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CHARACTERISTICS OF SOIL ORGANIC MATTER  
IN ECTOHUMUS HORIZONS OF FOREST SOILS  
IN THE STOŁOWE MOUNTAINS\*\*

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*Abstract.* This paper describes the fractional composition of humus substances and physico-chemical properties of ectohumus horizons in forest soils (Haplic Cambisols (Distric) and Albic Podzols) developed from various parent materials and in various forest sites: mountain mixed forest with beech tree, spruce forest with spruce monoculture, mountain mixed forest with beech, sycamore maple and larch and mountain mixed forest with spruce and larch. Reactions of the analyzed soils were strongly acidic. Organic C content was in the range of 21-48% and total N reached values between 0.68-1.63%. The fractional composition of humus substances was analyzed using the Tiurin method. Fraction Ia (extracted with  $0.05 \text{ mol dm}^{-1} \text{ H}_2\text{SO}_4$ ) constituted a rather insignificant part (1.03-3.63% of  $C_{\text{org}}$ ) of humus compounds. Humus was dominated by fraction I (extracted with  $0.1 \text{ mol} \cdot \text{dm}^{-1} \text{ NaOH}$ ) (27.4 - 42.5% of  $C_{\text{org}}$ ). The ratio of  $C_{\text{HA}}:C_{\text{FA}}$  was within the range of 0.75-1.35 and increased in deeper organic subhorizons. Non-extracted C was within the range of 55.7-69.7% of  $C_{\text{org}}$ . In all the ectohumus samples investigated, the highest humification degree was found in the deepest organic subhorizon.

The amount and quality of organic matter and the directions of its transformation play an important role in the functioning of forest ecosystems [5, 6]. Plant remains that are present in forest soil horizons are a store of nutrients, determine their availability and determine ecosystem stability [3, 4]. The basic source of organic matter in forests is the overground fall of plants, trees and bushes, and ground cover, and also the withering of the underground parts of plants. Plant fall is

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an important element since a considerable amount of nutrients returns to the soils with the fall [18, 20]. Quantitative analysis of fractional composition of humus substances in forest soils of mountain areas has been presented in the works of Kowaliński *et al.* [15], Niemyska-Łukaszuk [19], Licznar and Mastalska-Cetera [16], Drozd *et al.* [2-4], Licznar *et al.* [17], and Jamroz [10,11]. In soils of the Stołowe Mountains, quantitative and qualitative studies concerning humus substances have so far not been conducted on a wider scale.

The aim of this paper is an attempt to determine the influence of tree stand species on the physico-chemical properties and fractional composition of humus substances of the ectohumus of selected types of mountain soils present in the area of the Stołowe Mountains National Park. Also, the properties of ectohumus under various geological conditions have been taken into consideration in the study.

#### MATERIAL AND METHODS

The study included the following subhorizons of ectohumus: O<sub>l</sub> – raw, O<sub>f</sub> – fermentation, O<sub>fh</sub> – detritus and O<sub>h</sub> – epihumic of 2 profiles of podzols formed from Cretaceous sandstones (profile 1 and profile 2) and 2 profiles of acid brown soils formed from Permian sandstones (profile 3 and profile 4). The analyzed soils were accepted as Albic Podzols (profile 1 and profile 2) and Haplic Cambisols (Distric) (profile 3 and profile 4) following the WRB classification [22].

Profile 1. Mountain mixed forest with beech tree stand and ectohumus of moder type.

Profile 2. Spruce forest with spruce monoculture and ectohumus of mor type.

Profile 3. Mountain mixed forest with beech, sycamore maple and larch and ectohumus of mull-moder type.

Profile 4. Mountain mixed forest with spruce and larch tree stand, and ectohumus of moder-mor type.

