

CARBON SEQUESTRATION AND ITS DYNAMICS IN WATER-STABLE AGGREGATES

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Sequestration of organic carbon in soils is an effective strategy to mitigate global climate change. Carbon sequestration leads to an increase in carbon stocks in soil, thereby reducing greenhouse gas emissions while improving soil quality and crop production. There are several published articles containing information in which the authors explain carbon sequestration in different soil types under different climatic conditions or farming systems, but on the other hand there is less information about carbon sequestration in water-stable aggregates. In field experiment, the manner in which different soil management practices influence carbon sequestration and its dynamics in water-stable aggregates was studied. We evaluated the soil samples taken from Haplic Luvisol (Dolná Malanta – Slovakia) from all treatments of tillage (conventional, minimal and grassland) and fertilisation (without fertilisation, crop residues together with NPK fertilisers and

only NPK fertilisers). The maintenance of carbon concentration within soil under conventional tillage and in native grassland was due to an enhanced incorporation of new organic matter from the coarse fraction of particulate organic matter to macro-aggregates and in treatment with ploughed crop residue together with NPK fertilisers, there was besides of this caused by the reduction of carbon mineralisation from the fine fraction. Soil management practices have a significant effect on the re-distribution of soil organic matter in water-stable aggregates. In conventional and minimal tillage, very important sources of carbon sequestration are agronomical favourable size fractions of water-stable macro-aggregates and in native grassland, as well as in all fertiliser treatments, the most important source of carbon sequestration is water-stable micro-aggregates.

Key words: carbon sequestration, soil organic matter, water-stable aggregates, soil tillage, fertilisation

Soil organic matter (SOM) is one of the most important indicators for the quality of soil environment that affects the amount of chemical, biological (Zancani *et al.* 2009) and physical processes (Šimanský *et al.* 2013) going on within the soil. The SOM concentration is dependent on soil management (Kladivko 2001; Šimanský *et al.* 2008; Šimon *et al.* 2009; Balashov & Buchkina 2011; Šoltysová & Danilovič 2011; Brown & Huggins 2012; Šimanský & Tobiašová 2012), but in a stable fraction of organic matter, the significant changes can be observed for a long period of time (Hungate *et al.* 1996; Haynes 2005). Recent developments in SOM stud-

ies suggest that particulate organic matter (POM) is a good indicator of soil quality and is more sensitive to soil management practices such as tillage and fertilisation than total SOM concentration (Chan *et al.* 2002; Šimanský 2013). POM comprises of large particles of organic matter (250–2,000 µm) that exist as free POM, within a light fraction or encrusted with soil particles, which in turn offer physical protection from decomposition (Plante & McGill 2002).

Organic carbon is a quantitative indicator of the humus regime in soils and the soil environment is the largest source of carbon on Earth. It contains 3–4 times more carbon than what is within the at-

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mosphere (Lal 2004). Changes in land use significantly affect the carbon cycle. For example, as mentioned by Balashov and Buchkina (2011), only 75-year agricultural management of the clayey loam Haplic Chernozem resulted in a significant decrease in content of SOM and microbial biomass carbon. Burning fossil fuels and the incorrect management of agricultural land are causes of increases within the concentration of CO₂ in the atmosphere along with carbon loss within the soil throughout the past decades. The sequestration of organic carbon within soil is a relatively new aspect in the study of the biogeochemical carbon cycle within the framework of problems in global climate change on Earth. Ecosystems such as an agro-ecosystem, forest or meadow have different carbon sequestration capacities (Semenov *et al.* 2008). The soil carbon sequestration capacity (CSC) reflects the capacity of the soil to stabilise and retain carbon within the SOM, which can have a positive impact on the stability of aggregates (Tisdall & Oades 1982; Beare *et al.* 1994; Amézketa 1999; Bronick & Lal 2005). There are several published articles containing information in which the authors explain carbon sequestration in different soil types under different climatic conditions or farming systems (Martens 2000; Gonzalez & Laird 2003; Brown & Huggins 2012; Barančíková *et al.* 2013). The information about carbon sequestration in water-stable aggregates (WSA) is very important not only for scientists, but is necessary for ecologists as well as farmers. For example, Šimanský (2013) published information about carbon sequestration in WSA of Rendzic Leptosol under different soil management practices in a productive vineyard. The results showed that the most intensive changes in the SOM content in the highest size fractions of water-stable macro-aggregates were observed and the dynamics of organic and labile carbon in WSA, due to its relatively wide range, can be considered as an important and sensitive indicator of the quality of the soil environment under different soil management practices. On the basis of his results, farmers (winemakers) can improve their approaches and contribute to sustainable land management at the same time.

