Properties of Peat in Ombrotrophic Bogs Depending on the Humification Process

I. Silamiķele, O. Nikodemus, L. Kalniņa, O. Purmalis, J. Šīre, M. Kļaviņš

Faculty of Geography and Earth Sciences, University of Latvia, Raiņa Blvd 19, LV-1586, Rīga, Latvia

Studies of the humification process of living organic matter are essential for understanding of the carbon biogeochemical cycle. Considering this, the aim of this study is to analyse relations between the properties and humification degree of peat on the basis of an analysis of two peat profiles in ombrotrophic bogs in Latvia in order to identify the links between the age, decomposition degree, properties, and botanical composition of peat. As the study proves, the process of peat diagenesis can be described a using multiproxy analysis of the age, botanical composition, elemental composition, elemental ratios, and spectral characterization (UV-Vis, FTIR, fluorescence) of peat organic matter and peat alkaline extracts. This approach ensures both better understanding of peat properties and their relation to peat decomposition processes and original living organic matter. Multiproxy studies of peat properties assert the importance of the development of peat humification indicators.

Keywords: peat, Latvia, humification indicators, multiproxy study.

INTRODUCTION

In the carbon biogeochemical cycle of key importance is the transformation of living organic matter into a refractory part of organic matter – humic substances (humic acid, fulvic acid, and humin), i.e. humification. Both degradation and synthetic processes during the decay of living organic matter are described as humification, and in general it means 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) and, finally, into mineral carbon compounds. Understanding of transformation of living organic matter up to mineralization, especially formation of humic substances, is of key importance to understand the carbon biogeochemical cycle (Francioso et al., 2003). At the same time, the character of transformation of living organic matter is a very complex study subject considering the high variability of the environmental conditions under which living organic matter decays, and the large number of and structural differences

in organic molecules composing living organic matter. We can assume that the humification conditions may have an impact on the structure and properties of refractory intermediate transformation products of living organic matter – humic substances. From this perspective, it is important to study humification processes in such conditions that the transformation of living organic matter is studied in a relatively homogeneous and stable environment of bogs, identifying peat as the study subject.

Peat is a light brown to black organic material formed under waterlogged conditions by way of partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees (Coccozza et al., 2003). The interest in peat properties is because peat supports and influences bog and wetland ecosystems, and peat monoliths can serve as an archive indicating conditions in past environments (Yeloff and Mauquoy, 2006). Significant amounts of organic carbon are stored in the form of peat; therefore, peat reserves play major role in the carbon biogeochemical cycle and are especially important considering the ongoing climate change process (Bogmark, 2005). Industrial and agricultural use of peat is expanding (Brown et al., 2000; Ghaly et al., 1999), and significant amounts of peat are mined industrially not only in Northern countries, but also in tropical regions. Considering this, there is an increasing interest in the research of peat properties and processes influencing peat formation. Humification of peat takes place in diverse conditions both placewise (from tropical regions to the Arctic environment) and timewise (peat formation can take place for many thousands of years). During peat formation even at one site major changes in vegetation, temperature, amount of precipitation and, accordingly, in hydrological conditions of the bog and land use in the basin of the wetland can take place (Caseldine et al., 2000; Chapman et al., 2001; Zaccone et al., 2007).

To characterize the humification process, an important tool is the development of humification indexes that link the rate of transformation of living organic matter, development of humic substances with parameters that describe the properties of formed materials (Lu et al., 2001). Several humification indexes have been suggested to study the humification process during composting to evaluate maturity of compost (Jerzykiewicz et al., 1999; Domeizel et al., 2004) and to study soil formation processes (Zsolnay et al., 1999; Cavani et al., 2003; Ikeya and Watanabe, 2003; Rosa et al., 2005; Corvasce et al., 2006). Usually the humification process is evaluated using indirect measurements that describe structural changes occurring during the humification process. Several methods have been suggested, such as measurement of E_4/E_6 ratio that indicates the development of condensed macromolecules, the amount of organic/aliphatic carbon estimated with ¹³C CP MAS NMR. Furthermore, measurements of presence of free radicals, determined using EPR and studies of fluorescence properties of humic macromolecules, have been used to describe humification processes (Milori et al., 2002). However, only a few articles study the humification processes of peat (Schnitzer and Levesque, 1979; Preston et al., 1989; Hargitai, 1994; Baran, 2002; Francioso et al., 2003; Šīre et al., 2008) despite the fact that bogs and wetlands form one of the largest sources of refractory organic matter.

