

## HUMUS COMPOSITION OF CHERNOZEM, EUTRIC CAMBISOL AND LUVISOL IN CONTINENTAL CROATIA

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### Abstract

The aim of this study was to determine humus composition in the surface layer of Chernozem, Eutric Cambisol and Luvisol, major soil types used for crop production in continental Croatia. The study was conducted on 36 soil samples collected at 12 locations, of which 4 in each soil type. Humus content was determined by modified Walkey-Black method (1934) and the humus composition was analyzed by the version of Schnitzer method (1982) using a mixture of 0.1M NaOH and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. UV-VIS spectroscopic characterization of humic acid and fulvic acids was performed at wavelengths 465 and 665 nm. Average humus content decreased in the following order: Chernozem (2.99%) > Eutric Cambisols (2.23%) > Luvisols (1.71%). The average carbon content in humic acids decreased from 32.7% (Chernozem) to 14.72% (Luvisols), while in fulvic acids ranged from 15.97% (Chernozem) to 24.91% (Luvisols). The average ratio of humic acid and fulvic acids (Ch/Cf) decreased from 2.05 established in Chernozem to 0.60 in Luvisols. Structures of higher aromaticity – humic acids prevail in Chernozem and Eutric Cambisols, whereas aliphatic structures characteristic of fulvic acids are prevalent in Luvisols. The average ratio of optical densities (E<sub>4</sub>:E<sub>6</sub>) ranged from 2.4 (Chernozem) to 6.02 (Luvisols). Data obtained by the non-invasive - spectroscopic method are in agreement with data of carbon content in humic acid and fulvic acids obtained using the modified Schnitzer method.

**Key words:** humic acid, fulvic acid, Ch/Cf, E<sub>4</sub>:E<sub>6</sub>

### Introduction

Humus composition defines key soil characteristics and its fertility, and is an indicator of the processes in soil. Soils differs in the amount and composition of humus, and this diversity is closely related to human activity such as soil tillage, hydro ameliorations, fertilization, crop rotation etc. Monitoring of humus composition in soil is the key to understanding and predicting the future state of the soil. The aim of this study was to determine humus content and composition in the surface horizons of Chernozem, Eutric Cambisol and Luvisol, major soil types used for crop production in continental Croatia.

### Material and methods

The study was conducted at 12 locations, on which were taken 36 soil samples, four for each soil type (Chernozem, Eutric Cambisol and Luvisol). A three average soil samples were taken from depth 5-20 cm at each location. Soil samples were prepared for laboratory analysis according to HRN ISO 11464:2009. Humus content was determined by modified Walkey-Black method (1934) and the humus composition was analyzed by modified Schnitzer method (1982) using a mixture of 0.1M NaOH and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. UV-VIS spectroscopic characterization of humic acid and fulvic acids was performed on spectrophotometer SHIMADZU UV-1700, at wavelengths 465 and 665 nm. The total nitrogen content was determined by Kjeldahl method (HRN ISO 11261:2004). The soil samples were also analyzed on basic physical and chemical properties. Soil texture was determined by sieving and sedimentation (HRN ISO 11277:2004), the pH in distilled water and 1M solution of KCl (HRN ISO 10390:2005), and the base saturation of adsorption complex by Kappen method (JDPZ, 1966).

## Results and discussion

Basic chemical properties of soils and their texture are shown in Table 1. Chernozem has silty loam texture and weakly acid to neutral pH. The humus content is low and medium, average low (2.99%). Texture of Eutric Cambisol is silty loam, pH is acid to neutral, base saturation of adsorption complex is high and humus content low. Luvisol has also silty loam texture, very acid to acid reaction, low to medium base saturation of adsorption complex and very low humus content.

Table 1: Chemical properties and soil texture of P1 horizons

Soil type	Statistics	pH		V* %	Humus %	Percentage of mechanical particles diameter				
		H <sub>2</sub> O	KCl			2,0- 0,2	0,2- 0,063	0,063- 0,02	0,02- 0,002	<0,002
Chernozem	Mean	7,29	6,33	-	2.99	0.7	1.5	36.2	31.7	25.8
	Min	6,76	5,54	-	2.40	0,3	0,6	34,0	28,5	23,3
	Max	8,07	7,13	-	4.00	1,1	2,6	38,7	34,3	27,9
Eutric Cambisol	Mean	6,46	5,31	79,4	2.23	7.8	12.4	33.1	32.2	28.1
	Min	5,51	4,32	65,1	1.30	1,1	1,5	20,3	29,8	14,1
	Max	7,54	6,70	93,3	2.80	10,8	17,7	40,8	34,9	33,7
Luvisols	Mean	5,46	4,33	37,9	1.71	10.2	14.1	38.7	30.3	17.4
	Min	4,41	3,65	16,1	1.00	0,4	1,7	30,4	27,5	6,5
	Max	6,57	5,48	55,6	2.20	16,6	19,0	46,7	35,6	22,5

\*base saturation of adsorption complex

Properties of selected soils are very similar to typical (average) soils of wider research area described by Škori et al (1977).

