Labile Forms of Carbon and Soil Aggregates

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Abstract


Soil organic matter (SOM) and soil structure are in the mutual dynamic interaction and this relationship is influenced not only by soil properties (Martins et al. 2013; Wang et al. 2016), but also by the way of land use (Barreto et al. 2009; Wang et al. 2014). The positive influence of stable components of SOM (like humus substances) on the quality of soil and soil aggregates is evident (Bartlová et al. 2015). However, according to Yang et al. (2012), the labile pools of carbon also significantly affect the quality of soil and moreover they can be used to monitor the changes in SOM in a shorter time period. The lability of SOM depends on its chemical recalcitrance and physical protection against microbial activity (Sit-
VERIA et al. 2008). The increase in SOM amount is associated with the increase of the amount of carbon-rich macro-aggregates (Six et al. 2002) and with the enrichment of water-resistant macro-aggregates with new SOM (AnGers & Giroux 1996). Its components are incorporated into various levels of the soil aggregates hierarchy, from the first formation of basic organo-mineral complexes to stabilizing of larger aggregates (Six et al. 2004). Labile fractions include various components of organic matter in soil, which are characterized by a short turnover. Cold (CWEOC) and hot (HWEOC) water extractable organic carbons are the most active pools of SOM and play an important role in the global carbon turnover (Bu et al. 2011) and are a part of dissolved organic carbon (Zsolnay 2003; Fernández-Romero et al. 2016). Carbon that is oxidizable with KMnO₄ (Cᵢ) includes all organic components that are easily oxidizable with KMnO₄, including the labile humus material and polysaccharides (Conteh et al. 1999).

The objectives of this study were (i) to assess the influence of labile carbon fractions (CWEOC, HWEOC, and Cᵢ) on the proportions of dry-sieved (DSA) and wet-sieved (WSA) macro-aggregates, (ii) to determine the relationship between the content of total organic carbon (TOC) and its labile fractions (CWEOC, HWEOC, and Cᵢ) in the soil and in the fractions of macro-aggregates (DSA, WSA).

**MATERIAL AND METHODS**

**Characteristics of the territory.** The studied areas are located in different parts of Slovakia. Mollic Fluvisol comes from the locality Horná Kráľová (48°24′N, 17°92′E) and Haplic Chernozem comes from the locality Pata (48°16′N, 17°49′E), which are situated on the northern border of the Danube Basin. Geological structure is characterized by neogene strata, which consist mainly of claystones, sandstones, and andesites covered with younger quaternary rocks represented by different fluvial and eolian sediments (Biely et al. 2002). Natural vegetation consists mostly of ash-oak-elm-alder forests, and along the river, there are willow-poplar forests and floodplain forests. In the elevated areas and dunes, xerophilic communities of oak-elm forests are dominant (Korec et al. 1997). Eutric Fluvisol and Haplic Luvisol come from the locality Vráble (48°24′N, 18°31′E), which is situated in the Danube Lowland, in the unit of the Danube Plain, namely in the Nitra Upland. Geological structure is characterized by neogene sediments – loess and loamy loess. Neogene bedrock is formed by lake and brackish sediments (clays, gravels, and sands) (Biely et al. 2002). In the lower parts there are oak forests and higher beech forests dominate. Rendzic Leptosol comes from the locality Turá Lúka (48°44′N, 17°32′E), which is situated at the eastern foot of the White Carpathians, in the Myjava Upland, in the valley of the river Myjava. Geological structure is characterized by the limestones and marls of the klippen belt, chalk clay-marl layers and neogene conglomerates, sandstones, and sands. In the forests, oak and hornbeam dominate, with beech in higher parts and conifers on dolomites and limestones (Korec et al. 1997). Eutric Cambisol comes from the locality Spišská Belá (49°11′N, 20°27′E), which is situated in the northern part of the Poprad Basin. Geological structure is characterized by the “core mountains” of the Central Western Carpathians. This part of the mountains is composed of mica schists to gneisses, locally early palaeozoic phyllites, which are covered with deluvial sediments (Biely et al. 2002). In the forests, spruce dominates.

