WATER-STABLE AGGREGATES AS A KEY ELEMENT IN THE STABILIZATION OF SOIL ORGANIC MATTER IN THE CHERNOZEMS

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Abstract: The content of soil organic matter (SOM) with regards to soil structure was evaluated in Chernozems of the Danube Lowland (Slovakia). The content of water-stable macro-aggregates (WSA_{ma}) in the studied soils was on average 74.6%. Important from the agronomical viewpoint aggregates fraction 0.5–3.0 mm amounted on average 29.9%. The average content of soil organic carbon (SOC) was 13.5 ± 3.78 g kg^{-1} and it was significantly higher as compared to the content of this element in water-stable micro-aggregates (WSA_{mi}) (10.5 ± 4.22 g kg^{-1}). The highest content of SOC was in the WSA_{ma} (13.8 ± 4.36 g kg^{-1}). The content of labile carbon (C_L) was on average of 2.03 g kg^{-1}. On average, the contents of C_L in water-stable aggregates (WSA) were lower as compared to C_L in soil. SOC decreased with rising sand content. In contrast, SOC increased with increasing clay and silt contents in the soil. The content of SOC in WSA was conditioned by SOC concentration, the content of silt and clay fractions as well as by the content of WSA. The same trend was observed for C_L in WSA; however, C_L in WSA_{mi} was not affected by C_L in soil, rather by SOC with combination of other parameters such as: silt and clay contents and content of WSA_{mi}.

Keywords: Chernozems, labile carbon, soil organic carbon, water-stable macro-aggregates, Danube Lowland.

1. INTRODUCTION

South part of Slovakia is characterized by the presence of fertile black-earth soils known as Chernozems, which characterized by a thick, rich in organic matter, well-structured and dark-coloured humic horizon developed under the influence of steppe vegetation. The Russian soil scientist Dokuchaev coined the name "Chernozem" in 1883 to denote the typical zonal soil of the tall grass steppes in continental Russia. Many Chernozems correspond to: Calcareous Black Soils and Kalktschernoseme (Germany); Chernosols (France); Eluviated black soils (Canada); several suborders (especially Udolls) of the Mollisols (United States of America) and Chernossolos (Brazil). Chernozems cover an estimated 230 million ha worldwide, mainly in the middle latitude steppes of Eurasia and North America, north of the zone with Kastanozems (WRB, 2014). Chernozems occupies an area of 291 073 ha, accounting for 11.9% of agricultural land in Slovakia (Zaujec et al., 2009).

As it is above mentioned, the Chernozems are rich in organic matter. For example, Šimanský & Bajčan (2014) published ranges of soil organic carbon (SOC) from 0.93% to 1.64% (the depth 0–0.3 m), in Chernozems of Slovakia. SOC plays an important role in cycling plant nutrients, increasing grain yield and improving the physical, chemical and biological properties of soils (Bhattacharyya et al., 2010; Gaida et al., 2013) and it varies across space and time and is a result of the influence of many environmental and anthropogenic factors (Kalembasa & Becher, 2012; Jonczak, 2014). Since the changes in land use significantly affect the carbon cycle, it is very important stabilized its content in soils. There are few factors of stabilization and protection of carbon in soils. As mentioned von Lützov et al., (2008), SOC can be controlled by association with clay minerals or Fe and Al oxides, by sequestration into macro- and micro-pores of soil aggregates and biochemical stabilization, however the mechanism of SOC protection within aggregates is poorly understood (Zotarelli et al., 2005).

Very important factor of SOC stabilization is favourable soil structure, because SOC is one of the most significant binding agents which are responsible for association of mineral particles together into the aggregates (Rabbi et al., 2015). If aggregates are water-resistant they can protect carbon inside of aggregates (Šimanský & Bajčan, 2014) which is an effective strategy to mitigate global climate change. This knowledge is important for assessing the potential for forming optimal soil structure and carbon sequestration and its stabilization in water-stable aggregates in arable Chernozems of Slovakia.