The aim of this paper is to study how different soil management practices influence carbon sequestration and its dynamics in WSA of Haplic Luvisol.

Luvisols are soils that have a higher clay content in the subsoil than in the topsoil as a result of pedogenetic processes (especially clay migration) leading to an argic subsoil horizon. Luvisols extend over 500–600 million ha worldwide (WRB 2006). In Slovakia, Luvisols include 11.7% of agricultural land. The average content of SOM is 2.19% (Zaujec *et al.* 2009).

MATERIAL AND METHODS

An experiment was started in 1999 and is still in progress at the experimental station of Slovak University of Agriculture in Nitra (Dolná Malanta), located east of Nitra, on the Žitavská upland (latitude 48°19'00"; longitude 18°09'00"). The total annual rainfall is 573 mm and the mean air temperature is 9.8°C. The soil in the area was developed on Young Neogene deposits of various clays, loams and sand gravels on which loess was deposited in the Pleistocene Epoch in accordance with the World Reference Base for Soil Resources, Haplic Luvisol (WRB 2006). The particle-size distribution was 360.4 g/kg of sand, 488.3 g/kg of silt and 151.3 g/kg of clay. Bulk density was in the range of 1.50–1.68 t/m³. Soil carbon content was 1.29%, while the cation exchange capacity was 147.18 mmol/kg and base saturation percentage was 92.6%. On average, the soil pH was 6.96.

The field experiment had four repetitions of each of the studied factors. Except for two plots of tillage practices (conventional, minimal), soil samples for comparison were also taken from native grassland. Conventional tillage means the annual ploughing to the depth of 0.20 m and the minimal tillage means the annual disking to the depth of 0.10 m. Three levels of fertilisation were used: (1) without fertilisation, (2) crop residues together with NPK fertilisers (crop residues were returned to the soil and the doses of NPK were calculated by the balance method) and (3) NPK fertilisers (the doses of NPK were calculated by the balance method). The field experiment had the following crop rotation: (1) red clover (*Trifolium pratense* L.); (2) pea (*Pisum sativum* L. *subsp. Hortense* (Neitr.)); (3) winter wheat (*Triticum aestivum* L.); (4) maize (*Zea mays* L.); (5) spring barley (*Hordeum vulgare* L.).

Every spring, from 2008 to 2010, soil was sampled to the depth of 0.20 m. For each sampled zone (included all treatments of tillage + grassland as control and fertilisation), five different locations were chosen randomly. Soil samples were mixed in an average sample, air dried and ground. The concentration of organic carbon within the soil (TOC) was assessed by the wet combustion method (oxidation of organic matter by a mixture of H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ with titration using Mohr's salt) according to Tyurin in modification of Nikitin (Dziadowiec & Gonet 1999). The labile carbon content (TC_L) (Łoginow *et al.* 1987) and the fraction composition of humus substances according to Belchikova and Kononova (Dziadowiec & Gonet 1999) along with the optical parameters of humus substances and humic acids was determined. The soil pH (1 : 2.5 – soil : water) was determined potentiometrically and sorptive characteristics of the soil that include exchangeable cations as Ca^{2+} , Mg^{2+} , K^+ and Na^+ (Fiala *et al.* 1999) were also determined. To determine parameters of soil structure stability, samples were taken with the aid of a spade to maintain the soil within its natural aggregates. Soil samples were also air dried and pre-sieved over a series of sieves, before being bulked into seven size fractions (>7, 7–5, 5–3, 3–1, 1–0.5, 0.5–0.25, <0.25 mm). These size fractions (dry sieve) were used for the determination of WSA. The size fractions of WSA were the following: >5, 5–3, 3–2, 2–1, 1–0.5, 0.5–0.25 (macro-aggregates – WSA_{ma}) and <0.25 mm (micro-aggregates – WSA_{mi}). The sum of size fractions from 0.5 to 3 mm are agronomical favourable macro-aggregates (WSA_{ma} 0.5–3 mm). In the size fractions of WSA, the following were determined: organic carbon (C_{org}) by Tyurin in modification of Nikitin (Dziadowiec & Gonet 1999) and labile carbon content (C_L) (Łoginow *et al.* 1987).

