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PEAT HUMIFICATION CHARACTER IN TWO OMBROTROPHIC BOGS DEPENDING ON PEAT PROPERTIES

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Study of the living organic matter humification process is essential for understanding of the carbon biogeochemical cycle. The aim of this study is to determine the relations between peat properties and humification degree in two peat profiles in ombrotrophic bogs in Latvia, to identify the links between peat age, decomposition degree, peat properties, peat botanical composition and peat properties. The peat diagenesis process was described using multiproxy analysis of peat age, botanical composition, elemental composition, elemental ratios of the peat organic matter and peat alkaline extracts. This approach supports a better understanding of the peat properties and their relation both to peat decomposition processes, and also to original living organic matter. Multiproxy study of peat properties supports development of peat humification indicators.

Key words: *peat, Latvia, humification indicators, multiproxy study.*

INTRODUCTION

A key process in the carbon biogeochemical cycle is the transformation of living organic matter into the refractory part of organic matter — humic substances (humic acid, fulvic acid, and humin). Both degradation and synthetic processes during decay of living organic matter are described as humification and in general it describes 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 until their mineralisation, and especially formation of humic substances, are of key importance to understand carbon biogeochemical cycling (Francioso *et al*., 2003). It is important to study humification processes in conditions where the transformation of living organic matter can be studied in a relatively homogeneous and stable environment, such as in peat of bogs.

Peat is a light brown to black organic material formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees (Coccozza *et al*. 2003). Interest inpeat properties is growing since peat as a substance supports and influences bog and wetland ecosystems, and peat monoliths can serve as an archive indicating conditions in past environments (Yeloff and Mauquoy 2006). Peat conains significant amounts of stored organic carbon and thus peat reserves play a major role in the carbon biogeochemical cycling and have a special role in climate change (Borgmark, 2005b). Industrial and agricultural uses of peat are growing (Ghaly *et al*., 1999; Brown *et al*., 2000) 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 into studies of peat properties and processes influencing their formation. During peat development, even at a specific site major changes in vegetation, temperature, amount of precipitations and correspondingly of the bog hydrological conditions, land use changes in the basin of wetland can take place (Caseldine *et al*., 2000; Chapman *et al*., 2001; Zaccone *et al*., 2007).

To characterise the humification process, an important tool can be development of humification indexes linking the rate of transformation of living organic matter, development of humic substances with parameters describing 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 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 describing structural changes occurring during the humification process. Several methods have been suggested to describe the humification, such as measurement of the E_4/E_6 ratio indicating development of condensed macromolecules, and amount of organic /aliphatic carbon estimated by ^{13}C CP MAS NMR. Also presence of free radicals, determined using EPR and studies of fluorescence properties of humic macromolecules has been used to describe humification processes (Milori *et al*., 2002). However, humification processes of peat have been studied only in few articles (Schnitzer and Levesque, 1979; Preston *et al*., 1989; Hargitai, 1994; Baran, 2002; Francioso *et al*., 2003; Šīre *et al*., 2008), which is surprising considering that bogs and wetlands form one of the largest sources of refractory organic matter.

The aim of this study was to determine the relations between peat properties and humification degree in two peat profiles of ombrotrophic bogs in Latvia.

MATERIALS AND METHODS

Site location. The study area includes ombrotrophic bogs located in the central part (Rīga District) of Latvia (Fig. 1). The bogs are located in the Coastal Latvia Lowland and their origin is similar and characteristic not only for ombrotrophic bogs in Latvia, but also for the North European region. Indepth studies were made on two bogs — Eipurs and Dzelves–Kroņu bogs. The two bogs have developed by ground paludification after the Ice age. Presently, the bogs are typical raised bogs with a number of bog lakes and pools. Dzelves–Kroņu Bog (coordinates N 57° 13' 58,2", E 024° 30' 12,2") is in a semi pristine condition in spite of peat cutting areas in the north-western part. Eipurs Bog (coordinates N 57° 14' 53,4", E 024° 37'00,3") is influenced by drainage and peat cutting, and the largest part is covered by pine forest.

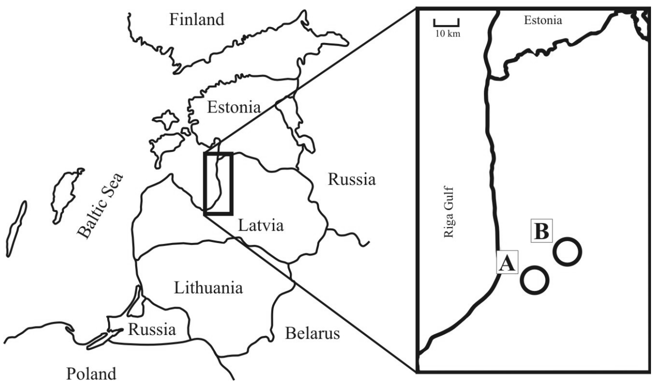

Fig. 1. Sampling sites: A – Dzelves–Kroņu bog; B – Eipurs bog.

