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HUMIC ACID PROPERTIES IN THREE DIFFERENT PEAT PROFILES

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SUMMARY

The similarity in the structure and properties of humic substances from peat column suggests the importance of intensity of biological transformation of organic matter on their structure. Comparative and complex characterization of peat humic acids (HAs) isolated from 3 different peat profiles in Latvia was done. Elemental and functional analysis of the isolated HAs was done, their acidity, hydrophobicity and spectral characterization estimated. Comparatively, the studied peat humic acids are at the start of the transformation process of living organic matter. Results of research shows degradation of unstable compounds (polysaccharides and others) and forming more stable compounds - increasing decomposition degree of peat, increase of HAs acidity and aromaticity.

KEYWORDS: peat, humic acids, spectral properties

INTRODUCTION

Peat composition is subjected to miscellaneous impacts: changes of climate and vegetation, geological impacts - like hydrological regime, surficial mass movements, seasonality, decomposing of organic material. Analysis of variation of peat composition and humic substances within peat profiles can give information on the character of transformation of organic matter, important for carbon biogeochemical cycling, but also on impacts of climate change and human activities (Zaccone, 2007).

The character of transformation of living organic matter is a very complex object of study, considering the high variability of environmental conditions under which living organic matter decay, slow pace of humification reactions and large number and structural differences of the organic molecules composing living organic matter. It can be supposed that 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 a relatively homogeneous and stable environment – bogs.

Humic substances are the most widely found naturally occurring organic substances and they may be described as a general category of naturally occurring, biogenic, heterogeneous organic substances that can be characterised of high molecular weight and refractory. They consists of several groups of substances that depending on their solubility can be grouped as: humin is the fraction of humic substances that is not soluble in water at any pH; humic acid (HA) is the fraction of humic substances that is not soluble in water under acidic conditions (below pH 2), but becomes soluble at greater pH; fulvic acid is the fraction of humic substances that is soluble under all pH conditions (Tan 2003).

The aim of the present paper is to analyze the properties of peat HAs isolated from peat profiles with different vegetation, humification degree and age.

MATERIALS AND METHODS

From profiles of 3 bogs peat samples were collected and after peat dating (^{14}C) and characterization, humic acids were isolated. The analysis of peat botanical composition was performed microscopically decomposition degree was determined. HAs were extracted and purified using procedures recommended by the International Humic Substances Society (Tan, 2005).

Elemental analysis (C, H, N, S and O) was carried out using an Elemental Analyzer Model EA-1108 and the found values were normalized in respect to ash content.
FTIR spectra were collected using Spectrum BX (Perkin Elmer) spectrophotometer in KBr pellets.

UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermo electron Co) spectrophotometer in a 1-cm quartz cuvette. The ratio E_4/E_6 (Chen et al. 1977): ratio of absorbance at 465 and 665 nm has been determined for the solution of 5 mg of the humic acid in 200 ml of 0.05 N $NaHCO_3$.

An automatic titrator TitroLine easy (Schott-Geräte GmbH) was used to measure carboxylic and phenolic acidity of each HA. The known Ca-acetate method (Tan, 2005), based on the formation of acetic acid, was used for determination of the total amount of carboxylic groups. HA (20 mg) were weight into 100 ml Erlenmeyer flask and under N_2 10 ml of the 0.2 N calcium acetate solution were added. Samples were potentiometrically titrated to pH 9.0 with 0.1 N NaOH.
To estimate total acidity (Tan, 2005), the known amount of humic acid, about 20 mg, were dispersed in 10 ml 0.1 M $Ba(OH)_2$ solution, which was then shaken overnight under N_2, filtered and washed with water. The filtrate together with washing solution were potentiometrically titrated with 0.1 M HCl down to pH 8.4 under N_2 flow.