The soil CSC in size fractions of WSA was quantitatively characterised by the ratio between the organic carbon resistant to mineralisation and the potentially mineralisable organic carbon according to Equation (1):

$$\text{CSC} = \frac{\text{C}_{\text{org}} - \text{C}_L}{\text{C}_L} \quad (1)$$

where C_{org} is the content of organic carbon [mg/100 g]

in size fraction of WSA, and C_L is the content of labile carbon [mg/100 g] in the same size fraction of WSA.

Changes in each size fraction of WSA from 2008 to 2010 are expressed as a percentage [%] of change within the organic carbon of the soil (TOC) and are calculated according to Equation (2):

$$\text{C}_{\text{org}} \text{ change [\%]} = \frac{\text{C}_{\text{org}} \text{F2010} - \text{C}_{\text{org}} \text{F2008}}{\text{TOC2010} - \text{TOC2008}} \times 100 \quad (2)$$

where $\text{C}_{\text{org}} \text{F2010}$ is organic carbon in size fractions of WSA from 2010, $\text{C}_{\text{org}} \text{F2008}$ is organic carbon in size fractions of WSA from 2008, TOC2010 is organic carbon in the soil from 2010 and TOC2008 is organic carbon in the soil from 2008.

Changes in the labile organic carbon (C_L) were calculated according to Equation (3):

$$\text{C}_L \text{ change [\%]} = \frac{\text{C}_L \text{F2010} - \text{C}_L \text{F2008}}{\text{TC}_L 2010 - \text{TC}_L 2008} \times 100 \quad (3)$$

where $\text{C}_L \text{F2010}$ is labile carbon in the size fractions of WSA from 2010, $\text{C}_L \text{F2008}$ is labile carbon in size fractions of WSA from 2008, $\text{TC}_L 2010$ is labile carbon in the soil from 2010 and $\text{TC}_L 2008$ is labile carbon in the soil from 2008.

The statistical treatment of the data was performed with the use of Statgraphics Centurion XV.I (Statpoint Technologies, Inc., USA). Treatment differences (ANOVA) were considered significant at P values ≤ 0.05 by the LSD multiple-range test. A correlation analysis to determine the relationships between chemical properties and CSC in the size fractions of WSA was used. The correlation coefficients with the significance level $P \leq 0.05$ were discarded.

RESULTS AND DISCUSSION

The dynamics of organic (C_{org}) and labile carbon (C_L) in size fractions of WSA expressed in percent of change in organic (TOC) and labile carbon (TC_L) within soil from 2008 to 2010, which has a dependence on tillage and fertilisation, are given in Figures 1 and 2. TOC and TC_L concentrations in soil are shown in Figure 3. In all of the tillage treatments with a higher concentration of TOC, a low-

er content of C_{org} in water-stable micro-aggregates (WSA_{mi}) was determined. The highest negative change (a decrease of C_{org} in WSA_{mi} from 2008 to 2010) was observed in conventional tillage. Six *et al.* (2004) as well as Lobe *et al.* (2001) reported, as a result the tillage leads to the lowest losses of organic carbon in micro-aggregates due to its stabilisation by chemical agents (Tisdall & Oades 1982; Amézketeta 1999; Bronick & Lal 2005). Content of C_{org} in size fractions of water-stable macro-aggregates (+4%) and agronomical favourable size fractions of WSA_{ma} 0.5–3 mm (+8%) contributed positively to TOC concentration changes in soil under conventional tillage. In native grassland, an increase of C_{org} in WSA_{ma} (+3%) and in WSA_{ma} 0.5–3 mm (+5%) was observed as well. It is likely due to higher level of POM from plant residue and microscopic hyphae of fungus (Tisdall & Oades 1982; Elliott & Coleman 1988; Cambardella & Elliott 1992). From 2008 to 2010, C_{org} contents within WSA had a significant impact to TOC change in soil for all fertilisation treatments. The content of C_{org} in WSA_{mi} contributed