Low humus content in P1 horizon of Chernozem and Eutric Cambisol, as well as very low humus content in Luvisol are results of human activity such as deep ploughing, fertilization and crop rotations with reduced proportion of grasses, as pointed by Kibblewhite et al (2005). These data fit into status and trends of humus in anthropogenized soils of Europe. Around 45% of the mineral soils in Europe have low or very low organic carbon content (0-2%) and 45% have a medium content (2-6%) (Rusco et al 2001). 74% of the land in southern Europe is covered by soils that have less than 2% of organic carbon in the topsoil (Zdruli et al 2007).

Statistical data for total inorganic carbon and nitrogen, C/N and humus composition in P1 horizon of studied soils are shown in Table 2.

The C/N ratio in the studied soils are in agreement with earlier research of Škori et al (1977) who determined range of C/N ratio 10-13 in Chernozem and 9.5-15 in Eutric Cambisol of eastern Slavonia. Slightly wider C/N ratio in relation to the above mentioned study was determined only in Luvisol (average C/N 13.7) while mentioned authors listed C/N range 10.1-11.2.

Table 2: Mean minimal and maximal values of total inorganic C, nitrogen, C/N, humic acid, fulvic acid, Ch/Cf, humin and E4/E6 in P1 horizons

Soil type	Statistics	C org %	N %	C/N	Ch %	Cf %	Ch/Cf	Humin %	E4/E6
Chernozem	Mean	1.74	0.167	10.4	32.69	15.97	2.05	51.34	2.47
	Min	1.39	0.142	8.4	27.90	13.20	1.59	45.00	2.23
	Max	2.32	0.221	12.8	37.00	18.50	2.41	58.20	2.92
Eutric Cambisol	Mean	1.29	0.116	11.2	24.69	20.83	1.20	54.48	3.81
	Min	0.75	0.066	9.4	21.90	18.00	1.02	50.60	3.37
	Max	1.61	0.166	13.5	27.40	24.10	1.52	60.10	4.18
Luvisol	Mean	0.98	0.073	13.7	14.72	24.91	0.60	60.38	5.98
	Min	0.57	0.041	11.1	10.80	21.30	0.43	55.90	5.17
	Max	1.26	0.114	16.8	17.40	28.90	0.73	65.00	6.43

The average proportion of humic acid, fulvic acid and humin in humus of Chernozem, Eutric Cambisol and Luvisol is shown on Figure 1-3.

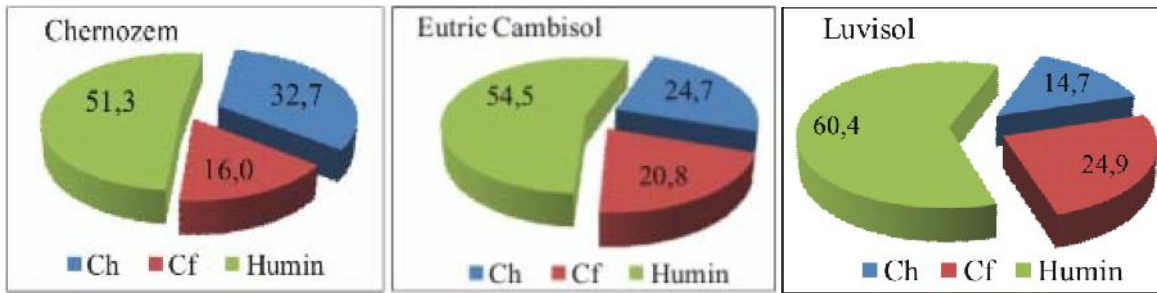


Figure 1-3: The average proportion of humic acid, fulvic acid and humin in humus of Chernozem, Eutric Cambisol and Luvisol

The average carbon content in humic acid decreased from 32.69% in Chernozem, over 24.69% in Eutric Cambisol to 14.72% in Luvisol, while in fulvic acid increased from 15.97% in Chernozem to 24.91% in Luvisol. The dominance of humic acid over fulvic acid in humus of Chernozem was recored in research of Pospišilova and Fasurova (2009), Nikolaishvili and Matchavariani (2008) and Gonet et all (2008).

The average ratio of humic acid and fulvic acid (Ch/Cf) decreased from Chernozem (2.05) over Eutric Cambisol (1.20) to Luvisol (0.60). About a similar ratio of humic acid and fulvic acid in humus of mentioned soils reports Stevenson (1994).

The relationships between humus fractions – humic acid, fulvic acid and humin are one of the most important indicators of humus properties in different soil types. Visualization of their relationships was given in the triangular diagram such as one for soil texture by Watanabe and Kuwatsuka (2001). In the 3D diagram (Figure 4) plots of humus composition of Chernozem, Eutric Cambisol and Luvisol were clearly separated. The diagram show that the separations between soil types are results of differences in all humus fractions, but the most pronounced are in humic acids. Humus composition presented in 3D diagram provides a clear visualization of the relationships between studied soil types.

