CONSIDERATIONS ON THE ORGANIC MATTER AND HUMUS DIVISION IN THE SOILS FROM MARAMUREŞ MOUNTAINS

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Abstract: In this paper some appreciations are made regarding the total organic matter and humic fractions in a few soils which are representative for Maramureş Mountains. Representative subtypes of soils from the Cambisoils class have been analyzed: typical eutricambosoil, typical prepodzol, skeletal prepodzol and lithic prepodzol. Comparing the data from the analyzed profiles, there is a difference in terms of organic accumulation: typical eutricambosoil has the best mineralization of organic matter; typical and skeletal prepodzol have high and similar values, organic material mineralization is decelerating and lithic prepodzol subtype has the highest organic accumulation. Qualitatively, there are some differences in the degree of humification of organic matter, the main distribution of humic fractions (fulvic acids, humic acids, humins) on soil horizons, and the emergence of accumulations horizons of fractions.

Keywords: *organic matter, humic fractions, soils, Maramureş.*

1. Introduction

Maramureş Mountains represent a central massive (together with Rodna Mountains and Suhard Mountains) lying in the northern group of the Eastern Carpathians, located on the right of Viseu up to the border and from Tisa River Gorge to Cârlibaba stream (tributary of Bistriţa Aurie). Mountains suffer a strong fragmentation between the tributariesof Viseu river, yielding five oblong peaks with heights ranging between 1,847 m (Cearcănu-Prislop) and 1,956 m (Pop Ivan). The temperate-continental climate is influenced by the high altitudes, configuration and orientation of the peaks, being marked by low temperatures with early frosts that extend until late spring. Vegetation is represented by forests and natural grasslands.

The pedologic cover is very related to the parent material. On the crystalline schists starting at 1,400 m altitude up to 1,800 m altitude podzolic soils are present, while podzols can be found up to 1,550-1,600 m altitude and feriluvic brown soils at higher altitudes. Regardless of the morphology and typology of profiles, the chemical parameters variation is relatively small, which argues in favour of a certain pedogenetic uniformity at this altitude (1,400-1,800 m).

2. Materials and methods

The method of humus fractionation was applied to four subtypes of cambisol soil class, respectively: typical eutricambosol subtype (920 m altitude), typical prepodzol (1,480 m), skeletal prepodzol (1,520 m) and lithic prepodzol (1,750 m). Five samples (taken according to horizons) were analzyed for each soil profile. For every soil sample we

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determined the pH in aqueous suspension, total organic carbon by wet oxidation method and titrimetrical dosage Walklay-Blak in changing humus (organic C total x 1,724).

Humic fractions (fulvic acids, humic acids, humins) were determined using the method developed by Kononova M. M. and Belcikova N. P. (1961), in which the soil sample is divided into several sub-samples and then there are made extractions with a mixture solution of sodium pyrophosphate (Na4P2O7 x 10H2O) 0,1 m – NaOH 0,1 n, pH approx. 13. The solution based on sodium pyrophosphate is considered the best for humic fractions extractant. The extract obtained is used in the determination of total carbon extractable (CET) and carbon in humic acids (CAHT), after first washing the fulvic acids (CAFT). Fulvic acids are determined by calculating the total. From the values obtained we calculated some indices to characterize the degree of humification of the organic matter and the degree of polymerization of humic compounds.

The data are presented as tables and charts in the following way: total organic carbon (C.org.tot.) % of the soil; total extractable carbon (CET): % compared to soil and % compared to C.org.tot.; humic acids carbon (CAHT) and fulvic acids (CAFT): % compared to soil, % compared to C.org.tot. and % to CET; residual carbon containing partially decomposed residuals, but also humic carbon (CH) is presented in percentage to the soil and percentage to the C.org.tot.

3. Results and discussions

The analyzed soils were identified and dignosed by a team led by Prof. dr. researcher Rusu Constantin („Al.I.Cuza" University of Iasi, Romanian Academy – Iasi Branch). They show a differentiation related to their taxonomic classification, parent rock, organic matter brought from the vegetal cover over time, by the dominant pedogenetic factors (temperature, precipitations, soil biological component) and altitude (Vasu, 1986, Perepeliţă, 1986).
Below we will present on each of the subtype of soil analysed.