The aim of this study is to analyse relations between the properties and humification degree of peat on the basis of analysis of two peat profiles from ombrotrophic bogs in Latvia.

MATERIALS AND METHODS

Site Location

In-depth studies on peat humification processes and peat composition have been done on two ombrotrophic bogs located in the central part of Latvia (Fig. 1). Properties, location of these bogs, their development process, sampling and analytical methods used for bog characterization are described in detail by Kuške and others in this volume (2009).



Figure 1. Sampling sites: A - Dzelve-Kronis Bog; B - Eipurs Bog

Analysis of Peat Properties

The ¹⁴C dating was done at the Institute of Geology of Tallinn Technical University (Estonia).

Carbon, hydrogen, nitrogen, and sulphur concentrations in peat samples (elemental analysis of C, H, N, S) were determined using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments) with the combustiongas chromatography technique. The instrument was calibrated using cystine (Sigma – Aldrich Inc.), and all peat samples were analysed twice. The ash content was measured after heating 50 mg of each peat sample at 750 °C for 8 h. The elemental composition was corrected considering the ash content, but the oxygen amount was calculated as a difference. Elemental analysis was used to calculate elemental ratios and the degree of oxidation ω (Fong and Mohamed, 2007) and the index of hydrogen deficiency ϕ .

$$\phi = \frac{(2C+2) - H}{2}$$
$$\omega = (2O+3N) - \frac{H}{C}$$

UV-Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co) spectrophotometer in a 1 cm quartz cuvette. The E₄/E₆ ratio (Chen et al., 1977), ratio of absorbance at 465 and 665 nm, was determined for the extract of 0.25 g of peat in 10 ml of 0.05 M NaOH.

Organic carbon concentration in peat extracts was determined with Shimadzu TOC – VCSN.

The FT-IR spectra were acquired in transmittance mode using a Thermo Nicolet FT-IR spectrophotometer. Potassium bromide pellets were obtained by pressing, under vacuum, a homogenized mixture of 400 mg of infrared-grade KBr and 1 mg of sample (dried, milled peat). Spectra were recorded in the range of 4000–400 cm⁻¹.

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

Scanning electron microscopy (SEM) was done by placing the peat samples from each corresponding depth into the SEM sample holder and covering them with gold. Prepared samples were investigated using the JEOL ISM T–200 scanning electron microscope with magnification 200 times.

Humification Degree

Humification (according to Blackford and Chambers, 1993, modified by Borgmark, 2005)

1.00 g of peat sample was treated for 1.5 h with 25 ml of 8% NaOH in 25 ml plastic tubes in a boiling water bath (95 °C) and filtered. 12.5 ml of the filtrate were diluted to 100 ml, and absorption was measured at 540 nm. The peat humification degree was expressed as absorption.

Humification degree (HD, Šīre et al., 2008)

1.00 g of peat sample was shaken for 24 h with 50 ml of 1.0 N NaOH and filtered. The total organic carbon of the alkaline extract containing humic substances (C_{HS}) was determined in the filtrate (mg·C/g). The peat humification degree was calculated as

$$HD = \frac{C_{HS}}{C_{peat}} \times 100,$$

where C is carbon in the sample (mg/g).

Data Treatment

Statistical analyses were performed using SPSS 16 software. Fitting of the obtained data to normal distribution was checked with the Kolmogorov-Smirnov tests. For further analysis, non-parametric methods were used. Relationships between different characteristics were assessed with Spearman rank correlation coefficients. In all cases the significance was p = 0.05.

RESULTS AND DISCUSSION

Peat Composition and Its Changes

The aim of this study was to analyse relations between the variability of peat properties and the humification degree with the help of analysis of peat profiles from ombrotrophic bogs in Latvia. For this in-depth study of the pattern of the peat humification process in peat columns, two ombrotrophic bogs located the central part of Latvia were selected.

