

# HAPLIC CHERNOZEM PROPERTIES AS AFFECTED BY DIFFERENT TILLAGE SYSTEMS

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## Abstract

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During 2007–2011 we assessed content and quality of humic substances with relationship to soil structure. Object of study was *Haplic Chernozem* (Hrušovany nad Jevišovkou, Czech Republic) under three different tillage systems: – conventional ploughing to a depth of 0.22 m (CP); – reduced tillage with shallow harrowing to a depth of 0.15 m (RTSH); – reduced tillage with subsoiling to a depth of 0.35–0.40 m (RTS). Isolation of humic acids was made according to IHSS standard method using spectrometer Shimadzu 8700. Aggregates stability was determined by wet sieving method. Results showed that macrostructure stability was directly connected with time of sampling and content and quality of humic substances. After five years of experiment statistically significant differences in humic substances content were found. The highest structure stability, quantity and quality of humic substances were achieved under reduced tillage with shallow harrowing.

Keywords: aggregates stability, humic substances, FTIR spectroscopy

## INTRODUCTION

Soil humic acids (HA) are essential for the stable aggregates formation, good chemical and biological properties. It directly influences soil water regime and aeration. Their chemical composition depends on plants residues composition, soil tillage practices, fertilizing, crop rotation system, liming and others (Gerzabek *et al.*, 2006). Soil structure has a significant impact on the ability of the soil to support plant, further directly influence carbon cycle and nutrient regime, retention and water movement, and erosion processes. The soil structure is one of very important soil properties and depends on the capability of soil particles to aggregate or disaggregate and create structural aggregates. It is the result of joint action of physical, chemical, and biological processes taking place in soil, which is based on the ability of soil particles combine solid phase or break up larger units of soil mass and thereby creating structural aggregates (Bronick and Lal, 2005). Aggregates

stability is also affected by soil type, texture class, particle size distribution, humic substances content and quality, exchangeable cations and sesquioxides, and by soil biological parameters such as microbial biomass content and activity (Anabi *et al.*, 2007; Javůrek and Vach, 2009). Aggregates stability can be also enhanced by growing catch crops, reducing application of mineral fertilizers and pesticides, and by promoting biological activity. One of the most important binding agents for forming stable aggregates are humic substances. Organic material is a very important soil additive to improve soil physical properties. Degradation of soil structure occurs mostly due to humic substances decreasing caused by excessive soil cultivation (Grandy *et al.*, 2002). Content and quality of HA is often used as one of the important parameter to assess soil quality/ health. Humic acids are not easily decomposed by soil microorganisms and consist of hydrophenols, hydrobenzoic acids and others aromatic structures with linked peptides, amino acids, fatty acids,

polysaccharides etc. (Hayes and Malcolm, 2001). Knowledge of the basic structures is required for a full understanding of the role and function of their constituents in the environment. FTIR spectroscopy offers a wide variety of techniques and could be a powerful method that can be used in the identification of complex compounds. FTIR spectra can identify a variety of chemical groups and bands in HA molecule, which characterized their reactivity, chemical properties, and evolution (Michel *et al.*, 2009). According to Stuart *et al.* (1996) attenuated total reflectance (ATR) spectroscopy utilises the phenomenon of total internal reflection. The development of an attachment mounted onto FTIR spectrophotometer allowed us to apply the golden gate single reflection attenuated total reflectance (SRATR) technique. Infrared spectroscopy allow us to assess index aromaticity, hydrophobicity, and O/R ratio in HA molecule according to Caprieli *et al.* (1995, 1997) and Wander and Train (1996). To obtain suitable FTIR spectra it is necessary to use a HA sample of certain purity and ash content.

The aim of our study was to evaluate chemical and physical soil properties under different soil tillage system (ploughing and reduced tillage). Mainly we consider aggregates stability and humic substances content and quality as the main factor of soil fertility.

