Differential Thermal Analysis of Peat and Peat Humic Acids in Relation to Their Origin

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We studied the thermal decomposition of peat and peat humic acids of two peat profiles from ombrotrophic bogs in Latvia in relation to their origin. The results of differential thermal analysis show that the character of peat decomposition significantly depends on the composition, age, and origin of peat. Studies of parameters of thermal decomposition help to identify the differences between peat and the corresponding humic acids, as well as links between the peat age, decomposition degree, and character of the decomposition process, thus ascertaining maturity of organic material. Hence, thermal analysis methods can be used for identification of the origin of peat and peat humic acids.

Keywords: peat, humic substances, TG, DTA.

INTRODUCTION

Thermal analysis methods are powerful analytical tools to study the properties of organic matter, and thermogravimetry (TG) and differential thermal analysis and gravimetry (DTA and DTG) have been used to study and compare the properties of peat and soil organic matter (Almendros et al., 1982; Montecchio et al., 2006). During the decomposition process of living organic matter, at first, degradation of more labile structures takes place, but at later stages processes that are similar to coalification processes, pyrolitic decomposition dominate (Esteves and Duarte, 1999). The characteristics of the thermal decomposition process in the case of peat profile studies are related to the stage in which the transformation of organic matter takes place and thus can reveal the first stages of diagenesis of fossil carbon-containing deposits – lignite, brown coal, coal, etc (Gonet and Cieslewicz, 1998). To better understand diagenesis of fossil fuel deposits, comparative studies of the thermal decomposition behavior of peat and corresponding humic substances can be useful (Tikhova et al., 1998). A study of the thermal degradation behavior of model compounds allows to correlate the decomposition process of natural materials with well-identified model compounds (Kucerik, 2006). Thermal analysis of humic substances can help to identify their structural elements and the stage in the transformation process of living organic matter (Leinweber and Schulten, 1992). However, a study of synchronous changes in the thermal decomposition character of material from peat profiles and humic substances isolated from the corresponding layers has not been done until now.

The aim of this study was to analyse the character of thermal decomposition of peat and peat humic acids of two peat profiles from ombrotrophic bogs in Latvia in relation to their origin.

MATERIALS AND METHODS

Thermal analysis has been done using peat isolated from the profiles of two ombrotrophic bogs located in the central part of Latvia. The properties and location of these bogs, their development process, sampling and analytical methods used for bog characterization are described in detail by Kušķe and others (2009), Silamiķele and others (2009) in this volume.

Thermal analyses were performed with SII EXSTAR 6300 TG/DTA derivatograph using 20 mg of peat or humic acids within a temperature range of 25–550 °C with the heating rate of 10 °C per min. The recorded curves were: thermogravimetric (TG), differential thermogravimetric (DTG), and differential thermoanalytic (DTA). The area under the DTA curve is proportional to the amount of heat released in the process of exothermic oxidation of organic matter. Weight losses were calculated from the TG curves.

RESULTS AND DISCUSSION

In this study, thermal analysis was performed on peat and humic acids isolated from peat profiles of two ombrotrophic bogs. Despite the relative similarity of the genetical pattern and location of the bogs, they differ much in the composition and properties of peat as well as in the homogeneity of the peat profiles (Kušķe et al., 2009, Silamiķele et al., 2009).

The first most important process during the thermal decomposition of peat is the loss of hygroscopic moisture happening around 100 °C and represented in the curves by a slight weight loss and a slight endothermic process (Fig. 1, 2). Although in the upper layer of the peat profile the decomposition degree and the TGA curves significantly differ, these differences depend more on sample pre-treatment rather than on the way how the hygroscopic moisture is fixed into the structure of peat and humic substances. Some similarities between humic acids and peat can be observed, however, and we can state that the amount (the intensity of signal related to elimination) of hygroscopically bound water in humic acids is higher than in peat from the corresponding layer. It has been suggested that the extent and intensity of this exothermic reaction is inversely related to the degree of humification of the corresponding samples (Leinweber and Schulten, 1992).