Under this context, we hypothesised that in such soils as Chernozems, the water-stable aggregates can be considered as a key element in the stabilization of soil organic matter (SOM), and therefore the aim of our work was to evaluate the content of SOM with regards to soil structure of Chernozems. The objectives of the present study were: 1) to quantify the content of individual size fractions of WSA and SOM content in Chernozems of Danube Lowland (Slovakia), 2) to determine the relationships between SOM, texture and individual size classes of WSA, and 3) to determine the threshold limits for SOM which are significant for formation of individual size fractions of WSA.

2. MATERIAL AND METHODS

Sixteen soils with a wide range of SOM contents and texture (Table 1) were studied in selected localities of the Danube Lowland (Fig. 1) during the years 2003-2011. The soils were classified according to the World Reference Base for Soil Resources (WRB, 2014) based on whole-profile morphology as Chernozems. Mean annual temperatures in the studied localities ranged from 9.0 to 10.4^{o}C and mean annual precipitation varied from 564 to 580 mm.

Table 1. Soil organic matter and particle size distribution of the Chernozems - Danube Lowland (0–0.3 m)

Locality	Soil type	Soil management	SOC	C_L	Clay	Silt	Sand	Soil texture
			g kg^{-1}		%			
Svätoplukovo	Haplic Chernozem	arable soil conventional tillage	19.6	3.80	11	52	38	silt loam
Nové Sady	Haplic Chernozem	arable soil conventional tillage	15.6	1.91	14	60	26	silt loam
Voderady	Haplic Chernozem	arable soil conventional tillage	21.7	2.27	21	54	25	silt loam
Kalná nad Hronom	Haplic Chernozem	arable soil minimal tillage	15.6	1.88	15	62	23	silt loam
		arable soil conventional tillage	13.7	1.82	16	57	28	silt loam
Borovce	Luvi-Haplic Chernozem	arable soil minimal tillage	13.6	2.61	20	57	23	silt loam
	Haplic Chernozem	grassland	13.9	2.45	20	51	29	silt loam
	Haplic Chernozem	arable soil conventional tillage	13.0	1.69	9	61	30	silt loam
Bajč	Haplic Chernozem	vineyard intensively cultivated rows	9.30	1.60	7	31	62	sandy loam
		vineyard grassy strips between rows	10.5	1.80	7	21	72	sandy loam
Dúlovce	Haplic Chernozem	vineyard intensively cultivated rows	7.50	2.18	6	16	78	loamy sand
		vineyard grassy strips between rows	9.30	1.64	7	15	78	loamy sand
Dvory nad Žitovou	Haplic Chernozem	vineyard intensively cultivated rows	10.5	1.03	8	25	67	sandy loam
		vineyard grassy strips between rows	12.0	1.33	8	25	67	sandy loam
Malá Máňa	Luvi-Haplic Chernozem	vineyard intensively cultivated rows	13.1	1.86	21	25	54	sandy clay loam
		vineyard grassy strips between rows	6.40	2.55	21	25	54	sandy clay loam

SOC – total soil organic carbon, C_L – labile carbon

The soil samples were collected from the topsoil (0–30 cm) of all the 16 Chernozems. After sampling, the soil samples were air dried at a laboratory temperature, homogenized and soil samples for determination of SOM parameters and particle-size distribution were grinded. SOC content was measured using the wet combustion method, it means: oxidation of SOM by a mixture of 0.07 M H_2SO_4 and $K_2Cr_2O_7$ with titration using Mohr's salt as is described in Hrivňáková et al., (2011).

