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Peat humic acid properties and factors influencing their variability in a temperate bog ecosystem

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Abstract. Studies of the properties of soil organic matter are essential for understanding the humification reactions and soil diagenesis processes. The aim of this study is to analyse properties of peat and peat humic acids as well as factors influencing their variability. Humic acids isolated from an ombrotrophic bog peat profile were used as study objects. Relations among peat age, decomposition and humification degree, botanical composition, and properties of peat humic acids (elemental, functional composition, spectral characteristics) were studied. The variability of peat properties was found to be less significant than the differences in the properties of peat-forming living matter, which indicates the dominant impact of humification processes on the properties of peat. Correspondingly, the composition of peat humic acids was insignificantly affected by the differences in the composition of the precursor living organic material.

Key words: peat, humic acids, structure of humic acids, humification.

INTRODUCTION

In the carbon biogeochemical cycle the transformation of living organic matter into the refractory part of organic matter (humic substances such as humic acids, fulvic acids, and humin) or humification is of key importance. Humification can be defined as the transformation of numerous groups of substances (proteins, carbohydrates, lipids, etc.) and individual molecules present in living organic matter into groups of substances with similar properties (humic substances) (Francioso et al., 2003). Humification plays an important role in the diagenesis of fossil carbon deposits (Houghton, 2003). Humification is a sum of very complex processes, including degradation and synthetic reactions, and is affected by the high variability of environmental conditions under which living organic matter decays, slow pace of humification reactions, as well as by the large number and structural differences of the organic molecules composing living organic matter. It can be supposed that humification conditions have an impact on the structure and properties of the refractory intermediate transformation products of living organic matter – humic substances. From this perspective, it is important to study humification processes in a relatively homogeneous and stable environment, for example in bogs, to reduce the impact of natural environmental variability.

Peat is a light brown to black organic material, which is formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees (Cocozza et al., 2003). The interest in peat properties is growing, as peat is a substance that supports and influences bog and wetland ecosystems, while peat profiles can serve as 'archives' indicating conditions in past environments (Yeloff & Mauquoy, 2006; Zaccone et al., 2007a). Significant amounts of organic carbon are stored in the form of peat. Therefore, peat reserves play a major role in the carbon biogeochemical cycling, which is of key importance in the context of the ongoing process of climate change (Falkowski et al., 2003; Borgmark, 2005a). Industrial and agricultural uses of peat are growing, and significant amounts of peat are mined industrially (Ghaly et al., 1999; Brown et al., 2000). Considering this, there is an increasing interest in studies of properties and diagenesis of peat.

Humification in peat has been taking place in very different conditions both geographically (from tropical regions to the Arctic environment) and temporally (peat development can last for many thousands of years). During peat formation even at one particular site, significant changes could have happened in vegetation, temperature, amount of precipitation and, correspondingly, in the bog hydrological conditions and land use in the basin of the wetland (Caseldine et al., 2000; Chapman et al., 2001; Zaccone et al., 2007b). As a result, not only changes in the properties of peat humic substances should be understood, but also the molecular descriptors of organic matter diagenesis should be identified. Notwithstanding the importance of this subject, the relations between the properties of peat (especially in full peat profiles) and those of peat humic substances have been studied comparatively little (Anderson & Hepburn, 1986; Zaccone et al., 2007b, 2008).

The aim of this study is to analyse the relations among the properties of peat, peat humic acid (HA), and peat humification degree.

MATERIALS AND METHODS

Site location

In-depth study of peat composition, humification degree, and peat HA properties was carried out in an ombrotrophic Eipurs Bog, which is located in the central part of Latvia (lat 57°14′53.4″N, long 24°37′00.3″). Full peat profiles were obtained and cut into 5 cm layers for the analysis of peat properties and isolation of HAs. The analysis of botanical composition was performed microscopically, using a Carl-Zeiss binocular microscope, thereby determining the decomposition degree (Lishtvan & Korol, 1975).

Isolation of peat humic acids

Procedures recommended by the International Humic Substances Society (IHSS) (Tan, 2005) were used to extract and purify HAs.

Analysis of peat and humic acid properties

The ^{14}C dating was done in the Institute of Geology at Tallinn University of Technology (Estonia). Carbon, hydrogen, nitrogen, and sulphur concentrations in the peat and humic acid samples (elemental analysis of C, H, N, S) were determined by the combustion-gas chromatography technique, using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). Ash content was measured after heating 50 mg of each peat sample at 750 °C for 8 h.

Atomic ratios were calculated from elemental analysis using the following equations:

$$\mathrm{O/C} = \frac{(M_{\mathrm{C}} \cdot \mathrm{O\%})}{(M_{\mathrm{O}} \cdot \mathrm{C\%})}, \tag{1}$$

$$\mathrm{H/C} = \frac{(M_{\mathrm{C}} \cdot \mathrm{H\%})}{(M_{\mathrm{H}} \cdot \mathrm{C\%})}, \tag{2}$$

where M_{X} is the element's molecular mass, and $\mathrm{X\%}$ is the percentage of the element in the sample.

The UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co) spectrophotometer in a 1 cm quartz cuvette. The ratio E_4/E_6 (Chen et al., 1977), i.e. the ratio of absorbance at 465 and 665 nm, was determined for 10 mg of humic acid solutions in 10 mL of 0.05 M NaOH.

Humification degree

To determine the humification degree (according to Blackford & Chambers (1993) modified by Borgmark (2005b)) 1.00 g of peat sample was treated for 1.5 h with 25 mL of 8% NaOH in a 25 mL plastic tube in a bath of boiling water (95 °C) and, afterwards, filtered. Then 12.5 mL of the filtrate was diluted to 100 mL, and absorption was measured at 540 nm. The humification degree of peat was expressed as absorption at 540 nm.

Carboxylic groups and total acidity

An automatic titrator TitroLine easy (Schott-Geräte GmbH) was used for measuring carboxylic and phenolic acidity of each HA. The known Ca-acetate method (Tan, 2005), based on the formation of acetic acid, was used for determining the total number of carboxylic groups. HAs (20 mg) were weighed into a 100 mL Erlenmeyer flask, and 10 mL of 0.2 N calcium acetate solution was added under N_2. The samples were potentiometrically titrated to pH 9.0 with 0.1 N NaOH. To estimate the total acidity, 20 mg of HA was dispersed in 10 mL of 0.1 M $Ba(OH)_2$

solution, which was then shaken overnight under N_2 atmosphere, filtered, and washed with water. The filtrate, together with the washing solution, was potentiometrically titrated with 0.1 M HCl down to pH 8.4 under N_2 flow.

Hydrophobicity

Hydrophobicity of humic substances was characterized by their distribution between water and polyethylene (PEG) phases (PEG 20000, Fluka) as distribution coefficient K_{PEGW} (analogous to the octanol/water distribution coefficient K_{ow}) (Zavarzina et al., 2002). The 10% PEG-10% $(NH_4)SO_4$–HA–H_20 systems were prepared by mixing 2 mL of 30% PEG solution with 2 mL of ammonium sulphate solution and 2 mL of HA (2 mg mL^{-1} in 0.05 M NaOH). The mixtures were shaken for 10 min. After complete phase separation, 1 mL was taken from each phase and diluted by 10 times in 0.05 M $NaHCO_3$. Then the absorbances at 465 nm were measured on a DR/2000 spectrophotometer (Hach Co). The distribution coefficients were calculated as follows: K_{PEGW} = absorbance at 465 nm of the top (PEG-rich) phase/ absorbance at 465 nm of the bottom phase.

Fluorescence spectra

Fluorescence spectra were recorded using a Perkin Elmer LS 55 fluorescence spectrometer on aqueous solutions of each sample at a concentration of 25 mg L^{-1}, adjusted to pH 7 with 0.5 M HCl. Emission spectra were recorded at a fixed excitation wavelength of 350 nm (scan speed 500 nm min^{-1}, with slit 10.0 nm over the wavelength range of 380 to 650 nm). The ratio of fluorescence intensity at 460 nm to the intensity at 510 nm (I_{460}/I_{510}) was used as the humification indicator previously suggested by Milori et al. (2002).

^{13}C nuclear magnetic resonance spectra

Solid-state ^{13}C-NMR spectroscopy was carried out using the technique of cross-polarization with magic angle spinning (CP/MAS). The spectra were recorded on a Bruker Avance Wide bore 600 MHz Solid state NMR spectrometer equipped with a 4 mm MAS double resonance probe. A 2 ms contact time and 2 s repetition time were used. The sample MAS was 10 kHz, and chemical shifts were referenced to Adamantane (left peak) at 38.48 ppm.

Data treatment

Statistical analyses were performed using SPSS 16 Software. The obtained data correspondence to the normal distribution was checked with the Kolmogorov–Smirnov tests. In further analysis non-parametric methods were used. Relationships among different characteristics were assessed by Spearman’s rank correlation coefficients. In all cases the significance level was $p = 0.05$.

RESULTS AND DISCUSSION

Peat composition and its changes

The humification process of peat and the development of peat HAs were studied in the peat profile from a heterogeneous ombrotrophic bog (Eipurs) in Latvia. The results of the palaeobotanical investigations (botanical composition, pollen analysis) indicate the development character and peat properties of the bog. Eipurs Bog has formed due to the paludification of the sandy ground as a result of rising groundwater level and wet conditions during the small depression after the Ice Age. The lowest part of Eipurs Bog is formed of fen wood–grass peat, *Hypnum* peat, and sedge–*Hypnum* peat (Fig. 1). These layers are covered with transition-