The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate both differences and similarities in the development of the studied bogs and peat properties. The Dzelve-Kronis Bog has formed due to paludification of sandy ground as a result of increase of the groundwater level and wet conditions in the small depression. A raised bog cotton grass peat layer covers sandy bottom, which is overlaid by pine-cotton grass peat. The upper part of the peat section is represented by a 3.2 m thick Sphagnum fuscum peat layer with decomposition 9 to 17% (Fig. 2). The botanical composition of the Dzelve-Kronis Bog is not varied: Sphagnum fuscum (60-75%), Eriophorum vaginatum (10-15%), Sphagnum rubellum (10-15%), and dwarf shrubs (10–15%). The botanical composition of the Eipurs Bog is completely different, although its origin is similar (Fig. 3). The lowest part of the Eipurs Bog is formed by fen wood-grass peat, Hypnum and sedge-Hypnum peat (Fig. 3) covered by a transition type wood peat. The upper part is represented by a 3.45 m thick raised bog peat of different types and decomposition degrees. For example, well decomposed (40-48%) pine-cotton grass peat occurs at the depth interval of 1.18–1.39 m (Fig. 3). It can be explained by possible accumulation during the Second Climatic Optimum. Although these bogs are comparatively close to each other, conditions of peat formation have been different. Pollen data indicate the start of development during the Late Atlantic Time or the Subboreal. The surface vegetation of the studied bogs is typical of ombrotrophic bogs in Latvia and is described in detail in Kušķe et al., 2009.



Figure 2. Peat stratigraphy, the Eipurs Bog

Peat humification can be visually traced, observing the peat structure and morphological and structural changes in the remains of peat forming plants (Fig. 4).

As we can see in the figures, during the peat development process in the Dzelve-Kronis Bog, gradual destruction of the Sphagnum leaves takes place,

evidently involving not only mechanical destruction of the original plant material, but also alteration of its composition. With the Eipurs Bog, the differences in the botanical composition of peat influence the image of peat material more than decomposition (Figure 5).



Figure 3. Peat stratigraphy, the Dzelve-Kronis Bog

The elemental compositions of the studied peat cores are summarized in Fig. 6 and Table. The ash content in the studied bogs ranges between $0.30 \pm 0.05\%$ and $6.10 \pm 0.05\%$, the average content being 1.8 ± 0.05 . The C concentration ranges from 40 to 55\%, H from 5.4 to 6.7\%, N from 0.5 to 1.5\%, S from 0.2 to 1.7\%, and O from 38 to 49%.



A 0 cm depth



B 65–70 cm depth



C 195-200 cm depth



D 245-250 cm depth



E 365-370 cm depth

Figure 4.

Visual changes in the peat material from the peat column of the Dzelve-Kronis Bog. A – decomposed Sphagnum leaves;

- B raised bog Sphagnum-fuscum peat, decomposition degree 10%;
- C raised bog cotton grass-Sphagnum peat, decomposition degree 29%;
- D raised bog Sphagnum-fuscum peat, decomposition degree 18%;

E – low moor-type sedge-Hypnum peat, decomposition degree 24%. Magnification 200 times I. Silamiķele, O. Nikodemus, L. Kalniņa, O. Purmalis, J. Šīre, M. Kļaviņš Properties of Peat in Ombrotrophic Bogs Depending on the Humification Process 79





B 120–125 cm depth

25kV X200 100µm 0000 23 36 SEI

C 230–235 cm depth



D 335-340 cm depth



E 390-395 cm depth

Figure 5.

Visual changes in the peat material from the peat column of the Eipurs Bog.

- A raised bog fuscum peat;
- B raised bog cotton grass-Sphagnum peat, decomposition degree 40% ;
- C raised bog fuscum peat, decomposition degree 18%;
- D transitional bog sedge-wood peat, decomposition degree 58%;
- E low moor-type grass peat, decomposition degree 56%. Magnification 200 times



Figure 6. The elemental composition of peat from the Eipurs Bog



Figure 7. The elemental ratio of peat from the Eipurs Bog

To characterize peat composition, elemental ratios have been used (Fig. 8). H/C and O/C values showed a decreasing trend with peat depth, but the N/C ratio in general increases with the depth of the peat core: this ratio is high in the upper layer (possibly due to the presence of proteinaceous materials of living organic matter), followed by significant fluctuations with increasing depth (starting from 250 cm), then, in more decomposed peat layers, the values of the N/C ratio increase again. This demonstrates that the elemental ratio cannot be correctly used to study the humification process due to the significant impact of the original plant composition and peat formation conditions.