The maximal depth of the peat layer in Eipurs bog is 4.70 m. The bog is in the transformation process from raised bog to *Pinus sylvestris* forest. Among the mosses the *Sphagnum* species, *S. fuscum* and *S. magellanicum*, dominate.

Dzelves–Kroņu Bog is a developing raised bog and is included in the list of Natura 2000 protected areas. In the sampling area, the plant communities are typical of a raised bog with hummocks covered by *Sphagnum* moss and hollows and small bog lakes. Dzelves–Kroņu bog is an active raised bog and is included in the list of Natura 2000 protected areas.

Sampling. Sampling was made using previously suggested approaches for peat core sampling to study peat properties (Borgmark, 2005b). Coring and peat sampling was conducted by peat sampler in the cupola area of each bog, where the surface peat layers are clearly elevated up to 2–4 m above that at the edge of the bog and has not been influenced by peat sliding. The peat samples (50 cm long monoliths) were placed in a special cartridge and wrapped in polyethylene film to preserve natural moisture, brought to the laboratory and sliced into 3 cm sections using a stainless steel knife. The outside edges were systematically discarded, as those could have been contaminated during the sampling. The first slice (+3 to 0 cm) corresponds to the living plant material on the bog surface. The peat material was oven dried at 105 ^{o}C in Teflon bowls and ground in a centrifugal mill.

Peat botanical composition. Peat botanical composition is closely related to plant nutrition conditions, characteristics of bog depression, relief, underlying deposits and groundwater mineralisation degree, which substantially affect peat decomposition degree, moisture and properties (Тюремнов, 1976).

The analysis of botanical composition was performed using a Carl-Zeiss binocular microscope and the decomposition degree (Lishtvan and Korol, 1975) was determined using common methods. Peat type and H-value (according to von Post and Granlund, 1926) were determined in the field and later adjusted in the laboratory.

Analysis of peat properties. The ^{14}C dating was conducted at the Institute of Geology of the Tallinn Technical University (Estonia). Carbon, hydrogen, nitrogen and sulphur concentrations in peat samples (elemental analysis of C, H, N, S) was carried out using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments) by combustion-gas chromatography technique. The instrument was calibrated using cystine (Sigma – Aldrich Inc.) and all peat samples were analysed in duplicate. Ash content was measured after heating 50 mg of each peat sample at 750 °C for 8 h. Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference. Elemental analysis has been used to calculate elemental ratios and degree of oxidation ω (Fong and Mohamed, 2007) and 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 E_4/E_6 ratio (Chen *et al*., 1977): ratio of absorbance at 465 and 665 nm was determined for extracts of 0.25 g of peat in 10 ml of 0.05 M NaOH.

Organic carbon concentration of peat extracts was determined using a Shimadzu TOC – VCSN.

Humification degree

Humification degree (HD) according to Blackford and Chambers, 1993, as modified by Borgmark 2005: 1.00 g of peat sample was treated for 1.5 hrs with 25 ml of 8% NaOH in 25 ml plastic tubes in a boiling water bath (95 ^{o}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 according to Šīre *et al.*, 2008: 1.00 g of peat sample was shaken for 24 hrs with 50 ml of 1.0 M NaOH, filtered and in the filtrate the total organic carbon of the alkaline extract, containing humic substances (C_{HS}) was determined (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. The fit of the obtained data to the normal distribution was checked with the Kolmogorov-Smirnov tests. In further analysis non-parametric methods were used. Relationships between different characteristics were assessed by Spearman rank correlation coefficients. In all cases the significance level was $P = 0.05$.

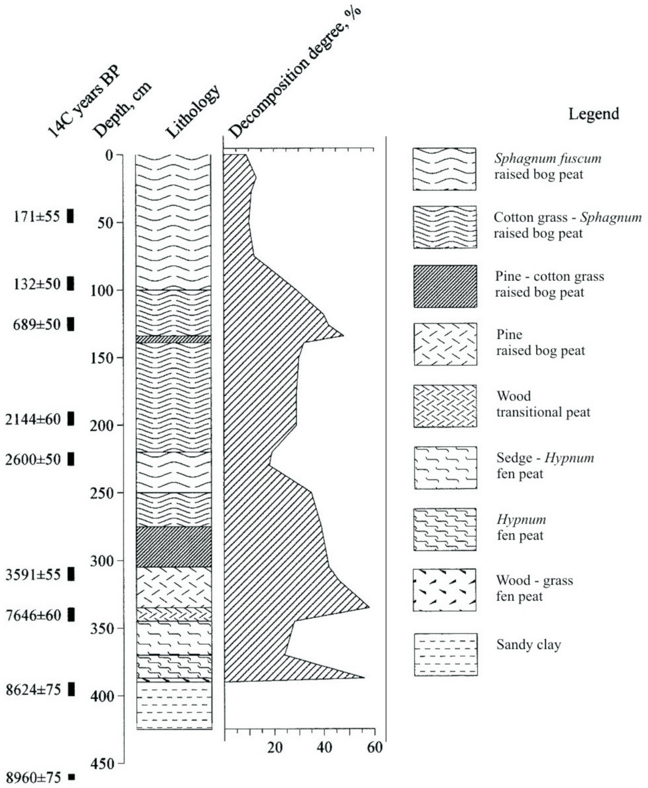

Fig. 2. Peat stratigraphy in Eipurs bog.

