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ELEMENTAL COMPOSITION OF HUMIC ACIDS ISOLATED FROM CHERNOZEM, VERTISOL, REGOSOL, PLANOSOL AND HISTOSOL

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INTRODUCTION

Humic acid (HA) is one of the main components of soil humic substances. HAs reflect characteristics of the environment forming them in an internal state, which affects their composition, structure and properties. Hence, they can be used as indicators of pedogenetic. Elemental composition, particularly the ratio of main elements, is one of features of HAs specifically related to natural environment. Nowadays, HAs are considered to be group of high-molecular weight compounds with heterogenous molecular and elemental composition. So, elemental composition of HAs is an important and informative characteristic, which indicates humification level, oxidation and condensation degree. It is also possible to assess the level of soil organic matter stabilization by assessment of atomic ratios and HA oxidation degree.

In this study, elemental composition was determined for humic acids isolated from five soils of Serbia, developed under different pedogenetic conditions, and related to soil properties and origin. Chernozem (CH), Smonica/Vertisol (VR) and Rendzina/Regosol (RG) were developed under terrestrial conditions, while Pseudoglej/Planosol (PL) and Prelazni treset/Histosol (HI) pedogenesis proceeded under hydrogenic conditions. Furthermore, difference in basic physical and chemical properties of these soils can effect HA elemental composition.

MATERIAL AND METHODS

Chernozem soil originates from Novi Banovci, 44º57′N, 20º16′E; 85 m above sea; mean annual precipitation (MAP) 690.9 mm; mean annual air temperature (MAAT) 12.5°C. Smonica/Vertisol soil originates from Umka, 44º39′N, 20º17′E; 111 m a.s; 690.9 mm; MAAT 12.5 °C. Rendzina/Regosol soil originates from Pirot, 43º07′N, 22º34′E; 370 m a.s; 605.8 mm, MAAT 11.4 °C. Pseudoglej/Planosol soil originates from Varna, 44º41′N, 19º38′E; 110 m a.s.; 693.3 mm, MAAT 11.2°C. Prelazni treset/Histosol soil originates from Divčibare (44º06′N, 19º59′E; 975 m a.s; 1017.3 mm; MAAT 7.7 °C). Prelazni treset/Histosol was under swamp vegetation, while other soils were used as cropland.

Soil samples were collected at 0-30 cm depth. Soil texture, organic C (soil organic matter for HI), and pH were determined by common methods.

HA samples were isolated using a modified (HA gel was dried at 35 °C, powdered, and sieved using a 0.05 mm sieve) IHSS method. The C, H, and N contents of HA samples were determined using elemental analyzer (CHNS 628, LECO Corporation, USA) after drying the samples over P_2O_5 under vacuum. Their percentages were calculated on the ash-free basis. The oxygen content was obtained as the difference. Ash content was determined by a dry combustion method (50 mg HA at 750 °C for 8 h). The C/N, O/C, H/C and O/H atomic ratios were calculated by determining the ratio of C to N, O to C, H to C, and C to H contents, respectively. Internal oxidation degree (ω) was calculated by the equation: ω=(2O+3N-H)/C, where: O, N, H and C are element contents (atomic %).

The correlation analysis were processed using StatSoft, Inc. Statistica software package for Windows, Version 8.

Table 1. General soil properties

Soil	Coarse fragm. (%)	Sand (%)	Silt (%)	Clay (%)	$CaCO_3$ (%)	pH in H_2O	Organic C (%)	Organic matter (%)
Chernozem	0	35.4	35.7	28.9	2.51	7.87	1.93	3.33
Vertisol	0	20.7	34.1	45.2	0	6.08	1.91	3.29
Regosol	18.0	53.2	23.4	23.4	14.5	7.98	1.15	1.98
Planosol	0	24.7	39.8	35.6	0	5.20	1.28	2.21
Histosol	0	ND[a]	ND	ND	0	5.09	ND	64.7

[a]ND

Table 2. Elemental composition, ash content, atomic ratios and internal oxidation degree (ω) of humic acids

Humic acids	C	H	O	N	Ash
	(wt. %, ash and moisture-free basis)				(%)
Chernozem	52.5	4.33	39.3	3.85	0.230
Vertisol	52.5	4.37	39.2	3.87	1.48
Regosol	50.5	4.78	41.0	3.70	0.648
Planosol	49.5	5.78	39.9	4.74	0.071
Histosol	49.8	5.55	40.8	3.75	0.416
	C/N	H/C	O/C	O/H	ω
	(atomic ratio)				
Chernozem	16.8	0.974	0.550	0.565	0.3049
Vertisol	15.8	0.991	0.560	0.565	0.3191
Regosol	15.8	1.14	0.614	0.541	0.2829
Planosol	12.2	1.39	0.605	0.435	0.0663
Histosol	15.5	1.33	0.615	0.464	0.0970