**Experimental design.** The experiment included four types of ecosystems representing different land use (forest, meadow, urban, and agro-ecosystems) of six soil types (Eutric Fluvisol, Mollic Fluvisol, Haplic Chernozem, Haplic Luvisol, Eutric Cambisol, and Rendzic Leptosol) (WRB 2006) most frequent in Slovak lowlands and uplands and intensively agriculturally used. The forest ecosystems are natural forests with human control, the meadow ecosystems were established by man 30 years ago, the urban ecosystems are represented by soils of urban landscape (grasses in a town influenced by human activities), and the fields in agro-ecosystems are located at different farms under real production conditions.

**Soil samples and analytical methods used.** The soil samples for chemical and physical analysis were collected in three replicates to a depth of 0.30 m, and dried under a constant room temperature of 25 ± 2°C. Basic chemical and physical properties of the soils are characterized in the Table 1. For conducting the chemical analysis, the soil samples were ground. To determine the fractions of soil aggregates, the soil samples were divided by a sieve (dry and wet sieve) to size fractions of the net aggregates (Sarkar & Halder 2005). The particle size distribution was determined after dissolution of CaCO₃ with 2 mol HCl/dm³ and oxidation of the organic matter with 30% H₂O₂. After repeated washing, samples were dispersed using Na(PO₃)₂. Silt, sand, and clay fractions were determined according
to the pipette method (van Reeuwijk 2002). In the soil and soil macro-aggregates (dry and wet sieve), the TOC by wet combustion (Orlov & Grišina 1981) and C\(_\text{L}\) by KMnO\(_4\) oxidation (Loginov et al. 1987) were determined. In the soil, CWEOC and HWEOC were determined according to the method by Ghani et al. (2003) with the final determination of organic carbon by wet combustion (Orlov & Grišina 1981).

The pH of the soil was potentiometrically measured in a supernatant suspension of a 1:2.5 soil:liquid mixture. The liquid is 1 mol KCl/dm\(^3\) (pH\(_\text{KCl}\)) (van Reeuwijk 2002); total exchange basis (T) was determined according to Soil Survey Staff (2014).

The obtained data were analyzed using Statgraphic Plus statistical software (Ver. 4, 1994). A multi-factor ANOVA model was used for individual treatment comparisons at \(P < 0.05\), with separation of the means by Tukey’s multiple range test. Correlation analysis was used to determine the relationships between the chemical properties and the parameters of soil structure stability. Significant correlation coefficients were tested at \(P < 0.05\) and \(P < 0.01\).

### RESULTS AND DISCUSSION

**Labile fractions of carbon and the proportion of soil aggregate fractions.** The proportion of fractions of soil aggregates is influenced not only by the amount of carbon, but also its stability and/or lability. The relationships between the individual fractions

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Ecosystem</th>
<th>pH</th>
<th>TOC (g/kg)</th>
<th>T (mmol/kg)</th>
<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
</tr>
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<td>Haplic Chernozem</td>
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<td>347.20</td>
<td>14.61</td>
<td>42.34</td>
<td>43.05</td>
</tr>
<tr>
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<td></td>
<td>6.46</td>
<td>20.13</td>
<td>389.90</td>
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<tr>
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</tr>
<tr>
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<td>50.13</td>
<td>32.53</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>11.44</td>
<td>347.93</td>
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<td>36.78</td>
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</tr>
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<td>11.17</td>
<td>70.55</td>
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<td>17.11</td>
<td>371.49</td>
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<td>15.11</td>
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<td>11.07</td>
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<tr>
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<td>5.87</td>
<td>8.63</td>
<td>321.44</td>
<td>17.47</td>
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</tr>
<tr>
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<td>353.32</td>
<td>11.74</td>
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<td>9.33</td>
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<td>69.25</td>
<td>19.27</td>
</tr>
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<td>23.52</td>
<td>470.89</td>
<td>11.00</td>
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<td>14.95</td>
</tr>
<tr>
<td>UE</td>
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<td>7.37</td>
<td>20.07</td>
<td>468.66</td>
<td>10.64</td>
<td>72.75</td>
<td>16.61</td>
</tr>
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<td>7.16</td>
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<td>12.14</td>
<td>68.54</td>
<td>19.32</td>
</tr>
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<td>259.53</td>
<td>12.54</td>
<td>51.50</td>
<td>35.96</td>
</tr>
<tr>
<td>ME</td>
<td></td>
<td>5.99</td>
<td>33.92</td>
<td>283.63</td>
<td>10.11</td>
<td>55.39</td>
<td>34.50</td>
</tr>
<tr>
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<td></td>
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<td>48.84</td>
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<tr>
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<td>19.10</td>
<td>258.63</td>
<td>8.02</td>
<td>49.42</td>
<td>42.38</td>
</tr>
</tbody>
</table>