negatively to TOC change in soil under NPK treatment. At the same time, the content of C_{org} in WSA_{ma} (+6%) and in WSA_{ma} 0.5–3 mm (+12%) contributed positively to TOC change in soil under NPK treatment. Ploughing crop residue together with NPK fertilisers into the soil had a significant influence on increase of C_{org} contents in all size fractions of WSA during 2008–2010.

From 2008 to 2010, the content of C_L in WSA_{mi} contributed negatively to TC_L change in conventional as well as in minimal tilled plots of soil (Figure 2). A possible reason for the decrease of C_L in WSA_{mi} is the newly formed bonds between more labile organic substances and mineral components (Santos *et al.* 1997) (labile organic substances were encapsulated by mineral components) during the period of time from 2008 to 2010. It means that the C_L in WSA_{mi} was physically protected against a microbial attack. On the other hand, the increase of C_L in WSA_{ma} was also the result of the microbial decomposition of coarse intra-aggregates POM (Six *et al.* 1999) as well as the newly formed bonds of easily

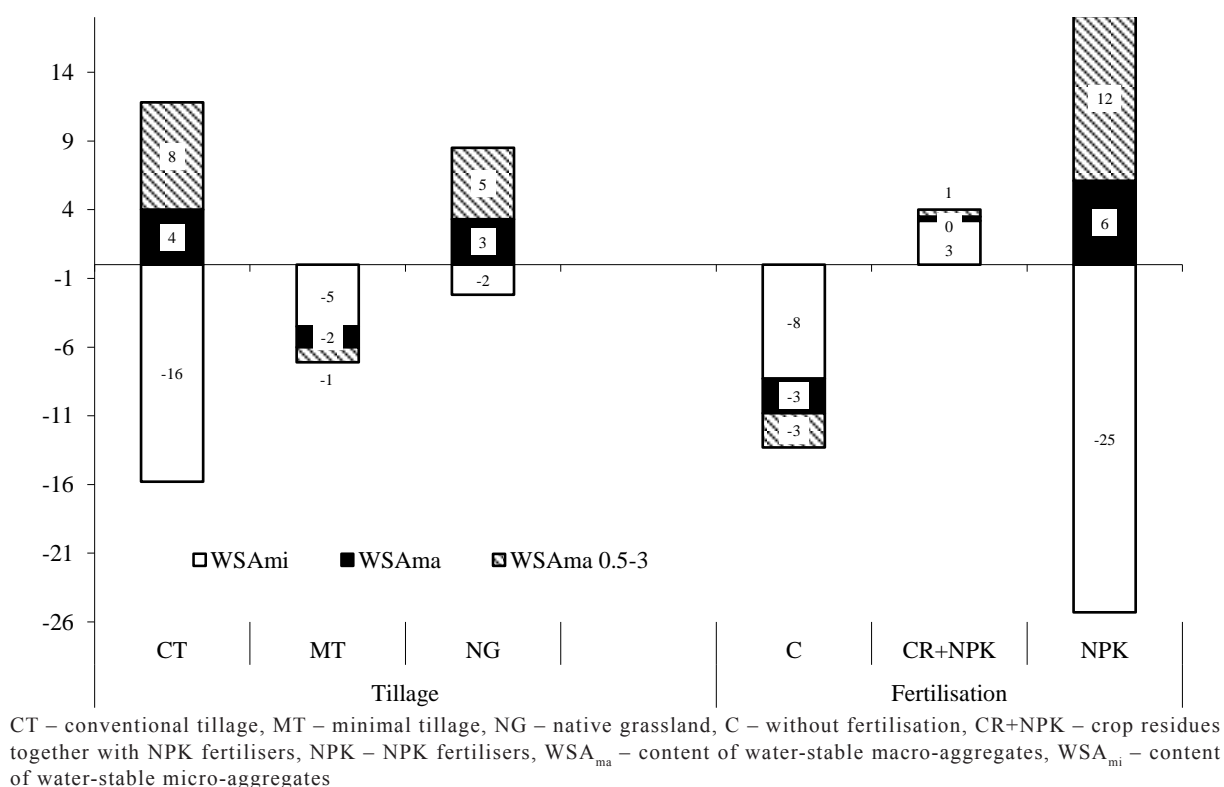


Figure 1. Dynamics of organic carbon (C_{org}) in water-stable aggregates as a percentage change in total organic carbon in soil (TOC) from 2008 to 2010