Depth, cm	Decomposition, %	C, %	H, %	N, %	S, %
-5	12	44.77	5.91	0.73	0.89
-105	14	45.68	5.78	0.53	0.88
-160	12	46.05	5.81	0.55	0.88
-205	10	45.53	5.60	0.47	0.81
-240	9	44.84	5.47	0.45	0.88
-305	13	47.42	5.75	0.76	0.87
-320	12	45.73	5.55	0.62	1.22
-325	24	44.73	5.44	0.60	0.64
-335	30	52.10	5.20	1.51	0.73
-340	38	52.70	5.20	1.70	0.77
-350	> 60	55.53	6.20	1.23	1.19

Table. The decomposition degree and elemental composition of peat from the Dzelve-Kronis Bog

Peat Spectral Characterization

For characterization of peat, both analysis of different peat extracts and peat itself can be used. UV-Vis spectra of peat alkaline extracts are featureless and their intensity monotonically decreases with increased wavelength (Fig. 8). Spectra of peat core extracts differed in optical density, especially if they were from deeper horizons. These changes can help to identify relative amounts of aromatic structures in the peat composition. For qualitative description, the curvature of the peat extract absorption spectra can be characterized by either the specific absorbance at one wavelength (A₂₈₀) or by the absorption E_4/E_6 ratio at two wavelengths.



Figure 8. UV spectra of alkaline extracts of peat core samples from the Eipurs Bog

The FT-IR spectra (Fig. 9–11) of the examined peat are in general similar to one another in the main position of adsorption, but differences of various entities are apparent in the relative intensity of some bands, depending of the origin (depth and age) of the sample. IR spectra of the analysed peat layers can be divided by regions depending on informativity and the presence of important functional groups. Absorption bands in the spectral region of 3600–2800 cm⁻¹ are very broad. Absorbance in this spectral region is determined by the presence of -OH groups. Sorption at wavelengths of 2950 and 2850 cm⁻¹ identifies the presence of CH₃- and CH₂- groups. Typical intensive sorption lines are common to the region around 1700 cm⁻¹ (1725–1700 cm⁻¹), which is characteristic of carbonylgroups in aldehydes, ketones, and carbonic acids. The actual sorption maximum greatly depends on the conjugation degree, presence of substituents, and hydrogen bonding. In the spectral region of 1690-1500 cm⁻¹, it is possible to identify the sorption maximum of amide bonds $(1620-1640 \text{ cm}^{-1})$ and 1550–1540 cm⁻¹). In the region between 1625 and 1610 cm⁻¹, sorption indicates the presence of aromatic C=C and carbonylgroups, hinones. At wavelengths between 1470 and 1370 cm⁻¹, there are bonds typical of C-H and O-H bonding and sorption maximums typical of C-O. For wavelengths below 1000 cm⁻¹, fingerprint patterns are evident. Sorption in this spectral region provides information about the possible role of carbohydrate percentage in the structure in humic molecules. Sorption at 1080 cm⁻¹ shows OH deformation or C-O stretch of phenole and alcohol OH groups, and at 1040 cm⁻¹ indicates C-O stretch of polysaccharide components.



Figure 9. IR spectra of peat of the peat column from the Dzelve-Kronis Bog

Changes in the relative intensities of sorption maximums in FT-IR spectra indicate the character of changes during the development of peat during humification, especially in comparison with the IR spectra of peat-forming plants. There are remarkable changes of sorption between peat and bog plants of the wide line around 3400 cm⁻¹. The intensity of the process increases as well. The absorption band centered at 1720 cm⁻¹ (indicating acidic carboxylic groups) was clearly stronger in peat with a higher degree of decomposition, especially in comparison with the intensity of sorption lines in bog plants. The absorption band centered at 1040 cm⁻¹ (C-O stretching, e.g., polysaccharides) was equally weak in all the studied peat samples, even if their decomposition degree was low, indicating that the decomposition of carbohydrates takes place at very early stages of humification. Such pattern of changes illustrating the development of peat structure is common for all the studied samples.



Figure 10. IR spectra of peat of the peat column from the Eipurs Bog



Figure 11. FT-IR spectra of peat-forming plants

To obtain more detailed information about the changes in the structure of peat extracts, fluorescence spectra in emission scanning mode were recorded. All peat alkaline extract fluorescence spectra obtained in this research have similar characteristics, showing maximum peaks at around 450 nm and weak shoulder curves at about 500 nm (Fig. 13, 14), but the intensity of fluorescence gradually decreases with depth. These results correspond with similar data given by Sire et al. (2008), which show that fluorescence emission spectra (excitation at 330 nm) of peat humic acids are characterised by maximums at the same wavelengths. The exact properties of the fluorescing groups are still unclear. Many scientists agree that fluorescence at higher wavelengths is typical of more humified organic matter and may be attributed to either highly substituted aromatic nuclei, possibly bearing at least one electron-donating group, or/and conjugated unsaturated systems capable of high degrees of resonance (Senesi and Steelink, 1989). Furthermore, lignin-derived structural units and conjugated phenolic aldehydes which have $\lambda_{_{em}}$ max = 485-510 can be suggested as possible contributors to fluorescence of soil organic matter (Senesi and Sakellariadou, 1994).