Genetic soil horizons were separated according to Annex 1 of the Systematics of Polish Soils [21], where the following indices were determined: organic C<sub>org</sub> using the Tiurin oxidometric method, pH using the potentiometry method in 1 mol KCl dm<sup>-3</sup> and in distilled water, the content of total N using the Kjeldahl method on a Buchi analyzer, total content of Ca<sup>+2</sup> and Mg<sup>+2</sup> dissolved in 70% HClO<sub>4</sub> and analyzed using the AAS method, fractional composition of humus substances using a modified Tiurin method [7] separating the following groups of humus substances:

- fraction Ia (fulvic) - substances passing to solution while treating the soil with 0.05 mol H<sub>2</sub>SO<sub>4</sub> dm<sup>-3</sup>;
- fraction I - humic substances separated by multiple soil treatment with 0.1 mol NaOH dm<sup>-3</sup> and humic acids (C<sub>HA</sub>) and fulvic acids (C<sub>FA</sub>) were isolated.

Non-extracted C – including so-called post-extraction residue including non-humificated organic residues. This fraction was calculated from the difference: Non-extracted C = organic C - ( $C_{\text{fraction Ia}} + C_{\text{fraction I}}$ ).

Absorbance with wavelengths of 464 and 665 nm was determined for humic acid extracts, and also the absorbance coefficients  $A_{4/6}$  were calculated.

## RESULTS AND DISCUSSION

The analyzed subhorizons of ectohumus, i.e. Ol, Of, Ofh and Oh, of profiles under beech tree, spruce monoculture or mixed forest differed both morphologically and as regards the analyzed physico-chemical parameters. The thickness of ectohumus was noticeably higher at sites where coniferous (spruce or spruce-larch) fall predominated, irrespective of soil type and bed-rock character. The reaction in all the profiles analyzed, according to forest soils classification [12], was determined as highly acidic and demonstrated lower pH values under spruce (profile 2) and spruce-larch tree stands (profile 4) (Table 1). Differences were also observed in terms of organic C content. Higher  $C_{\text{org}}$  contents were noted under spruce and spruce-larch tree stands where, due to the chemical composition of conifer needles rich in lignins, the ectohumus formed was less susceptible to

TABLE 1. PHYSICO-CHEMICAL AND CHEMICAL PROPERTIES OF SOILS

Profile No.	Soil horizon	Depth (cm)	pH		TOC (g kg <sup>-1</sup> )	N <sub>tot</sub>	C/N	Ca <sup>+2</sup> (mg kg <sup>-1</sup> )	Mg <sup>+2</sup> (mg kg <sup>-1</sup> )
			H <sub>2</sub> O	1MKC1					
Mountain mixed forest (beech tree) / Albic Podzols									
1	Ol	6-4	4.7	3.9	357	12.6	28	5 075	665
	Of	4-1	4.1	3.2	424	15.8	27	3 360	595
	Oh	1-0	3.8	2.8	281	11.6	24	1 950	1 045
Spruce forest (spruce monoculture) / Albic Podzols									
2	Ol	10-8	4.2	3.5	480	14.3	34	4 500	447
	Of	8-3	3.6	2.8	468	16.3	29	3 060	640
	Oh	3-0	3.6	2.3	231	8.3	28	1 160	805
Mountain mixed forest (beech, sycamore mapie, larch) / Haplic Cambisols (Distric)									
3	Ol	4-3	5.0	4.4	463	15.2	30	9 570	1 220
	Ofh	3-0	4.8	3.9	396	15.1	26	8 530	1 360
Mountain mixed forest (beech, larch) / Haplic Cambisols (Distric)									
4	Ol	10-9	4.3	3.7	472	13.6	35	7 020	1 050
	Of	9-7	3.8	3.0	456	14.9	31	6 440	1 210
	Oh	7-0	3.6	2.7	210	6.82	31	1 400	1 830

