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DISTRIBUTION OF HUMIC FRACTION IN REPRESENTATIVE SOILS FROM GURGHIU MOUNTAINS

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Abstract. The analysis of organic matter components was perfomed for 4 soil subtypes, which were identified and diagnosed in Gurghiu Mountains: one andic, histic Districambosol (830 m altitude), one cambic Andosol (1200 m altitude), one cambic-histic Andosol (1495 m altitude) and one typic Prepodzol (1725 m altitude). The research aimed to identify qualitative and quatitative differences in organic matter. The results show that the organic matter accumulation is high and it correlates with soil subtype, altitude and vegetation. The cambic Andosol presents high organic matter contents throughout the profile. The highest degree of humification characterizes the typic Prepodzol, while the other analysed soils present lower and comparable values. The polymerization degree of humic acids shows the dominant formation of fulvic acids, excepting the cambic-histic Andosol, in which case the ratio between the two types of acids is close to one.

Introduction

Gurghiu Mountains are part of the volcanic chain of Oriental Carpathians – the group of Căliman-Gurghiu-Harghita – made up of lava and pyroclastic rocks, with appreciable heights up to 1776m in Saca Peak. Two types of relief can be noticed: the volcanic cones and the lower volcanic plateaus (Rusu C., 2008). The pedogenesis reflects the influence of the volcanic material, climate conditions, which are tightly related to altitude and the forest vegetation.

The soils were identified, diagnosed 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

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samples were taken from Salard area (830 m), Borzont area (1200 m and 1495 m) and Saca Peak (1725 m) (Fig.1).

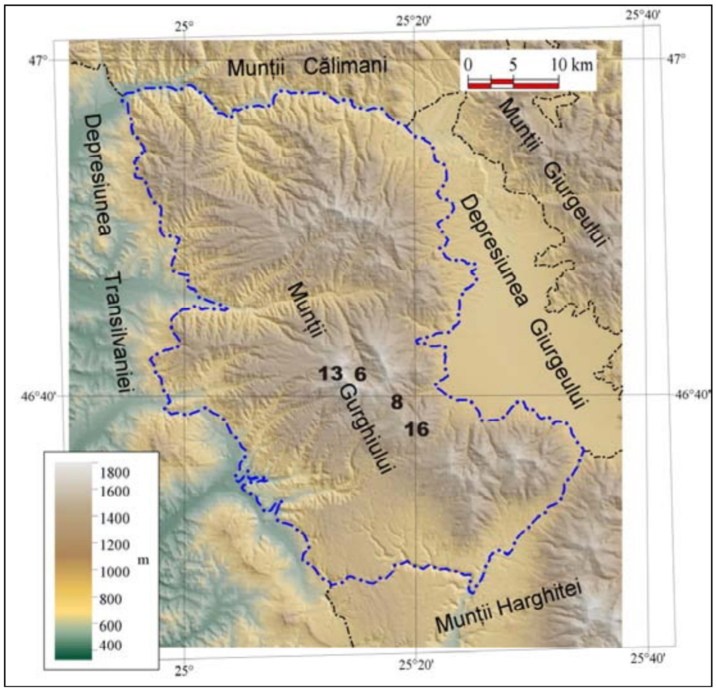

Fig. 1 Location of the analysed soil profiles within Gurghiu Mountains area: 6 - andic-histic Districambosol; 8 - cambic Andosol; 13 - cambic-histic Andosol; 16 - typic Prepodzol

1. Materials and methods

The humus fractioning analysis was performed for four soil subtypes: an *andic, histic Districambosol* (830 m altitude), a *cambic Andosol* (1200 m altitude), a *cambic-histic Andosol* (1495 m altitude) and a *typic Prepodzol* (1725 m altitude) from Saca Peak. For each soil profile, five soil samples were taken, according to the pedogenetic horizons.

For each soil sample, the pH in water suspension was measured, while the total organic carbon was determined by humid oxidation method and Walklay-Blak titrimetric dosage, modified by Gogoaşă. Then the humus content was determined by multiplying the total organic carbon with 1.724. Humus components were measured using the Kononova and Belcikova (1961) method, 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 generally 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 first 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 disscusions

The analysed soils show differences in respect to their taxonomical membership, parental rock, organic matter accumulated over time, dominant soil forming factors (temperature, precipitations, soil biological component), altitude etc. (Vasu A., 1986) . The soil profiles were selected along a toposequence in order to reveal the influence of altitude (Lupaşcu A, 1996).