## MATERIALS AND METHODS

Long term field experiments were established in 2007 to study the influence of various agro technical processes on physical and chemical soil characteristics. *Haplic Chernozem* (Hrušovany nad Jevišovkou) is located at GPS: 48° 51.899' (N), 16° 23.984' (E), at an altitude of 210 metres a.s.l., with an annual rainfall of 461 mm. The region is warm and dry. During the monitoring period (2007–2011) following crop rotation system was applied to all monitored plots: *winter rape pre-crop, then winter wheat, maize, winter wheat, spring barley*. Soil cultivation in the following variants was chosen: – conventional ploughing to a depth of 0.22 m (CP); – reduced tillage with shallow harrowing to a depth of 0.15 m (RTSH); – reduced tillage with subsoiling to a depth of 0.35–0.40 m (RTS). For each variant a plot of land 30×100 m was established considering the type of machinery. Fertilization and plant protection were relevant to the needs of individual crops in studied area. Basic soil properties are given in Tab. I and II. Total organic carbon content was determined by oxidimetric titration method according to Nelson and Sommers (1982). Fractional composition of HS was determined by short fractionation

method (Kononova-Belchikova, 1963). Sum of HS, HA and FA were determined by titrimetric method (Pospisilova *et al.*, 2011). Humic acids were isolated from three variants mentioned above according to IHSS standard method (Swift, 1996). Fourier transform infrared spectra (FT-IR) were recorded over the range of 4000–400 cm<sup>-1</sup> using spectrometer Shimadzu 8700. Aromaticity index ( $I_{ar}$ ) was calculated as a ratio of absorbance intensity at 1729 cm<sup>-1</sup> (aliphatic carboxylic groups) and at 1670 cm<sup>-1</sup> (Caprieli *et al.*, 1995, 1997). Hydrophobicity index (HI) was calculated as a ratio of integrated area at 3000–2800 cm<sup>-1</sup> (P) and total organic carbon content in soil. Integrated area at 3000–2800 cm<sup>-1</sup> characterized content of aliphatic C-H groups in HA molecule (Caprieli *et al.*, 1995, 1997). O/R ratio was used for labile and recalcitrant groups content in HA molecule evaluation. This ratio indicates HA biological activity. Calculation of O/R ratio was made according to Wander and Train (1996).

Aggregates stability was determined by wet sieving method according to Kandeler (1996). This method is based on investigations by Kemper and Koch (1966) and Murer *et al.* (1993). For determination of WSA, air dried aggregates (1–2 mm) are wet sieved in distilled water in a machine providing a mechanical stroke. After wet sieving the mass of stable aggregates is determined. Stable aggregates are destroyed by the addition of Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub> solution, leaving only the sand fraction. Aggregate stability is expressed as the percentage of stable aggregates of the total aggregates after correction of sand content. All measurements were done triplicate in spring and autumn during 2008–2012. Percentage of water stable aggregates was calculated according to Bartlová and Badalíková (2011). Results were statistically processed by the multifactorial analysis of variance and then by Tukey's test of simple contrast. Average values of WSA in topsoil and subsoil, in different variants of tillage and time of testing, were expressed in a bar graph with confidence intervals. Statistical evaluation was carried out using the Stat graphic, version 7.0, and statistical system.

## RESULTS AND DISCUSSION

Soil type was classified according to the Taxonomic system of soils in the Czech Republic (Němeček *et al.*, 2011) as *Haplic Chernozem*. Molic horizon thickness is 0.30 m. Chroma of molic horizon is 10 YR 2/Z. Textural Class is clay-loam (WRB, 2006). Active soil reaction was slightly alkaline, exchangeable soil reaction was slightly acid. Soil was loamy textured. Cation exchange capacity was high – see Tab. I.

I: Basic physical and chemical parameters of *Haplic Chernozem* (locality Hrušovany)

Soil type	Particles	Sand	Silt	Clay	pH/H <sub>2</sub> O	pH/KCl	CEC (cmol/kg)
	< 0.01 mm	2.00–0.05 mm	0.05–0.002 mm	< 0.002 mm			
	(%)	(%)	(%)	(%)			
Haplic Chernozem (Hrušovany)	38.84	41.16	33.24	25.60	7.35	6.52	22.00

Base saturation is middle. Humus content is low (3.33%). Fractional composition of humic substances in *Haplic Chernozem* before experiment (2007) is given in Tab. II. As it is evident, quality of humic substances and humification degree was very high and color index ( $Q_{4/6}$ ) achieved low values (less

than 4). After five years of experiment statistically significant differences in Corg content, HS content, and HA content between conventional ploughing and reduced tillage with shallow harrowing was determined – see Tab. III. Dynamic of humic substances content is given in Fig. 1. Increasing of