In the ***typical Eutricambosol*** soil, located at 920 m altitude, under a forest of *Fagus silvestris* mixed with *Acer pseudoplatanus, Picea abies* and *Dryopteris filix-mas, Rubus hirtus* in the shrub layer, the organic matter content varies along the soil profile, the values being placed on a descendent curve from 5.96% in horizon A/B (8-17 cm depth) to 0.56% in horizon Bv/C (68-88 cm); the values decrease gradually between the two horizons. These values (10.27-0.9% humus) are the result of a lower mineralization due to the environmental conditions, primarily to a high acidity in the upper horizons (pH – 4.93 in horizon A/B).

Regarding the quality of the organic matter, the degree of humification is of 39.59% in horizon A/B, 50% in Bv1 and 53% to the base of the profile (Tab. 1). Extractable organic matter is formed mainly throughout the profile of fulvic acids, whose concentration increases gradually with the depth; they represent 57.64% in A/B of CET, up to 84.06% in Bv3. Otherwise expressed: CAF/CAH ratio ranges between 1.36 in A/B and 5.27 in Bv3. Huminic acids are better represented in the upper horizons, where they are formed, and represent 16.77% of the organic matter.

The amount of humins varies along the profile between 3.6% and 0.26%; in respect of the total organic matter, it has high values (60,4%) in the upper horizons, in which the partially decomposed organic compounds are abundantly found; low values (46%) are recorded from Bv1 to Bv/C, where humins are represented by old humic acids, very intimately related to the mineral part of the soil and which do not solubilize in the extractant solution. The small-value CAH/CAF ratio indicates unfavorable conditions for the reactions of heteropolicondensation indicating humic acids.

In *typical Prepodzol* soil (Tab. 2), located at an altitude of 1,480 m, under a meadow with *Nardus stricta, Festuca rubra, Poa violacea, Anthoxanthum odoratum, Juncus trifidus,* *Rumex acetosella*, *Campanula carpathica*, the content in organic matter is very high throughout the profile, with percentages between 12.6% and 2.7% of total organic carbon and between 21.72% and 4.65% of humus. The distribution of the data on the profile looks like a sinuous curve with high values in horizons Aou and middle A, with lower values in horizon B1 and rising values in Bs2 and BV-Bs. This organic accumulation is closely linked to severe humification conditions (climate, soil pH value of 4-4.2 in horizons A, that slow down the mineralization processes of organic waste by reducing the microbiological activity (Lupascu, 1994, 1996).

Table 1. Variation with depth of organic matter and humic fraction in the typical Eutricambosoil (920 m altitude)

Horizon (depth, cm)	**pH**	**TOC**	**Humus**	**TEC**	**HA**	**FA**	**Residual C**	***CFA/ CHA***
A/B 8-17	4.03	5.96	10.27	2.36 39.59	1.00 16.77 42.37	1.36 22.81 57.63	3.60 60.40	1.36
Bv1 17-30	4.70	3.72	6.41	1.86 50.00	0.61 16.39 32.79	1.25 33.61 67.20	1.86 50.00	2.04
Bv2 30-44	4.92	2.63	4.53	1.41 53.66	0.38 14.45 26.95	1.03 39.21 73.05	1.22 46.38	2.71
Bv3 44-68	4.80	1.30	2.24	0.69 53.07	0.11 8.46 15.94	0.58 44.60 84.06	0.61 46.92	5.27
Bv/C 68-88	5.10	0.56	0.9	0.30 53.57			0.26 46.42	

TOC – total organic carbon (% of soil mass); Humus (% of soil mass); TEC – total extractible carbon (% of soil mass / % of TOC); HA – carbon from huminic acids (% of soil mass / % of TOC / % of TEC); FA – carbon from fulvic acids (% of soil mass / % of TOC / % of TEC); residual C – non-extractible carbon and humines (% of soil mass / % of TOC)

Table 2. Variation with depth of organic matter and humic fraction in typical Prepodzol (1,480 m altitude)

Horizon (depth, cm)	**pH**	**TOC**	**Humus**	**TEC**	**HA**	**FA**	**Residual C**	**CAF/ CAH**
Aou 0-5	4.09	12.60	21.72	5.59 44.36	1.95 15.47 34.88	3.64 28.88 65.11	7.01 55.63	1.86
A/Bs(Es) 5-11	4.22	6.89	11.87	2.36 34.25	1.78 25.83 75.42	0.58 8.41 24.57	4.53 65.74	0.32
Bs1 11-23	4.52	2.70	4.65	1.81 67.03	0.77 28.52 42.54	1.03 39.21 73.05	1.22 46.38	1.35
Bs2 23-40	4.46	4.17	7.18	1.53 36.69	1.05 25.18 68.63	0.48 11.51 31.37	0.61 46.92	0.46
Bv-Bs 40-55	4.74	3.77	6.49	0.80 21.22	0.44 11.67 55.0	0.36 9.55 45.0	2.97 78.78	0.81

