

The long-term changes in soil organic matter contents and quality in Chernozems

JAN HORÁČEK^{1,*}, PAVEL NOVÁK², PETER LIEBHARD³, EDUARD STROSSER¹, MÁRIA BABULICOVÁ⁴

¹*Department of Applied Plant Biotechnologies, Faculty of Agronomy, University of South Bohemia, České Budějovice, Czech Republic*

²*Research Institute for Soil and Water Conservation, Prague, Czech Republic*

³*Division of Agronomy, Department of Crop Sciences, BOKU University of Natural Resources and Life Sciences, Vienna, Austria*

⁴*Agricultural and Food Centre – Research Institute for Plant Production Piešťany, Piešťany, Slovak Republic*

*Corresponding author: horacek@zf.jcu.cz

ABSTRACT

Horáček J., Novák P., Liebhard P., Strosser E., Babulicová M. (2017): The long-term changes in soil organic matter contents and quality in Chernozems. *Plant Soil Environ.*, 63: 8–13.

For the purposes of assessment of long-term changes, two sets of Chernozems soil samples were analysed and compared in parallel: 'old' file samples obtained during the Soil Survey 1960–1970 in the former Czechoslovakia and a 'present' (2013) set of samples from exactly the same sites as the archive samples. The recently collected samples revealed worse qualitative parameters (lower humic acid to fulvic acid (HA/FA) ratios and higher colour quotient Q4/6 values) than the file samples, for all the localities. On the other side, the quantitative soil organic matter (SOM) parameters (oxidizable carbon (C_{ox}) and all its determined components) showed contrary results. The amount of total SOM at the same sites is higher now than it was about 50 years ago. It can be concluded that the current decline in SOM quality in Chernozems is partly compensated for by higher accumulation of SOM in the soils. All the analysed Chernozem samples were found to have much worse qualitative SOM parameters than the values mentioned for this soil type in the older literature. However, a comparison of the current data and the file data of Chernozem SOM quality can still be considered an open issue and require more complex research.

Keywords: soil organic matter quantity and quality; soil organic matter changes in time, organic substances

Characteristics and importance of soil organic matter. Soil organic matter (SOM) is a complex of heterogeneous, polydisperse organic substances of varied origins, variable compositions, levels of dispersity, activities as well as relations to other components of soil matter and live organisms (Sotáková 1982, Stevenson 1994).

The importance of soil organic matter to soil fertility and in general to soil quality has been known and valued over the long-term (Stockman

et al. 2013). There is no doubt that soil organic matter positively influences physical and chemical properties of soil and it is a factor fundamentally influencing soil fertility and to a large degree is conditional to the existence of rich and diversified soil biota (Kubát et al. 2008, Baum et al. 2013).

Besides the agronomic significance of soil organic matter, its importance to the environment has been valued recently, especially regarding the organic carbon accumulation and sequestration in

soil, and further to the preservation of ecological functions of soil (Kubát et al. 2008, Kolář et al. 2014). In connection with these questions, a model-based approach for the determination of organic carbon stock in agricultural soils is frequently taken (Lugato et al. 2014). Therefore, the condition of SOM in soil cannot only be determined on its total quantity or total organic (oxidizable) carbon (C_{ox}) content. This is the reason for which this quantitative parameter is largely accompanied with qualitative SOM parameters. The summary of provided parameters is presented by Maia et al. (2013). The most commonly used parameter is a humic acid to fulvic acid (HA/FA) ratio, colour quotient Q4/6 and degree of humification (Dh) (Stevenson 1994, Kubát et al. 2008). The recent values of these qualitative parameters in a number of Chernozemic soil localities were found to be considerably worse than those mentioned for this soil type in earlier literature (Pospíšil 1980, Sprague and Triplett 1986) and this would mean a decline in quality of Chernozemic SOM over the latest decades. It is assumed though that the major part of Chernozemic C_{ox} is present mainly in the humidified fraction of SOM, of which the quality in humic horizons in the form of ratio HA:FA 2.5–3.5 and colour quotient Q4/6 = 1.0–1.5 (Pospíšil 1980, Sotáková 1982, Stevenson 1994) is very high.