Although not very markedly, our study confirms this suggestion, as we can see in the comparison of the decomposition pattern of humic acids from the upper layer in the Dzelve–Kronis bog (with a very low decomposition degree) with humic acids isolated form peat with a higher decomposition degree.

At higher temperatures (up to 300 °C) destruction takes place of the less condensed components, such as the polysaccharides or the more thermolabile components of peat organic matter or humic acids. Finally, at about 500 °C, the thermal effects are attributed to the pyrolysis of the more condensed materials, such as the aromatic components of lignin and the core structures of humic materials.

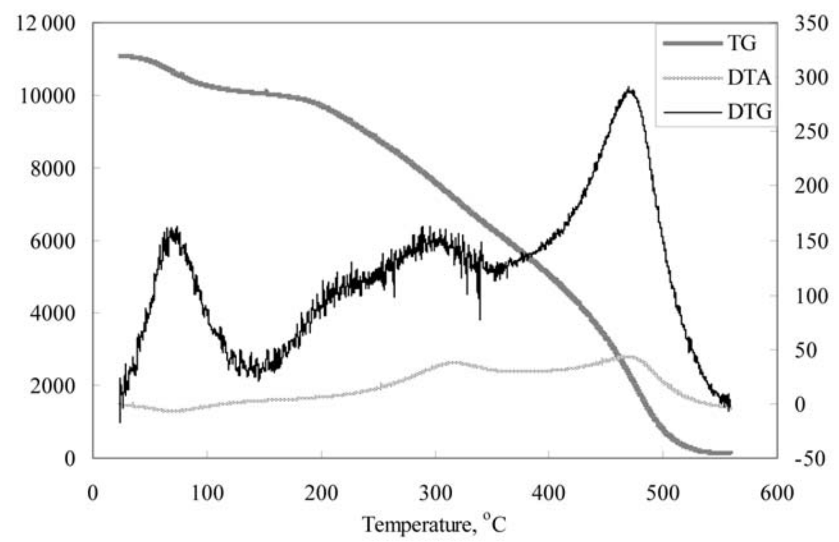

Figure 1. **TG, DTA, DTG curves of peat samples taken from the Eipurs Bog, depth 0.00–0.25 cm**

The studied peats of the profile have a different degree of decomposition and botanical composition, as described previously. The changes in the intensity of released water upon heating are not significant throughout the profile and possibly can be explained not only by the way of bonding of hygroscopical water, but also by differences in the peat drying conditions.

The intensity of the second thermal effect (280–330 °C) increases with depth in peat from the Eipurs Bog peat profile, indicating presence of polysaccharides or more thermolabile components of peat organic matter or humic acids. In the older (7700 ^{14}C years) peat samples, a shift of temperatures at which decomposition happens can be observed, and a new peak appears, indicating a different character of the processes of peat decomposition evidently affected by the different peat botanical composition in the deeper layers of the peat sample. In peat from the Dzelve-Kronis Bog consisting predominantly from Sphagnum moss peat, the changes of peat decomposition peak around 300 °C are not so expressed but at the same time more uniform. Finally, the third peak in the DTA spectra, characterizing thermal effects attributed to the pyrolysis of the more condensed materials, such as aromatic components in the core structures of humic materials, demonstrate presence of relatively homogeneous structures (a comparatively sharp peak in the case of the Dzelve-Kronis Bog peat and much less expressed intensity in peat from the Eipurs Bog, especially from the deeper, more decomposed peat layers).