Figure 1. Selected sites in Slovakia. *1: Svätoplukovo, 2: Nové Sady, 3: Voderady, 4: Kalná nad Hronom, 5: Borovce, 6: Bajč, 7: Dúlovce, 8: Dvory nad Žitavou, 9: Malá Máňa*

Labile carbon (C_L) content was determined using 0.005 M $KMnO_4$ (Loginov et al., 1987). The particle-size distribution was determined after dissolution of $CaCO_3$ with 2 M HCl and removing of organic matter with 6% H_2O_2. After repeated washing, soil samples were dispersed using sodium hexametaphosphate solution. Content of silt, sand and clay fractions was determined with the pipette method as described in Hrivňáková et al., (2011). The soil samples for determination of water-stable aggregates were air-dried at a laboratory temperature, sieved through a set of sieves, and then bulked into seven size fractions (>7, 7–5, 5–3, 3–1, 1–0.5, 0.5–0.25, <0.25 mm). These air-dried aggregates were used to measure the size fractions of water-stable aggregates (WSA). Water-stable aggregates in size fractions more than 0.25 mm are macro-aggregates (WSA_{ma}) and less than 0.25 mm are micro-aggregates (WSA_{mi}). Size fractions of WSA were determined by a Baksheev method. Briefly, soil sample (30 g) was overflowed with distilled water (water level 1 cm above aggregates). Two hours later, the sample was transferred to the top sieve (>5 mm) in a cylindrical container (Baksheev device), which has been filled with distilled water. Cylinder was hermetically closed and the sample was sieved 12 minutes. The size fractions of WSA were following: >5, 5–3, 3–2, 2–1, 1–0.5, 0.5–0.25 and <0.25 mm. The material retained was quantified in each sieve except micro-aggregates (<0.25 mm). Their content was calculated as difference between total weight of soil sample and sums of macro-aggregates (>0.25 mm). In the size fractions of WSA we measured organic carbon content (SOC in WSA) by the Tyurin method (Hrivňáková et al., 2011) and labile carbon content (C_L in WSA) by the Loginov method (Loginow et al., 1987). The stability coefficient of WSA_{ma} (Sw) was calculated according to equation 1:

$$Sw = \frac{WSA_{ma}(\%) - 0.09\,sand(\%)}{silt(\%) + clay(\%)} \quad (1),$$

where WSA_{ma} is the content of water-stable macro-aggregates.

Pearson *r* coefficient was calculated to test the one to one relationships between variables (soil parameters) and t-tests were applied to inform on the significance of the differences. For determination of relationships between SOM in WSA and other soil parameters the multiple regressions analyse was used. All statistical analyses were carried out with the statistical software Statgraphics Centurion XV.I (Statpoint Technologies, Inc., USA).

3. RESULTS AND DISCUSSION

The contents of individual fractions of WSA of Chernozems in selected localities of the Danube Lowland are shown in Table 2. In Chernozems, the content of WSA_{mi} on average was 25.4% and content of WSA_{ma} 74.6%. Bartlová et al., (2015) presented contents of WSA_{ma} in range 30-60%, however better soil structure is connected with upper level of mentioned interval. The content of macro-aggregates in size from 0.5-3 mm is important from the agronomical point of view (Šimanský & Bajčan, 2014) and their average content was 29.9% in Chernozems. Content of WSA decreased by larger size fractions of WSA ($WSA_{mi} > WSA_{ma}$: size fractions 0.25–0.5 mm > 0.5–1 mm > 1–2 mm > 5–3 mm and > more than 5 mm). Very important stability parameter of soil structure is stability coefficient of WSA_{ma} (Sw) and its values are in Table 2. The Sw values above 1 indicate higher macro-aggregate stability. Aggregate stability is affected by soil intrinsic factors as electrolyte concentration, types of exchangeable cations, clay mineralogy (Paradelo et al., 2013), content of carbonates (Vaezi et al., 2008), SOM (Saha et al., 2011; Šimanský & Bajčan, 2014), iron and aluminium "free" oxides (Barthes et al., 2008) and soil texture. Parameters of SOM in the studied soils are presented in Table 3. The average content of SOC was 13.5 ± 3.78 g kg^{-1}. As mentioned above it the content of SOC in Chernozems of Slovakia is different (Šimanský & Bajčan, 2014) and it depends on a lot of factors and management practices (Balashov & Buchkina, 2011). Based on t-tests, in soils the content of SOC was significantly higher (P ≤ 0.05) than the content of