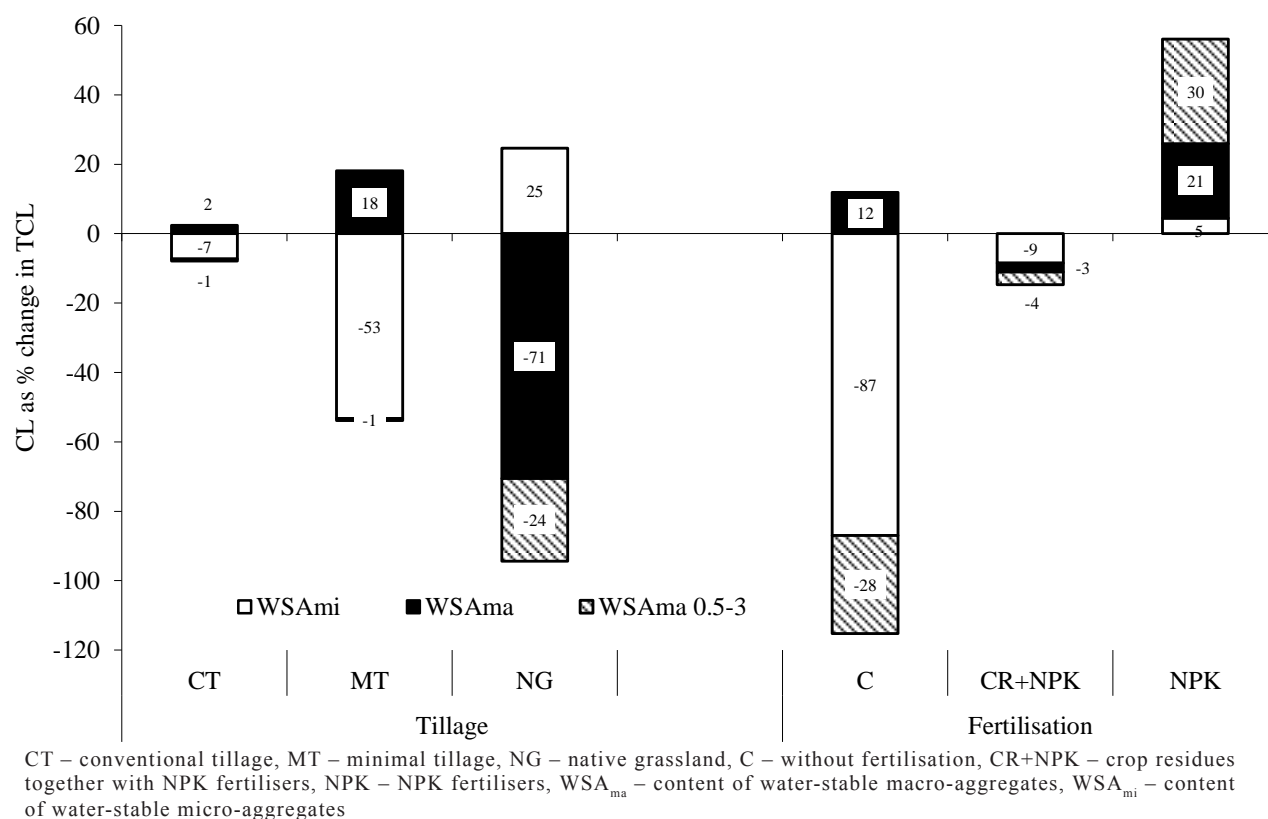


Figure 2. Dynamics of labile carbon (C_L) in water-stable aggregates as a percentage change in labile carbon in soil (TC_L) from 2008 to 2010