Unfortunately, insufficient input values for the sampled sites do not allow for comparative and more reliable assessment of the abovementioned qualitative SOM parameters (Kubát et al. 2008).

This discussion focuses on the quantitative and qualitative parameters of treated Chernozems in view of their relatively worse values, particularly in comparison with the figures presented earlier for this soil type.

MATERIAL AND METHODS

The abovementioned lack of data was solved by comparing two sets of samples taken at the same sites during different time periods. The file soil samples were taken during the Soil Survey in 1960–1970 in the former Czechoslovakia at Special Soil Profile Pits with a precise field location (Němeček et al. 1967). The samples were deposited by the Research Institute for Soil and Water Conservation in Prague. They have been

stored since 1963, in sealed sample containers in dark and at stable temperature of 15°C. Perennial fodder crops such as winter wheat, barley and sugar beet were the most used in crop rotations in the regions before 1990. After 1990, the proportions of cereals and particularly of winter rape considerably increased. Current yields of crops have increased by approximately 2.5 times. The ‘new’ soil samples were collected in June 2013 at the exactly same sites as the file samples. All selected localities of Chernozem profiles in the Central Bohemia were middle-textured with the depth of active humus horizons up to 50–60 cm. Both old and new samples were taken from the plough horizon A_p . The localities at Klapý, Libčeves, Libochovice, Nová Ves and Račiněves were chosen for their flat land reliefs in order to minimise potential negative influence of erosion. They were treated with conventional deep tillage. The time difference of nearly 50 years was regarded as sufficient for the purpose of demonstration of SOM changes. The old and present soil samples were analysed and evaluated in parallel. The samples were air-dried, ground for 2-mm sifting, using a Pulverisette 8 (Fritsch, Germany) grinding mill, homogenised, and part separated using a Laborette 27 (Fritsch, Germany) for 0.25 mm sifting. The soil organic matter was characterised by the following fractions: oxidizable carbon content (C_{ox}); oxidizable carbon of humic substances ($C_{ox}^{HS} = C_{ox}^{HA} + C_{ox}^{FA}$); humic acids (C_{ox}^{HA}) and fulvic acids (C_{ox}^{FA}) in alkaline extracts (0.1 mol/L sodium pyrophosphate in sodium hydroxide) and hot-water soluble carbon (C_{hws}) according to Weigel et al. (1998). For the carbon analyses, chemical oxygen demand (COD) analysis were performed using acid potassium dichromate method (0.0667 mol/L $K_2Cr_2O_7$ at 125°C during 45 min) with 0.1 mol/L Fe^{2+} retitration with the automatic titrator DL 50 (Mettler-Toledo, Switzerland). The procedure of SOM fractionation (Kononova 1963, Zbiral et al. 2011) was modified (Horáček et al. 2008) as follows: < 0.25 mm soil fraction was used instead of < 2 mm fraction, and the extracts were obtained using centrifugation instead of filtration. Before the COD determination the C_{ox}^{HS} , C_{ox}^{HA} , C_{ox}^{FA} and C_{hws} extracts were evaporated at 60°C. Qualitative parameters of SOM were characterized using HA:FA ratio, colour quotient Q4/6 and degree of humification Dh ($Dh = C_{ox}^{HS}/C_{ox} \times 100$ (%)). The Q4/6 values were established using a Jenway 6

doi: 10.17221/274/2016-PSE

100 spectrophotometer (Bibby Scientific Limited, UK) in stabilised alkaline extracts at 465 nm and 665 nm. The HS concentrations were treated prior to measurements using extracting agents so that their absorbance values at 465 nm ranged around 0.7.

The characteristics of sorption complex, cation exchange capacity (CEC), exchangeable base cations (EBC) and degree of sorption saturation (DS): $DS = BC/CEC \times 100$ (%), were established using the method originally used for the Soil Survey in 1960–1970 (Sirový et al. 1967). Analytical repetitions were processed using common statistical procedures in the program Statistica (Stat Soft. Inc., Tulsa, USA). It was not possible to carry out a more detail statistical survey because of the limited set of samples and low number of repetition, and therefore the results obtained are only given as ranges of established values.