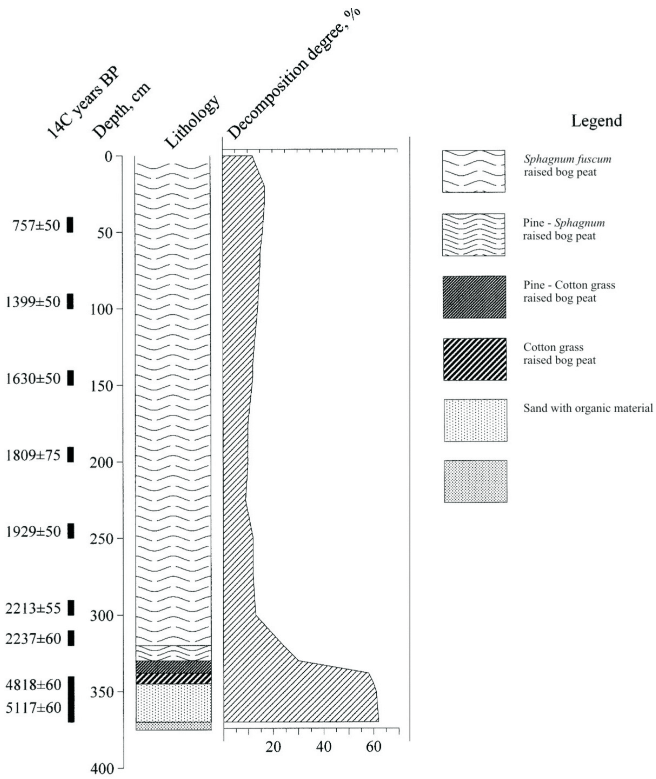

Fig. 3. Peat stratigraphy in Kroņu–Dzelves bog.

RESULTS

The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate both differences and similarities of bog development and peat properties. Kroņu–Dzelve Bog was formed by paludification of sandy ground after a raised groundwater level and wet conditions in a small depression. A raised bog cotton grass peat layer covers the sandy bottom, which is overlain by pine-cotton grass peat. The upper part of peat section is represented by a 3.2 m thick *Sphagnum fuscum* peat layer with a decomposition level 9 to 17% (Fig. 2). Botanical composition is not very variable: *Sphagnum fuscum* (60–75%), *Eriophorum vaginatum* 10–15%, *Sphagnum rubellum* 10–15% and dwarf shrubs 10–15%. The botanical composition of Eipurs Bog differs, although its origin is similar (Fig. 3). The deepest part of Eipurs is formed by fen wood-grass peat, *Hypnum* and sedge-*Hypnum* peat (Fig. 3) which is covered by a transition type wood peat. The upper part is represented by 3.45 m thick raised bog peat of different types and decomposition degree. For example, well decomposed (40–48%) pine-cotton grass peat occurs at a depth of 1.18–1.39 m (Fig. 3), which possibly accumulated during the second climatic optimum. Although these bogs are located comparatively close, their local conditions for peat formation have been different. Pollen data indicate the start of development during the late Atlantic Period or the subboreal. The surface vegetation of the studied bogs is typical for ombrotrophic bogs in Latvia and in detail is described elsewhere (Silamiķele *et al.*, 2008).

The elemental composition of the studied peat cores are summarised in Figure 4 and Table 1. The ash content in the studied bogs ranged between 0.30 ± 0.05% and 6.10 ± 0.05%, with an average content of 1.8 ± 0.05 and the C concentration from 40 to 55% and 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%.