organic C in the water-stable aggregates (SOC in WSA) (12.2 ± 3.99 g kg^{-1}) as well as in water-stable micro-aggregates (SOC in WSA$_{mi}$) (10.5 ± 4.22 g kg^{-1}). The highest content of C was noticed in water-stable macro-aggregates (SOC in WSA$_{ma}$) (13.8 ± 4.36 g kg^{-1}), but this was not significantly higher (P > 0.05) than the SOC in soils (on average). As reported by Šimanský (2013) higher carbon content is in macro- rather than in the micro-aggregates mainly due to the increase of particulate organic matter (de Moraes Sa et al., 2014) and also its content is influenced by the land uses or soil management practices (Balashov & Buchkina, 2011; Gaida et al., 2013). The content of labile carbon (C$_L$) in Chernozems was on average of 2.03 g kg^{-1} and ranged between 1.03 g kg^{-1} at the Dvory nad Žitavou (intensively cultivated rows of vine) and 3.80 g kg^{-1} at Svätoplukovo locality. On average, the C$_L$ contents in WSA (macro and micro) were lower compared with C$_L$ in the soil. On average, the content of C$_L$ in soil represented 15% from SOC. Similar the content of C$_L$ in WSA, WSA$_{ma}$ and WSA$_{mi}$ represented 15, 17 and 14 % from SOC in WSA, WSA$_{ma}$ and WSA$_{mi}$, respectively. It means that WSA have capacity for retain of C$_L$ from soil. As reported Parton et al., (1995) labile components of SOM as roots exudates have a very important influence on the changes of both the physical and chemical properties in soils. The SOC positive correlated with C$_L$; however, the most significant correlation was observed between SOC in WSA$_{ma}$ and C$_L$ in WSA$_{ma}$ (r = 0.885, P ≤ 0.001) and then follows: SOC in WSA (r = 0.835, P ≤ 0.001) > SOC in WSA$_{mi}$ and C$_L$ in WSA$_{mi}$ (r = 0.631, P ≤ 0.01) > SOC in soil and C$_L$ in soil (r = 0.593, P ≤ 0.05). The average values of SOC and C$_L$ in WSA

were different depending on the size fractions of WSA. Biswas et al., (2009) observed increased (linear) concentration of C for larger size fractions of aggregates, which corresponded with our results. We observed increase (linear) of C concentration for larger size fractions of aggregates: SOC = 0.05x (size fraction of WSA) + 1.13; R^2 = 0.709 and C$_L$ = 34.79x (size fraction of WSA) + 1730; R^2 = 0.833.

The studied Chernozems had different particle-size distribution and it ranged from loamy sand to sandy clay loam (Table 1). Table 4 shows the correlations between SOM parameters and soil texture as well as content of WSA. SOC decreased with rising sand content (r = −0.716, P ≤ 0.01) in Chernozems. In contrast, SOC increased with increasing clay (r = 0.637, P ≤ 0.01) and silt (r = 0.636, P ≤ 0.01) contents in the soil. Higher clay content in the soil, results in higher organic matter content (Wang et al., 2013).

Most of the SOC in soils is associated with the fine fraction and the dominant mechanism is chemical protection (Basile-Doelsch et al., 2007). Between C$_L$ and particle-size distribution significant correlations were not observed what is surprising. The fine fraction of soils consists of silt and clay-sized organo-mineral associations, and it is believed that mainly labile carbon is primarily sorbed to the fine fraction (Christensen, 2001). SOM can be physically protected from microbial mineralization through sorption to clay minerals and enclosure within soil aggregates (Peth et al., 2008). At the same time, we determined positive correlations between SOM in WSA and texture, however, any statistical significant correlation was not observed between SOM and individual size fractions of WSA (Table 4).