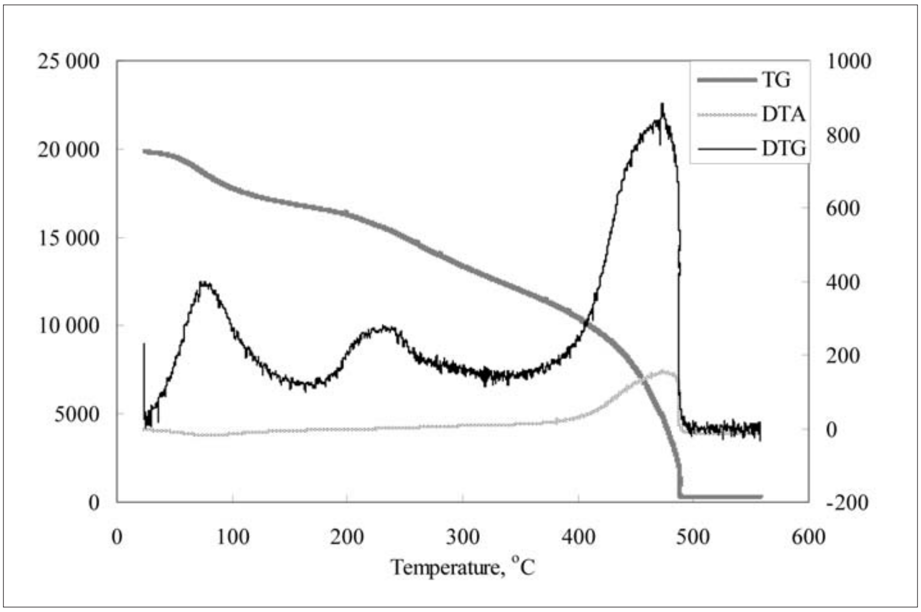

Figure 2. **TG, DTA, DTG curves of peat samples taken from the Eipurs Bog, depth 4.56–4.62 m**

The character of thermal analysis of humic acids isolated from peat profiles significantly differs from the character of peat decomposition. The first peak indicating loss of hygroscopically bound water does not demonstrate significant changes along the peat profile, but the second peak characterizing the character of thermal decomposition of more labile structures in humic acids is at first much lower for peat humic acids than for peat, but its intensity decreases with increasing peat decomposition degree. The most pronounced changes are evident in the decomposition character at 450–500 °C. The signal intensity in peat humic acids at higher temperatures is much higher than in peat. As far as decomposition at this interval of temperatures can be associated with decomposition of more condensed aromatic structures, we can conclude that such structures are significant

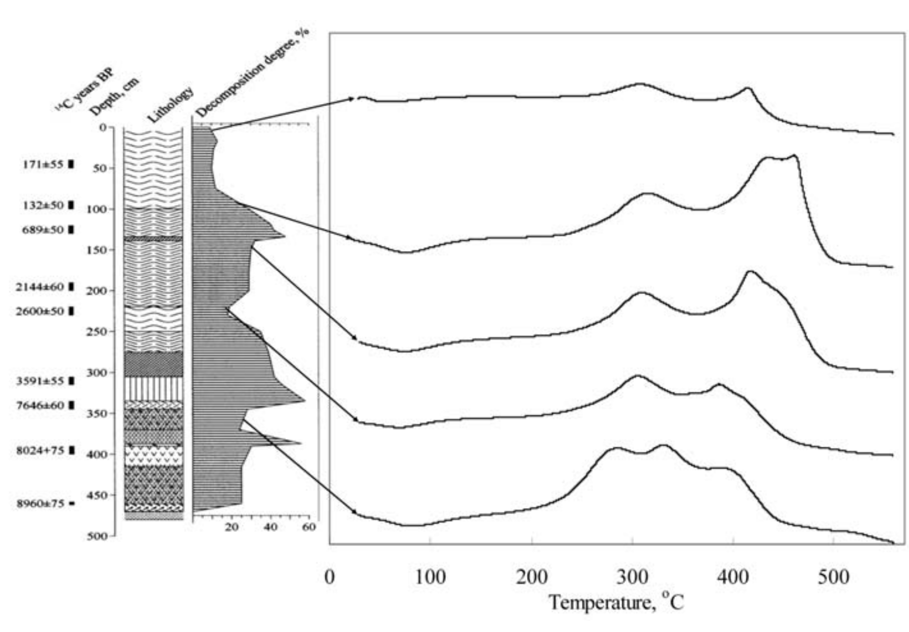

Figure 3. **Differential thermal analysis (DTA) curves of the Eipurs Bog peat profile**