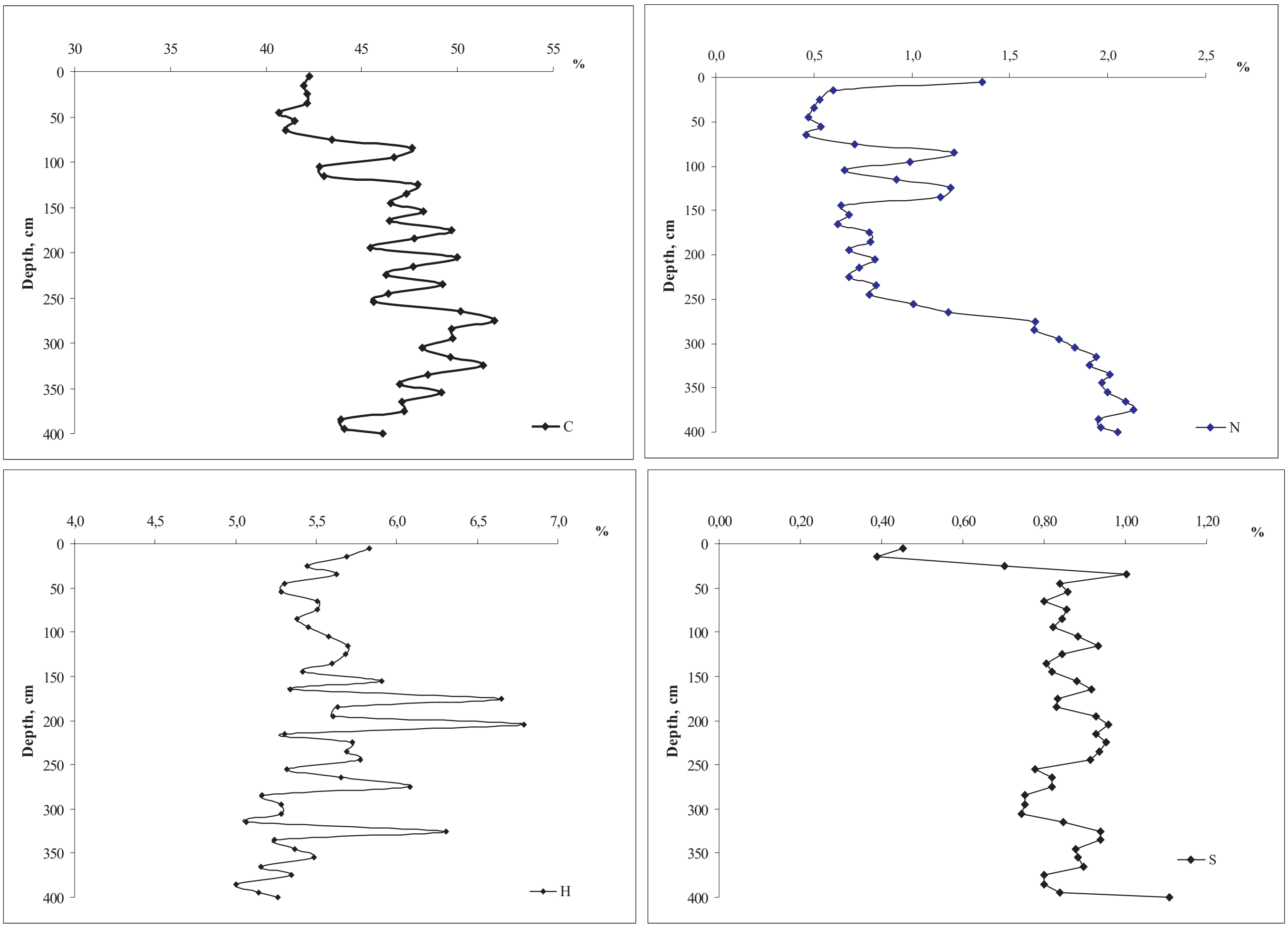

Fig. 4. Elemental composition of Eipurs bog peat.

Table 1

PEAT DECOMPOSITION DEGREE AND ELEMENTAL COMPOSITION OF PEAT IN KROŅU–DZELVES BOG

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

Element ratios were used to characterise peat composition (Fig. 5). H/C and O/C values showed a decreasing trend with peat depth and N/C ratio in general increased with depth of the peat core. However, this ratio is high in the upper layer (possibly due to the presence of proteinaceous materials of living organic matter), variable with increasing depth (starting from 250 cm), but increased in more decomposed peat layers. This demonstrates that atomic ratio cannot be used alone to study the humification process due to the significant impact of the original plant composition and peat formation conditions.

DISCUSSION

Studies of living organic material transformation (humification) is of utmost importance for better understanding of carbon biogeochemical cycling. From this perspective studies are needed on peat properties in cores and identification and the links or correlations between peat age, decomposition degree, peat properties, peat botanical composition (describing and much depending on the bog development conditions, climatic and hydrological factors as well as changes of land use within the bog catchment). Important are also information on changes of peat properties that describe humification process at the molecular level, which can provide new understanding of chemical and biochemical processes behind the humification. We selected two ombrotrophic bogs of similar age, located spatially closely (Fig. 1), but with very much differing peat column stratigraphy (Figs. 2, 3) and peat column botanical composition as well as decomposition degree. The major part of the bog volume of Kroņu–Dzelves bog consists from relatively homoge-