RESULTS AND DISCUSSION

Chernozem soil is used as a comparative soil type both for laboratory incubation and field experiments. Resulting values of Chernozems SOM qualitative parameters recently obtained by several laboratories rather vary from those presented in earlier works (Horáček et al. 2008). Our recent results (Pospíšilová et al. 2010, Babulicová et al. 2011, Liebhard et al. 2012) show a proof that the Chernozem SOM quality has continued to worsen, especially in relation to the data presented earlier for this soil type. They are simplified to a large extent, and averaged data are not possibly fully

uniform from the point of view of varied research intentions. For this reason, only most frequent indicators have been discussed, i.e. the total quantity of oxidizable carbon C_{ox} , HA:FA ratio values, and Q4/6 colour quotient values, or possibly Dh humification degree values. Unfortunately, those characteristics were not determined for the file samples during the respective sampling period.

Nevertheless, the SOM quality can still be partially evaluated by assessing the soil sorption complex characteristics, in particularly using CEC. The initial sorption complex characteristics of Central Bohemia Chernozems are known, and therefore the same method was chosen to determine the characteristics of both file and present soil samples.

Elementary soil characteristics of the analysed file samples and recently taken soil samples of Central Bohemia Chernozems are shown in Table 1.

In terms of grain composition, the Chernozem soil in the Klapý locality has developed in loess and marl substrates and has been classified as clay-loam (USDA); out of five probes, it contains the highest number of particles < 0.01 mm (Table 1). Further, it contains the highest percentage of carbonates, which can explain why the soil reaction values have remained unchanged for both the former and recently taken soil samples. Further, the soil complex in this locality shows the highest CEC and EBC values in combination with the highest DS, which corresponds to the high carbonate content. The degree of sorption of the present soil samples dropped when compared to the file and formerly declared soil samples. The C_{ox} content and other SOM components (Table 2) increased over app. 50 years of treatment by about 0.5%, but the quality

Table 1. Elementary soil characteristic of Central Bohemia Chernozems

Locality	Grain composition		C _{ox}	CaCO ₃	pH _{KCl}			CEC			CEC for base			DS (%)		
	(%) (a.d.)		(%)	(%)				(mmol ₊ /100 g soil)			(mmol ₊ /100 g soil)					
	0.01 mm	0.001 mm	a.d.	a.d.	a.d.	a.s.p.a.	p.s.	a.d.	a.s.p.a.	p.s.	a.d.	a.s.p.a.	p.s.	a.d.	a.s.p.a.	p.s.
Klapý	70.4	44.2	2.21	14.0	7.10	7.19	7.17	36.8	35.5	39.2	36.1	34.8	38.1	98.1	98.0	97.2
Libčeves	31.7	19.3	1.32	1.3	7.10	7.16	7.30	19.0	16.5	19.9	17.9	15.5	18.6	94.2	94.1	93.4
Libochovice	48.7	28.5	2.06	2.1	7.30	7.30	7.26	27.1	26.8	31.8	25.5	25.4	29.8	94.1	94.8	93.7
Nová ves	33.5	21.3	1.51	0.32	7.20	7.18	6.90	20.5	20.4	26.3	17.5	17.9	22.1	85.3	87.7	84.2
Račíněves	48.7	26.9	0.88	0.94	6.60	6.48	6.61	24.5	25.6	25.7	23.3	23.9	23.6	95.1	93.3	91.8
Mean	46.6	28.0	1.60	3.73	7.06	7.06	7.05	25.6	25.0	28.6	24.1	23.5	26.4	93.4	93.6	92.1

a.d. – archived data; a.s.p.a. – archived samples, present analysis; p.s. – present samples; C_{ox} – oxidizable carbon; CEC – cation exchange capacity; DS – degree of sorption saturation

Table 2. Quantitative parameters of soil organic matter (SOM) in selected Ap horizons of Central Bohemia Chernozems

