

# Differential Thermal Analysis of Peat and Peat Humic Acids

Oskars Purmalis<sup>1</sup>, Dmitrijs Porsnovs<sup>2</sup>, Maris Klavins<sup>3</sup>,  
<sup>1-3</sup>University of Latvia, Faculty of Geography and Earth Sciences

**Abstract:** This article describes 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. 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 the parameters of thermal decomposition help to identify the differences between peat and the corresponding humic acids, as well as the links between the peat age, decomposition degree, and character of decomposition process, thus ascertaining maturity of organic material. Accordingly, thermal analysis methods can be used for identification of the origin of peat and peat humic acids. Thermal treatment of peat helps to accelerate the changes in the peat properties and thus significantly increase the oil sorption capacity. Thermally treated peat is much more hydrophobic and could be considered as a prospective sorbent for oil sorption.

**Keywords:** peat, humic substances, TG, DTA, oil sorbents

## I. INTRODUCTION

Thermal analysis is an efficient method 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 [1, 2]. During the decomposition process of living organic matter, at first, degradation of more labile structures takes place, but at later stages the processes that are similar to coalification processes, pyrolytic decomposition dominate [3]. The characteristics of the thermal decomposition process in the case of peat profile studies are related to the stage at 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 [4]. For a better understanding of fossil fuel diagenesis of key importance could be studies of the transformation products of living organic matter within peat – humic substances. To better understand diagenesis of fossil fuel deposits, comparative studies of the thermal decomposition behavior of peat and corresponding humic substances have been used [5, 6, 7]. Previous results of thermal analysis have shown the differences between the humic acid samples, depending on their origin in respect to their coalification rank and higher thermal stability of lignite humic acids than others [6, 7, 8]. A study of the thermal degradation behavior of model compounds allows to correlate the decomposition process of natural materials with well-identified model compounds [9]. Thermal analysis of humic substances can help to identify their structural elements and the stage in the transformation process of living organic matter [10]. It could be hypothesized that during thermal treatment

(heating) the processes naturally occurring during peat transformation take place and more labile structures are released, thus increasing peat and humic acid hydrophobicity. However, the correct relation of peat properties to its thermal decomposition character is not yet fully understood [1] and 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. Another important aspect of the peat and humic matter thermal treatment includes studies of their ability to absorb oil products.

The aim of this study was to analyze 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 as well as to look at the oil sorption capacities of thermally treated peat.

## II. EXPERIMENTAL

Thermal analysis has been done using peat isolated from the profiles of the 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 and peat characterization are described in detail by [11]. Humic acids from peat were extracted and purified using procedures recommended by the International Humic Substances Society [12].

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.

To increase oil sorption capacity, peat was treated with solutions of industrially manufactured HA in 0.1 molar NaOH, with concentrations: 1.5-100 g/l, then heated in a laboratory oven for 5 hours, at the temperature: 240-250 °C.

### *Oil sorption experiment*

4 ml (3.23 g) of crude oil and 0.25 g of peat sorbent were added into laboratory bottles (volume 100 ml) with 50 ml of MilliQ water. Samples were placed on a shaker and shaken at 120 rpm for 5 hours. Then the samples were filtered through filter paper. The resulting mass (peat with sorbed oil) was placed into laboratory bottles, treated with 20 ml of hexane and extracted on the rotary shaker for 30 minutes, then once again filtered through filter paper. The mass collected on the

filter was washed with 20 ml of hexane. Pooled filtrate was placed in the bottles with known mass and evaporated at room temperature to a constant weight. At the same time and in identical conditions, the evaporated samples of oil with known mass were dissolved in hexane. The mass content of non-volatile hydrocarbons in the oil was calculated using mass difference. The sorbed oil mass was calculated using derived factor.

### III. RESULTS AND DISCUSSION

In this study, thermal analysis was performed on the peat and humic acids isolated from peat profiles of two ombrotrophic bogs. Despite the relative similarity of the genetic 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 [13, 14].

As can be seen from Figures 1-4, thermal decomposition curves of the samples (both peat and peat humic acids) can be described as a five peak system, with well manifested exothermic effects at the following temperature intervals: ~ 100°C, 170 – 250°C, 250 – 340°C, 300-350°C, 380 – 420°C and 480 - 530°C regions. Such systems are typical for the materials with plant origin, they are independent of dilution and hence do not represent sporadic oxidation and incomplete combustion, but rather indicate a series of discrete chemical reactions [15].

According to [1], thermal decomposition of peat occurs as follows: at low temperature (about 100 °C) evaporation of hygroscopic moisture can be observed, this process is shown as a pronounced depression of a decomposition velocity on the DTG curve and as slight endothermic effect on the DTA curve (Figures 1-2). In the temperature interval around 300 °C decomposition of less condensed peat compounds (cellulose and other polysaccharides, external functional groups of humic matter, aliphatic compounds) takes place. As we can see, these processes are manifested as the first exothermic peak on a DTA curve, and as the second interval of depression of a decomposition velocity on a DTG curve. It is found that the area of the first exothermic peak is proportionally related to the content of slightly decomposed biomass in peat and respectively inversely related to the degree of humification [1, 16]. The second exothermic peak manifests a decomposition of more condensed compounds, for example aromatic structure of lignin and humic matter [16]. According to [17] results, high bitumen content in peat can also significantly increase the intensity of the second peak.

The first most important process during the thermal decomposition of peat humic acids 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 (Figures 1, 2). Although in the upper layer of the peat profile the decomposition degree and the TGA curves of peat humic acids significantly differ, these differences depend more on sample pretreatment rather than on the way how the hygroscopic moisture is fixed into the structure of humic acids. 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 [10].