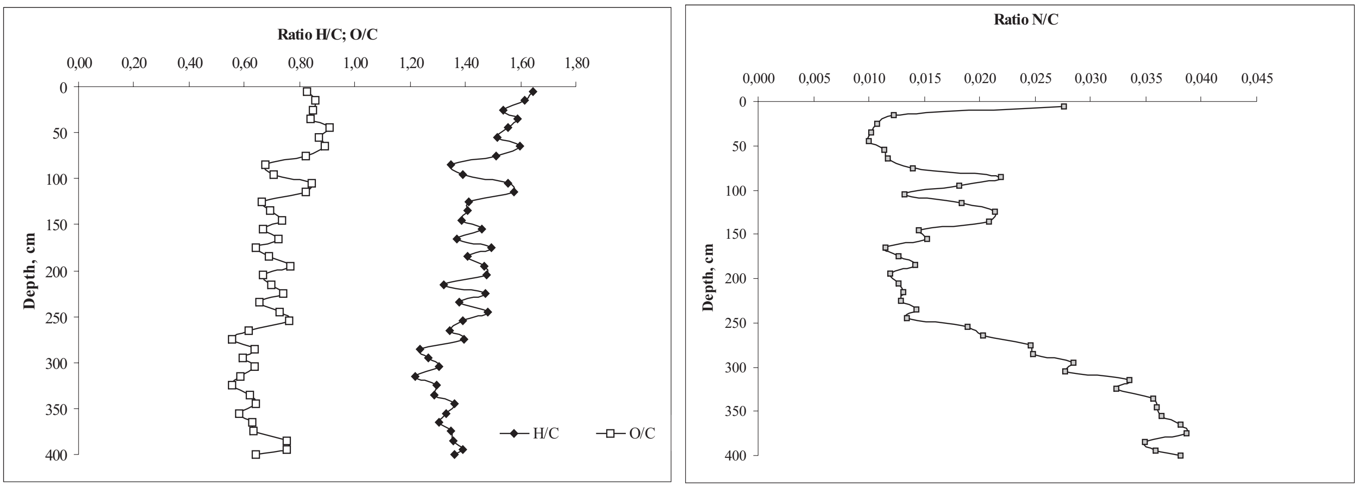

Fig. 5. Element ratio in peat from Eipurs bog.

neous sphagnum peat with a comparatively low decomposition degree, while the composition of the Eipurs bog peat is very much heterogeneous and reflects high variability of local bog development conditions.

Basic peat properties can be analysed using peat elemental (C, H, N, O, S) composition. The elemental composition of peat in the Eipurs bog is comparatively variable and reflects the changes in the peat decomposition degree and peat type. C concentration in the peat increases starting from a depth of 1 m and reaches a level of 53% at about 3 m depth and then again decreases. H concentrations demonstrate significantly higher variability. N concentrations are higher in the upper and lower horizons of the bog and demonstrate increased values coinciding with the changes in the peat composition and formation conditions, which might be associated with changes in the peat botanical composition and decomposition degree. S concentrations are significantly lower just in few upper centimetres of the peat bog, but comparatively stable along the peat column. The elemental composition (Table 1) of Kroņu Dzelves bog is very much different and largely reflects the peat column composition: the C content in the upper layers is much lower (~ 45%) and comparatively uniform up to a depth of 3.25 m, but then rapidly increases reaching 55% for highly decomposed peat.

The elemental ratio is much more informative than elemental composition of peat is (Table 1, Fig. 5. C/N ratio can be considered as an 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. Decreasing C/N ratios indicate increasing peat decomposition (due microbial decay) and vice versa. The H/C ratio is an index of molecular complexity (but at the same time of aromaticity) and ranges from 1.6 to 1.2 (Anderson and Hepburn, 1987). It is relatively constant with depth; below 50 cm, it decreases. On the other hand, O/C ratio is considered an indicator of carbohydrate and carboxylic contents and can be directly related to aromatisation of the organic matter forming peat (Anderson and Hepburn, 1987). O/C ratio decreases with depth, however in layers with higher decomposition degree also values of this indicator are high.

Elemental analysis data can be used also for calculation of hydrogen deficiency ϕ and degree of oxidation ω indexes (Fong and Mohamed, 2007). However in this case these indexes have only weak relation with the high variability of peat properties in Eipurs bog peat core and peat hydrogen deficiency ϕ and degree of oxidation ω can be considered as relatively homogeneous (Fig. 6).

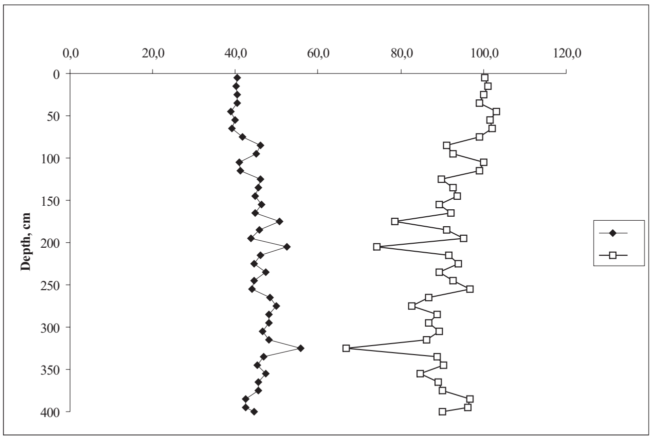

Fig. 6. Index of hydrogen deficiency ϕ and degree of oxidation ω versus depth in peat from Eipurs bog.