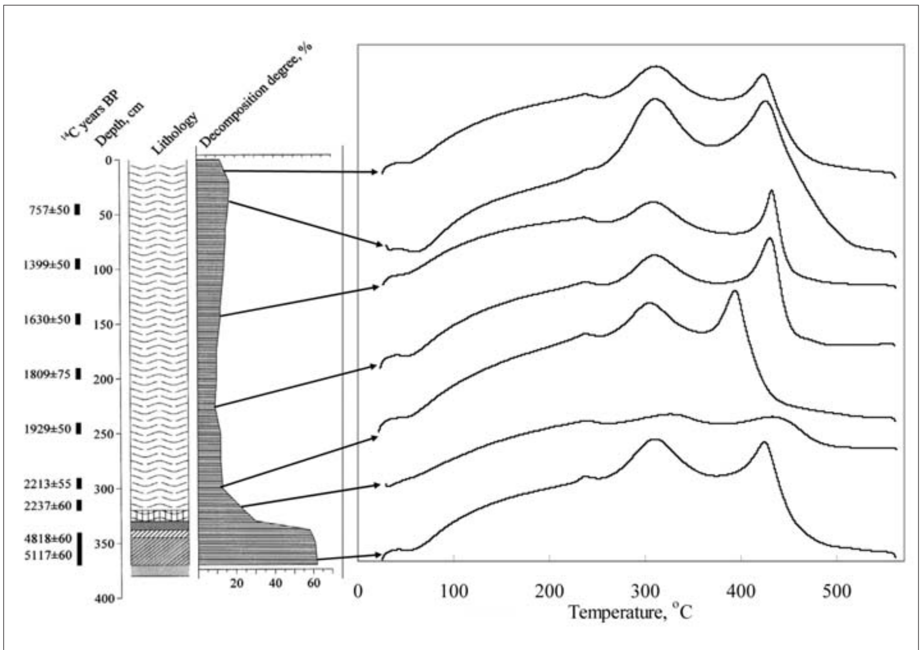

Figure 4. **Differential thermal analysis (DTA) curves of the Dzelve-Kronis Bog peat profile**

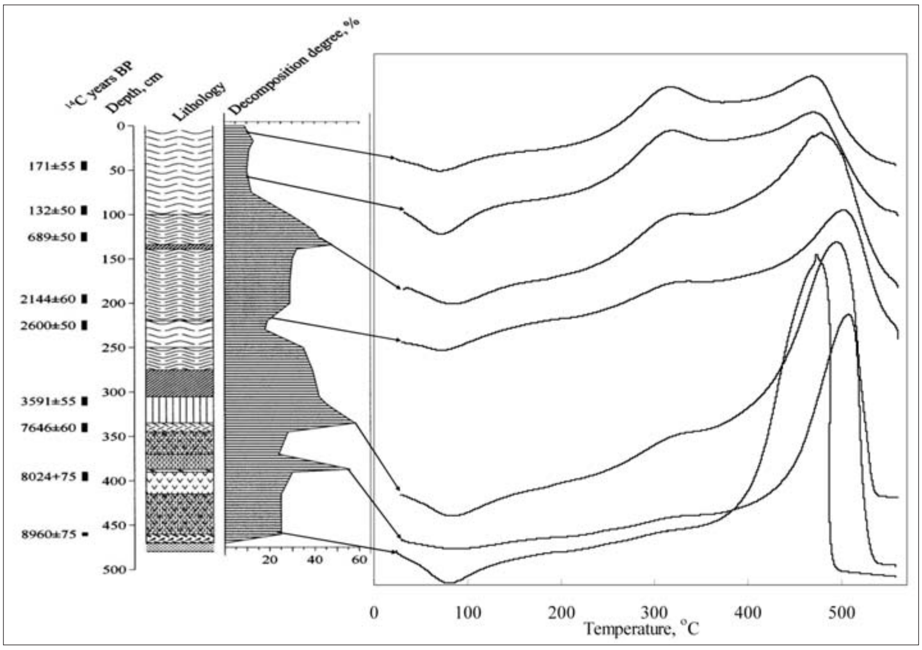

Figure 5. **Differential thermal analysis (DTA) curves of humic acids isolated from the Eipurs Bog peat profile**