FE – forest ecosystem; ME – meadow ecosystem; UE – urban ecosystem; AE – agro-ecosystem; TOC – oxidizable organic carbon; T – total exchange bases
of DSA and WSA and individual fractions of labile carbon are different (Table 2). In the case of the proportion of smaller fractions of WSA (0.25–1.0 mm), a negative correlation between these fractions and the content of carbon that is oxidizable with KMnO₄ (C₇) were recorded, and in the case of WSA (0.5–1.0 mm) also with HWEOC. A deterioration of the soil structure condition is reflected in the increased proportion of the smallest fractions of soil aggregates (Whalen & Chang 2002). These smallest fractions of macro-aggregates contain the lowest amounts of carbon (Sohi et al. 2001), however more stabilized than in the larger fractions. In the case of larger DSA fractions (3–7 mm), a positive correlation between these fractions and water extractable carbon was recorded. Larger fractions of aggregates contain higher amount of carbon, however subjected to more intensive mineralization (Six et al. 2000; Wang et al. 2014). One of the reasons is a higher proportion of more labile fractions of carbon; the second is greater access of the pores for soil microorganisms that participate in these transformation processes. According to Ranjard and Richaume (2001), the limitation of decomposers access to organic substances is a key factor in the physical stabilization of carbon. At the beginning of the carbon accumulation, it decides about the carbon next stabilization in DSA and hence its subsequent content in WSA. The tendency was similar when comparing within a set of six soil types and also in one soil type (Table 2). Water-resistant macro-aggregates of the 0.5–3.0 mm size fraction are agronomically the most valuable aggregates. However, it was revealed that a lower limit (0.5–1.0 mm) does not correspond to optimal condition of the soil structure. Many soils with deteriorated soil structure exhibited an increased content of macro-aggregates of 0.5–1.0 mm size fraction. On the contrary, this fraction seems to be an important indicator of changes in the ecosystems.

If we compare the contents of the 0.5–1.0 mm size fraction of WSA in individual ecosystems within the Haplic Luvisol soil type (Figure 1a), the highest proportion of this fraction was in the agro-ecosystem. Emadi et al. (2009) also reported that in the ploughed soil a higher proportion of micro-aggregates and small macro-aggregates remains. In the case of other ecosystems, the contents of the 0.5–1.0 mm size fraction were in a balance. If we compare the contents of the 0.5–1.0 mm size fraction in the individual ecosystems in the set of different soils (Figure 1b), the tendency is the same, but the differences between the ecosystems are more significant. The lowest content of this fraction was in the meadow ecosystem. In this ecosystem, the root system has a high impact on the Table 2. Dependence between the fractions of dry-sieved (DSA) and wet-sieved (WSA) macro-aggregates and carbon in the set of six soil types and Haplic Luvisols