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 low amounts 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 the present study, the variability of the E_4/E_6 ratios in the peat profile of the Eipurs bog was relatively high (Fig. 7) and can be related to the transformation processes of organic matter within peat profiles.

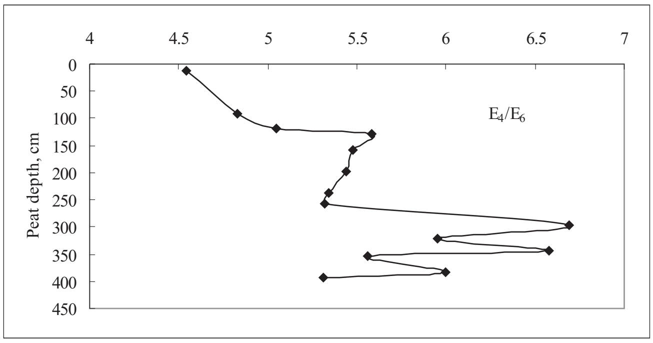

Fig. 7. Sectral absorption ratio E_4/E_6 versus depth in peat from Eipurs bog.

Absorption at 540 nm in the UV-Vis spectra of peat alkaline extracts can be used as an simple indicator of humification process as has been suggested and recently improved by Borgmark (2005a). This humification index demonstrates the expected differences (Fig. 8) when used for description of Kroņu–Dzelves and Eipurs bogs and the changes can be associated both with the peat decomposition degree and with the differences in peat composition.

In order to provide reliable and quantity information about the diagenesis of peat, we carried out further studies of the dependence of the peat humification indicators (humification indexes) on the peat decomposition (correspondingly peat age, depth and decomposition degree (Figs. 9, 10).

As it can be seen from Figure 9, the peat decomposition is very well and statistically significantly correlated with the humification index according to Borgmark (2005b) and humification degree, an index suggested by Šīre *et al.* (2008). Correlation between fluorescence intensity ratios fluorescence intensities (I_{380}/I_{330} and I $_{460}/I_{380}$) is much poorer. Both of these humification indexes describe basic changes in the peat properties and are well correlated with the elemental ratios of the peat in the peat cores, thus depicting changes of peat organic materials during humification of living organic matter, and can be suggested for characterisation of humification process also in other environments.

The conclusions are that studies of living organic matter humification are essential for understanding of the carbon biogeochemical cycle. From this perspective, the study of peat properties of peat cores can help to identify the links between peat age, decomposition degree, peat properties, peat botanical composition and peat properties An important tool in carbon biogeochemical cycle studies can be humification indicators, which might provide new understanding of chemical and biochemical processes behind the humification.

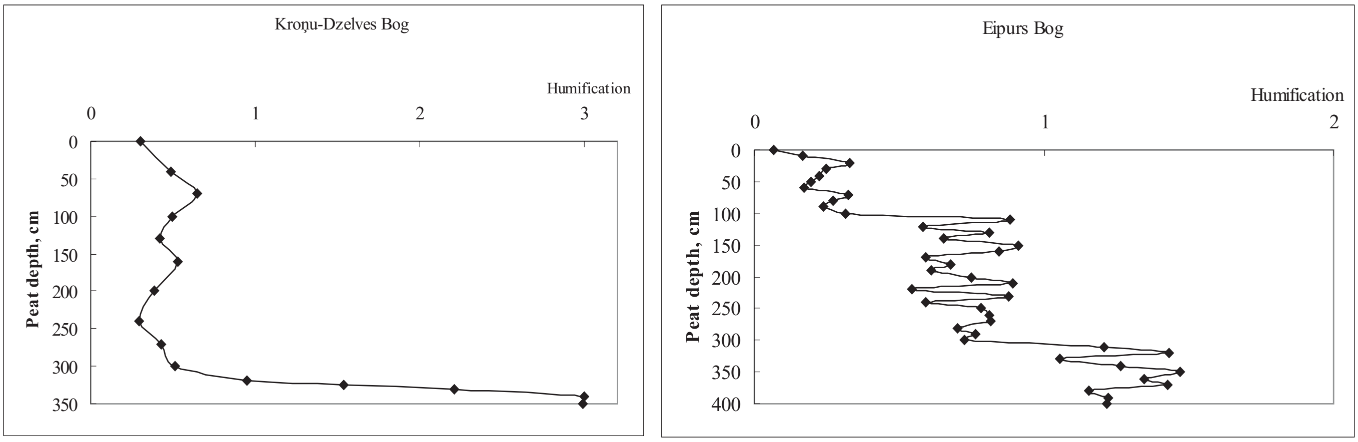

Fig. 8. Changes of the Humification Index according to Borgmark (2005a) (adsorption of peat extract at 540 nm) versus depth in peat from Eipurs bog.