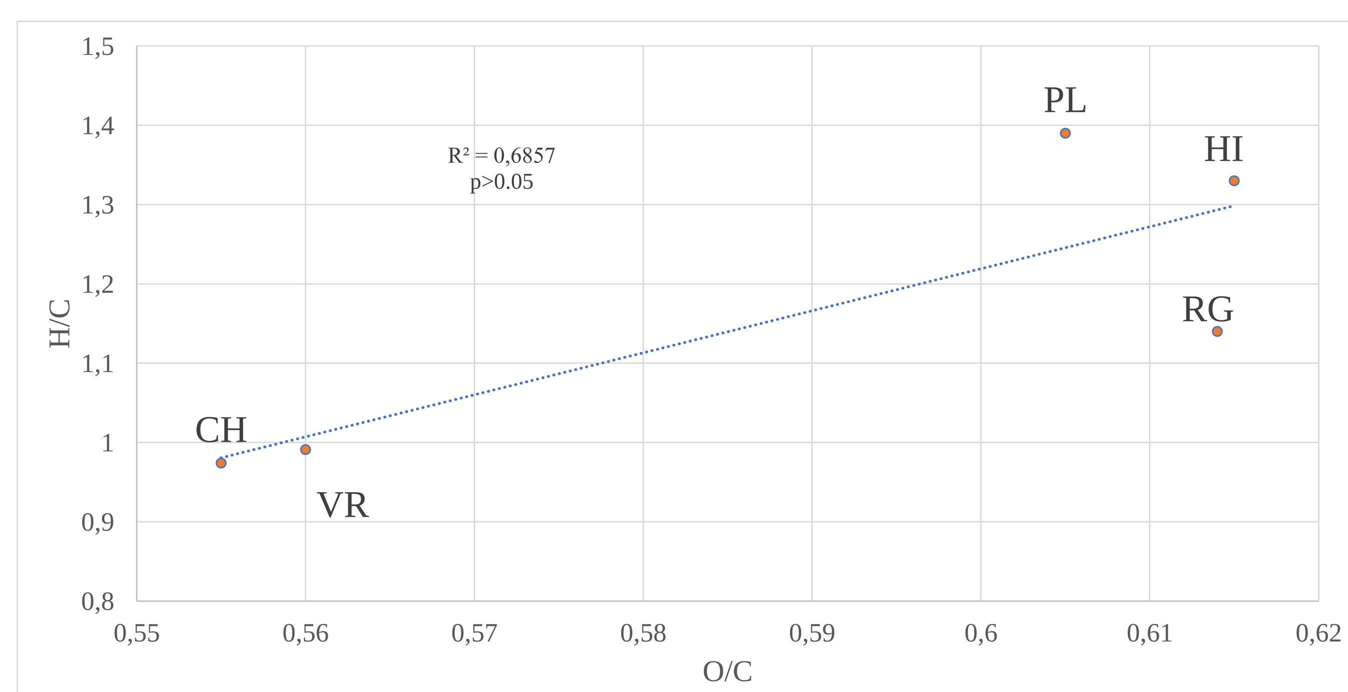

Figure 1. Atomic ratios of elements in humic acids (CH - Chernozem, VR - Smonica/Vertisol, RG - Rendzina/Regosol, PL - Pseudoglej/Planosol and HI - Prelazni treset/Histosol)