RESULTS AND DISCUSSION

This study analysed the peat humification process and development of peat humic acids in the peat profiles from three heterogeneous ombrotrophic bogs in Latvia.
The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate differences and similarities in the development and peat properties of the studied bogs. Dzelve

Bog has been formed due to paludification of sandy ground as result of groundwater level increase and wet conditions during the small depression after the Ice Age. A raised bog cotton grass peat layer covers the sandy bottom, overlaid 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 %. The botanical composition of most of the bog is relatively heterogeneous: *Sphagnum fuscum* (60-75%), *Eriophorum vaginatum* (10-15%), *Sphagnum rubellum* (10-15%) and dwarf shrubs (10-15%). The botanical composition of Eipurs Bog is completely different, although it is of a similar origin. The lowest part of Eipurs Bog is formed by fen wood-grass peat, *Hypnum* and sedge-*Hypnum* peat, and these layers are covered by transition type wood peat. The upper part is represented by a 3.45 m thick layer of 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. It can be explained by accumulation, possibly during the Second Climatic Optimum. Although these bogs are located comparatively close to each other, their local conditions for peat formation have been different. In the same time, third bog - Dizpurvs differ from previous bogs and located in links near the Baltic Sea. In Dizpurs bog sedge-*Hypnum* peat layer covers the sandy bottom, overlaid by *Hypnum*-sedge and sedge peat. The upper part of peat section is represented by a 2.0 m thick *Sphagnum*-cotton grass and cotton grass peat layer with a decomposition level 15 to 30 %. The botanical composition of the bog is relatively heterogeneous, but sedge is come across all profile. Presence of sedge and wood in peat profiles demonstrates higher values of decomposition degree. This effect can explain due to microbial activity and intensive decay processes of these peat layers.