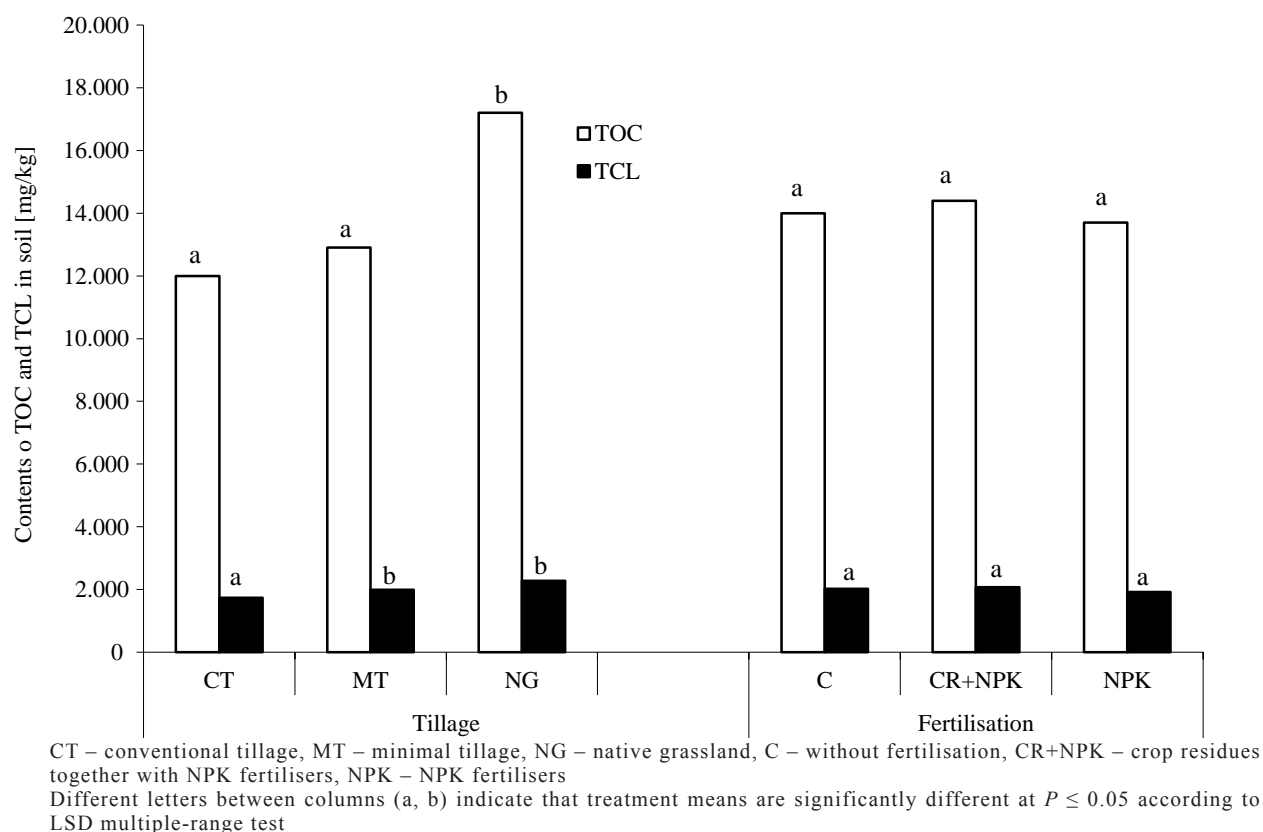


Figure 3. Total organic (TOC) and labile carbon (TC_L) concentrations in soil (2008–2010)

decomposable organic substances (Jastrow 1996; Plante & McGill 2002), which have been cementing agents in the WSA_{ma}. Tisdall and Oades (1982) reported that the formations of temporary/unstable aggregates are mainly contributing substances from initial decomposition of organic residues, specific-

ly polysaccharides. The labile fractions have a much shorter turnover time (Janzen *et al.* 1997) and thus are affected much more rapidly by management-induced changes in organic matter inputs or losses. Tobiašová and Šimanský (2009) recorded that in the long term a higher content of SOM in labile form