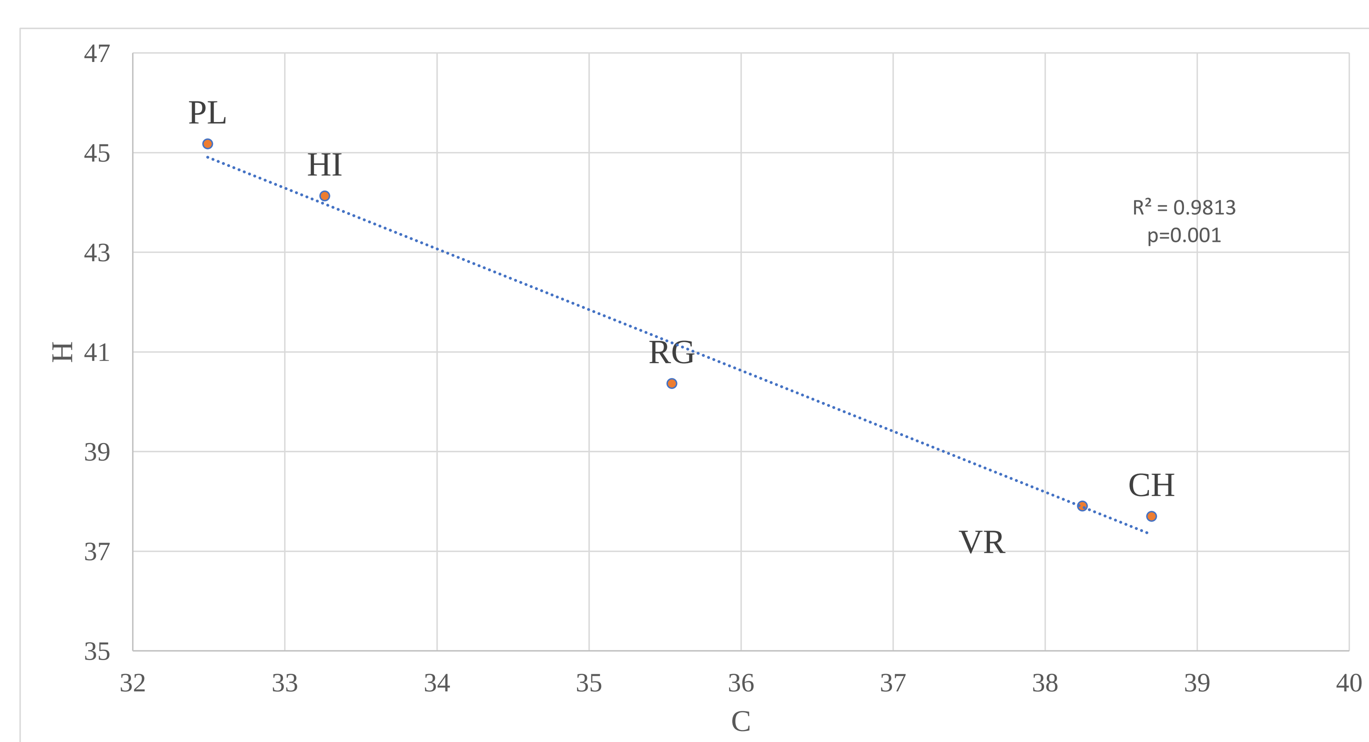

Figure 2. H versus C (atomic %) in humic acids (CH - Chernozem, VR - Smonica/Vertisol, RG - Rendzina/Regosol, PL - Pseudoglej/Planosol and HI - Prelazni treset/Histosol)

RESULTS

Soil texture of investigated soils (Table 1) was RG - sandy clay loam, CH and PL - clay loam, and VR - clay. CH and RG were calcareous and moderately alkaline, while other soils were acid: VR slightly, PL strongly and HI - very strongly acid. Organic matter content was 64.7% in HI, and 1.98-3.33% in other mineral soils.

Elemental compositions of investigated CH, VR, RG, HI and PL HAs (Table 2) fall within the range of average values reported for soil HAs.

Generally, high C/N and O/H and low O/C and H/C reflect high degree of aromatic condensation, maturity and stability of HAs, i.e., the degree of HA humification. According to the humification degree obtained, HAs studied are ranged as follows: CH>VR>RG>HI>PL.

Both correlations done (H/C versus O/C and H versus C) separate HAs in three groups: CH and VR - the most dehydrogenated and demethylated, i.e. the most stable; RG - the most oxidated; and HI and PL - the most hydrogenated (Figs.1 and 2).

Internal oxidation degree values are obviously lower in hydromorphic HI and PL HAs compared to terrestrial RG, CH and VR HAs, but positive values indicate predominance of aerobic under anaerobic conditions in surface layer of hydromorphic soils.

Soil organic C of mineral soils was in negative significant correlation with O/C ratio (r=-1.00, p<0.01), and non-significant with H/C (r=-0.77), and in positive non-significant correlation with C/N and O/H (r=0.56 and 0.62, respectively), indicating higher HAs humification degree in more humified soils.

Soil pH was non-significant positivelly correlated with C/N, O/H and negative with O/C and H/C (r=0.71, 0.75, -0.24 and -0,66, respectively). HA humification degree was higher in slightly acid (VR) and alkaline (CH and RG) than in strongly and very strongly acid (PL and HI) soils. HA from the most calcareous RG soil showed lower humification degree compared to those from less calcareous CH soil.

Correlations of soil sand, silt and clay with HA elements content and ratios were very weak.

CONCLUSION

Results obtained in this study are in agreement with the literature data, indicating HA characteristics as particularly dependant on environmental conditions.

More pronounced differences in HA elemental composition were consequences of various hydrological regimes in terrestial (CH, VR and RG) and hydrogenic (Pl and HI) soils, while climate (precipitation) and chemical properties (soil organic matter, pH and carbonate) possibly had minor influence.