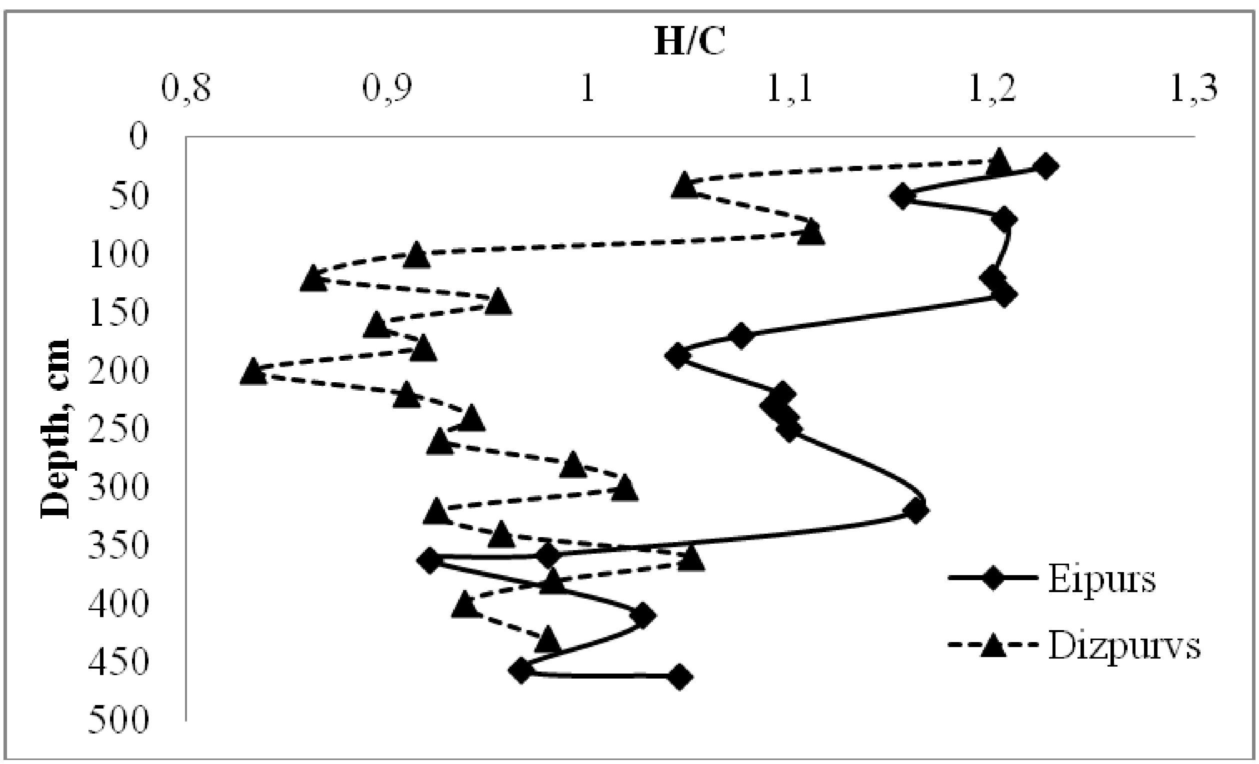

Fig. 1. Element ratio (H/C) in humic acids isolated from Eipurs and Dizpurvs.

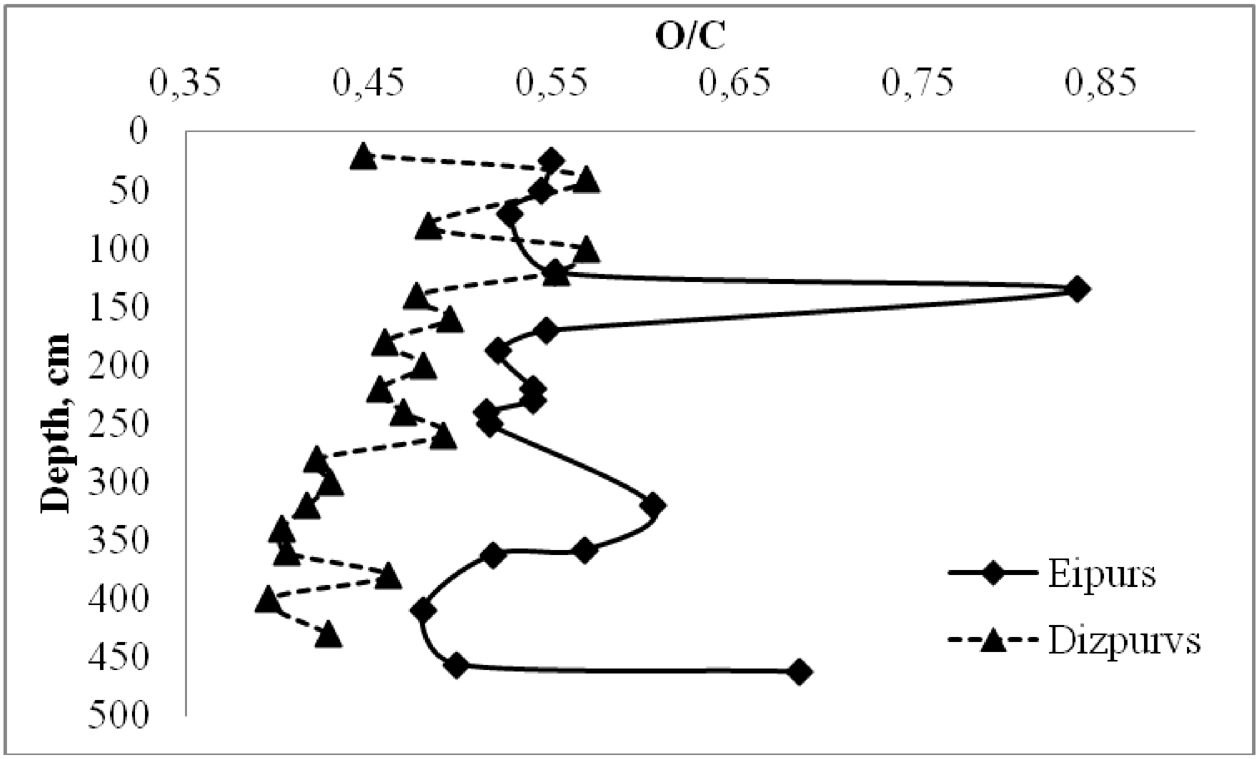

Fig. 2. Element ratio (O/C) in humic acids isolated from Eipurs and Dizpurvs.