Table 2. Contents of water-stable aggregates (%) and values of index stability of water-stable macro-aggregates

Locality	WSA$_{mi}$	WSA$_{ma}$	Individual size fractions of water-stable macro-aggregates in mm						Sw
			0.25–0.5	0.5–1	1–2	2–3	3–5	>5	
Svätoplukovo	26.1	73.9	13.8	13.5	15.2	20.6	7.8	3.2	1.13
Nové Sady	30.5	69.5	36.2	13.9	15.2	2.7	1.7	0.1	0.91
Voderady	23.1	76.9	24.2	25.6	19.0	5.2	1.5	1.5	1.00
Kalná nad Hronom	41.1	58.9	27.0	17.4	8.3	4.3	1.7	0.4	0.74
	12.2	87.8	23.8	22.5	28.2	8.5	1.2	3.6	1.18
Borovce	41.5	58.5	21.7	16.4	10.3	6.0	3.3	0.8	0.74
	32.0	68.0	16.9	21.9	19.0	7.3	3.3	1.1	0.92
	23.7	76.3	20.7	23.7	18.6	7.2	2.3	0.2	1.06
Bajč	13.2	86.8	19.8	21.0	24.6	12.9	4.5	4.0	2.14
	17.7	82.3	18.3	27.9	14.8	8.4	8.8	4.1	2.71
Dúlovce	23.2	76.8	36.6	29.9	7.8	1.8	0.6	0.1	3.17
	18.6	81.4	22.5	15.8	13.4	12.5	11.3	5.9	3.38
Dvory nad Žitovou	35.9	64.1	30.0	25.6	7.2	1.1	0.1	0.1	1.76
	12.0	88.0	15.2	28.5	16.4	10.2	9.8	7.9	2.48
Malá Máňa	30.6	69.4	23.0	23.0	16.5	6.6	0.2	0.1	1.40
	25.0	75.0	23.1	40.8	7.8	2.9	0.3	0.1	1.53
Average	25.4	74.6	23.3	15.1	7.4	7.4	3.7	2.1	1.64

WSA$_{mi}$ – content of water-stable micro-aggregates, WSA$_{ma}$ – content of water-stable macro-aggregates, Sw – stability coefficient of water-stable macro-aggregates

Table 3. Content of soil organic matter in water-stable aggregates

Locality	SOC (g kg^{-1})			C$_L$ (g kg^{-1})		
	average in WSA	in WSA$_{mi}$	average in WSA$_{ma}$	average in WSA	in WSA$_{mi}$	average in WSA$_{ma}$
Svätoplukovo	18.9	16.2	21.6	2.85	2.59	3.11
Nové Sady	12.4	12.5	12.3	1.39	1.29	1.49
Voderady	19.5	20.5	18.5	2.36	2.58	2.13
Kalná nad Hronom	16.0	14.9	17.0	2.34	2.35	2.34
	14.0	10.7	17.3	2.18	2.26	2.11
Borovce	13.9	11.1	16.7	2.51	2.50	2.51
	13.5	10.2	16.7	2.30	2.39	2.22
	12.8	11.5	14.0	1.61	1.63	1.58
Bajč	7.20	5.20	9.20	1.48	1.50	1.46
	5.90	5.40	6.40	1.11	0.83	1.40
Dúlovce	7.50	6.80	8.20	0.97	0.81	1.13
	10.5	5.30	15.7	1.96	1.96	1.96
Dvory nad Žitovou	8.30	8.40	8.10	1.16	0.92	1.39
	8.80	7.50	10.0	1.73	1.85	1.61
Malá Máňa	12.3	10.2	14.3	1.38	1.25	1.52
	13.5	11.7	15.3	2.07	1.96	2.18
Average	12.2	10.5	13.8	1.84	1.79	1.88
Standard deviation	3.99	4.22	4.36	0.56	633	505
SOM in soil vs. SOM in WSA t-test	0.0080	0.0000	0.6136	0.1482	0.1379	0.1883

SOC – total soil organic carbon, C$_L$ – labile carbon, WSA – content of water-stable aggregates, WSA$_{mi}$ – content of water-stable micro-aggregates, WSA$_{ma}$ – content of water-stable macro-aggregates

Table 4. Correlation coefficients (r) between soil organic matter and particle-size distribution and water-stable aggregates

