÚKZÚZ. (in Czech) Available at https://eagri.cz/public/web/file/708532/Publikace_50_let_na_internet.pdf

IUSS Working Group WRB (2014): World Reference Base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. Rome, FAO.

IUSS Working Group WRB (2022): World Reference Base for Soil Resources 2022. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. Rome, FAO.

Klement V., Smatanová M., Trávník K. (2012): Fifty Years of Agrochemical Testing of Agricultural Soils in the Czech Republic and Forty Years of Long-Term Field Experiments in ÚKZÚZ. Brno, ÚKZÚZ (in Czech with partial English translation) Available at https://eagri.cz/public/web/file/216024/Publikace_50_a_40_let_AZZP_2012.pdf

Kochiieru M., Lamorski K., Feiziene D., Feiza V., Slepetiene A., Volungevicius J. (2022): Land use and soil types affect macropore network, organic carbon and nutrient retention, Lithuania. Geoderma Regional, 28: e00473.

Kopittke P.M., Hernandez-Soriano M.C., Dalal R.C., Finn D., Menzies N.W., Hoeschen C., Mueller C.W. (2018): Nitrogen-rich microbial products provide new organo-mineral associations for the stabilization of soil organic matter. Global Change Biology, 24: 1762–1770.

Lehmann J., Kleber M. (2015): The contentious nature of soil organic matter. Nature, 528: 60–68.

Leue M., Ellerbrock R.H., Gerke H.H. (2010): DRIFT mapping of organic matter composition at intact soil aggregate surfaces. Vadose Zone Journal, 9: 317–324.

Maryganova V., Szajdak L.W., Tychinskaya L. (2010): Hydrophobic and hydrophilic properties of humic acids from soils under shelterbelts of different ages. Chemistry and Ecology, 26: 25–33.

Nebbioso A., Piccolo A. (2012): Advances in humeomics: Enhanced structural identification of humic molecules after size fractionation of a soil humic acid. Analytica Chimica Acta, 720: 77–90.

Němeček J., Smolíková L., Kutílek M. (1990): Soil Science and Paleo Soil Science. Prague, Academia. (in Czech)

Nierop K.G.J., Van Bergen P.F., Buurman P., Van Lagen B. (2005): NaOH and $Na_4P_2O_7$ extractable organic matter in two allophanic volcanic ash soils of the Azores Islands – A pyrolysis GC/MS study. Geoderma, 127: 36–51.

Pavlů L., Kodešová R., Fér M., Nikodem A., Němec F., Prokeš R. (2021): The impact of various mulch types on soil properties controlling water regime of the Haplic Fluvisol. Soil and Tillage Research, 205: 104748.

Pavlů L., Kodešová R., Vašát R., Fér M., Klement A., Nikodem A., Kapička A. (2022): Estimation of the stability of topsoil aggregates in areas affected by water erosion using selected soil and terrain properties. Soil and Tillage Research, 219: 105348.

Pavlů L., Zádorová T., Pavlů J., Tejnecký V., Drábek O., Reyes Rojas J., Thai S., Penížek V. (2023): Prediction of the distribution of soil properties in deep Colluvisols in different pedogeographic regions (Czech Republic) using diffuse reflectance infrared spectroscopy. Soil and Tillage Research, 234: 105844.

Piccolo A. (2002): The supramolecular structure of humic substances: A novel understanding of humus chemistry and implications in soil science. Advances in Agronomy, 75: 57–134.

Piccolo A., Spaccini R., Nieder R., Richter J. (2004): Sequestration of a biologically labile organic carbon in soils by humified organic matter. Climatic Change, 67: 329–343.

Schmidt M.W.I., Torn M.S., Abiven S., Dittmar T., Guggenberger G., Janssens I.A., Kleber M., Kögel-Knabner I., Lehmann J., Manning D.A.C., Nannipieri P., Rasse D.P., Weiner S., Trumbore S.E. (2011): Persistence of soil organic matter as an ecosystem property. Nature, 478: 49–56.

Sedlář O., Balík J., Černý J., Kulhánek M., Smatanová M. (2023): Long-term application of organic fertilizers in relation to soil organic matter quality. Agronomy, 13: 175.

Sposito G. (2008): The Chemistry of Soils. New York, Oxford University Press, Inc.

Stevenson F.J. (1994): Humus Chemistry, Genesis, Composition, Reactions. 2nd Ed. New York, John Wiley and Sons, Inc.

Thai S., Pavlů L., Tejnecký V., Vokurková P., Nozari S., Borůvka L. (2021): Comparison of soil organic matter

composition under different land uses by DRIFT spectroscopy. Plant Soil and Environment, 67: 255–263.

Thai S., Davídek T., Pavlů L. (2022): Causes clarification of the soil aggregates stability on mulched soil. Soil and Water Research, 17: 91–99.

Tonneijck F.H., Jansen B., Nierop K.G.J., Verstraten J.M., Sevink J., De Lange L. (2010): Towards understanding of carbon stocks and stabilization in volcanic ash soils in natural Andean ecosystems of northern Ecuador. European Journal of Soil Science, 61: 392–405.

Van der Voort T.S., Zell C.I., Hagedorn F., Feng X., McIntyre C.P., Haghipour N., Graf Pannatier E., Eglinton T.I. (2017): Diverse soil carbon dynamics expressed at the molecular level. Geophysical Research Letters, 44: 840–850.

Vancampenhout K., De Vos B., Wouters K., Swennen R., Buurman P., Deckers J. (2012): Organic matter of subsoil horizons under broadleaved forest: Highly processed or labile and plant-derived? Soil Biology and Biochemistry, 50: 40–46.

von Lützow M., Kögel-Knabner I., Ekschmitt K., Matzner E., Guggenberger G., Marschner B., Flessa H. (2006): Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – A review. European Journal Soil Science, 57: 426–445.