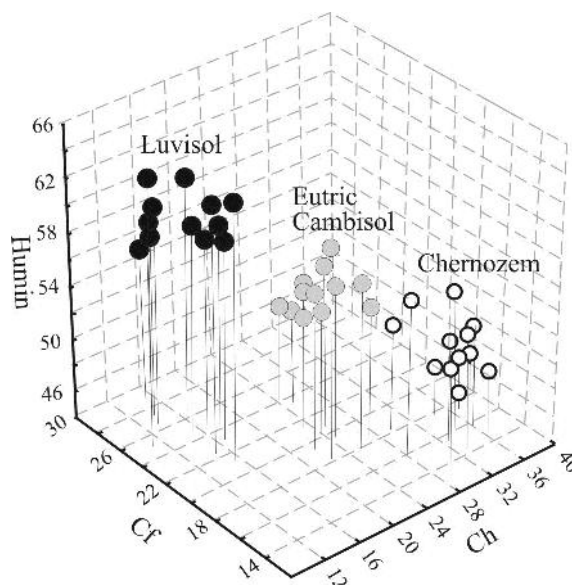


Figure 4: 3D diagram for humus composition of Chernozem, Eutric Cambisol and Luvisol

Quantitative values of humic acid and fulvic acids, as well as their relationships were compared to UV-VIS spectroscopy method. Figure 5 shows  $E_4/E_6$  ratio defined as the ratio of optical absorbance at 465 nm to that of 665 nm for humic substances in aqueous solution. This ratio has been correlated negatively with increasing content of condensed aromatic structures (Bravard and Righi 1991; Stevenson 1994). Therefore, the more refractory and complex the soil humus, the lower should be its  $E_4/E_6$  ratio. Described index was the lowest in Chernozem and the highest in Luvisol. Higher degree of aromaticity in humic acid of Chernozem, in comparison to Eutric Cambisol and Luvisol in their study showed Baran ikova et al (1997).

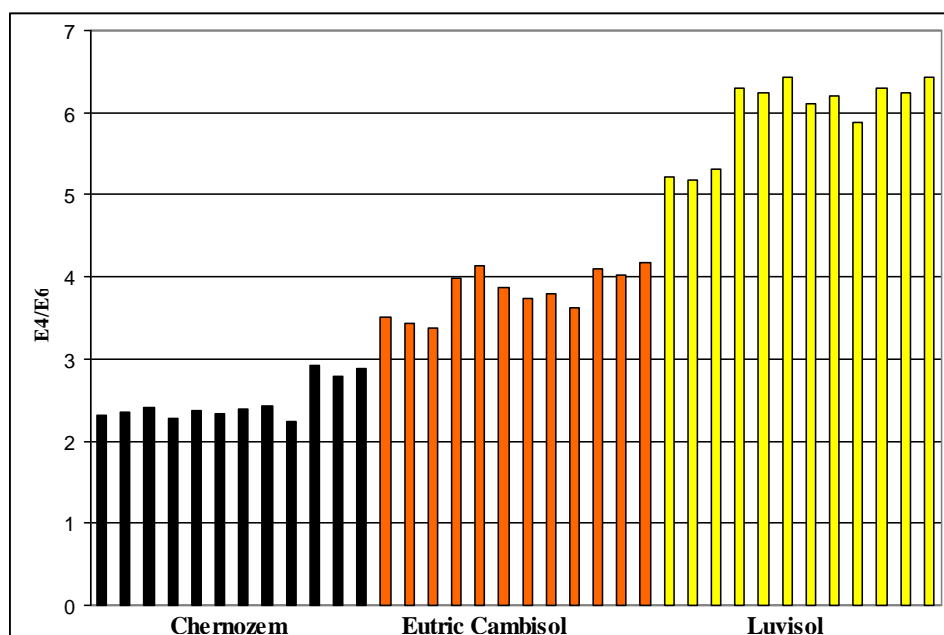


Figure 5: The optical indexes ( $E_4/E_6$ ) calculated as the ratio of  $A_{465} / A_{665}$  nm in soil samples

### Conclusion

The average humus content in studied soils are low and very low and decreased in the following order: Chernozem (2.99%) > Eutric Cambisol (2.23%) > Luvisol (1.71%). In humus of Chernozem and Eutric Cambisol prevail humic acid (Ch/Cf 2.05 and 1.21), while in Luvisol Ch/Cf is 0.60. UV-VIS spectroscopically established ratio  $E_4/E_6$  confirms above mentioned relationships of humus fractions. Humus composition refers to clear differences between the studied soil types and plot of humus fractions presented in 3D diagram provides a clear visualization of their separation.

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