Each of the analysed soil subtypes are presented as follows.

The andic, histic Districambosol (Dcan-tb), sampled in Salard area (Fig. 2) from a uniform slope at the altitude of 830 m, is developped on a pyroclastic deluvium and andezitic lava, with a profile depth of 125 cm structured in 10 horizons from which 5 samples were taken, from Oh to Bv2 horizon (Tab. 1).

Tab. 1 Distribution of humic fractions from the andic-histic Districambosol (Gurghiu Mountains, 830 m altitude)

Horizon (depth, cm)	**pH**	**TOC**	**Humus**	**TEC**	**HA**	**FA**	**Residual C**	**FA/HA**
Oh 11-0	4.96	16.98	29.27	8.23 48.46	4.31 25.38 52.37	3.92 23.07 47.63	8.75 51.53	0.9
Aou 0-15	5.11	9.83	16.94	5.81 59.1	1.94 19.73 33.39	3.87 39.36 66.61	4.02 40.89	2.0
A-B 15-25	5.28	7.28	12.55	4.72 64.83	1.56 21.43 33.05	3.16 43.4 66.95	2.56 35.16	2.0
Bv1 25-38	5.53	5.47	9.43	3.11 56.85	0.87 15.9 27.97	2.24 40.94 72.03	2.36 43.14	2.6
Bv2 38-52	5.89	5.31	9.15	2.75 51.79	0.38 7.15 13.81	2.37 44.63 86.18	2.56 48.21	6.2

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); residual C – non-extractible carbon and humines (% from soil mass / % from TOC)

The vegetation cover is represented by a mixed forest, with spruce and beech and other deciduous trees. The herbaceous cover is dominated by *Dryopteris filix mas, Rubus caesius, Oxalis acetosella, Salvia glutinosa.*

Soil reaction is acid troughout the profile, the pH values increasing with depth from 4.96 in Oh horizon to 5.89 in Bv2.

The organic matter content decreases with depth (TOC = 16.98% from soil mass in Oh, TOC = 5.31% from soil mass in Bv2), revealing a good mineralisation of organic debris and a relatively intense biologic activity. In AB and Bv horizons, it is noticed a slight accumulation of non-extractible humines.

The humification degree of organic matter, the extractibility of organic matter respectively, varies between 48.46% and 64.83%. Lower values are encountered at the base of the profile, where the aged extractible material is partially stable bounded to soil mineral components.

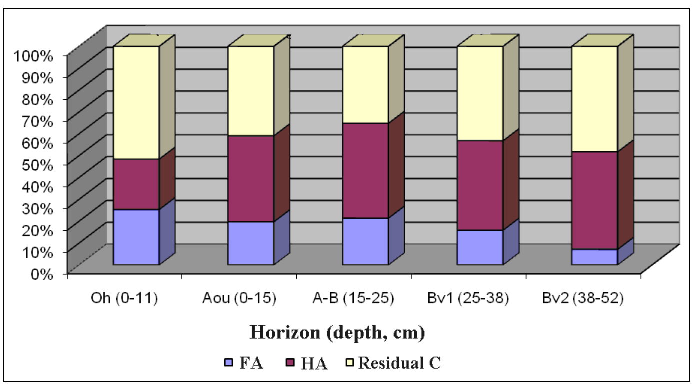

Fig. 2 Percentages of humic fractions from the andic-histic Districambosol (Gurghiu Mountains, 830 m altitude)

The extractible component indicates the dominance of fulvic acids all over the profile, excepting the Oh horizon, in which case the huminic acids are slightly dominant. The FA/HA ratio reveals the leaching of fulvic acids from Aou horizon, in which they form, to AB and Bv horizons, in which they accumulate. The huminic acids have higher values in the forming horizon (Oh), in which they represent 4.31% from soil mass and 52.37% from TEC, and much lower values at the base of the profile. The HA/FA ratio decreases with depth from 1.09 to 0.16. These values indicate a low nitrogen humus, containing mobile humic acids with low polymerisation degree. The distribution curve of aggresive fulvic acids points out the gradual increase of this fraction, within total fulvic acids, with soil depth, representing between 47.63% and 86.18% from TEC).