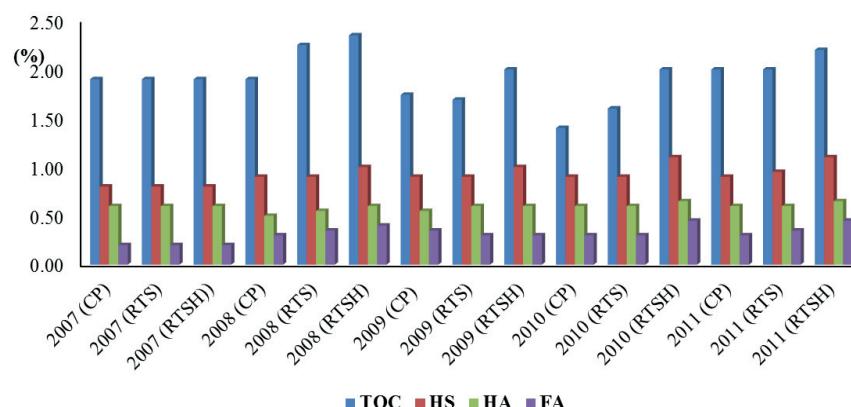
II: *Fractional composition of humic substances in Haplic Chernozem (locality Hrušovany)*

Soil type	C <sub>org</sub>	HS	HA	FA	HA/FA	HD	Q <sub>4/6</sub>
	%	%	%	%		%	
Haplic Chernozem (Hrušovany)	1.93	8.00	6.00	2.00	3.00	41.45	3.17

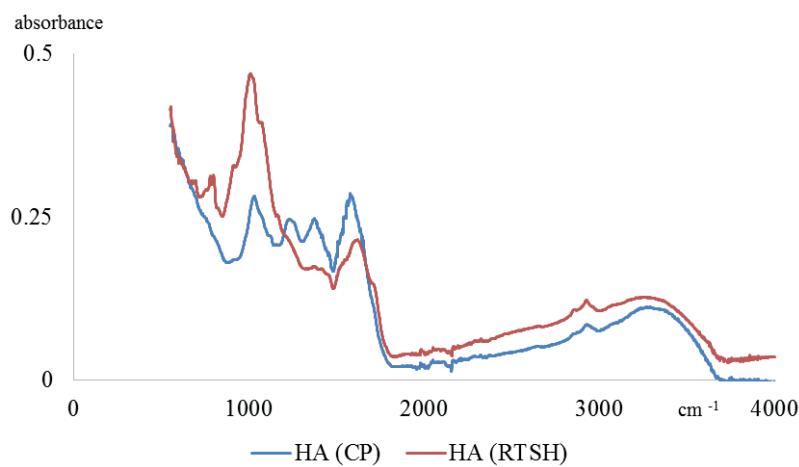
III: *Statistically significant differences in humic substances content between conventional ploughing and reduce tillage with shallow harrowing in Haplic Chernozem (n = 14;  $\alpha = 0.05$ ;  $r_{critic} = 2.160$ )*

Source	Number	Sum	Average	Variance			
Corg (CP)	14	25.66	1.832857	0.0674			
Corg (RTSH)	14	31.285	2.234643	0.096886			
Source of j variability	SS	Difference	MS	F	P	F <sub>crit</sub>	
Between sources	1.130022	1	1.130022	<b>13.75675</b>	0.000994	4.225201	
All sources	2.135721	26	0.082143				
Total	3.265744	27					
Source	Number	Sum	Average	Variance			
HS(CP)	14	113.2	8.085714	0.796703			
HS (RTSH)	14	138.8	9.914286	0.835165			
Source of variability	SS	Difference	MS	F	P	F <sub>crit</sub>	
Between sources	23.40571	1	23.40571	<b>28.68579</b>	1.32E-05	4.225201	
All sources	21.21429	26	0.815934				
Total	44.62	27					
Source	Number	Sum	Average	Variance			
HA (CP)	14	78.2	5.585714	0.405934			
HA (RTSH)	14	96.7	6.907143	0.553022			
Source of variability	SS	Difference	MS	F	P	F <sub>crit</sub>	
Between sources	12.22321	1	12.22321	<b>25.49275</b>	2.95E-05	4.225201	
All sources	12.46643	26	0.479478				
Total	24.68964	27					

Dynamic of humic substances in Haplic Chernozem (2007-2011)