mineralization processes and was characterized by a wider C/N ratio when compared to ectohumus with a predominant deciduous fall. Lower content of organic C, and also a narrower C/N ratio in profiles under beech (profile 1) and beech-sycamore maple-larch tree stands (profile 3) are the result of an intense period of the mineralization process of plant fall that was more susceptible to decomposition. Maciaszek *et al.* [18] and Gonet *et al.* [9] noted that ectohumus, where predominant plant residues are spruce and pine needles, are usually characterized by base reaction, a high content of organic C, a low content of organic N and a wide C/N range reaching even values of 50 or more, especially in the Ol or Ofh subhorizons. This leads to a distinct increase in the abundance of organic matter at sites with a predominant coniferous tree stand, a fact which was also observed in the present study. The differences in pH values, amount of organic C and C/N ratio values observed both in ectohumus of podzols and acid brown soils confirm the thesis that physico-chemical features of ectohumus are substantially influenced by plant fall character, which may in particular be observed in profiles 1 and 2. Less clear differences in the content of organic C in profiles 3 and 4 are probably the effect of the addition of larch needles to beech and sycamore maple fall.

The analysis of the total content of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  cations in subhorizons of soil ectohumus demonstrated a clear tendency towards a decrease in the amount of  $\text{Ca}^{+2}$  cations and an increase in the amount of  $\text{Mg}^{+2}$  cations in deeper layers (Table 1). In the case of calcium this is the result of its intense elution from subhorizons of soil ectohumus irrespective of plant fall, soil type and bed-rock character. The most abundant  $\text{Ca}^{+2}$  was ectohumus formed on acid brown soils. The rate of calcium elution was connected to ectohumus thickness. The lowest amounts of  $\text{Ca}^{+2}$  cations were accumulated in subhorizons Oh of ectohumus characterized by high thickness, and under a coniferous tree stand. The total content of  $\text{Mg}^{+2}$ , similar to the content of  $\text{Ca}^{+2}$ , was considerably higher in the ectohumus of acid brown soils when compared to podzols. Accumulation of  $\text{Mg}^{+2}$  cations was observed in the deepest subhorizons of ectohumus in all the analyzed sites, while the lowest amounts of  $\text{Mg}^{+2}$  were accumulated in ectohumus under spruce monoculture on podzol.

The differences in the amount of organic carbon, pH values and C/N ratios between the analyzed ectohumus samples influenced the differentiation in the contribution of particular fractions of humus compounds in the organic carbon pool. Quantitative changes of the analyzed fractions of humus compounds were seen very clearly between the analyzed subhorizons. The analysis of fractional composition demonstrated a low contribution of low-molecular, highly mobile organic compounds (fraction Ia) (Table 2). The highest content of this fraction was noted in raw subhorizons Ol with predominant residues of spruce and larch needles both in podzols and acid brown soils. The distinct decrease in the contribution of fraction Ia in fermentation subhorizons Of and their re-increase in epihumus subhorizons Oh confirms the mobility of those kinds of organic compounds. An increase in

TABLE 2. FRACTIONAL COMPOSITION OF HUMUS IN % OF ORGANIC C (TOC)

Profile No.	Soil horizon	TOC (g kg <sup>-1</sup> )	Fraction Ia	Fraction I			CHA: CFA	C-non extracted	IH*	A 4/6
				C-extracted	CHA	CFA				
				(% )						
Mountain mixed forest (beech tree) / Albic Podz										
1	Ol	357	2.84	27.46	11.58	15.87	0.73	69.70	30.30	7.50
	Of	424	1.70	35.32	16.07	19.24	0.84	62.99	37.01	7.03
	Oh	281	1.81	42.48	23.93	18.55	1.29	55.71	44.29	6.41
Spruce forest (spruce monoculture) / Albic Podzols										
2	Ol	480	3.38	29.31	13.03	16.28	0.80	67.30	32.70	8.19
	Of	468	1.40	37.71	18.92	18.78	1.01	60.89	39.11	7.11
	Oh	231	1.50	39.28	20.71	18.57	1.12	59.22	40.78	6.78
Mountain mixed forest (beech, sycamore maple, larch) / Haplic Cambisols (Distric)										
3	Ol	463	2.59	29.07	12.34	16.73	0.74	68.35	31.65	7.62
	Ofh	396	2.16	36.23	15.82	20.40	0.78	61.61	38.39	6.37
Mountain mixed forest (beech, larch) / Haplic Cambisols (Distric)										
4	Ol	472	3.63	29.46	12.62	16.83	0.75	66.92	33.08	8.04
	Of	456	1.03	36.01	17.99	18.02	1.00	62.96	37.04	6.65
	Oh	210	1.65	42.48	24.40	18.08	1.35	55.86	44.14	6.28