The humines content varies between 35% and 51% form TOC.

The cambic Andosol (ANcb) was sampled near Borzont settlement, at 1200 m of altitude, on a slope developped on andesite deluvium. The profile is 80 cm thick, to which it adds 13 cm above 0 soil level, and it is structures as presented in table 2.

The natural vegetation is a mixed forest with spruce *(Picea excelsa)* and beech *(Fagus silvestris)*, the litter being dominated by acidophilic species: *Vaccinium myrtilus, Oxalis acetosella, Rubus idaeus, Polytrichum commune* etc.

Soil reaction is acid throughout the profile (Tab. 2), the pH values increasing slightly form Oh horizon towards the base of profile. This acidity is explained by the parent rock but also by the chemical reaction of the coniferous litter.

TOC analysis shows a slow mineralisation process and hence an intense organic accumultation throughout the profile (Tab. 2). The highest values are recorded in the surface Of and Oh horizons (13 cm thick), with a finely grained aspect. The TOC values reach here 47.09% in Of horizon, dropping to 17.54% in the Oh horizon bellow. The Aou horizon has 9.68% TOC and 16.68% humus respectively. The organic matter accumulation descreases slightly with profile depth, down to 6.67% in Bv1 horizon. The degree of humification, revealed by the TEC/TOC ratio, has high values all over the profile, starting from Oh horizon.

Tab. 2 Distribution of humic fractions from the cambic Andosol
(Gurghiu Mountains, 1200 m altitude)

Horizon (depth, cm)	**pH**	**TOC**	**Humus**	**TEC**	**HA**	**FA**	**Residual C**	**FA/HA**
Of 9-5	5.09	47.09	80.99	15.91 33.78	8.28 17.58 52.04	7.63 16.19 47.96	31.18 66.22	0.9
Oh 5-0	5.14	17.54	30.23	10.69 60.94	4.69 26.74 43.87	6.00 34.2 56.13	6.85 39.06	1.3
Aou 0-15	5.25	9.68	16.68	6.19 63.94	1.74 17.97 28.11	4.45 45.96 71.89	3.49 36.06	2.6
A-Bv 15-26	5.28	7.91	13.63	4.52 57.14	1.22 15.42 26.99	3.3 41.72 73.01	3.39 42.86	2.7
Bv1 26-31	5.31	6.67	11.49	3.79 56.82	0.73 10.94 19.26	3.06 45.87 80.74	2.88 43.18	4.2

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); residual C – non-extractible carbon and humines (% from soil mass / % from TOC)

The extractible component is mainly formed of fulvic acids, which dominate down all over the profile: the FA/HA ratio is 0.9 in Of horizon and more than 1 down to profile base (1.3 in Oh, 2.6 in Aou and 4.2 in Bv1). This variation indicates qualitative differences in humification, with high contents of huminic acids in the upper horizon and dominance of the fulvic component towards profile base with high leaching potential.

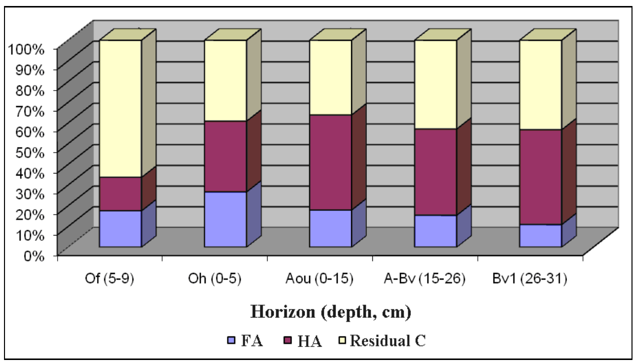

Fig. 3 Percentages of humic fractions from the cambic Andosol (Gurghiu Mountains, 1200 m altitude)

The non-extractible component, formed in the Of horizon, dominanted by partially decomposed organic debris, represents 66.22% of the total organic matter. In undelying horizons, the humines are less present due to formation and accumulation of humic acids.

