PRESENT ENVIRONMENT AND SUSTAINABLE DEVELOPMENT, VOL. 5, no. 1, 2011

HUMIC FRACTIONS FROM TWO SOIL TYPES LOCATED IN HARGHITA MOUNTAINS

Angela Lupaşcu [1], Daniela Chelariu [2], Cristian-Valeriu Patriche[3]

Key words: humic fractions, Luvosols, Prepodzols, Harghita Mountains.

Abstract. The analysis of organic matter components was carried out for 3 soil subtypes, identified and diagnosed in Harghita Mountains, namely a Stagnic Luvosol, a Histic and a Histic-Skeletic Prepodzol. The purpose of our research was to identify some qualitative and quantitative differentiations within the organic matter. In this respect, the organic matter accumulation is high and it correlates with altitude and land cover. The lowest degree of humification characterises the stagnic Luvosol, while the highest is present in the histic-scheletic Prepodzol. The polymerization degree of humic acids reveals the dominant formation of fulvic acids (among which, the aggressive fraction dominates in the lower half of the soil profile). The non-extractible fraction has the highest values in the case of the stagnic Luvosol (which does not provide favourable conditions for the development of microbial flora) and the lowest ones in the case of the histic skeletic Prepodzol.

Introduction

Harghita Mountains are part of the volcanic chain of Oriental Carpathians and belong to Calimani-Gurghiu-Harghita group, being made up of lava and pyroclastic rocks. These materials form the volcanic plateau situated at approximately 1000m of altitude in the western part of Harghita Mountains, which in fact represents a lithological surface on pyroclastic rocks.

The soils were identified, diagnosed, according to the Romanian Soil Taxonomy System (Florea and Munteanu, 2003) and sampled as part of a research theme, coordinated by prof. dr. Rusu Constantin (“Al. I. Cuza” University of Iaşi, Faculty of Geography and Geology), to whom we wish to thank for his efforts. Soil samples were taken from Harghita Băi region, Vârful Ascuțit and Vlăhița (fig. 1).

[1] Assoc. Prof. PhD., Alexandru Ioan Cuza University, Iaşi, lupascua@yahoo.com
[2] Researcher**,** Romanian Academy, Iaşi, dana_chelariu@yahoo.com
[3] Senior Researcher, Ph.D., Romanian Academy, Iaşi, pvcristi@yahoo.com