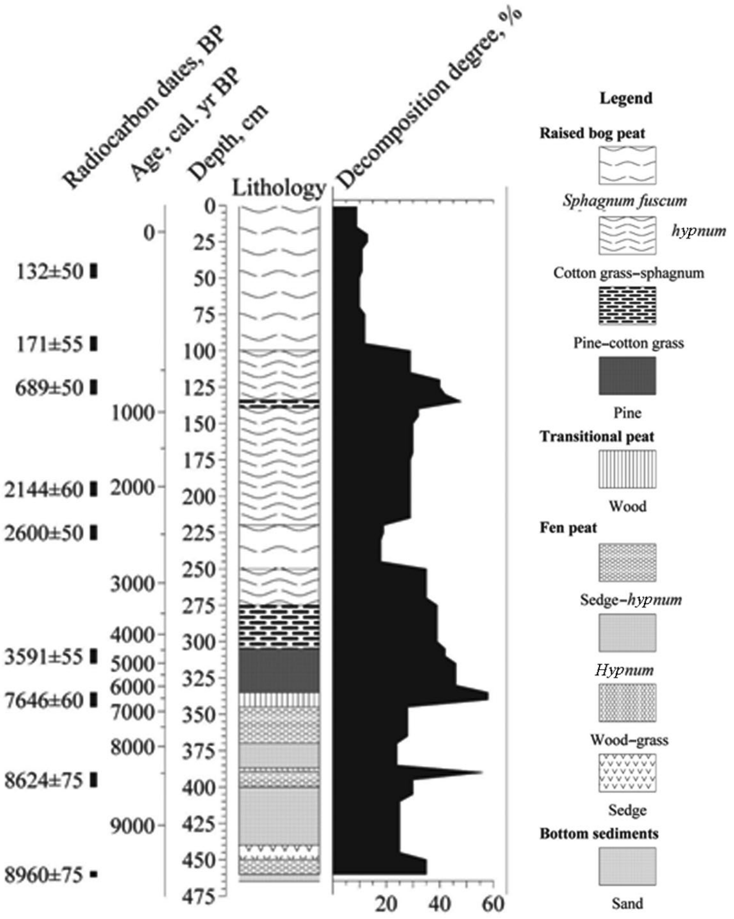

Fig. 1. Peat stratigraphy in Eipurs Bog.

type wood peat. The upper part is represented by a 3.45 m thick layer of raised bog peat of different type and decomposition degrees. For example, well-decomposed (40–48%) pine–cotton grass peat occurs at a depth of 2.75–3.00 m (Fig. 1).

Basic peat properties were analysed using the peat elemental (C, H, N, O, S) composition. The elemental composition of the studied peat cores is summarized in Fig. 2. The ash content of the peat in the bog ranges between 0.30±0.05% and 6.10±0.05% with an average content of 1.8±0.05%. The C concentrations range from 40% to 55%, H concentration is 5.4–6.7%, of N 0.5–1.5%, S 0.2–1.7%, and O 38–49%. The elemental composition of peat in Eipurs Bog is comparatively variable and reflects changes in the peat decomposition degree and peat types. The concentration of C in peat increases, starting from the depth of 1 m, reaches 53% at the level of 2.8 m, and then decreases again. The concentrations of H demonstrate a significantly higher variability. Variations in the N concentrations (elevated in the upper and lower horizons of the bog, and also demonstrating higher values concurrently with the changes in the peat composition and formation conditions) could be associated with changes in the peat botanical composition and decomposition degree. The concentrations of S are significantly lower than elsewhere in the comparatively stable peat column just in a few upper centimetres of the peat.

The elemental ratios are much more informative than the elemental composition of peat. The N/C ratio can be considered as a good indicator of the humification process mainly due to specific microbial activity in the anaerobic, acidic environ-

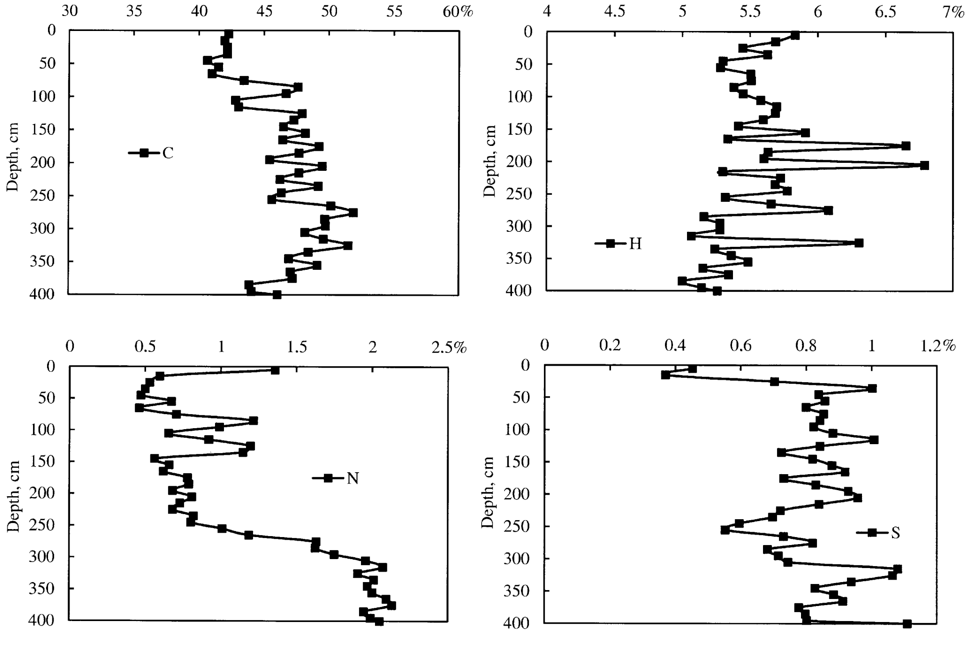

Fig. 2. Elemental composition of peat in Eipurs Bog.