TOC – total organic carbon (% of soil mass); Humus (% of soil mass); TEC – total extractible carbon (% of soil mass / % of TOC); HA – carbon from huminic acids (% of soil mass / % of TOC / % of TEC); FA – carbon from fulvic acids (% of soil mass / % of TOC / % of TEC); residual C – non-extractible carbon and humines (% of soil mass / % of TOC)

The content of extractable organic matter is related to the total organic matter, but the curve feature data is descendent and not sinuous. The humification degree varies along the profile, which indicates a more dynamic evolution of the pedogenetic processes, so, it has values of 44.36% in Aou, 34.25% in A/Bs (Es), especially of fulvic acids, with smaller molecules floating and accumulating in Bs1, where the degree of humification rises to 67.03% in horizons Bs2 and Bv-Bs, due to the intimate ties between humic acids and mineral matter, the degree of humification having very low values, even if the amount of humins represents 78.78% of the total organic carbon.

Humic acids, through their distribution, reflect the same dynamic evolution. Thus, in Aou horizon, where mainly fulvic acids are formed, the CAF/CAH ratio is of 1.86. In the forming horizon, A/Bs (Es), fulvic acids represent only 24.57% of the extractable material, compared to 65.11% in Aou horizon and to 57.46% in underlaying horizon. Humic acids decrease toward the base of profile, with a slight trend of accumulation in Bs2 horizon. The CH/CF ratio is variable, with low values in Bs1, Bs2 and high values (7.81) in A/Bs (Es) and Bv-Bs (8.25), indicating conditions of heteropolicondensation, but only in these horizons. Humins represent another humic fraction, well represented in this profile, with high values aligned on a decreasing curve with depth. The values decrease from 7.01% in Aou to 0.61% in Bs2, in the base of the profile being deposited in a high quantity, respectively 2.97% of the soil (78.78% of total organic carbon), which escapes the phyrophosphate extraction.

Table 3. Variation with depth of organic matter and humic fraction in skeletal Prepodzol (1,520 m altitude)

Horizon (depth, cm)	pH	TOC	Humus	TEC	HA	FA	Residual C	*CFA/ CHA*
Oh 9-0	4.09	11.90	20.51	5.37 45.13	2.34 19.66 43.57	3.03 25.47 56.43	6.53 54.87	1.29
Aou 0-9	3.88	5.6	9.66	4.09 73.04	3.06 54.64 74.81	1.03 18.39 25.19	1.51 26.96	0.33
A/Bs 9-18	4.11	8.78	15.14	2.92 33.25	1.08 12.30 36.98	1.84 20.95 63.02	5.86 66.74	1.70
Bs1 18-32	4.19	7.08	12.21	2.81 39.68	0.94 13.84 33.45	1.87 25.83 66.55	4.27 60.32	1.98
Bs2 32-50	4.78	6.11	10.53	2.64 43.20	0.52 8.51 19.69	2.12 34.69 80.31	3.47 56.79	4.07

TOC – total organic carbon (% of soil mass); Humus (% of soil mass); TEC – total extractible carbon (% of soil mass / % of TOC); HA – carbon from huminic acids (% of soil mass / % of TOC / % of TEC); FA – carbon from fulvic acids (% of soil mass / % of TOC / % of TEC); residual C – non-extractible carbon and humines (% of soil mass / % of TOC)

Skeletal Prepodzol soil (Tab. 3) is located at an altitude of 1,520 metres under a small spruce forest *(Picea excelsa)* mixed with *Alnus viridis* and *Dryopteris filix-mas, Luzula luzuloides, Poa* sp. in the grassy layer; it contains, just like typical prepodzol, a large quantity of organic matter along the whole profile. The total organic carbon values, as well as humus, are disposed on a sinuous curve that reveals a slight floating in Aou horizon; thus, the values for total organic carbon drop from 11.9% in Oh to 6.11% in Bs2 at 50 cm depth. This organic accumulation throughout the profile is consistent with the unfavorable conditions for mineralised micro-organisms, respectively the altitude, litter in mix with spruce needle leaves, acid pH especially in the upper horizons. The highest degree of humification is in Aou horizon, in which the extractable material represents 73.94% of total organic carbon, a part coming from Oh horizon, where the humification is intense.