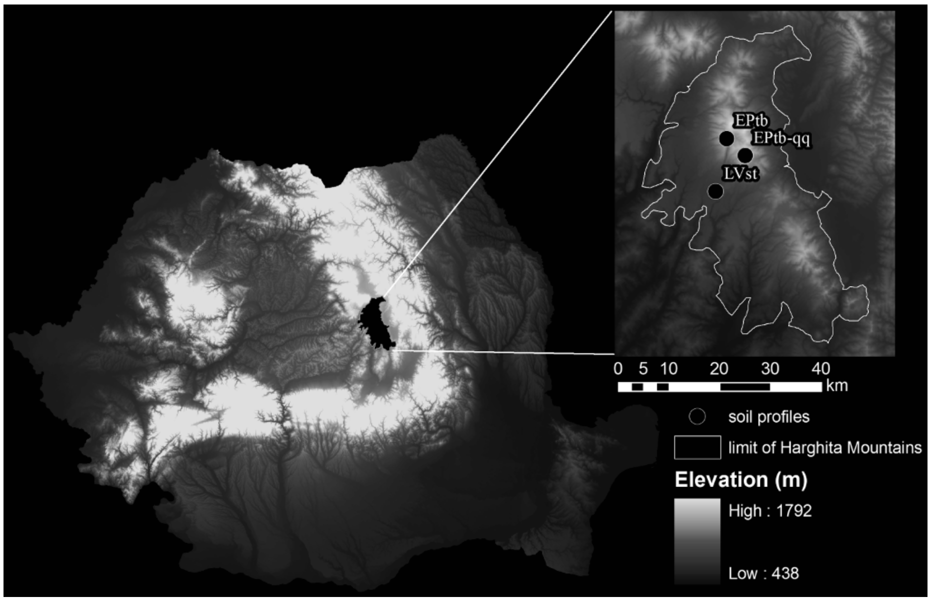

Fig. 1 - Location of the analysed soil profiles within Harghita Mountains area

Generally, the soil cover altitudinal distribution departs from Cambisols, which dominate at altitudes lower than 1000m. Luvisols are also present at these altitudes, dominating the soil cover in the western and southwestern part of the mountains. These soils are followed by Spodisols, found most frequently at altitudes between 1400m and 1800m (Păunescu, 1975). From this class, the Prepodzols represent the dominant type, while the Podzols do not generally meet the necessary formation conditions (Rusu et al., 2006). Andisols, most of them of skeletic subtype, appear most frequently at altitudes between 1000m and 1500m, their genesis being conditioned by the volcanic parent material (Perepeliţă et al., 1986).

Our study continues previous researches regarding organic matter components from mountain soils (Lupaşcu, 2007, Lupaşcu et al., 1998), focusing this time on soils belonging to Harghita Mountains.

1. Materials and methods

The humus fractioning analysis was performed for three soil subtypes: a stagnic Luvosol, sampled at 835m altitude (Harghita Băi), a histic Prepodzol at 1660m altitude (Vârful Ascuţit) and a histic-scheletic Prepodzol situated at 1725m altitude (Vlăhița). For each soil profile, five soil samples were taken, according to the pedogenetic horizons.

For each soil sample, we measured the pH in water suspension, the total organic carbon by humid oxidation method and Walklay-Blak titrimetric dosage, modified by Gogoașă, and the humus content (total organic carbon multiplied by 1.724). Humus components were measured using the method proposed by Kononova and Belcikova (1961), by dividing the soil sample into several subsamples and by performing extractions with sodium pyrophosphate solution ($Na_4P_2O_7$ x $10H_2O$, 0.1 m – NaOH 0.1 n, pH ≈ 13). The solution based on sodium pyrophosphate is considered to be the best extractant for humic fractions. The resulting extract is used for measuring the total extractible carbon (TEC) and the carbon from huminic acids (HA), after removing the fulvic acids (FA). The total content of fulvic acids results from calculations. The values achieved were further used for computing certain indices characterising the humification and polymerisation degree of humic compounds.

2. Results and discussions

The analysed soils show differences related to their taxonomical membership, parental rock, organic matter accumulated over time, dominant soil forming factors (temperature, precipitations, soil biological component), altitude etc.

The stagnic Luvosol (LVst) (Stagnic Luvisols according to FAO, 1998), sampled in Vlăhița area (Fig. 2) on a plateau situated at 835m altitude, is formed on a fine volcanic-sedimentary formations and has a 140cm deep profile comprising 8 horizons, from which 5 samples were taken from the interval 0-73cm and analysed (tab.1).

The vegetation cover is represented by cultivated pasture, dominated by meso-hygrophile species belonging to *Poaceae, Fabaceae, Cyceraceae* families.

Soil reaction is acid all over the profile, the pH values gently increasing with depth from 5.32 in Ao horizon to 5.89 in Bt_1W horizon.

The organic matter, showing a decrease with soil depth (3.86% TOC in Ao horizon, 0.51% in BtElw), indicates a good mineralisation of organic debris, therefore an intense biological activity. In Bt_1W horizon, we notice a slight accumulation of non-extractible humines.

The degree of organic matter humification, hence the organic matter extractability, varies between 42.26% and 64.89%. Higher values indicate the accumulation of fulvic acids down from Elw horizon, while lower values characterise the topsoil, on one hand, where the organic debris is partially decomposed and easier to levigate and the bottom of the soil profile, on the other hand, where the aged extractible material is partially stable linked to soil mineral fraction.

Tab. 1 - Humic fractions from Stagnic Luvosol (LVst) – 835m altitude

Horizon (depth)	pH	TOC	Humus	TEC	HA	FA	Humines	HA/FA	FA/HA	Aggressive FA
Ao 0-18 cm	5.32	3.86	6.65	1.76 45.59	0.62 16.06 35.22	1.14 29.53 64.78	2.1 54.41	0.54	1.84	0.37 32.45
AoEl 18-30 cm	5.53	1.72	2.96	0.85 49.41	0.10 5.81 11.76	0.75 43.60 88.24	0.87 50.59	0.13	7.5	0.23 30.66
Elw 30-41 cm	5.53	0.94	1.62	0.61 64.89	0.02 2.12 3.27	0.59 62.77 96.73	0.33 35.11	0.03	29.5	0.24 40.67
BtElw 41-54 cm	5.36	0.51	0.87	0.27 52.94	0.02 3.92 7.40	0.25 49.02 92.59	0.24 47.06	0.08	12.5	0.13 52.00
Bt_1W 54-73 cm	5.89	0.97	1.67	0.41 42.26	0.04 4.12 9.75	0.37 38.14 90.25	0.56 57.74	0.11	9.25	0.28 75.67