		Clay	Silt	Sand	WSA$_{mi}$	WSA$_{ma}$
SOC	in soil	0.637[**]	0.636[**]	−0.716[**]	ns	ns
C$_L$		ns	ns	ns	ns	ns
SOC	average in WSA	0.649[**]	0.708[**]	−0.781[***]	ns	ns
	in WSA$_{mi}$	0.601[*]	0.704[**]	−0.763[***]	ns	ns
	average in WSA$_{ma}$	0.606[*]	0.615[*]	−0.690[**]	ns	ns
C$_L$	average in WSA	0.520[*]	0.584[*]	−0.640[**]	ns	ns
	in WSA$_{mi}$	0.540[*]	0.608[*]	−0.665[**]	ns	ns
	average in WSA$_{ma}$	ns	0.520[*]	−0.570[*]	ns	ns

SOC – total soil organic carbon, C$_L$ – labile carbon, WSA – content of water-stable aggregates, WSA$_{mi}$ – content of water-stable micro-aggregates, WSA$_{ma}$ – content of water-stable macro-aggregates. ns – non-significant; [*] – $P \leq 0.05$, [**] – $P \leq 0.01$, [***] – $P \leq 0.001$

The SOC has relatively few reactive functional groups to support the sorption and stabilization of SOC tends to occur by the stabilization of soil aggregates in combination with other pedological factors, such as particle-size distribution. Since we wanted to know which parameters are essential for stabilization of C in WSA in Chernozems, we identified multiple regression models for SOM (Table 5). Content of SOC in WSA on average depended on SOC concentration, contents of silt and clay as well as content of WSA. The same trend was observed for C$_L$ in WSA; however C$_L$ in WSA$_{mi}$ was not dependent on C$_L$ in soil, but on SOC in combination with other parameters, such as: silt and clay contents and content of WSA$_{mi}$. The ratios of SOM content in WSA to that in soil were different in Chernozems. These results demonstrated that Chernozems had a rather wide ability to a sequestration of SOC from soil to individual size fractions of WSA. In our study, we observed that changes in contents of SOC and C$_L$ in size fractions of WSA were accompanied by those in the size fractions of WSA of the studied Chernozems.

However, maximum absolute values of contents of SOC and C$_L$ did not correspond to maximum values of individual size fractions of WSA in the studied Chernozems. These results did not enable us to distinguish the maximum formation of individual size fractions of WSA by SOM in Chernozems; therefore we did not give any threshold limit for SOM in WSA. The contents of individual size fractions of WSA did not demonstrate their clear contribution to the accumulation of SOM.

Table 5. Multiple regression models for the soil organic matter in water-stable aggregates of Chernozems

Multiple regression models	Probability
SOC in WSA_{mi} = -0.455 + 0.927 SOC in soil + 0.002 Clay+Silt + 0.006 WSA_{mi}	0.0000
SOC in WSA_{ma} = 0.158 + 0.532 SOC in soil + 0.008 Clay+Silt + 0.001 WSA_{ma}	0.0061
C_L in WSA_{mi} = 489.4 + 579.3 SOC in soil + 14.5 Clay+Silt − 10.0 WSA_{mi}	0.0177
C_L in WSA_{ma} = 465.1 + 0.490 C_L in soil + 8.407 Clay+Silt − 0.335 WSA_{ma}	0.0026

SOC – total soil organic carbon, C_L – labile carbon, WSA – content of water-stable aggregates, WSA_{mi} – content of water-stable micro-aggregates, WSA_{ma} – content of water-stable macro-aggregates

4. CONCLUSION

The content of soil organic carbon in water-stable aggregates on average depended on the contents of soil organic carbon, silt and clay and water-stable aggregates. The same trend was observed for labile carbon in water-stable aggregates; however labile carbon in water-stable micro-aggregates was not dependent on labile carbon in soil, but on soil organic carbon in combination with other parameters, such as: silt and clay contents and content of water-stable micro-aggregates. If the content of C in the water-stable aggregates is smaller than the C content in the soil, water-stable aggregates can retain of C within of them from the soil. The higher stability of water-stable aggregates means the more C protected within the aggregates and therefore we can consider the water-stable aggregates for a key factor in the stabilization of soil organic matter in the Chernozems; however, mainly in combination with higher contents of silt and clay.

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