Figure 12. Fluorescence spectra of the humic matter isolated from the Dzelve-Kronis Bog peat column

In the case of the Dzelve-Kronis Bog, it is evident that the fluorescence spectra of peat extracts isolated from the upper layers (comparatively homogeneous poorly decomposed peat) are very similar, characterized by maximum peaks at around 450 nm and weak shoulder curves at about 480 nm. The fluorescence spectra of peat extracts isolated from more decomposed peat are of much lower intensity; however, the peat at around 450 nm is more intensive than at 480 nm, clearly indicating higher importance of more aromatic structures in the peat organic matter. The heteregeneous structure of the Eipurs Bog also confirms the changes of the character of the fluorescence spectra, which can possibly be used for characterization of peat humification degree as well.



Figure 13. Fluorescence spectra of the humic matter isolated from the Eipurs Bog peat column

Factors Affecting Peat Humification Process

Studies of living organic material transformation (humification) are of utmost importance for better understanding of the carbon biogeochemical cycling. Studies of peat core properties from this perspective identify the links or correlations between the age, decomposition degree, and properties of peat, and peat botanical composition (that describes and depends much on the bog development conditions, climatic and hydrological factors, as well as changes of land use within the bog catchment). On the other hand, the changes of peat properties that influence the humification process at a molecular level and help to enhance the understanding of chemical and biochemical processes behind the humification are also important. Following this approach, we selected two ombrotrophic bogs of similar age located close to each other for this study (Fig. 1); nevertheless, the bogs had very different peat column stratigraphy (Fig. 2, 3) and peat column botanical composition as well as the decomposition degree. The major part of peat from the Dzelve-Kronis Bog consists of relatively homogeneous sphagnum peat with a comparatively low decomposition degree, whereas the composition of peat from the Eipurs Bog is very heterogeneous and reflects the high variability of local bog development conditions. The changes in the peat core properties are represented in Fig. 4 and Fig. 5. The peat core microphotographs (magnification 200 times) reveal not only changes in the different peat forming plants during their decay (in the Eipurs Bog), but also show that sphagnum tissues during their decay process are well preserved in the Dzelve-Kronis Bog. The selected study objects thus confirm the importance of analysis of the relations between peat development conditions and peat properties as well as identification of the humification indicators that best describe the process of transformation of living organic material.

Basic peat properties can be analysed using peat elemental (C, H, N, O, S) composition. The elemental composition of peat from the Eipurs Bog is comparatively variable and reflects the changes in the decomposition degree and type of peat. C concentration increases starting from the depth of 1 m up to 53% and then decreases again. H concentrations demonstrate significantly higher variability, but changes of N concentrations (increased concent ration in the upper and lower horizons of the bog, also demonstrating increased values coinciding with the changes in the peat composition and formation conditions) could be associated with changes in the botanical composition and decomposition degree of peat. S concentratively stable along the peat column. The elemental composition (Table 1) of the Dzelve-Kronis Bog, however, differs very much and largely reflects the peat column composition: C content in the upper layers is much lower (~ 45%) and comparatively stable to the depth of 3.25 m, but then rapidly increases, reaching 55% in highly decomposed peat.

The elemental ratio gives much more information than the elemental composition of peat. (Table 1, Fig. 7.) C/N ratio can be considered a good index of the humification process due to specific microbial activity in anaerobic, acidic environment and enrichment of the peat mass with nitrogen-containing compounds of bacterial origin (Borgmark, 2005a). This ratio can be efficiently used as a measure of peat degradation. The decreasing C/N ratios indicate increasing peat decomposition (due to microbial decay) and vice versa. H/C ratio is an index of molecular complexity (and at the same time of aromaticity), and it ranges from 1.6 to 1.2 (Anderson and Hepburn, 1987). It is relatively constant with depth; below 50 cm it decreases. O/C ratio is considered to be an indicator of carbohydrate and carboxylic contents and is directly related to aromatization of the organic matter forming peat (Anderson and Hepburn, 1987). O/C ratio decreases with depth; however, in layers with higher decomposition degree, the values of this indicator also are high.