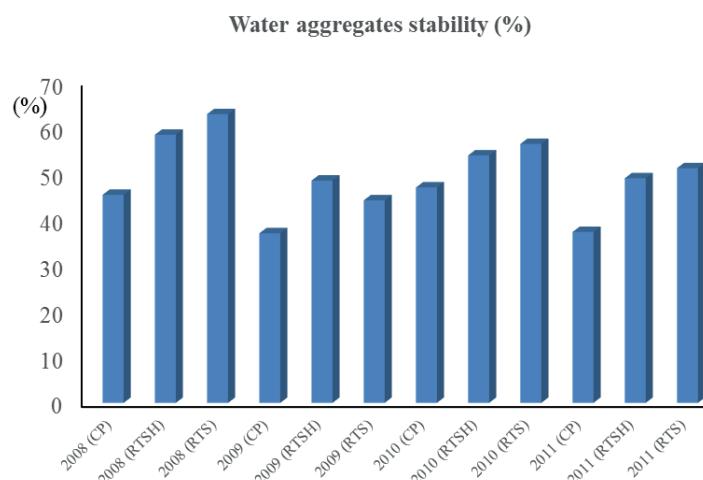
1: *Dynamic of total organic carbon (TOC), humic substances (HS), humic acids (HA), and fulvic acids (FA) in Haplic Chernozem (Hrušovany)*



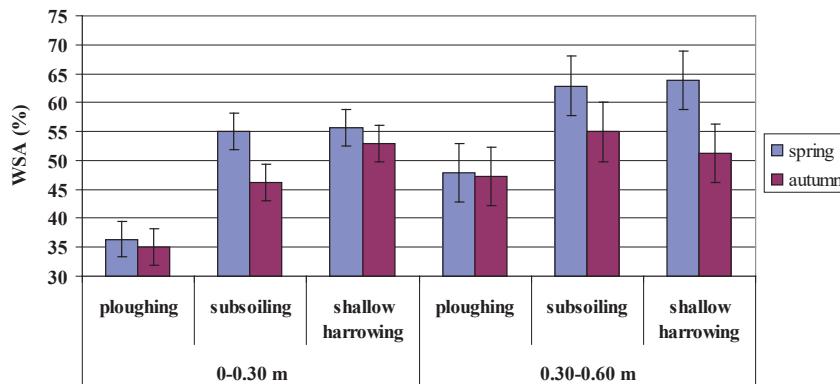
2: Infrared spectra of humic acids isolated from Haplic Chernozem (Hrušovany)

humic substances (HS), humic acids (HA) and fulvic acids (FA) is evident. Quality of humic substances was evaluated by chemical characterization of isolated humic acids samples from conventional ploughing and reduced tillage with shallow harrowing variants. Comparison of both HA-samples in FTIR spectral range is listed in Fig. 2. Both spectra suggested stretch vibration and deformation of the following functional groups: SO<sub>3</sub>H groups at 900–1100 cm<sup>-1</sup>; polysaccharides at 900–1045 cm<sup>-1</sup>; various ether and alcoholic groups -O-H at C-O 1127–1123 cm<sup>-1</sup>; carbonyl and carboxylic groups at 1225–1223 cm<sup>-1</sup>; phenolic groups at 1404–1419 cm<sup>-1</sup>; aromatic C=C groups at 1624–1619 cm<sup>-1</sup>; carboxylic and amido groups at 1655–54 cm<sup>-1</sup>; C=O bands at 1690–1716 cm<sup>-1</sup>; carbonyl and carboxylic groups at 1719–1718 cm<sup>-1</sup>; -C-H, CH<sub>2</sub> and CH<sub>3</sub>, aliphatic groups at 2942–2920 cm<sup>-1</sup>; amino and amido groups -N-H at 3500–3200 cm<sup>-1</sup>. HA isolated from conventional ploughing variant contained more aromatic and phenolic groups to compare with HA-reduce tillage variant. We can conclude that the variant with reduced tillage with

shallow harrowing contained more young humic acids, which are supposed to be more biologically active. They contained more O-H groups, aliphatic C-H groups, amino and amido groups -N-H, various ether and alcoholic groups, polysaccharides and SO<sub>3</sub>H groups (see Fig. 2). Our results also showed that chemical composition of soil HA was influenced not only by soil type but also by tillage system. Similar to us Rosell *et al.* (1990, 1995) and Beyer *et al.* (1993) showed that chemical composition, functional groups content and elemental composition of soil HA are directly affected by tillage systems, crop rotation systems and lands management. Calculated values of hydrophobicity index was higher in HA-minimum tillage to compare with HA-plough. We can conclude that HA-minimum tillage contained more labile O-C groups and less recalcitrant C=C groups to compare with HA-plough. High values of HI indexes (HI > 2) are connected with higher aggregability of soil aggregates and better soil structure formation. Aromaticity index ( $I_{ar}$ ) was calculated according to Capriel *et al.* (1995, 1997) as a ratio of absorbance intensity at 1729 cm<sup>-1</sup> (aliphatic