The humic acids resulting from humification processes indicate a favorable ratio of fulvic acids production (CAF/CAH = 1.29) in Oh horizon; in the next horizon the production of humic acids continues, representing 3.06% of the soil and 54.64% of C.E.T., but in this horizon the humic acids are floating; the CAF/CAH ratio is of 0.33, fulvic acids represent 18.39% of the extractable material. In the underlying horizons, fulvic acids predominate (the CAF/CAH ratio is of 1.7 and 1.98), at the base of the profile they accumulate, representing 80.31% of the extractable material. The CH/CF ratio has small values along the entire profile, except for horizon A/Bs with a value of 3.18.

Humins are well represented along the entire profile, except for Aou horizon.

Prepodzol lithic soil (Tab. 4), taken from an altitude of 1,750 m, has formed in a subalpine meadow vegetation with *Agrostis tenuis, Festuca rubra*, *Nardus stricta*, *Cynosurus cristatus,* rare *Vaccinium sp.* and *Juniperus communis*. It is the soil subtype with the most intense organic accumulation, both under the form of humic acids and of humins (Donisă, 1998). As a chemical reaction, the acidity is lower in comparison to other podzol subtypes analyzed. The total organic carbon, namely humus, is distributed on a decreasing curve with depth: total organic carbon gradually decreases from 19.69% in Aou1 to 8.94% at the base of profile – horizon Bs+C (47-70 cm); in the same way, the humus decreases from 33.94% to 15.41%. The humification degree slightly increases from 38.86 in Aou1 up to 56.93 in Bs+C.

Table 4. Variation with depth of organic matter and humic fraction in Prepodzol lithic (1750 m altitude)

Horizon (depth, cm)	**pH**	**TOC**	**Humus**	**TEC**	**HA**	**FA**	**Residual C**	**CFA/ CHA**
Aou1 0-7	4.77	19.69	33.94	7.65 38.86	4.80 24.37 62.74	2.85 14.49 37.26	12.04 61.14	0.59
Aou2 7-14	4.84	13.54	23.34	6.82 50.37	4.32 31.90 63.34	2.50 18.46 36.66	6.72 49.63	0.57
Aou/Bs 14-26	4.99	11.40	19.65	5.87 51.49	4.18 36.66 71.21	1.69 14.82 28.79	5.53 48.51	0.40
Bs 26-47	5.02	10.97	18.91	5.42 49.40	2.66 24.24 49.07	2.76 25.15 50.93	5.55 50.60	1.03
Bs+C 47-70	5.03	8.94	15.41	5.09 56.93	1.82 20.36 35.75	3.27 36.57 64.25	3.85 43.07	1.79

TOC – total organic carbon (% of soil mass); Humus (% of soil mass); TEC – total extractible carbon (% of soil mass / % of TOC); HA – carbon from huminic acids (% of soil mass / % of TOC / % of TEC); FA – carbon from fulvic acids (% of soil mass / % of TOC / % of TEC); residual C – non-extractible carbon and humines (% of soil mass / % of TOC)

The extractable material is distributed on the same decreasing trendline with depth, the values being high, ranging between 7.54% of soil in Aou1 and 5.09% at the base of the profile. A peculiarity of this soil is the formation of a large quantity of huminic acids on behalf of organic rests rich in nitrogen from the grassy vegetal cover (Lupascu, 2006). Huminic acids represent between 4.8% of soil and 1.82% at the base of the soil profile, respectively between 62.74% and 71.21% in horizons A and Aou/Bs and 49.07%-35.75% in B horizons. The CAF/CAH ratio is much subunitary in the first three horizons (0.59-0.4), unitary in Bs horizon, and of 1.79 at the base of the profile, where fulvic acids accumulate.

Humins, containing partially decomposed remains, represent about 60% of the total organic carbon in Aou1 horizon and about 50% in the rest of the profile; at the base of the profile, humins represent 43.07% of the total organic carbon.

4. **Conclusions**

By comparing the data in the profiles there can be found a differentiation in terms of organic accumulation: typical eutricambosoil has the best mineralization of organic matter, in connection with the altitude and vegetal cover; typical and skeletal prepodzol have the same high values throughout the profile, the mineralization of organic matter being slightly slowed down, while the lithic prepodzol subtype found at 1,750 m altitude in a spruce forest record the most intense organic accumulation, according to the environmental conditions (climate, vegetal cover, altitude).

Qualitatively, there are some differences in the degree of humification of organic matter, the main humic fractions repartition on horizons, the emergence of accumulation horizons of frations. Typical and lithic prepodzol have a slightly higher content of humic acids, typical eutricambosoil and skeletal prepodzol accumulate a quantity of fulvic acids 5.3 – 4 times larger than the humic acids.

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