Locality	Treatment	C_{ox}	C_{ox} HS	C_{ox} HA	C_{ox} FA	C_{hws}	Remainder C_{ox} after extraction
		(g/100 g soil)					
Klapý	archived	2.05 ± 0.02	0.98 ± 0.06	0.56 ± 0.03	0.42 ± 0.03	0.073 ± 0.002	0.93 ± 0.04
	present	2.52 ± 0.03	1.09 ± 0.07	0.62 ± 0.04	0.47 ± 0.03	0.088 ± 0.002	1.22 ± 0.05
Libčeves	archived	1.32 ± 0.03	0.70 ± 0.04	0.37 ± 0.02	0.33 ± 0.02	0.059 ± 0.002	0.90 ± 0.04
	present	2.27 ± 0.01	0.90 ± 0.06	0.44 ± 0.02	0.46 ± 0.03	0.117 ± 0.003	1.16 ± 0.05
Libochovice	archived	2.06 ± 0.02	0.96 ± 0.02	0.56 ± 0.04	0.42 ± 0.03	0.073 ± 0.002	1.01 ± 0.05
	present	2.42 ± 0.01	1.02 ± 0.07	0.60 ± 0.04	0.46 ± 0.03	0.083 ± 0.002	1.32 ± 0.06
Nová Ves	archived	1.51 ± 0.01	0.73 ± 0.04	0.41 ± 0.02	0.32 ± 0.02	0.056 ± 0.002	0.73 ± 0.04
	present	2.18 ± 0.02	0.91 ± 0.06	0.51 ± 0.03	0.41 ± 0.02	0.064 ± 0.002	1.00 ± 0.04
Račíněves	archived	0.88 ± 0.03	0.51 ± 0.03	0.26 ± 0.02	0.25 ± 0.01	0.032 ± 0.002	0.48 ± 0.03
	present	1.53 ± 0.02	0.69 ± 0.05	0.35 ± 0.02	0.33 ± 0.02	0.052 ± 0.002	0.93 ± 0.03
Mean	archived	1.56 ± 0.02	0.78 ± 0.04	0.43 ± 0.03	0.35 ± 0.02	0.058 ± 0.002	0.81 ± 0.04
	present	2.18 ± 0.02	0.92 ± 0.06	0.50 ± 0.03	0.43 ± 0.03	0.080 ± 0.002	1.13 ± 0.05

C_{ox} – oxidizable carbon; HS – humic substances; HA – humic acid; FA – fulvic acid; C_{hws} – hot-water soluble carbon

of this SOM has decreased (however, not with a statistically significant result, Figures 1–3).

On the contrary, Libčeves locality soil has been classified as sandy clay loam. This is reflected in relatively low CEC and EBC (the lowest within the whole set) with the present sample having its CEC value a little bit higher than the file sample. The degree of sorption is classified as saturated (Němeček et al. 2011), which corresponds to the carbonate contents and neutral or slightly alkaline pH_{KCl} . In this locality, the C_{ox} content and other components (Table 2) increased most markedly, but

the quality of this SOM along with the Račíněves site has fallen in the greatest extent (Figures 1–3).

As to the grain composition, the Chernozem soil from the Libochovice samples has been classified as clay loam; it contains 2.1% $CaCO_3$ and is slightly alkaline (pH_{KCl}). Consequently, its CEC and EBC values are relatively high with the present samples showing higher values than the archived samples. The SOM content has increased by app. 0.5%, but the SOM quality has fallen slightly, but conclusively.

The Chernozem soil from the Nová Ves probe has been classified as loam; it is relatively low in carbonate

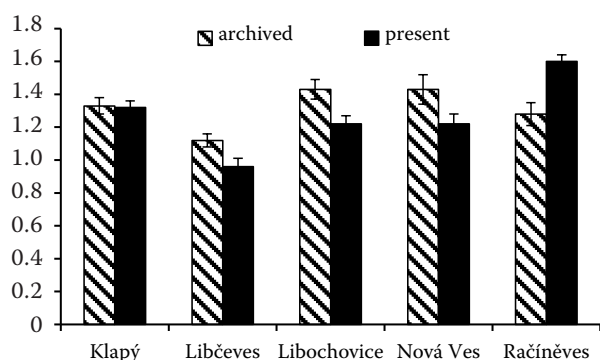


Figure 1. Humic acid (HA): nFA (fulvic acid) ratio of Ap horizons in selected Central Bohemia Chernozems