TOC – total organic carbon (% from soil mass); Humus (% from soil mass); TEC – total extractible carbon (% from soil mass / % from TOC); HA – carbon from huminic acids (% from soil mass / % from TOC / % from TEC); FA – carbon from fulvic acids (% from soil mass / % from TOC / % from TEC); Humines (% from soil mass / % from TOC); Aggressive FA (% from soil mass / % from FA)

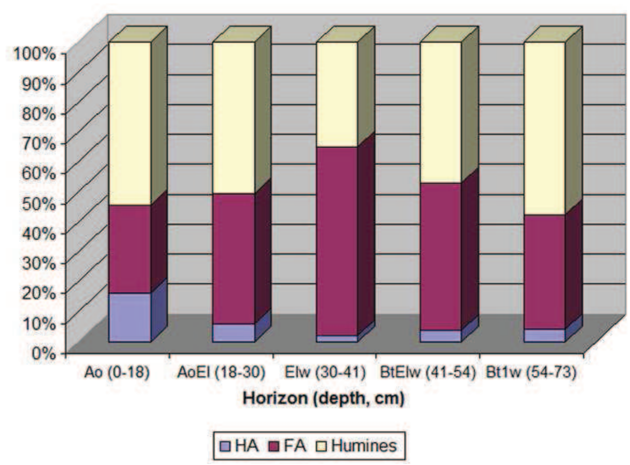

Fig. 2 - Percentages of humic fractions from Stagnic Luvosol (835m, Harghita Mountains)

Tab. 2 - Humic fractions from histic Prepodzol (EPtb) – 1660m altitude

Horizon (depth)	pH	TOC	Humus	TEC	HA	FA	Humines	HA/FA	FA/HA	Aggressive FA
Oh 17-0 cm	5.23	0.18	0.31	0.10 55.55	0.03	0.07	0.08 44.44	0.42	2.33	0.03 42.85
					16.66	38.88				
					30.00	70.00				
Aou 0-14 cm	4.39	11.55	19.91	4.07 35.23	1.64	2.43	7.48 64.77	0.67	1.48	1.31 53.91
					14.19	21.04				
					40.29	59.71				
AoBs 14-26	4.15	16.84	29.03	7.02 41.68	2.96	4.76	9.82 58.32	0.47	2.10	2.46 51.68
					13.42	28.26				
					32.19	67.81				
BsC+R 43-55 cm	5.57	1.97	3.39	1.25 63.45	0.07	1.18	0.72 36.55	0.06	16.85	0.98 83.05
					3.55	28.26				
					5.6	67.81				

TOC – total organic carbon (% from soil mass); Humus (% from soil mass); TEC – total extractible carbon (% from soil mass / % from TOC); HA – carbon from huminic acids (% from soil mass / % from TOC / % from TEC); FA – carbon from fulvic acids (% from soil mass / % from TOC / % from TEC); Humines (% from soil mass / % from TOC); Aggressive FA (% from soil mass / % from FA)

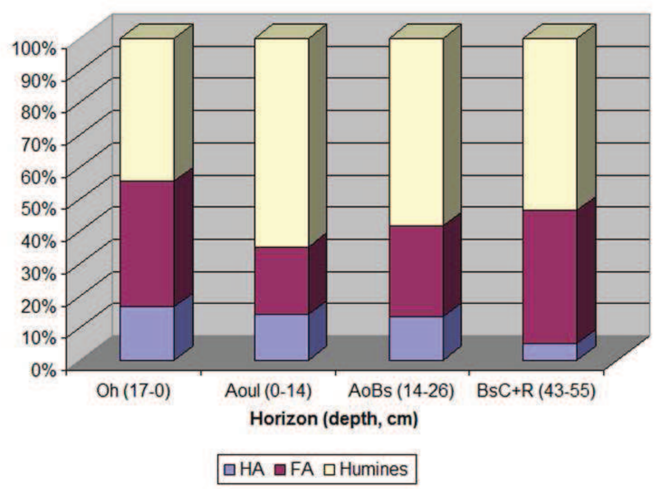

Fig. 3 - Percentages of humic fractions from Histic Prepodzol (1660m, Harghita Mountains)