IH\* – humification index (100%-C non extracted).

fraction Ia contribution was also observed in spruce woods of the Karkonosze [3, 15], in moder beddings of brown soils in the area of the Jaworowy Wood [10] and in mor beddings of podzols in the area of the Śnieżnik Mountains [11].

The dominant group in the fractional composition of humus compounds was represented by fraction I. The contribution of fraction I, in all analyzed profiles, increased from subhorizon Ol towards Oh, according to the humification index (HI). An increase in the contribution of fraction I, C<sub>HA</sub> fraction and also the value of the C<sub>HA</sub>:C<sub>FA</sub> ratio in subhorizons pF, Ofh and Oh, irrespective of the character of plant residues, was also emphasized in the study by Dziadowiec [6]. The lowest values of the C<sub>HA</sub>:C<sub>FA</sub> ratio in subhorizons Ol are connected first of all to an inflow of fresh organic matter to the soil, which leads to formation of a considerable amount of organic connections of a simple molecular structure [1, 2]. The lowest humification degree in raw horizons Ol was confirmed by the highest contribution of non-extracted carbon fraction including above all non-humified plant residues. The observed decrease in non-extracted carbon fraction content in deeper

ectohumus horizons has already been noted by Kowaliński *et al.* [15], Niemyska-Lukaszuk [19], Drozd *et al.* [4], Gonet *et al.* [9] and Jamroz [10, 11]. The relatively higher value of the humification index HI in ectohumus under spruce and spruce-larch tree stands, especially in horizons O1, was mainly connected to the higher amount of organic C, and also to the higher contribution of low-molecular organic compounds (fraction Ia). Similar to the cases of both fraction I and C<sub>HA</sub> of that fraction, a distinct differentiation in non-extracted carbon fraction content between ectohumus of podzols and acid brown soils could not be demonstrated.

One of the basic physico-chemical properties determining the internal structure of humic acids is optical density. As was demonstrated by Kononowa [14], optical density of humus substances depends on the ratio of carbon content in the aromatic nucleus to carbon in lateral radicals. The author revealed that 'younger', as regards their chemistry, humic acids are characterized by lower optical density when compared to 'mature' acids. This results from a high condensation of the aromatic nucleus in 'mature' humic acids, and the predominance of lateral chains in 'younger' acids. Changes in the optical density of sodium humates solutions from subhorizons O1, Of and Oh were expressed by absorbance values with wavelengths of 465 nm and 665 nm, and the absorbance ratio  $A_{465}:A_{665}$  ( $A_{4/6}$ ), (Table 2). It is accepted that the  $A_{465}$  value determines the absorbance of the substances in an initial humification stage, and  $A_{664}$  of the substances of a high humification degree [8, 13]. Lower values of the ratio of absorbance  $A_{4/6}$  in subhorizons Of, Ofh and Oh, when compared to O1, confirm an increase in the degree of humification of horizons lying deeper in all the sites analyzed. The calculated values of the ratio of absorbance  $A_{4/6}$  indicate, moreover, that ectohumus of soils on the beech site (profile 1) and on the beech-sycamore maple-larch site (profile 3) is characterized by the presence of humic acids of higher molecular weight and a higher degree of condensation of aromatic structure when compared to humus of soils in the spruce (profile 2) and the spruce and larch sites (profile 4).