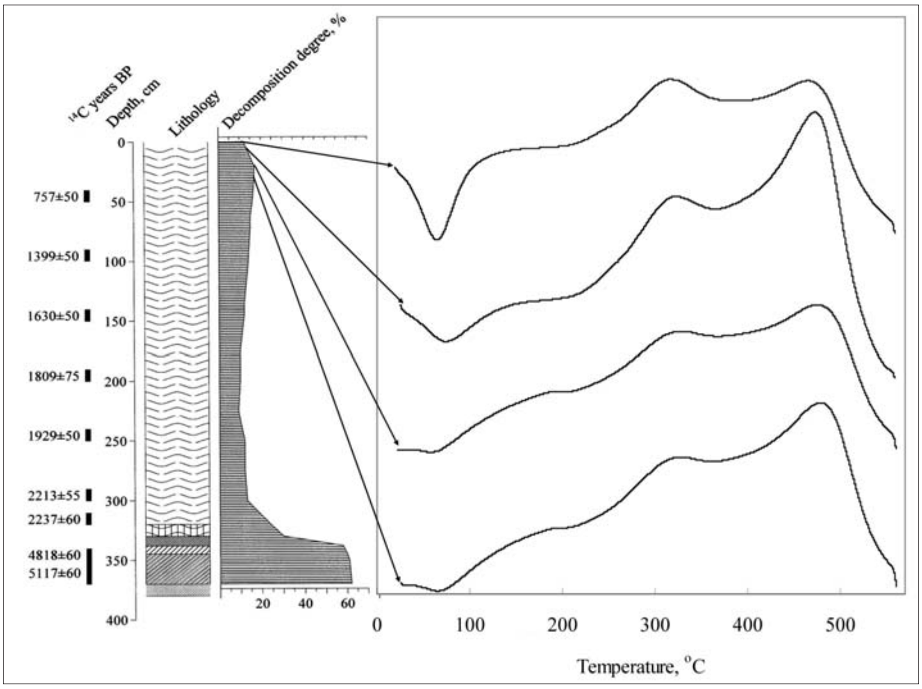

Figure 6. **Differential thermal analysis (DTA) curves of humic acids isolated from the Dzelve-Kronis Bog peat profile**

in the molecules of peat humic acids. Intensity of this signal (the area of the peak indicating weight loss at the corresponding temperature) is well correlated with the peat decomposition degree (Figure 7).

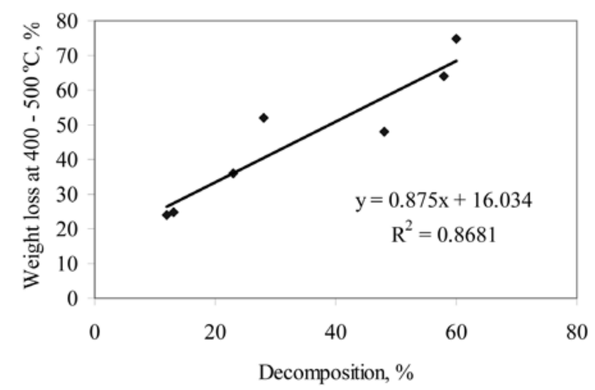

Figure 7. **Changes in the percentage of the weight loss at 400–500 °C in humic acids isolated from the Eipurs Bog peat profile depending on the peat decomposition degree**

CONCLUSIONS

Thermal analysis of peat profiles and corresponding humic acids allows to determine structural changes in the studied material and improve understanding of the diagenesis of peat deposits and corresponding humic materials.

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