ment and the enrichment of the peat mass with nitrogen-containing compounds of bacterial origin (Borgmark, 2005b). This ratio can be efficiently used as a measure of peat degradation. The decreasing N/C ratios indicate increasing peat decomposition (due to microbial decay) and vice versa. The H/C ratio is an indicator of molecular complexity (also of aromaticity), and it ranges from 1.2 to 1.6 (Anderson & Hepburn, 1986). It is relatively constant with depth, but decreases below 50 cm. The O/C ratio is considered as an indicator of carbohydrate and carboxylic group contents and can be directly related to aromatization of the peat-forming organic matter (Anderson & Hepburn, 1986). The O/C ratio decreases with depth; however, the values of this indicator are high in the layers with higher decomposition degrees.

In Eipurs Bog the H/C and O/C values are rather fluctuating (Fig. 3) around the average values common for peat and do not reflect a high variability of peat decomposition and high diversity of precursor living biota. The N/C ratio is high in the upper layer (possibly due to the presence of proteinaceous materials of living organic matter) and in general it increases with the depth of the peat core. Significant fluctuations follow with increasing depth (starting from 250 cm). After that, the values of the N/C ratio increase again for more decomposed peat layers. Our findings demonstrate that the atomic ratio is only of a limited value for the study of the humification process due to the significant impact of the original plant composition and peat formation conditions.

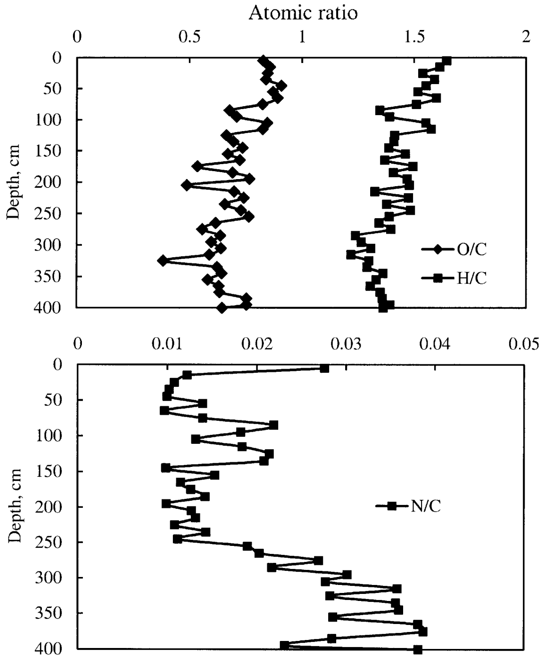

Fig. 3. Elemental ratio of the peat from Eipurs Bog.

Peat humification character

Studying the transformation (humification) of living organic material is of utmost importance for a better understanding of the carbon biogeochemical cycling. From this perspective, there is a need for studies of peat diagenesis within profiles and identification of correlations among peat properties (age, decomposition degree, and botanical, elemental, and functional composition), peat humification and the properties of HAs isolated from peat. Such studies can help describe the process of humification at a molecular level, supporting thus the development of new knowledge of chemical and biochemical processes behind humification. Therefore, an ombrotrophic bog with a highly differing peat column stratigraphy (see Fig. 1), botanical composition of the bog profile, and the decomposition degree was chosen for this study. Thus, the selected study object is suitable for both analysing the relations among peat formation conditions and peat properties and identifying the humification indicators that best describe the transformation process of living organic material.

Absorption at 540 nm (D_{540}) in the visible spectra of peat alkaline extracts can be used as a simple indicator of the humification process, an approach suggested and recently improved by Borgmark (2005a). As seen in Fig. 4, this humification index demonstrates the expected differences when used for describing Eipurs Bog, and the changes can be associated with both the peat decomposition degree and the differences in peat composition.

Further studies into the dependence of parameters describing peat humification (age and depth of the studied peat layer, decomposition, HA/FA, D_{540}, E_4/E_6, and I_{460}/I_{510}) and peat composition (O/C, H/C, N/C) (Fig. 5, Table 1) were carried out in order to provide reliable quantitative information about the diagenesis of peat. The found correlations allow identifying the parameters most suitable for characterizing the transformation of living organic matter into peat organic matter.

As seen in Fig. 5, the parameter describing peat composition (atomic ratio H/C) is well correlated with the peat decomposition degree, thus indicating molecular mechanisms behind peat humification: dehydrogenation (hydrogen

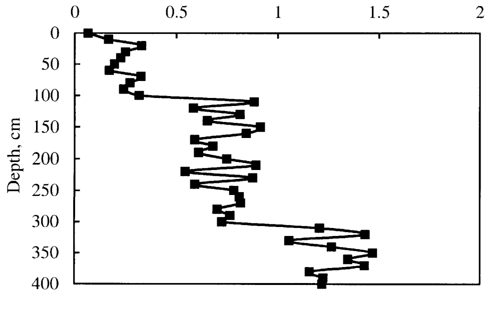

Fig. 4. Changes in the humification index (absorption of peat extract at 540 nm) versus depth in peat from Eipurs Bog.