<table>
<thead>
<tr>
<th>DSA (mm)</th>
<th>Six soil types</th>
<th>Haplic Luvisols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOC</td>
<td>C₇</td>
</tr>
<tr>
<td>&gt; 7</td>
<td>−0.242</td>
<td>−0.047</td>
</tr>
<tr>
<td>5–7</td>
<td>0.343*</td>
<td>0.202</td>
</tr>
<tr>
<td>3–5</td>
<td>0.445**</td>
<td>0.346*</td>
</tr>
<tr>
<td>1–3</td>
<td>0.267</td>
<td>0.142</td>
</tr>
<tr>
<td>0.5–1.0</td>
<td>−0.049</td>
<td>−0.173</td>
</tr>
<tr>
<td>0.25–0.50</td>
<td>−0.140</td>
<td>−0.297</td>
</tr>
<tr>
<td>WSA (mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt; 5</td>
<td>0.081</td>
<td>0.287</td>
</tr>
<tr>
<td>3–5</td>
<td>0.303</td>
<td>0.445**</td>
</tr>
<tr>
<td>2–3</td>
<td>0.393**</td>
<td>0.387*</td>
</tr>
<tr>
<td>1–2</td>
<td>0.155</td>
<td>−0.017</td>
</tr>
<tr>
<td>0.5–1.0</td>
<td>−0.247</td>
<td>−0.368*</td>
</tr>
<tr>
<td>0.25–0.50</td>
<td>−0.305*</td>
<td>−0.479**</td>
</tr>
</tbody>
</table>

TOC – total organic carbon; C₇ – labile carbon; CWEOC – cold water extractable organic carbon; HWEOC – hot water extractable organic carbon; **P < 0.01; *P < 0.05
aggregation (Tisdall & Oades 1982) that may subject the mechanical linking of these smaller aggregates. Moreover, according to Verchot et al. (2011), the polysaccharides coming from the microbial activity play a crucial role in the formation of stable micro-aggregates and the carboxyl carbon supports in turn the stabilization through the occlusion. In addition to the dominance of more labile forms of carbon in the meadow ecosystem, there are also drier conditions in the root zone. Drying influences the stabilization of organic matter and also the formation of stronger linkages with soil mineral components.

More significant differences in the proportion of WSA of the 0.5–1.0 mm size fraction between the soil types were not recorded (Figure 2). Of the studied soil types, this fraction showed a more significantly lower proportion only in Rendzic Leptosol, in which also WSA of the > 5 mm size fraction had the highest proportion. The process of aggregation in Rendzic Leptosol compared to other soil types is different. This soil contains free calcium and in the case of skeletal Rendzic Leptosols also drought plays an important role. Such conditions were during most of the year also in the meadow ecosystem, in which the lowest content of WSA of the 0.5–1 mm size fraction was also recorded. The drying may contribute to the formation of linkages between the organic molecules and mineral surfaces (Denev et al. 2002). However, in the case of meadow ecosystem, the lowest content of this fraction was a result of higher contents of the labile forms of carbon, so the influence was direct. In the case of Rendzic Leptosol, the influence of labile forms of carbon was indirect. A greater part of SOM was bonded primarily in the larger aggregates, which had, in this case, significantly higher proportion. The strength of their linkages with the mineral components is also higher, which limits the disruption and the proportion of smaller fractions of aggregates. A significant role in the aggregation is played by exchangeable Ca\(^{2+}\), which supports the uptake and retention of water-soluble carbon (Setia et al. 2013).

**Labile fractions of carbon and their proportion in the fractions of soil aggregates.** Carbon content and its forms in the soil also influence its contents in the fractions of soil aggregates. In the WSA and DSA of the 0.5–1.0 mm size fraction, the highest variability in their contents was observed in the forest ecosystem. In this ecosystem, the highest inputs of carbon into the soil are reflected, and at the same time the highest variability of the forest communities, which results from the highest differences in the quality of organic substances inputs into the soil. The litter composition in coniferous and deciduous forests differs, or also the variability of the forest floor. The variability in carbon contents was more significant in the case of C\(_1\) (Figure 3) than
in TOC (Figure 4). The forest ecosystem was followed by meadow and urban ecosystems with grass vegetation cover. Organic inputs in these ecosystems were influenced by the inputs from aboveground biomass, left in place after mowing. The variability in the agro-ecosystem was clearly the lowest, with the lowest inputs into the soil. From the above given it follows that the higher were the inputs of organic substances, the greater was the variability in their incorporation into the soil aggregates.