The peat formation process was examined using the van Krevelen graphs frequently applied in the analysis of the carbon biogeochemical cycle and genesis of fossil fuel (Van Krevelen, 1950). Figure 14 shows the elemental ratios of the studied peat samples. According to Steelink (1985), the atomic ratio O/C, H/C, and N/C indices are useful in the identification of structural changes and the degree of maturity of peat in different depositional environments. The graph of H/C atomic ratio versus O/C atomic ratio reveals changes in the properties associated with coalification reactions.



Figure 14. The van Krevelen (H/C vs O/C atomic ratio) graph of bog plants (\blacklozenge), peat samples from the studied bogs in Latvia (\blacklozenge), reference peat samples (IHSS), and peat samples from common peat bogs (\blacksquare), brown coal (\blacktriangle), coal (\blacktriangleleft), lignite (∇)

Figure 14 shows the relation between H/C atomic ratio and O/C atomic ratio of organic material of a differing decomposition degree – beginning with bog plants up to brown coal, lignite, and coal. The graph in Figure 14 could be considered a graphical statistical representation of the impact of the humification process on elemental composition of organic material, indicating the degree of maturity and intensity of degradation processes such as dehydrogenation (reduction of H/C ratio), decarboxylation (reduction of O/C ratio), demethylation occurring during the decay of peat-forming plants, and peat maturation into coal. These changes are especially evident when atomic ratios of peat-forming plants are compared to the atomic ratio of organic matter of a high decomposition degree (low moor peat, coal). From the point of view of chemistry, humification can be considered a process in which more labile structures (carbohydrates, amino acids, etc) are destroyed, but thermodynamically more stable aromatic and

polyaromatic structures emerge. It follows that the atomic ratios are associated with the processes transpiring during peat humification. As shown in Figure 14, H/C ratio decreases with an increasing decomposition degree of the original living matter, starting with peat-forming plants, cellulose, and proteins, and up to bituminous coal. Comparatively, the studied peats demonstrate an increasingly intensive transformation process of living organic matter. The van Krevelen graph (Figure 14) also indicates a decrease in O/C ratio, illustrating the decrease in the number of oxygen-containing functional groups, such as methoxyl, carboxyl, and carbonyl functional groups, in the fossil material with an increasing humification degree.

Elemental analysis data can also be used for calculation of indexes of hydrogen deficiency ϕ and oxidation ω (Fong and Mohamed, 2007). However, in this case these indexes have only weak relations with the high variability of properties of the peat core from the Eipurs Bog, and peat hydrogen deficiency ϕ and degree of oxidation ω can be considered relatively homogeneous.



Figure 15. Changes of indexes of hydrogen deficiency ϕ and degree of oxidation ω in peat from the Eipurs Bog

Spectral analysis of both intact peat and peat alkaline extracts confirms for the most part the aforementioned conclusions, but allows to identify the structural and molecular changes ongoing during the humification process (Fig. 8–13). UV and fluorescence spectra allow to study the development of aromatic structures during the humification process. Growing intensity of absorption at 280 nm in UV spectra characteristic of benzene (aromatic) rings (especially if we compare

absorption at 280 nm with absorption at 410 nm) with increasing depth and decomposition degree of peat from the Eipurs Bog illustrate increasing growth of aromaticity during the humification process.

The E_4/E_6 ratio is often used to describe the extent of condensation of the aromatic C-containing structures; low ratios reflect high degrees of condensation of aromatics, while high ratios mean the presence of large quantities of aliphatic structures and small numbers of condensed aromatics (Chen et al., 1977). This ratio is also inversely related to the degree of aromaticity and acidity (Uyguner et al., 2004).

In this study, the variability of E_4/E_6 ratios in the peat profile from the Eipurs Bog was relatively high (Fig. 16) and can refer to the transformation processes of organic matter within peat profiles.

Absorption at 540 nm in the Vis spectra of peat alkaline extracts can be used as a simple indicator of the humification process, as suggested and recently improved on by Borgmark (2005a). We can see in Figure 17 that this humification index demonstrates expected differences when used for description of the Dzelve-Kronis Bog and Eipurs Bog, and the changes can be associated with the peat decomposition degree and the differences in peat composition.