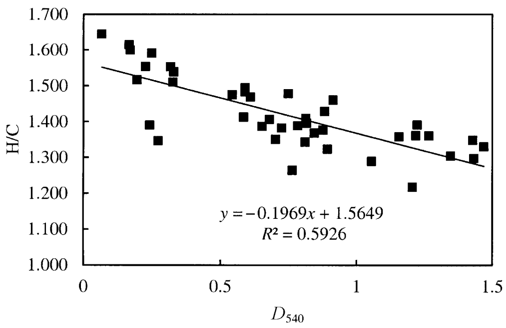

Fig. 5. Correlation between peat atomic ratio H/C and humification indicator D_{540}.

Table 1. Correlations among indicators describing the decomposition of the precursor living materials (age and depth of the studied peat layer, decomposition, HA/FA, D_{540}, E_4/E_6, and I_{460}/I_{510}) and peat composition parameters (O/C, H/C, N/C) in Eipurs Bog. Boldface type indicates significant correlation

	O/C	H/C	N/C	Age, ^{14}C years	E_4/E_6	I_{460}/I_{510}	HA/FA	D_{540}
Decomposition, %	**0.585**	**0.616**	**0.626**	**0.575**	0.055	0.330	0.437	**0.860**
Depth, cm	**0.517**	**0.588**	**0.624**	**0.858**	0.175	0.393	0.201	**0.794**
O/C		**0.667**	0.487	0.292	0.051	**0.568**	0.474	**0.543**
H/C			**0.582**	0.476	0.008	**0.555**	**0.543**	**0.592**
N/C				**0.636**	0.242	0.387	**0.578**	**0.667**
Age, ^{14}C years					0.313	0.250	0.323	**0.741**
E_4/E_6						0.239	0.260	**0.664**
I_{460}/I_{510}							**0.843**	**0.857**
HA/FA								**0.776**

Significance level $p = 0.05$.

removal from organic molecules) during the humification process. The humification index describing the basic changes in the properties of peat is well correlated with the elemental ratios in the peat cores, thereby reflecting changes in peat organic materials during the humification of living organic matter. Other indicators of peat organic matter that describe well the peat transformation process include HA/FA, D_{540}, and E_4/E_6, whereas I_{460}/I_{510} describes humic matter properties rather than those of peat (Table 1).

The UV–Vis absorption ratios were measured to provide information about the humification of peat samples. The ratio E_4/E_6 is often used to describe the extent of the condensation of aromatic C-containing structures: low ratios reflect high degrees of aromatics condensation, while high ratios mean the presence of large quantities of aliphatic structures and low amounts of condensed aromatics (Chin et al., 1997). This ratio is also inversely related to the degree of aromaticity, particle size, molecular weight, and acidity (Uyguner et al, 2004). In the present study, the variability of the E_4/E_6 ratios in the peat profile was generally low (Table 1).

Elemental composition and functional characteristics of peat humic acids

Studying the elemental composition of peat HAs extracted from a peat column can give information about ongoing humification reactions during peat development. Humification has recently been mostly studied to analyse the composting and soil formation processes. However, the humification process in peat is significantly different from that in composts and soils, where the decomposition of organic matter is quite rapid in early humification stages. In contrast to that, in waterlogged environments, under the impact of anaerobic and acidic conditions, the humification process in the saturated peat layers is much retarded. Therefore, it is possible to follow the humification process in peat for very long periods (thousands of years).

In the studied Eipurs Bog significant variations were observed in the elemental composition of HAs within peat profiles. Depending on the bog stratigraphy and the intervals of changes of peat properties, the elemental compositions of the studied peat HAs (Fig. 6) were highly variable: C made up 42.74–59.49%, H 3.98–5.41%, N 1.80–2.79%, S 0.23–1.71%, and ash 0.34–1.46%. The O content

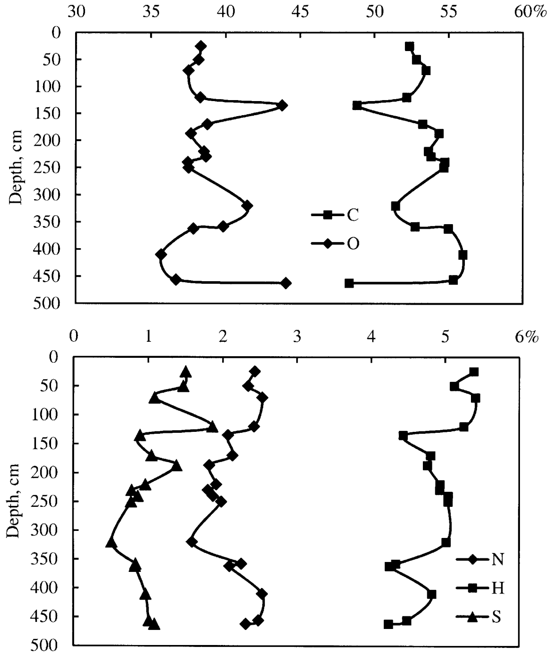

Fig. 6. Elemental composition of peat humic acids from Eipurs Bog.

was determined by mass balance; it was within the range of 32.52–48.78%. In general, the concentrations of N decreased with depth, whereas the C and H concentrations accordingly increased; the concentration of S was very variable throughout the profile. The concentrations of elements in HAs from peat in Latvia are of similar magnitude as those for peat HAs from other regions of the world (Anderson & Hepburn, 1986; Qiamg et al., 1993; Yamaguchi et al., 1998; Garnier-Sillam et al., 1999; Zaccone et al., 2007b).