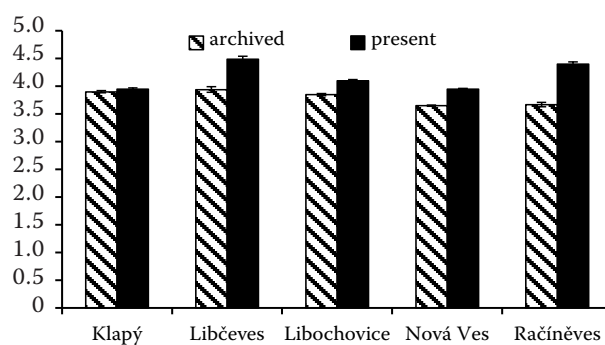


Figure 2. Colour quotient Q4/6 of Ap horizons in selected Central Bohemia Chernozems

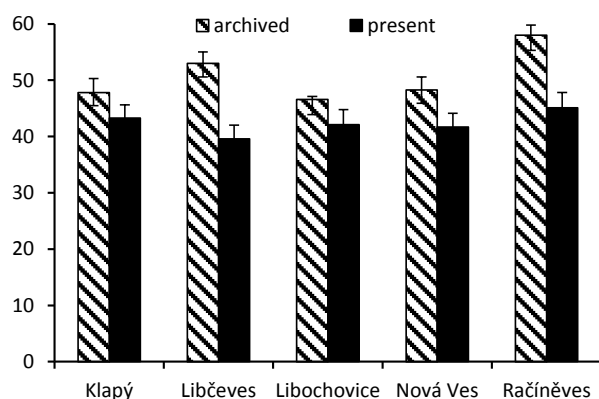


Figure 3. Degree of humification (Dh) of Ap horizons in selected Central Bohemia Chernozems

contents (Table 1). The Nová Ves site is the only one in the set, for which the soil reaction has fallen over the 50-year period of treatment from 7.20 to 6.90 pH_{KCl} . It shows the lowest sorption saturation values (Table 1) within all five Central Bohemian Chernozems soils, but similarly to the other sites the CEC value of the present sample has increased. The SOM content and other components also have increased (Table 2), but in parallel with the SOM quality decline (Figures 1–3).

In terms of grain composition, the Račíněves Chernozem soil has been classified as clay loam, but the carbonate content is not available in the file. The present analysis has shown 0.94% CaCO_3 content. This locality shows the lowest pH_{KCl} (Table 1) within the whole set, but no soil reaction decline has been registered when comparing the present and file samples. There has been registered a moderate DS decline of the sorption complex, along with a moderate rise in CEC. The total SOM content and contents of other components (Table 2) have risen significantly, but similarly to the other sites, their quality has fallen (Figures 1–3).

Using the set of selected Central Bohemian Chernozems, analytical file data of deposited soil samples analysed together with the present samples are compared with data of samples collected at present at the same sites. The resulting values of SOM parameters in Ap horizons are rather inconsistent. Established SOM quality indicators, i.e. the HA:FA ratio (Figure 1), colour quotient Q4/6 (Figure 2) and possibly the degree of humification Dh (Figure 3), indicate the worsening (relatively) quality of SOM (Stevenson 1994) in all the localities over past approx. 50 years, even so not much noticeably in some localities (Klapý, Libochovice).

However, values of qualitative parameters of SOM from the selected Central Bohemian Chernozem localities are generally relatively low for this soil type, primarily in contrast to the oldest reported data (Pospíšil 1980, Stevenson 1994). On the contrary, the data shown in Table 2 indicate a considerable increase (improvement) in all quantitative values of SOM in present A_p horizons compared to deposited samples. However, contents of C_{ox} can be regarded as corresponding to the given soil type (Stevenson 1994). The sorption complex values cannot be regarded as relating to the SOM quality, because the increase of CEC values can be apparently attributed to the increase of total SOM content (Němeček et al. 2011, Maia et al. 2013). The increase of CEC values could be caused by the clay mineral component of sea sediments due to lower ploughing in recent decades. However, the quantification concerning this factor would require additional analyses.

Moreover, it is also possible to speculate about certain diversity of the used analytical methods or variances between the methods.

However, the comparison of the current and old data of Chernozemic SOM quality can still be considered an open issue.

Acknowledgements

Special thanks belong to the workers of the Research Institute for Soil and Water Conservation in Prague engaged by the Ministry of Agriculture of the Czech Republic, Project No. MZE0002704902.

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Received on April 11, 2016

Accepted on January 17, 2017