The cambic-histic Andosol (ANcb-tb), sampled in Borzont settlement area, at 1495 m of altitude, is situated on a mountainous plateau. The parent material is made up of andesites with pyroxenes and amphiboles. The profile is 90 cm thick and it is structured as presented in table 3. The litter cover is 25 cm thick.

The natural vegetation is made up of forests from the limit with the subalpine zone, with representative species such as spruce *(Picea excelsa)*, *Vaccinium mirtillus, V. uliginosus, Luzula silvatica, Rubus idaeus* etc.

Soil reaction is acid throughout the profile, the pH values increasing with depth. The coniferous litter determines the acid pH values in the upper horizons, while the influence of parent rock manifests at profile base.

The analyses of TOC and humus reveal the active mineralisation of organic matter, through the low values of these parametrs (Fig. 4). Comparing the two analysed andosols profiles, the altitude difference is marked mainly in the organic matter accumulation: 17.54% TOC in Oh at 1200 m altitude and 1.73% at 1495 m. In this profile, the mineralisation is activated and the organic debris is lower. The

Oh horizon has a TOC value of 1.73%, which decreases gradually along the profile. The degree of humification indicates a good humification of organic matter, beginning with Oh horizon (56.07). It increases slightly in Bv1 horizon (77.27) and decreases towards profile base (64.29 in Bv3).

Tab. 3 Distribution of humic fractions from the cambic-histic Andosol
(Gurghiu Mountains, 1495 m altitude)

Horizon (depth, cm)	pH	TOC	Humus	TEC	HA	FA	Residual C	FA/HA
Oh 14-0	5.01	1.73	2.98	0.97 56.07	0.51 29.48 52.57	0.46 26.59 47.43	0.76 43.93	0.9
Bv 5-12	5.23	0.64	1.1	0.35 54.69	0.1 15.62 28.57	0.25 39.06 71.43	0.29 45.31	2.5
Bv1 12-32	5.27	0.22	0.38	0.17 77.27	0.1 45.45 58.82	0.07 31.81 41.17	0.05 22.73	0.7
Bv2 32-54	5.34	0.22	0.38	0.14 63.63	0.07 31.81 50.0	0.07 31.81 50.0	0.08 36.37	1.0
Bv3 54-70	5.48	0.14	0.24	0.09 64.28	0.03 21.42 33.33	0.06 42.85 66.66	0.05 35.72	2.0

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); residual C – non-extractible carbon and humines (% from soil mass / % from TOC)

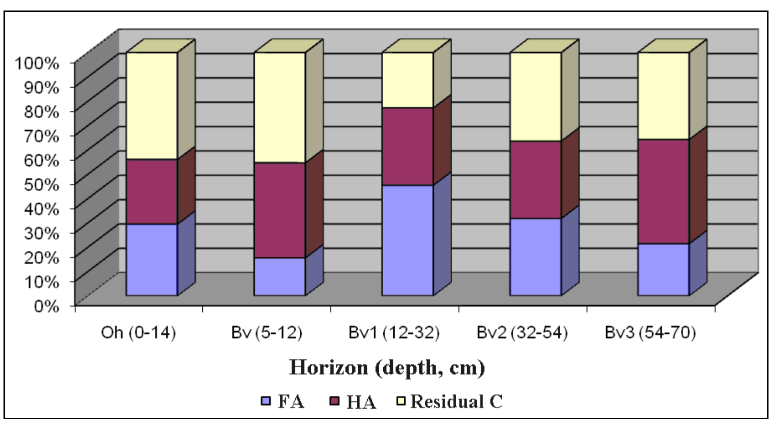

Fig. 4 Percentages of humic fractions from the cambic-histic Andosol
(Gurghiu Mountains, 1495 m altitude)

The extractible component, formed of huminic and fulvic acids, presents variations along the soil profile (Donisa C., 1998). The fulvic acids dominate, but with a maximum value of FA/HA index of 2.5 in Bv horizon.

The non-extractible component decreases down to Bv1 horizon, after which the values slightly increase.

The typic Prepodzol (EPti), sampled on a plateau from Saca Peak, at 1775 m altitude, has a thickness of 70 cm and, in addition, 10 cm of litter. The parent material is represented by an andesitic eluvium. The natural vegetation is constituted mainly of *Juniperus communis,* with *Picea excelsa* (rarely encountered) and acidophile herbaceous species such as *Festuca rubra, Nardus stricta, Vaccinium vitis-idaea* etc.