There was significant variation in elemental composition of HAs within the peat profiles. Depending on the bog and the intervals of changes, the elemental compositions of the studied peat HAs were highly variable: C was 48–60%; H was 3.9–5.7%, N was 0.8–3.2%, S was 0.5–1.5% and ash was 0.1–1.2%. The O content, with range 32–49%, was determined by mass balance. In general, C concentrations increased with depth, but H and N concentrations decreased with depth, but S concentration was very variable down the profile.
The same tendency there was in variation of atomic ratios of HAs representing humification process, indicating the degree of maturity and intensity of degradation processes such as dehydrogenation (reduction of H/C ratio) (Fig. 1), decarboxylation (reduction of O/C ratio) (Fig. 2). Different results of dehydrogenation shows bottom parts of Dizpurvs and Eipurs peat profiles, indicating importance of peat lithology. Peat profile layers formed from fen peat shows stable or even a little increase of H/C ratio and thickness of these layers depend on genesis of the bog (1.70 m – Dizpurvs, 1.2 m – Eipurs).

Changes in concentrations of acidic functional groups in peat humic acids illustrate the character of peat humic matter diagenesis: relatively rapid increase of concentration of carboxylic functional groups due to microbial decay of living organic matter and in general increasing concentrations of it at the same time reflecting the composition of precursor biological material. On the other hand, the humification is characterized with decrease of phenolic acidity in structure of humic acids.

The slope of the adsorption curves as measured by the ratios of UV absorbancy at 465 and 665 nm, have been suggested to be inversely related to the condensation of aromatic groups (aromaticity), and also to particle size and molecular weight (Chen *et al.* 1977). Higher E_4/E_6 ratios are characteristic for humic substances with higher degree of condensed aromatic systems and smaller particle sizes or molecular weights measured (Chen *et al.* 1977). In studied bogs E_4/E_6 ratio increase with depth and decomposition degree, but there is some exceptions, in Dzelve and Dizpurvs bog. In Dzelve bog decomposition degree is inversely related to depth, only bottom layers of bog shows the same character of increasing of aromaticity. It can be explained by very high accumulation ratio in beginning of subatlantic (3000 - 2000 yr. ago) period. Peat formed in that time causes very low concentration of carboxylic groups of HA's. In Dizpurvs peat profile E_4/E_6 ratio is relative stable, without significant changes and it's related to homogenous decomposition degree. Presence of grass in peat profile reflecting with higher decomposition degree and concentration of carboxylic groups, these layers differ in distribution of E_4/E_6 ratio.