The extractible component indicates the dominance of fulvic acids all over the profile. FA/HA ratio reveals a levigation of fulvic acids from Ao horizon, where they form, to Elw horizon, where they accumulate. Huminic acids content is higher in Ao horizon, where they represent 0.62% from soil mass, 16.06% from TOC and 35.22% from TEC and much lower in the other soil horizons. These values suggest the presence of low quality humus, with a low nitrogen supply, containing weakly polymerised, easy to levigate humic acids. The vertical distribution of aggressive fulvic acids shows a gradual increase with soil depth, representing 30.66% up to 75.67% from the total fulvic acids.

The humines content varies along the profile, with lower values in Elw horizon (0.33% from soil mass, 35.11% from TOC) and higher values in B horizon (0.56% from soil mass, 57.74% from TOC), in which part of this fraction bonds with the mineral fraction.

The histic Prepodzol (EPtb) (Histi-entic Podzol according to FAO, 1998), belonging to Spodisols class, was sampled from Vârful Ascuțit, from the upper part of a 7-10^o slope, with South-East exposition and 1660m of altitude. The soil is formed on an andesitic eluvium situated over Harghita type andesites. Soil depth is 75cm and it is structured as shown in Tab. 2.

The natural vegetation under which soil evolved is represented by a young spruce forest (*Picea excelsa)* with acidophile litter species *Vaccinium myrtilus, Nardus stricta, Sphagnum* sp*., Polytrichum commune* etc.

Soil reaction is acid all over the profile, the pH values decreasing from Oh to AoBs horizon (5.23 – 4.15), then increasing towards profile base (5.57). This acidity is controlled by the parental rock, but also by the chemical reaction of coniferous litter.

The total organic carbon analysis shows a slow mineralisation and consequently an intense organic matter accumulation for the entire soil profile. Lower values characterise Oh horizon (17cm thick), which has a fibrous aspect and comprises slightly decomposed organic debris (TOC = 0.18%). The underlying Aou horizon has 11.55% TOC and 19.91% humus. The maximum accumulation takes place in AoBs horizon, which contains 16.84% TOC and 29.03% humus. Bs and BsC+R horizons display decreasing values, down to 1.97% TOC.

The humification degree, expressed by TEC/TOC x 100 formulae, has lower values in Aou and AoBs horizons (35-42%) and higher values in Bs horizons (63.45%) where levigable fractions accumulate.

The extractible component is formed mainly by fulvic acids, which dominate all over soil profile (FA/HA ratio is 1.5-2.1 in Aou and AoBs and 16.85 in BsC+R). This variation reveals both the high fulvic acids content and intensity of levigation processes within the histic Prepodzol. Huminic acids content is very low in Oh horizon, correlated with TOC and TEC). The fibrous structure itself does not favour humification. Aou horizon, displaying a degree of humification of 35.23%, „produces” over 40% of the huminic acids and almost 60% of the fulvic acids. The high humines quantity (7.48% of soil mass) is related to deceleration of microbiological activity within a very acid environment represented by coniferous debris. In the underlying horizon, the degree of humification increases, but the polymerisation of humic acids (HA/FA) decreases (from 0.67 to 0.47), resulting a quantity of fulvic acids at least 2 times higher than that of huminic acids. At the bottom of the soil profile, the 16.85 FA/HA ratio reveals an intense accumulation of fulvic acids, also explainable by the aggressive component representing 54% of the forming horizon and 83% of FA in BsC+C horizon.

The non-extractible component, dominated by partially decomposed debris and containing a smaller amount of humines in O and A horizons, explains the high values of residual carbon. At profile base, the actual content of 0.72% from soil mass represents 36.55% from TOC.