3: Dynamic of water aggregates stability in Haplic Chernozem (Hrušovany)



4: Average values of aggregates stability under different tillage systems (Haplic Chernozem, Hrušovany, 2008–2011)

IV: Correlation between fractional composition of humus and water aggregates stability (Haplic Chernozem, Hrušovany,  $n = 192$ ;  $\alpha = 0.05$ ;  $r_{crit} = 0.159$ )

	Sh (%)	WSA (%)	Sum HS (%)	Sum HA (%)
Sh (%)	1			
WSA (%)	<b>0.24725</b>	1		
Sum HS (%)	<b>0.323342</b>	<b>0.414596</b>	1	
Sum HA (%)	<b>0.30459</b>	<b>0.321336</b>	<b>0.852841136</b>	1

carboxylic groups) and at  $1670\text{ cm}^{-1}$  (aromatic chinone groups). Low values of aromaticity index are characteristic for high humic acids quality. Hydrophobicity index (HI) was calculated according to Capriela *et al.* (1995, 1997) as a ratio of integrated area at  $3000\text{--}2800\text{ cm}^{-1}$  (P) and total organic carbon content in soil. Integrated area at  $3000\text{--}2800\text{ cm}^{-1}$  characterized content of aliphatic C-H groups in HA molecule. High values of hydrophobicity index (HI) are typical for high humic acids quality. O/R ratio is used for characterization of reactive and recalcitrant labile groups in HA molecule. Their content allows us to evaluate HA biological activity. Calculation of HI was made according to Wander and Train (1996).

Aggregates stability during the experiment is documented in Fig. 3 and 4. Different tillage systems had different water stable aggregates. The highest values of stability were achieved in upper layer ( $0\text{--}0.30\text{ m}$ ) under the reduced tillage with shallow harrowing (RTSH). The lowest stability was under conventional ploughing (CP). We can conclude that reduce tillage caused higher aggregates stability to compare with conventional ploughing system. As

quoted Alvarez and Steinbach (2009); Daraghmeh *et al.* (2009); and Kasper *et al.* (2009) reduced tillage system had lower degradation effect on aggregates and soil structure to compare with ploughing system. We have also found out that aggregates stability in upper layer ( $0\text{--}0.30\text{ m}$ ) was lower to compare with the subsoil horizon ( $0.30\text{--}0.60\text{ m}$ ) – see Fig. 4. Aggregates stability depends also on time of sampling. Higher values were achieved during spring sampling to compare with autumn. Statistically significant differences were found after four years of experiment in reduced tillage with shallow harrowing (RTSH) variant. Increasing of aggregates stability during spring could be explained by higher biological activity and humic substances content. Similar results were published by Daraghmeh *et al.* (2009) and Bullock *et al.* (1988). Correlation between aggregates stability and humic substances content was determined ( $n = 192$ ;  $\alpha = 0.05$ ;  $r_{crit} = 0.159$ ) – see Tab. IV. Our results confirm that content and quality of humic substances and their humification degree directly influenced aggregates stability.

## CONCLUSION

During long-term field experiments (2007–2011) we assessed the influence of different tillage systems on soil humic substances content and quality and structure. Three tillage systems were chosen: – conventional ploughing (CP) to the depth of  $0.22\text{ m}$ ; – reduced tillage with shallow harrowing (RTSH) to the depth of  $0.15\text{ m}$ ; – reduced tillage with subsoiling to the depth of  $0.35\text{--}0.40\text{ m}$ . Object of study was *Haplic Chernozem* (locality Hrušovany nad Jevišovkou, Czech Republic). Basic soil properties were determined by standard methods. Total organic carbon content was determined by oxidimetric titration method. Fractional composition of humic substances was determined by short fractionation method and sum of HS, HA and FA were determined by titrimetric method. Humic acids were isolated according to IHSS standard method. Fourier transform infrared spectra (FT-IR) were

recorded over the range of 4000–400 cm<sup>-1</sup> using spectrometer Shimadzu 8700. Aggregates stability was determined using the wet sieving method and results were expressed as the percentage of water stable aggregates in the total amount of aggregates after subtracting the proportion of sand. The last was directly influenced by the time of sampling, quantity and quality of humic substances. After five years of experiment statistically significant differences between variants in humic substances content were found. The amount and quality of humic substances, as well as aggregates stability, were the best under reduced tillage with shallow harrowing (RTSH). Correlation between humic substances content and aggregates stability was found.

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