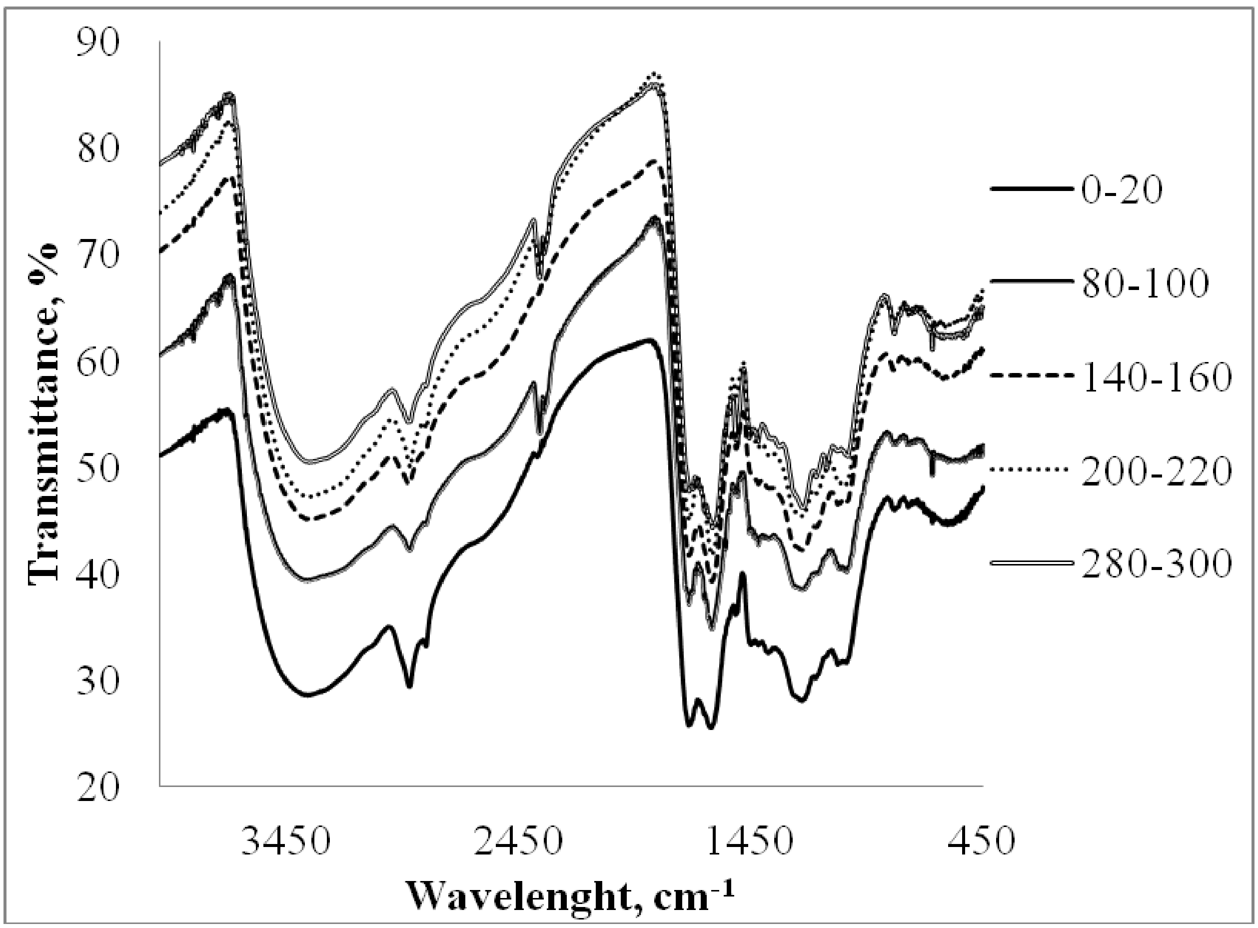

Fig. 3. FT-IR spectra of humic acids isolated form bog Dizpurvs.

The FT-IR spectra (Fig. 3) of the peat humic acids examined 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 origin (depth and age) of the sample. FT-IR spectra shows decreasing of polysaccharides (1040 cm^{-1}), phenol OH groups (1080 cm^{-1}) and carboxylic groups (1720 cm^{-1}) (Cocozza et. al., 2003), but in the same time CH_2 and CH_3 groups are relative stable. In peat forming biota during humification process degrade unstable compounds forming more stable ones (increase aromaticity, but decrease aliphatic compounds and polysaccharides).

Amongst the main objectives of the study was the identification of the dependence of the humic acid properties on the composition of original living matter in the peat, especially considering high variability of peat composition in the studied bogs. Despite some correlation between peat botanical composition and properties to exist, in general the similarities are much more expressed, thus indicating the significance of microbial decay processes on the properties of humic material.

CONCLUSIONS

Peat genesis, age and humification processes have influence on HS properties. During decomposing of peat, significantly varies intensity of humification process – it is slower in anaerobic layers of bog, but more rapid in layers with presence of higher vegetation residues. Characteristic features of studied bogs can be associated with climatic changes in past too. Use of peat profiles of 3 different bogs, allow us to perceive importance and probably resemble process of humification.

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