Variations in the main atomic ratios (H/C, N/C, and O/C) within the peat HA profiles are described in Fig. 7. The O/C versus N/C atomic ratios indicate that the decarboxylation processes were in line with the reduction of the N concentration relative to the C content in HAs.

Changes in the H/C ratio in HAs prove the importance of peat accumulation rate. The bottom to middle bog layers show an increasing H/C ratio. In the upper peat layers HAs have a relatively stable H/C ratio with comparatively high amounts of both carbon and hydrogen and a decreasing oxygen percentage. The H/C ratios in HAs from Eipurs Bog in fen peat were the lowest at a depth of 3.5–4.62 m. Lower C and H percentages and H/C ratio and a higher O/C ratio are common for peat that is fully or partly formed from wood (generally from pine). These findings indicate the presence of lignin. At the same time, wooden peat is usually more decomposed.

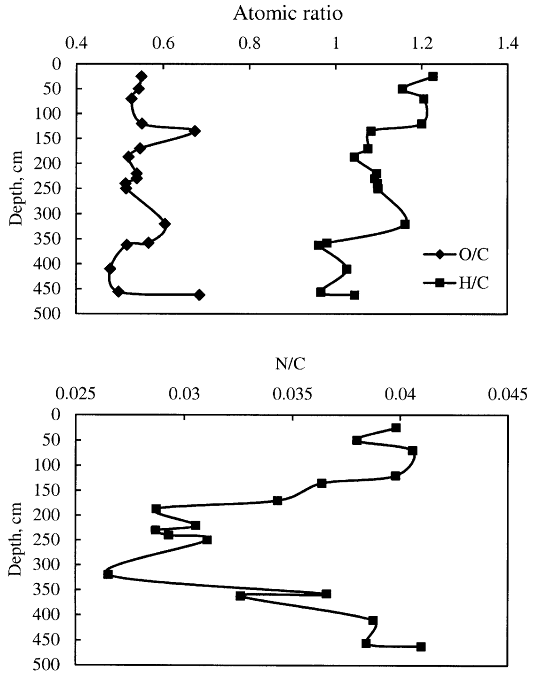

Fig. 7. Elemental ratios in peat humic acids from Eipurs Bog.

The relationship between the H/C and O/C atomic ratios (Fig. 8) of HAs reveals changes in the elemental composition of HAs and thus is useful in the identification of structural changes and the maturity degree of HAs (van Krevelen graphs are frequently applied in studies of humic substances and the C biogeochemical cycle) (Van Krevelen, 1950). Figure 8 can be considered as a graphical representation of the humification process indicating the degree of maturity and the intensity of the degradation processes such as dehydrogenation (reduction of the H/C ratio), decarboxylation (reduction of the O/C ratio), and demethylation, which occur during the genesis of humic acids. From the point of view of chemistry, the elemental ratios of peat HAs demonstrate changes in the HA composition during peat diagenesis, considering it as a process in which more labile structures (carbohydrates, amino acids, etc.) are destroyed, while thermodynamically more stable aromatic and polyaromatic structures emerge. The elemental composition of the studied peat HAs refers to the start of the transformation process of living organic matter.

To provide reliable and quantitative information about the diagenesis of HAs, further studies of the dependence on the elemental composition of peat and its HAs on the peat age (depth and decomposition degree) (Fig. 9) were carried out. The trends of dependence among H/C values and the depth of the peat samples were mostly negatively related, demonstrating that dehydrogenation is amongst the dominant processes during the ageing of peat HAs.

The structural features of peat HAs are directly characterized by their ^{13}C NMR spectra (Fig. 10, Table 2). The signals in these NMR spectra represent different types of carbon atoms. The use of cross-polarization and magic angle spinning techniques resulted in well resolved spectra, thus allowing division of the spectra into six main regions, which were attributed to carbon atoms in major structural units (Table 2). The ^{13}C NMR spectra can be divided into several chemical shift ranges (Fig. 10) indicating the presence of different major structural elements in the HA structure. Region A (0–50 ppm) consists primarily of aliphatic

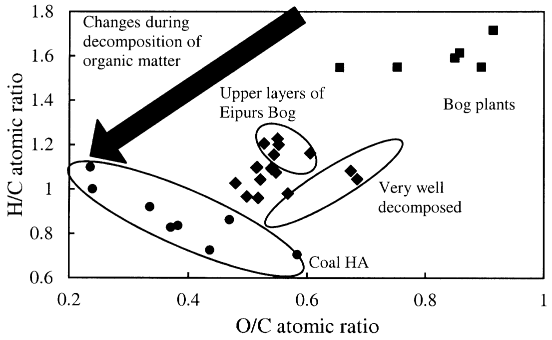

Fig. 8. Van Krevelen (H/C versus O/C atomic ratio) graph of peat humic acids from Eipurs Bog (♦), bog plants (■) (Van Krevelen, 1950), and coal HA (●) (Van Krevelen, 1950).