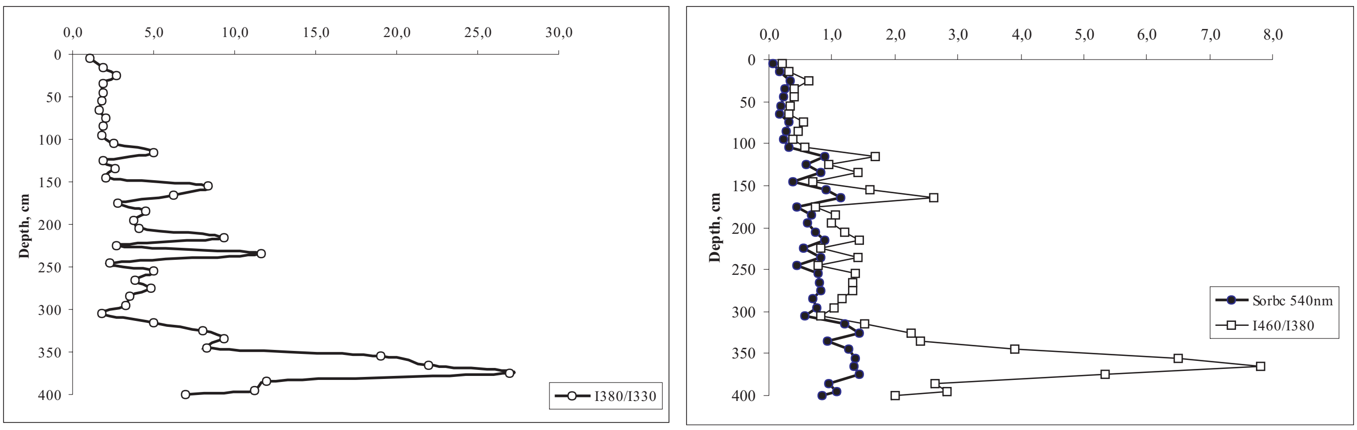

Fig. 9. Changes of the Humification Index according to Borgmark (2005a) (adsorption of peat extract at 540 nm) and ratios of fluorescence indexes (I $_{380}/I_{330}$ and I $_{460}/I_{380}$) versus depth in peat from Eipurs bog.