T a b l e 1

Statistical evaluation of carbon sequestration capacity in size fractions of water-stable aggregates

WSA [mm]	Tillage			Fertilisation		
	CT	MT	NG	C	CR+NPK	NPK
<0.25	5.29 ^a	5.58 ^a	6.23 ^a	5.02 ^a	6.00 ^a	6.08 ^a
0.25–0.5	5.44 ^a	5.48 ^a	5.99 ^a	5.32 ^a	5.73 ^a	5.86 ^a
0.5–1	5.54 ^a	5.47 ^a	5.67 ^a	5.26 ^a	5.45 ^a	5.98 ^a
1–2	5.98 ^a	5.92 ^a	4.95 ^a	5.90 ^a	5.69 ^a	5.25 ^a
2–3	6.03 ^a	6.34 ^b	4.81 ^a	6.01 ^a	6.04 ^a	5.13 ^a
3–5	5.48 ^a	6.22 ^b	5.08 ^a	5.74 ^a	5.66 ^a	5.40 ^a
>5	5.69 ^a	5.65 ^a	8.16 ^b	6.00 ^a	6.61 ^a	6.89 ^a
WSA _{mi}	5.29	5.58	6.23	5.02	6.00	6.08
WSA _{ma}	5.69	5.85	5.78	5.71	4.76	5.75
WSA _{ma} 0.5–3	5.85	5.91	5.14	5.72	5.73	5.45

CT – conventional tillage, MT – minimal tillage, NG – native grassland, C – without fertilisation, CR+NPK – crop residues together with NPK fertilisers, NPK – NPK fertilisers, WSA – water-stable aggregates
Different letters between columns (a, b) indicate that treatment means are significantly different at $P \leq 0.05$ according to LSD multiple-range test

T a b l e 2

Correlation coefficients among values of carbon sequestration capacity in size fractions of water-stable aggregates and chemical properties of soil

WSA [mm]	Soil characteristics													
	Ha	SBC	CEC	Bs	TC _L	TOC	pH	C _{HA} :C _{FA}	Q _{HS}	Q _{HA}	Exchangeable cations			
											Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
<0.25	0.544 ⁺	n.s.	n.s.	−0.501 ⁺	n.s.	n.s.	−0.444 ⁺	0.507 ⁺	n.s.	n.s.	−0.469 ⁺	n.s.	n.s.	n.s.
0.25–0.5	0.451 ⁺	n.s.	n.s.	n.s.	n.s.	n.s.	−0.479 ⁺	0.499 ⁺	0.473 ⁺	n.s.	n.s.	n.s.	n.s.	n.s.
0.5–1	0.438 ⁺	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.504 ⁺	n.s.	n.s.	n.s.	−0.445 ⁺	n.s.	n.s.
1–2	n.s.	0.587 ⁺⁺	0.637 ⁺⁺	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	−0.489 ⁺	n.s.	n.s.
2–3	n.s.	0.616 ⁺⁺	0.633 ⁺⁺	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	−0.439 ⁺	n.s.	n.s.
3–5	n.s.	0.557 ⁺⁺	0.546 ⁺	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
>5	0.771 ⁺⁺⁺	n.s.	n.s.	−0.742 ⁺⁺⁺	n.s.	n.s.	−0.585 ⁺⁺	0.557 ⁺⁺	0.542 ⁺	n.s.	−0.436 ⁺	−0.493 ⁺	n.s.	n.s.

WSA – water-stable aggregates, Ha – hydrolytic acidity, SBC – sum of basic cations, CEC – cation exchange capacity, B_s – base of saturation, TC_L – content of labile carbon in soil, TOC – content of organic carbon in soil, C_{HA}:C_{FA} – the carbon of humic acids to carbon of fulvic acids ratio, Q_{HS} – colour quotient of humic substances, Q_{HA} – colour quotient of humic acids
n = 21; n.s. – non-significant; ⁺ $P \leq 0.05$; ⁺⁺ $P \leq 0.01$; ⁺⁺⁺ $P \leq 0.001$