Figure 16. Changes of the spectral absorption E4/E6 ratio versus depth in peat from the Eipurs Bog

Fluorescence spectra with two well-expressed peaks prove better quantification of aromaticity during humification (Fig. 12, 13). One of the peaks (490–520 nm) is clearly associated with aromaticity of the studied material (Cocozza et al., 2003). In the upper layers of both bogs, the intensity of fluorescence signals of

aromatic structures is much lower than the intensity of signals associated with fluorophores in aliphatic structures (Anderson and Hepburn, 1987), whereas in deeper layers, the aromaticity of the studied materials evidently increases. Thus, the ratios of the fluorescence intensities at different wavelengths can be used as humification indicators. In this study we tested possibilities to use fluorescence intensities I_{380}/I_{330} and I_{460}/I_{380} (Fig. 18). As we can see in Figure 18, in the Eipurs Bog the fluorescence intensity ratios follow the pattern of peat decomposition degree quite well and even better than the humification index, which, according to Brogmark, helps to describe the character of peat development.





Figure 17. Changes of the humification index according to Borgmark (2005b) (adsorption of peat extract at 540 nm) versus depth in peat from the Eipurs Bog



Figure 18. Changes of the humification index according to Borgmark (2005a) (adsorption of peat extract at 540 nm) and ratios of fluorescence intensities (I_{380}/I_{330} and I_{460}/I_{380}) versus depth in peat from the Eipurs Bog

The changes in FTIR spectra (Fig. 9–11) show the changes in the intensity of functional groups with peat material humification (increasing age, depth, and decomposition degree). The changes in the functional groups of peat organic matter at first can be related to relative amounts of -OH, -COOH, -C=O, CH groups.

91



Figure 19. Correlation between peat decomposition (%, the Eipurs Bog and Dzelve-Kronis Bog) and humification indexes (humification according to Borgmark, D540, the humification degree HD, and fluorescence intensity ratios $I_{_{380}}/I_{_{330}}$ and $I_{_{460}}/I_{_{380}}$)

<u>92</u>



Figure 20. Correlation between the humification index according to Borgmark (D540) and N/C and H/C elemental ratios of peat

In order to provide reliable and quantity information about the diagenesis of peat, we carried out further studies on the dependence of the peat humification indexes on peat decomposition (the age, depth, and decomposition degree of peat, respectively, Figure 19, 20).

As we can see in Figure 19, peat decomposition very well and statistically significantly correlates with the humification index according to Borgmark (2005b) and the humification degree – an index suggested by Šīre et al. (2008). Correlation between fluorescence intensity ratios and fluorescence intensities (I_{380}/I_{330} and $I_{460/}I_{380}$) is much poorer. Both humification indexes describe basic changes in the peat properties and correlate well with the elemental ratios of peat in the peat cores, thus depicting changes of peat organic materials during humification of living organic matter. Both indexes can hence be suggested for characterization of humification processes in other environments as well.

CONCLUSIONS

Transformation (humification) of living organic matter into refractory organic material (peat) in wetlands is of key importance for genesis of carbon-containing deposits and carbon biogeochemical cycling. Analysis of peat profiles is an

93

important tool to study the peat humification process. As this study confirms, the transformation process of living organic matter can be described using multiproxy analysis of peat – analysis of the elemental composition, elemental ratios, and spectral characterization of peat organic matter and peat alkaline extracts. This approach facilitates better understanding of peat properties and their relation to peat decomposition processes as well as to original living organic matter. The multiproxy study of peat properties confirms the necessity of peat humification indicators.

ACKNOWLEDGEMENTS

The authors are grateful to Dr Enn Kaup (Institute of Geology, Estonia) for determination of peat age using ¹⁴C analysis, A. Diņķīte (Balt-Ost Geo) for analysis of the botanical composition and decomposition degree, I. Kļimenkovs for providing CHNS analysis, S. Kokoreviča for obtaining IR spectra, and A. Patmalnieks for obtaining SEM microphotographs. We thank the European Social Fund for financial support to I. Silamiķele.