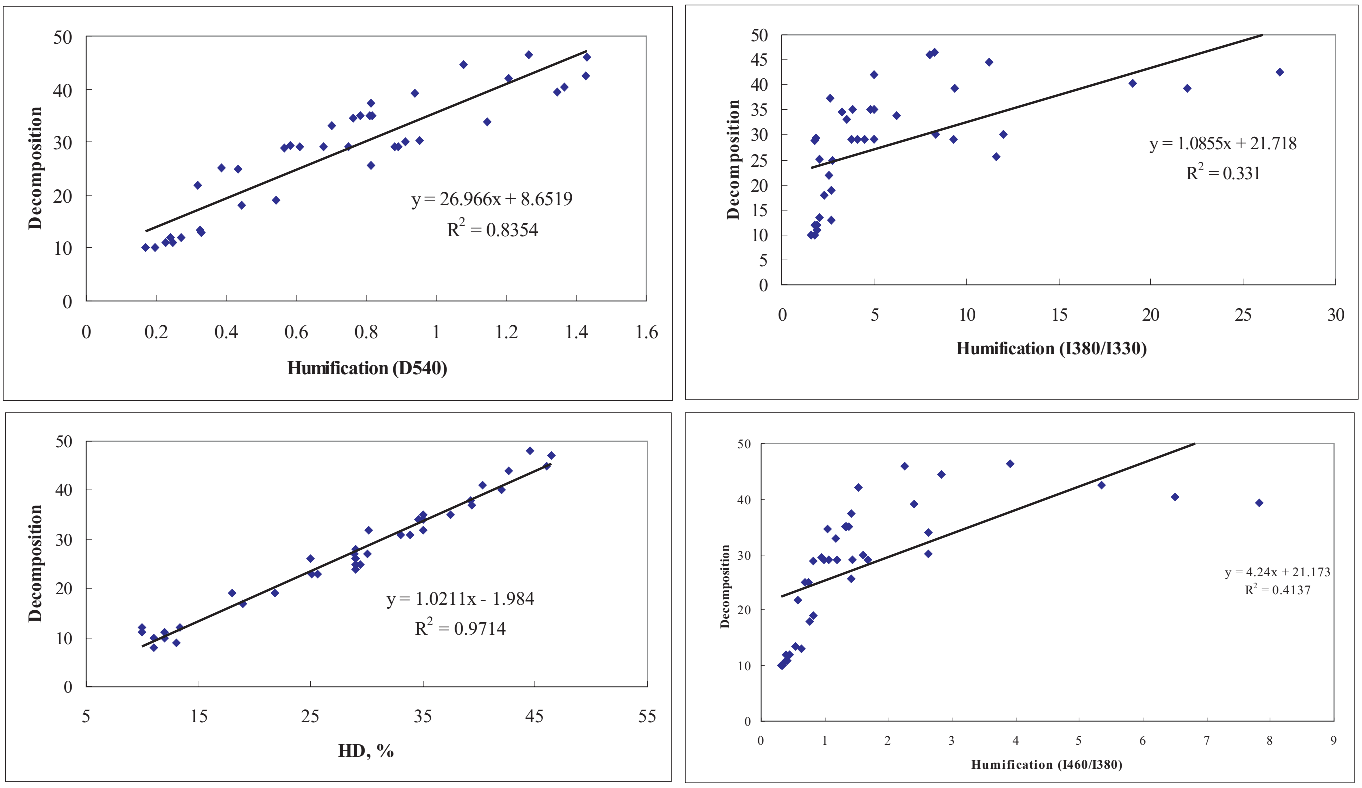

Fig. 10. Correlation between peat decomposition (%, Eipurs and Kroņu–Dzelves bog) and humification indexes (Humification Index according to Borgmark D540, Humification degree HD, and fluorescence intensity ratios I $_{380}$/I$_{330}$ and I $_{460}$/I$_{380}$)

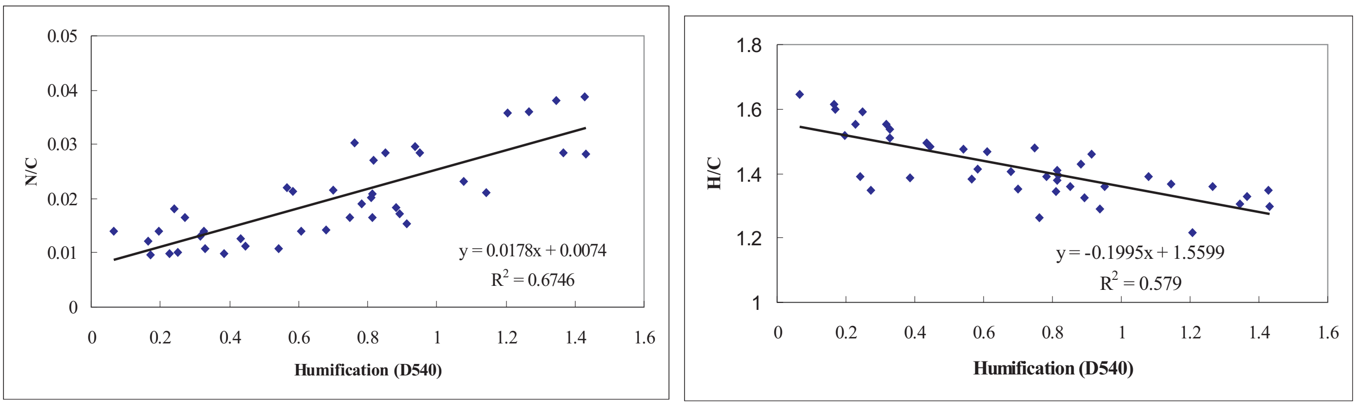

Fig. 11. Correlation between Humification Index (Eipurs and Kroņu–Dzelves bog) according to Borgmark (D540) and elemental ratio of peat N/C, H/C

The transformation process can be described using multi-proxy analysis of peat elemental composition, elemental ratios and spectral characterization of the peat organic matter and peat alkaline extracts. This approach supports not only better understanding of the peat properties but also their relation to both peat decomposition processes and original living organic matter. Multiproxy study of peat properties supports development of peat humification indicators.

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KŪDRAS HUMIFIKĀCIJAS RAKSTURA ATKARĪBA NO TĀS ĪPAŠĪBĀM DIVU AUGSTO PURVU KŪDRAS KOLONNAS ANALĪZES PIEMĒRĀ

Oglekļa bioģeoķīmiskās aprites cikla ietvaros notiekošo procesu izpētei svarīgi ir izprast dzīvās organiskās vielas pārvērtību raksturu, notiekot tās sadalīšanās – humifikācijas procesiem. Šī darba mērķis ir pētīt kūdras īpašības tās kolonnā atšķirīgas uzbūves augstā tipa purvos atkarībā no humifikācijas procesu rakstura, kā arī attīstīt risinājumus humifikācijas procesa raksturošanai. Pētījumā pierādīts, ka kūdras elementsastāva un īpašību analīze ļauj atsegt kopsakarības starp kūdras humifikācijas procesiem, kūdru veidojošo augu sastāvu un izstrādāt humifikācijas indeksus kūdras īpašību raksturošanai. Ieteikts humifikācijas pakāpes noteikšanai izmantot kopējās organiskās vielas kūdrā un humifikācijas gaitā veidoto humusvielu attiecību, kā arī kūdras sārmaina ekstrakta sorbcijas vērtību pie 540 nm.