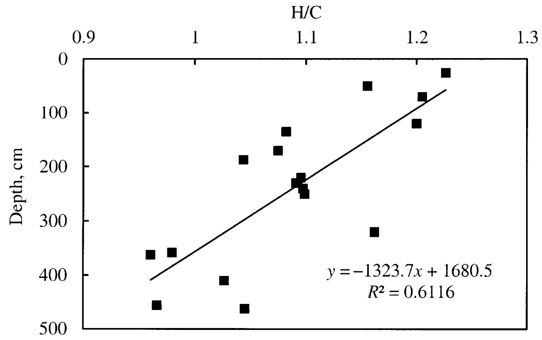

Fig. 9. Correlation between peat depth and the H/C atomic ratio of peat humic acids.

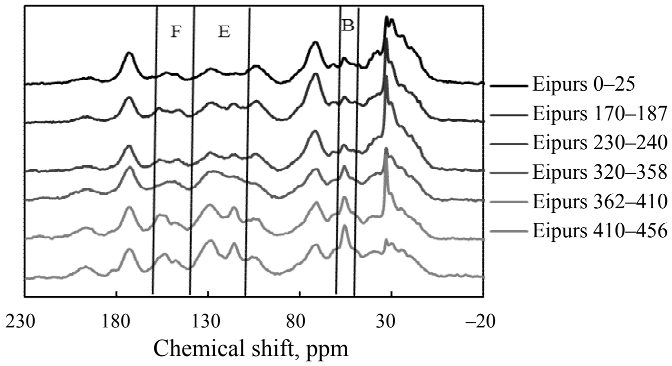

Fig. 10. ^{13}C CP MAS NMR spectra of peat humic acids from Eipurs Bog.

carbon resonances (methyl, methylene, and methine carbons). Region B (50–60 ppm) consists of methoxylcarbon (–OCH_3) resonance signals. Region E (110–140 ppm) is assigned to the resonance of unsubstituted and alkysubstituted aromatic carbons. Region F (140–160 ppm) consists of the resonance of the aromatic carbons substituted by oxygen and nitrogen (e.g. phenols, aromatic ethers, or amines). The analysis allowed direct evaluation of the substantial differences among peat humic substances of differing origin and revealed substantially lower aromaticity of peat HAs in comparison with commercial HAs and the ones from other terrestrial and aquatic sources. The ^{13}C NMR spectra illustrate major structural changes that take place during the peat diagenesis process: the reduction in the amount of aliphatic (alkyl) fragments (50–0 ppm) and structures characterizing ring carbon of carbohydrates (90–60 ppm) with increasing depth. The presence of unsaturated compounds is also increasing (140–110 ppm C_{AR} C in alkenes and aromatics) with increasing depth. Other major structures such as acidity (phenolic and carboxylic) did not show clearly expressed trends of changes with peat depth/ humification degree/age.

Table 2. Integrated areas of the main signal regions of the ^{13}C CP/MAS NMR spectra of peat humic acids isolated from Eipurs Bog

Depth, cm	220–190 ppm	190–160 ppm	160–140 ppm	140–110 ppm	110–90 ppm	90–60 ppm	60–50 ppm	50–0 ppm
	C=O, C in ketones and hinones	>CO–O, N C of carboxyls, esters, and amides	C_{AR}–O, N C of O, N-substituted aromatics	C_{AR} C in alkenes and aromatics	OC–O, N C bound by simple bonds to O, N, acetals in cyclic polysaccharides	O–C–O ring carbon of carbo-hydrates	CH_3O metoxyl C	CH_n C in aliphatic (alkyl) fragments
0–25	2.06	10.71	4.64	8.75	5.99	17.54	6.38	43.29
170–187	1.82	8.97	4.88	13.07	6.61	19.14	5.97	37.65
230–240	1.91	8.79	5.67	12.05	5.04	16.65	6.23	43.60
320–358	3.10	11.31	7.59	18.41	5.06	14.88	7.54	31.77
362–410	2.91	9.97	8.36	19.53	5.25	15.12	9.05	29.81
410–456	3.69	9.59	8.78	21.04	5.29	14.91	10.54	25.85
456–462	4.44	12.95	8.26	18.93	4.61	15.22	7.09	28.37

The distinctive distribution of the functional groups and major building blocks of HAs may reflect the way of their production and structural changes due to microbial degradation and geochemical alteration. The formation of HAs may occur through condensation reactions involving compounds derived from precursor organic materials or through the production of residual recalcitrant compounds in the microbial degradation of precursor organic materials. Lignin is not included in the set of precursor materials and carbohydrates for peat HAs; aliphatic structures are relatively abundant. Carbohydrate structures, however, are labile and may be rapidly degraded by microorganisms.