TOC content was in a direct relationship with the content of individual labile fractions. Yang et al. (2012) recorded a high positive correlation between TOC and $C_L$ ($r = 0.901; P < 0.01$) in soil and Xue et al. (2013) also between TOC and HWEOC. In this case, a positive correlation between TOC and $C_L$ in soil aggregates with the contents of all studied labile fractions of carbon ($C_L$, CWEOC, HWEOC) in soil was recorded (Table 3). The contents of TOC and its labile fractions in soil significantly influence the content of TOC in the soil aggregates sizing up to 7 mm.

The influence of TOC and $C_L$ in soil on the content of TOC in DSA increased with a reduction of the size fraction ($r = -0.900; P < 0.05$), and in the case of the influence of HWEOC in soil on TOC in DSA increased with the size fraction enlarging ($r = -0.815; P < 0.10$).

CONCLUSION

In the case of DSA, the contents of labile fractions of carbon, in particular CWEOC and HWEOC, had a higher impact on the proportions of larger fractions of macro-aggregates (3–7 mm), while in the case of WSA, the impact of labile fractions of carbon, mainly $C_L$, was higher on the proportions of smaller fractions of aggregates (0.25–1.00 mm).

WSA size fraction of 0.5–1.0 mm seems to be an important indicator of changes in the ecosystems and its amount was in negative correlation with $C_L$ and HWEOC, thus its lower proportion will be in the ecosystems with higher sources of less stabilized organic matter, as is confirmed by the lowest content

![Figure 3](image-url)  
Figure 3. Labile carbon ($C_L$, mg/kg) in the 0.5–1.0 mm fraction of dry-sieved macro-aggregates (a) and of water-resistant macro-aggregates (b)  
AE – agro-ecosystem, FE – forest ecosystem, ME – meadow ecosystem, UE – urban ecosystem

![Figure 4](image-url)  
Figure 4. Total organic carbon (TOC, mg/kg) in the 0.5–1.0 mm fraction of dry-sieved macro-aggregates (a) and of water-resistant macro-aggregates (b)  
AE – agro-ecosystem, FE – forest ecosystem, ME – meadow ecosystem, UE – urban ecosystem
in the meadow ecosystem, i.e. in the natural ecosystem with a higher proportion of labile organic substances.

In the WSA and DSA size fractions 0.5–1.0 mm, the highest variability in the contents of TOC and C_L was recorded in the forest ecosystem > meadow ecosystem > urban ecosystem > agro-ecosystem. The higher were the inputs of organic substances into the soil, the greater was the variability in their incorporation into the soil aggregates.

The influence of the content of TOC and its labile forms on its contents in the DSA and WSA was different, and the contents of TOC and C_L in the aggregates were more significantly affected by the C_L content than by water soluble carbon. In the case of the WSA fractions, their carbon content was more affected in the 1–2 mm than in the 0.5–1.0 mm fraction.

**Acknowledgements.** This work was supported by the Slovak Research and Development Agency under the contract No. APVV-14-0087.

**References**


Emadi M., Baghernejad M., Memarian H.R. (2009): Effect of land-use change on soil fertility characteristics within

<table>
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<tr>
<th>TOC in aggregates</th>
<th>DSA (mm)</th>
<th>WSA (mm)</th>
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<tr>
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<td>0.860**</td>
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<td>0.883**</td>
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<td>0.25–0.50</td>
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<td>0.843**</td>
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<table>
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<th>WSA (mm)</th>
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<td>0.858**</td>
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</tbody>
</table>

CWEOC – cold water extractable organic carbon; HWEOC – hot water extractable organic carbon; **P < 0.01

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