The histic-skeletic Prepodzol (EPtb-qq) (Histi-skeleti-entic Podzol, according to FAO, 1998), belonging to Spodisols class, sampled at Harghita Băi, 1 km South of the main peak, at 1725m altitude, is situated on a volcanic plateau, on a 3^{o} slope oriented towards North. The parental material consists in an andesitic periglacial eluvium, resting on in situ andesites. The soil profile is 55cm thick and it is structured as shown in Tab. 3, the litter layer being 22cm thick above 0 level.

The natural vegetation belongs to the transition from forest to subalpine zone, with representative species such as the spruce *(Picea excelsa)*, the mountain pine *(Pinus mugo)*, *Vaccinium mirtillus, V. uliginosus, Nardus stricta, Campanula* sp. etc.

Soil chemical reaction is acid throughout the profile, the pH values increasing with depth from 4.72 in Oh1 horizon to 6.23 in Bs1+R. As in the case of the previous soil, the coniferous litter confers the acid pH to the upper soil horizons, while at the bottom of the profile pH is influenced by the parental rock.

TOC and humus analysis reveal the slow mineralisation of organic debris, by their high values all over the profile. Comparing the two analysed Prepodzols profile, the altitudinal difference is reflected mainly in the organic accumulation. Hence, the Oh horizon, with clear separations of the 3 sub-horizons, show values between 6.03% and 14.92% for TOC and between 10.39% and 25.72% for humus, the latter values being the highest ones for the entire soil profile. In underlying horizons, the values slowly decrease, so as in Bs1+R horizon the TOC is 5.55% and the humus content is 9.56%. The organic matter is well humified, the degree of humification being 69.95 in Oh2 horizon, increasing to 73.12 in Aou horizon and then decreasing towards the profile base (65.82 in Bs1+R).

Tab. 2 - Humic fractions from histic-skeletic Prepodzol (EPtb) – 1725m altitude

Horizon (depth)	pH	TOC	Humus	TEC	HA	FA	Humines	HA/FA	FA/HA	Aggressive FA
Oh_1 22-17	4.72	6.03	10.39	2.22 36.81	0.24 3.98 10.81	1.98 32.82 89.19	3.81 63.19	0.12	8.25	0.92 46.46
Oh_2 17-10	5.01	14.92	25.72	9.84 65.95	4.03 27.01 40.95	5.81 38.94 59.05	5.08 34.05	0.69	1.44	2.68 46.12
Oh_3 10-0	5.10	13.57	23.39	9.68 71.33	4.03 29.69 41.63	5.65 41.64 58.37	3.89 28.66	0.71	1.40	2.71 47.96
Aou 0-10	5.23	9.60	16.55	7.02 73.12	1.96 20.42 27.92	5.06 52.7 72.08	2.58 26.88	0.38	2.58	2.64 52.17
AouBs 10-18	5.58	7.72	13.31	5.27 68.26	0.80 10.36 15.18	4.47 57.9 84.82	2.45 31.74	0.17	5.58	2.46 55.03
Bs_1+R 18-30	6.23	5.55	9.56	3.66 65.82	0.60 10.81 16.39	3.06 55.01 83.61	1.89 34.18	0.19	5.10	2.16 70.58

TOC – total organic carbon (% from soil mass); Humus (% from soil mass); TEC – total extractible carbon (% from soil mass / % from TOC); HA – carbon from huminic acids (% from soil mass / % from TOC / % from TEC); FA – carbon from fulvic acids (% from soil mass / % from TOC / % from TEC); Humines (% from soil mass / % from TOC); Aggressive FA (% from soil mass / % from FA)

As previously, the extractible component is dominated by fulvic acids, but with a FA/HA maximum index of 8.25. Towards the profile base, the fulvic acids concentration is 3 times lower than in the 1660m profile. Moreover, the amount of aggressive fulvic acids is lower towards the profile base. The polymerisation degree of humic components, given by HA/FA ratio, has values under 1 throughout the profile and a maximum value in Oh3 horizon (0.71). This degree is higher than the one determined for the histic Prepodzol, because humification leads to formation of higher quality huminic acids.