Study of correlations among the properties of HAs isolated from corresponding peat layers and peat decomposition degree proved the concept about the major processes behind humification and illustrated the diagenesis of peat organic matter (Fig. 11). At first, the increased peat decomposition degree might be associated with the dehydrogenation of peat HAs, probably leading towards the development of aromatic or other unsaturated (alkene) structures. Another evidently ongoing process is the development of acidity: genesis of carboxylic groups in peat humic substances during the decomposition and humification of peat organic matter, which mostly proceeds in upper bog layers and significantly depends on precursor biological material.

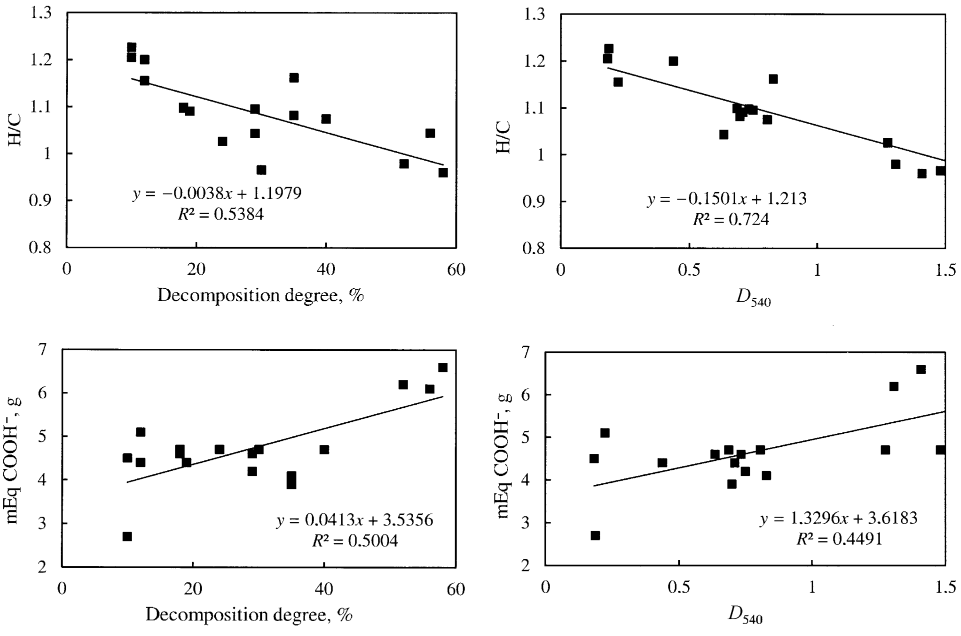

Fig. 11. Correlation among the properties of humic acids and peat decomposition degree and D_{540} of Eipurs Bog.

CONCLUSIONS

The transformation (humification) of living organic matter into refractory organic material (peat) in wetlands plays a key role in the genesis of carbon-containing deposits, as well as in the carbon biogeochemical cycling. Analysis of peat profiles can be considered as an important tool for studying the humification process in peat.

Elemental, functional, and spectral characterizations of peat HAs stress the role of the humification process as a major factor influencing the diagenesis of peat organic matter. The present study showed that the dominant properties of peat HAs were relatively homogeneous, unless there was a high variability in peat properties. The source of changes in the properties of peat HAs extracted from bogs could be natural variability and structural changes during the humification process. This approach supports better understanding of peat properties and their relation with peat decomposition processes and the original living organic matter.

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Turba huumushapete omadused ja nende varieerumist mõjutavad tegurid

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Turba omaduste uurimine on olulise tähtsusega turbasoode arenemisega seotud lagunemisprotsesside, humifikatsioonireaktsioonide, orgaanilise süsinikuga seotud biogeokeemilise aineringe ja fossiilse süsinikuga seotud diageneesiprotsesside seaduspärasuste mõistmisel. Käesolevas töös on käsitletud turba ja turbast ekstraheeritud huumushapete omadusi ning nende varieeruvust mõjutavaid tegureid. Uurimise objektiks olid Kesk-Lätis asuva Eipursi kõrgsoo ombrotroofse rabaturba profiilid ja selle erinevatest kihtidest väljutatud huumushapped. Peamiselt uuriti turba huumushapete omaduste (elemendiline ja funktsionaalne koostis, spektraalsed karakteristikud) seostatust turba vanuse, lagunemis- ning humifikatsiooniastme ja botaanilise koostisega. Süsiniku-, vesiniku-, lämmastiku- ja väävlisisaldus määrati nii turbas kui ka sellest väljutatud huumushappes. Töös on veel ka andmed turba tuhasuse, huumusainete hüdrofoobsuse ja karboksüülgruppide happesuse kohta. Uurimise tulemusena selgus, et turvast moodustava elusa orgaanilise aine omadused varieerusid tunduvalt enam, võrreldes vastavate turba omadustega. See näitab, et peamiseks turba omaduste kujunemise teguriks (mõjuriks) on humifikatsiooniprotsess. On järeldatud, et turba huumushapete koostis ei ole olulisel määral mõjutatud algse elusa orgaanilise aine koostise varieeruvustest. Turbasoode uurimine profiilidemeetodil aitab paremini mõista turba omaduste seoseid originaalse (algse) elusa orgaanilise ainega ja turbas kulgevate protsessidega.