had a negative effect on soil structure stability. However, the clay particles can form a protective coating around the labile forms of organic matter and this is a reason for inhibition of decomposition of the SOM inside aggregates by the bacterial colonies (Elliot 1986). In case of NG treatment, a similar effect is shown. In C treatment (without fertilization), higher changes in content of C_L were observed in WSA_{ma} 0.5–3 and WSA_{mi} . It can be connected with stability of SOM inside of aggregates. Stable forms of SOM or physically protected SOM inside of aggregates lower changes on contents of C_L in WSA. During the 2008–2010, a higher content of C_L in WSA_{ma} contributed positively to TC_L concentration within soil under NPK treatment (Figure 2). The same effect was observed in the treatment with ploughed crop residue together with NPK fertilisers. Such a mechanism was described by Six *et al.* (1999).

CSC in size fractions of WSA with a dependence on tillage and fertilisation is shown in Table 1. Soil tillage had a statistically significant influence on CSC in size fractions of $WSA_{ma} > 2$ mm. In conventional (by 8%) and minimal tillage (by 5%), the values of CSC were higher in WSA_{ma} than WSA_{mi} , with the highest values of CSC in agronomical favourable fractions (WSA_{ma} 0.5–3 mm). In native grassland, the CSC values decreased within the following sequence: WSA_{mi} (6.23) > WSA_{ma} (5.78) > WSA_{ma} 0.5–3 mm (5.14). The reason is that the proportion between the mineralisable and resistant fractions of the SOM is affected by different soil types (Gonzalez & Laird 2003; Bronick & Lal 2005). In some cases, the long-term application of high rates of organic fertilisers is accompanied by a continuous rise in the soil TOC concentration. In other cases, the soil saturation with organic carbon takes place relatively quickly, so that the additional inputs of organic matter are subjected to rapid mineralisation (Six *et al.* 2002). Values of CSC in WSA_{mi} were higher under NPK as well as under plots where ploughed crop residue was mixed together with NPK fertilisers. On the other hand, the values of CSC in WSA_{ma} were higher in the treatment without fertilisation. The highest values of CSC were in fertiliser treatments than without fertilisation and tilled treatments (conventional and minimal) than a no-till plot (native grassland). Semenov *et al.* (2008) also published that the CSC values in arable soil are 1.3–1.9 times

higher than those in the soils of natural ecosystems. Correlation coefficients between values of CSC in size fractions of WSA and chemical properties of soil are shown in Table 2. A positive correlation among hydrolytic acidity, humus quality and CSC in WSA_{mi} as well as a negative correlation among base saturation, pH, exchangeable Ca^{2+} and CSC in WSA_{mi} was determined. The same situation, but with stronger correlation relationships between the above mentioned chemical parameters and values of CSC in $WSA_{ma} > 5$ mm was determined (Table 2). The results of Varadachi *et al.* (1994) also showed a decrease of carbon retention in soil due to increasing of pH values. On the other hand, higher values of sum of basic cations and cation exchange capacity are reasons for increase of CSC values in WSA_{ma} 1–5 mm.

CONCLUSIONS

The maintenance of carbon concentration within the soil under conventional tillage and in native grassland was due to an enhanced incorporation of new organic matter from the coarse fraction of POM to macro-aggregates. In treatment with ploughed crop residue together with NPK fertilisers, there was besides of this caused by the reduction of carbon mineralisation from the fine fraction. The reduced decrease of carbon concentration combined with easily decomposable organic matter is controversial. If labile carbon in WSA is physically protected, its higher content will have a positive effect on aggregation. On the other hand, if labile carbon is not physically protected intra-aggregates, it will be liable to a microbial attack with a consequent reduction in aggregate stability.

All in all, soil management practices have a significant effect on the re-distribution of SOM (mainly, coarse POM) in WSA. The dynamics of organic and labile carbon in WSA, due to its relatively wide range, can be considered as an important and sensitive indicator of quality within the soil environment.

The results showed that in conventional and minimal tillage, a very important source of carbon sequestration is agronomical favourable size fractions of water-stable macro-aggregates. On the other hand, in native grassland, and also in all fertiliser

treatments, the most important source of carbon sequestration is water-stable micro-aggregates.

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