## CONCLUSIONS

1. Differentiated forest habitats with beech tree, spruce tree or mixed forest with various kinds of formed forest humus with clearly marked raw O1, fermentation Of, detritus Ofh and epihumic Oh are observed in the area of the Stołowe Mountains.

2. The analyzed ectohumus subhorizons under coniferous, deciduous or mixed tree stands differed in terms of their physico-chemical parameters. Higher values of organic C content and a wider C/N ratio show a slower mineralisation process and a higher accumulation of organic matter on spruce and spruce-larch sites when compared to beech and beech-sycamore maple-larch sites.

3. Quantitative analysis of fractional composition did not demonstrate any distinct differentiation between humus compounds of Ol, Of, Ofh and Oh subhorizons in the analyzed ectohumus. Only negligible higher amounts of released low-molecular organic connections (fraction Ia) were noted in raw subhorizons Ol with predominant residues of spruce and spruce and larch needles both on podzols and acid brown soils.

4. The higher value of the humification index HI in ectohumus under spruce and spruce-larch tree stands, especially in Ol horizons, was first of all connected to a higher content of organic C, and also to the higher contribution of low-molecular organic compounds.

5. Clear differentiation in the fraction of humus compounds was noted within the particular soil profiles. An increase in  $C_{HA}:C_{FA}$  ratio, decreases in non-extracted carbon fraction contributions, and a lower value for the absorbance ratio  $A_{4/6}$  in subhorizons Ofh and Oh prove the higher intensity of the humification process in those horizons when compared to subhorizons Ol.

6. The humus formed under deciduous and mixed tree stands is characterized by the presence of humic acids of higher molecular weight and a higher degree of aromatic structure condensation when compared to humus of soils under coniferous tree stands, which is reflected by lower values for the absorbance ratio  $A_{4/6}$ .

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#### CHARAKTERYSTYKA SUBSTANCJI ORGANICZNEJ POZIOMÓW EKTOHUMUSOWYCH GLEB LEŚNYCH GÓR STOŁOWYCH

Badania obejmowały analizę ilościową substancji humusowych na tle właściwości fizykochemicznych próchnic nadkładowych gleb leśnych (Haplic Cambisols (Distric) and Albic Podzols) występujących na terenie Parku Narodowego Gór Stołowych. Materiał do badań pobrany został z obszarów zróżnicowanych pod względem składu gatunkowego drzewostanów: bór mieszany górski, bór świerkowy, las mieszany górski. W zabranym materiale glebowym oznaczono: pH w 1 mol KCl dm<sup>-3</sup>, zawartość C<sub>org</sub>, zawartość Nog, całkowitą zawartość Ca<sup>+2</sup> and Mg<sup>+2</sup> oraz skład frakcyjny związków próchnicznych metodą Tiurina. Odczyn analizowanych gleb był silnie kwaśny. Zawartość C<sub>org</sub> kształtowała się w zakresie od 21 do 48 %, a zawartość Nog w zakresie 0,68 – 1,63 %. W składzie związków próchnicznych niewielki udział stanowiła frakcja Ia (1.03 - 3.63 % C<sub>org</sub>). Wśród związków próchnicznych dominującą grupą była frakcja I, której udział mieścił się w zakresie 27,4 – 42,5% C<sub>org</sub>. Wartość stosunku C<sub>kh</sub>:C<sub>kf</sub> kształtowała się w zakresie 0,73 – 1,35 i wzrastał w głębiej zalegających podpoziomach ektopróchnicy. Udział węgla poekstrakcyjnej pozostałości mieścił się w zakresie 55,7 – 69,7% C<sub>org</sub>. We wszystkich badanych ektopróchnicach najwyższy stopień humifikacji występował w najgłębszych jej podpoziomach.