REFERENCES

- Anderson H., Hepburn A. (1986) Variation of humic substances within peat profile. In: *Peat and water* (Ed. C. H. Fuchsman), N.Y.: Academic Press, 177–194.
- Blackford J. J., Chambers F. M. (1993) Determining the degree of peat decomposition for peat-based paleoclimatic studies. *Int. Peat J.*, 5, 7–24.
- Borgmark A. (2005a) Holocene climate variability and periodicities in south-central Sweden, as interpreted from peat humification analysis. *Holocene*, 15(3), 387–395.
- Borgmark A. (2005b) The colour of climate: changes in peat decomposition as a proxy for climate change – a study of raised bogs in South-central Sweden. PhD thesis, Stockholm: Stockholm University.
- Brown P. A., Gill S. A., Allen S. J. (2000) Metal removal from wastewater using peat. Water Res., 34 (16), 3907–3916
- Caseldine C. J., Baker A., Charman D. J., Hendon D. (2000) A comparative study of optical properties of NaOH peat extracts: implications for humification studies. *Holocene*, 10(5), 649–658.
- Chapman S. J., Campbell C. D., Fraser A. R., Puri G. (2001) FTIR spectroscopy of peat in and bordering Scots pine woodland: relationship with chemical and biological properties. *Soil Biol. Biochem.*, 33, 1193–1200.
- Chen Y., Senesi N., Schnitzer M. (1977) Information provided on humic substances by E₄/E₆ ratios. *Soil Sci. Soc. Amer. J.*, 41(2), 352–358.
- Cocozza C., D'Orazio V., Miano T. M., Shotyk W. (2003) Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties. *Org. Geochem.*, 34, 49–60.

Fong S. S., Mohamed M. (2007) Chemical characterization of humic substances occurring in the peats of Sarawak, Malaysia. Org. Geochem., 38(6), 967–976.

95

- Ghaly R. A., Pyke J. B., Ghaly A. E., Ugursal V. I. (1999) Remediation of Diesel-Oil-Contaminated Soil Using Peat Energy Sources: Recovery, Utilization, and Environmental Effects, *Chemosphere*, 21(9), 785–799.
- Kuder T., Kruge M. A., Shearer J. C., Miller S. L. (1998) Environmental and botanical controls on peatification – a comparative study of two New Zealand restiad bogs using Py-GC/MS, petrography and fungal analysis. *Int. J. Coal Geol.*, 37, 3–27.
- Kušķe E., Silamiķele I., Kalniņa L., Kļaviņš M. (2009) Peat Formation Conditions and Peat Properties: a Study of Two Ombrotrophic Bogs in Latvia, This volume, pp. 54–68.
- Lishtvan I. I., Korol N. T. (1975) *Basic Properties of Peat and Methods for Their Determination*. Minsk: Nauka I Teknika. (in Russian)
- Milori D. M. B. P., Neto L. M., Bayer C., Mielniczuk J., Bagnato V. S. (2002) Humification Degree of Soil Humic Acids Determined by Fluorescence Spectroscopy. *Soil Sci.*, 167(11), 739–749.
- Moore P. D., Webb J. A. (1978) *An illustrated guide to pollen analysis*. London: Hodder and Stought.
- Steiner G. M. (ed.) *Moore von Siberien bis Feuerland* (2005) Linz: Biologiezentrum der OÖ Landesmuseum.
- Šīre J., Kļaviņš M., Purmalis O., Melecis V. (2008) Experimental study of peat humification indicators. *Proc. Latv. Acad. Sci.*, B, 62(1/2), 18–27.
- Tan K. H. (2005) *Soil Sampling, Preparation, and Analysis* Second Edition. New York: Taylor & Francis Group, 623 p.
- Tjuremnov S. N. (1976) *Peat deposits and their exploration*. Moscow: Nedra.
- Uyguner C. S., Hellriegel C., Otto W., Larive C. K. (2004) Characterization of humic substances: Implications for trihalomethane formation. *Anal. Bioanal. Chem.*, 378, 1579–1586.
- Von Post L., Granlund E. (1926) Södra Sveriges torvtillgångar 1. Sver. Geol. Unders., C335, 19(2), 1–127.
- Yeloff D., Mauquoy D. (2006) The influence of vegetation composition on peat humification: implications for paleoclimatic studies. *Boreas*, 35, 662–673.
- Zaccone C., Miano T. M., Shotyk W. (2007) Qualitative comparison between raw peat and related humic acids in an ombrotrophic bog profile. *Org. Geochem.*, 38, 151–160.
- Zicheng Yu., Vitt D. H., Campbell I. D., Apps M. J. (2003) Understanding Holocene peat accumulation pattern of continental fens in western Canada. *Can. J. Bot.*, 81, 267–282.