The non-extractible component has high values throughout the profile (5.08-1.89% from soil mass), representing between 63.19% and 26.88% of TOC, the distribution curve indicating slightly lower values in Aou horizon. Comparing this soil with the histic Prepodzol, we notice a better humification, favoured by a lesser

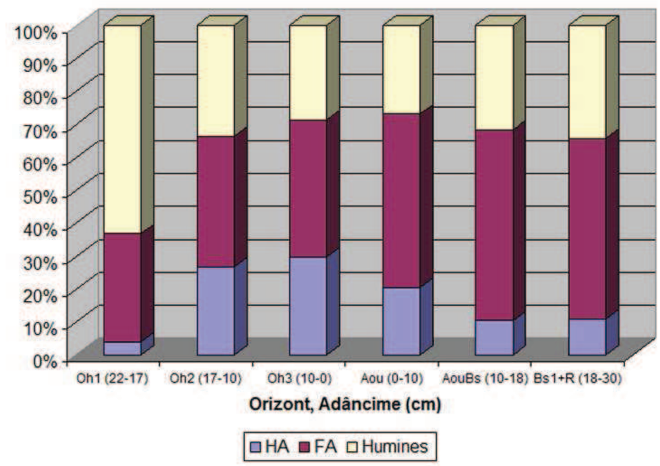

Fig. 4 - Percentages of humic fractions from Histic-Skeletic Prepodzol (1725m, Harghita Mountains)

acid soil reaction, with a value of 6.23 in Bs1+R horizon. In addition, the lower content of aggressive fulvic acids correlates with the higher pH.

Conclusions

The organic matter analysis of the three soil profiles reveals the following aspects:

a. The organic debris mineralisation is tightly related to the ecological conditions (pH, vegetation cover, altitude etc.) and it is reflected in the bioaccumulation process. Humus content is lower in the stagnic Luvosol (max. 6,65 % from soil mass) and much higher in the 2 Prepodzol subtypes (29,03 % in the histic Prepodzol and 25,72 % in the histic-skeletic Prepodzol).

b. The extractible component has values around 50% from TOC in the stagnic Luvosol and the histic Prepodzol (with maximum values of 65% and 63%) and much higher in the histic-skeletic Prepodzol, in which case the values are above 65% throughout the profile (excepting Oh_1 horizon) and the maximum value is 73.12% from TOC.

c. The humification processes favour the formation of fulvic acids, the fraction of aggressive fulvic acids dominating in the lower half of the profiles. The huminic acids content is the lowest in the stagnic Luvosol and the highest in the histic-skeletic Prepodzol.

d. The non-extractible component, represented by a mixture of humines and partially decomposed organic debris in the upper horizons and by humines in the lower horizons, shows the highest values in the stagnic Luvosol, which has a reduced biological activity and the lowest values in the histic-skeletic Prepodzol.

The humus of the histic-skeletic Prepodzol has superior quality compared to the other soil subtypes.

Acknowledgments

This study was carried out with support from project POSDRU/89/1.5/S/49944, coordinated by "Al. I. Cuza" University of Iaşi.

References:

Florea, N., Munteanu, I. (2003), *Romanian soil taxonomy system*. Ed. Estfalia, Bucharest. (In Romanian).

Kononova, M. M., Belcikova, N.P., (1961), *A rapid analysis of humus composition in mineral soil*. Pocivovedenie, **10**, 75–87. (In Russian)

Lupaşcu, A. (2007), *Considerations regarding the organic matter and humus fractioning for the dystric Cambisols from Giurgeu Mountains.* An. Şt. Univ. „Al.I Cuza" Iaşi, **LIII**, s. II-c, Geogr., Iaşi, 45-50.

Lupaşcu, A., Rusu, C., Donisă C., (1998), *Aspects regarding the organic matter from Andosols and andic soils from Oaş-Igniş Mountains*. Lucr. Sem. Geogr. „Dimitrie Cantemir", **17-18**, 151-159. (In Romanian).

Păunescu, C., (1975)*, Forest soils*. Ed. Academiei Române. (In Romanian).

Perepeliță, V., Florea, N., Vlad, L., Grigorescu A., (1986), *On diagnostic criteria of Andosols and andic soils from Carpathians Mountains.* An. ICPA, **XLVII**. (In Romanian).

Rusu, C., Niacsu, L., Roşca, B., Fiscutean, D., (2006), *The soils of the Harghita Mountains*. Programul celei de-a XVIII-a Conferinte Nationale de Stiinta Solului cu participare internationala, Cluj-Napoca, 20-26 august 2006, SNRSS, abstract, 88-89.

FAO (1998), *World reference base for soil resources*. World Soil Resources Reports, **84**, FAO, Rome.