Tab. 4 Distribution of humic fractions from the the typic Prepodzol (Gurghiu Mountains, 1775 m altitude)

Horizon (depth, cm)	**pH**	**TOC**	**Humus**	**TEC**	**HA**	**FA**	**Residual C**	**FA/HA**
Aou 0-10	5.04	10.95	18.87	5.01 45.75	1.45 13.24 28.94	3.56 32.51 71.06	5.94 54.24	2.4
A/Bhs 10-15	5.15	9.83	16.94	6.21 63.17	0.83 8.44 13.36	5.38 54.73 86.63	3.62 36.83	6.5
Bs1 15-25	5.28	6.55	11.29	5.37 81.98	1.16 17.71 21.6	4.21 64.27 78.39	1.18 18.01	3.6
Bs2 25-36	5.36	3.24	5.58	2.75 84.87	0.12 3.7 4.36	2.63 81.16 95.63	0.49 15.13	21.9
C-R 36-50	5.39	1.45	2.49	1.39 95.86	0.14 9.65 10.07	1.25 86.2 89.93	0.06 4.14	8.9

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); residual C – non-extractible carbon and humines (% from soil mass / % from TOC)

The total organic carbon (TOC) analysis shows a much slower mineralisation due to ecological conditions and hence, an intense organic matter accumulation all over the profile (Tab. 4, Fig. 5). Very high values are recorded in Aou horizon (10.95% TOC and 18.87% humus respectively), while the accumulation descreases slightly along the profile (3.24% TOC in Bs2 horizon). The degree of humification, revealed by the TEC/TOC x 100 index, has high values beginning with Aou horizon (45.75%) and they increase to 95.86% down to profile base.

The extractible component is mainly formed of fulvic acids, which dominate down to the profile base (HA/FA ratio is under 1 throughout the profile) and the FA/HA ratio is variable, with values between 2.45 in Aou and 21.91 in Bs2. This variation indicates both the non-qualitative humification (Perepelita V., 1986), with high contents of fulvic acids, and the intense leaching of these acids along the soil profile.

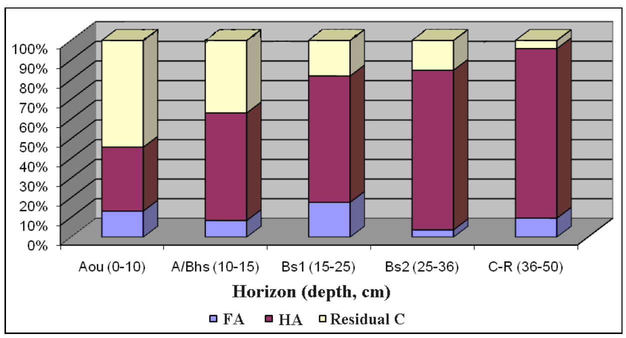

Fig. 5 Percentages of humic fractions from the the typic Prepodzol (Gurghiu Mountains, 1775 m altitude)

Compared with the other analysed soils, the non-extractible component decreases gradually from 54.24% to 4.14% of total organic matter. The fulvic acids, with low polymerisation degree, do not form complexes with the mineral part of soil, while the concentraction of huminic acids is reduced. In this way, it is explained the low value of humines from profile base.

Conclusions

The analysis of organic matter form the four soil profiles points out the following aspects:

The mineralisation of organic debris is tightly related to the ecological factors (acidity, microclimate, altitude etc.), the organic accumulation and intensity of microbiological activity and it is revealed in the bioaccumulation process. Humus content is maximum in the cambic Andosol, at 1200 m altitude, and minimum in the cambic-histic Andosol, at 1495 m altitude.

The extractible component has values of 54-77% from TOC in the cambic Andosol and 45-95% in the typic Prepodzol.

The humification processes favour the formation of fulvic acids, which can exceed 8.9 – 21.91 times the huminic acids content the huminic acids present the lowest values in the case of the typic Prepodzol.

The non-extractible component (residual C), represented by partially decomposed organic matter from the upper horizons and humines in the lower horizons, presents relatively high values in all analysed soils, with the exception of the typic Prepodzol, in which cased the humines vary from 54.24% in Aou and 4.14% in C+R.

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