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 bog (with a very low decomposition degree) with humic acids isolated from peat with a higher decomposition degree. Comparison of TG, DTA, DTG curves between peat and HAs isolated from peat in upper layer shows some similarities - HS forming most part of peat mass in upper layers or composition of HAs resembling their origin.

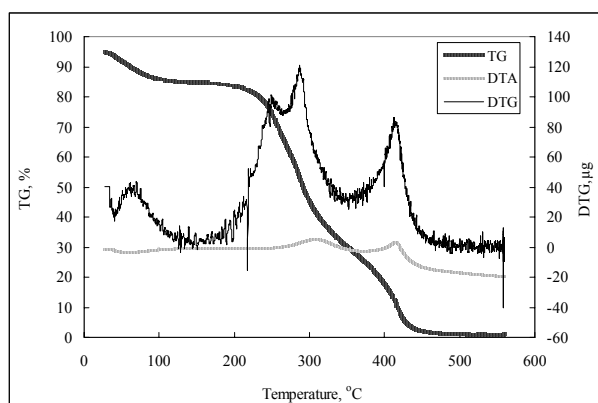


Fig.1. TG, DTA, DTG curves of peat samples taken from Eipurs Bog, depth 0.0 – 0.25 m

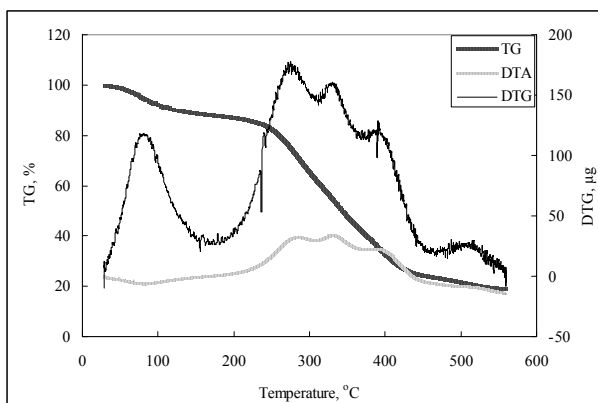


Fig.2. TG, DTA, DTG curves of peat samples taken from Eipurs Bog, depth 4.56 – 4.62 m

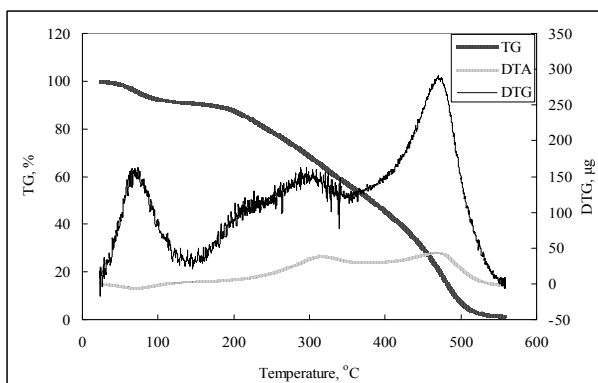


Fig.3. TG, DTA, DTG curves of peat humic acid isolated from Eipurs Bog, depth 0.0 – 0.25 m

HAs isolated from the bottom layers and HAs from the upper layers of peat profile differ in their origin. Comparison

of TG, DTA, and DTG curves between peat and HA shows that bottom layers forming more aromatic HAs and the difference shows that peat with HAs contains plenty of other compounds.

We can detect the first exothermic effect at 200 – 350 °C with the mass loss between 50 % (peat) and 20 % (HS). The peak shows results of thermal degradation of polysaccharides, decarboxylation of acidic groups and dehydration of hydroxylate aliphatic structures [6]. The second exothermic peak shows decomposition of more condensed compounds, for example aromatic structure of lignin and humic mater [16]. The second peak varies from 400 °C to 450 °C for peat and 400 °C to 550 °C for HA with mass loss – 18 % peat and 50 % HA.

The bottom layer of peat profile shows increase of aromaticity. This phenomenon we can interpret as presence of lignin structures in the bottom layers formed from fen peat and degradation of unstable compounds in Has structure.

The studied peats of the profile have a different degree of decomposition and botanical composition, as described above. The changes in the intensity of released water upon heating are not significant throughout the profile and possibly can be

explained not only by bonding of hygroscopical water, but also by the differences in peat drying conditions.

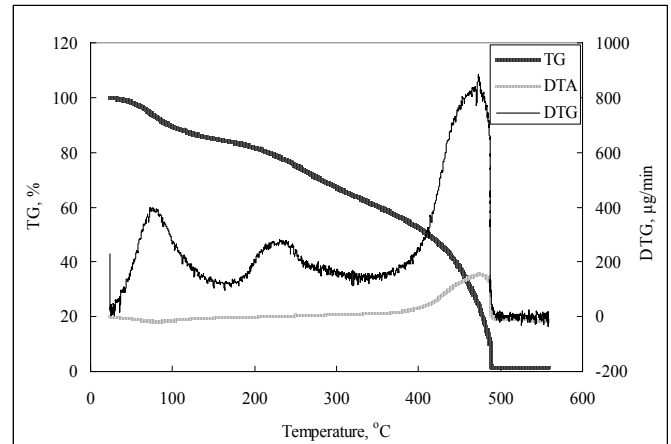


Fig.4. TG, DTA, DTG curves of peat humic acid isolated from Eipurs Bog, depth 4.56 – 4.62 m

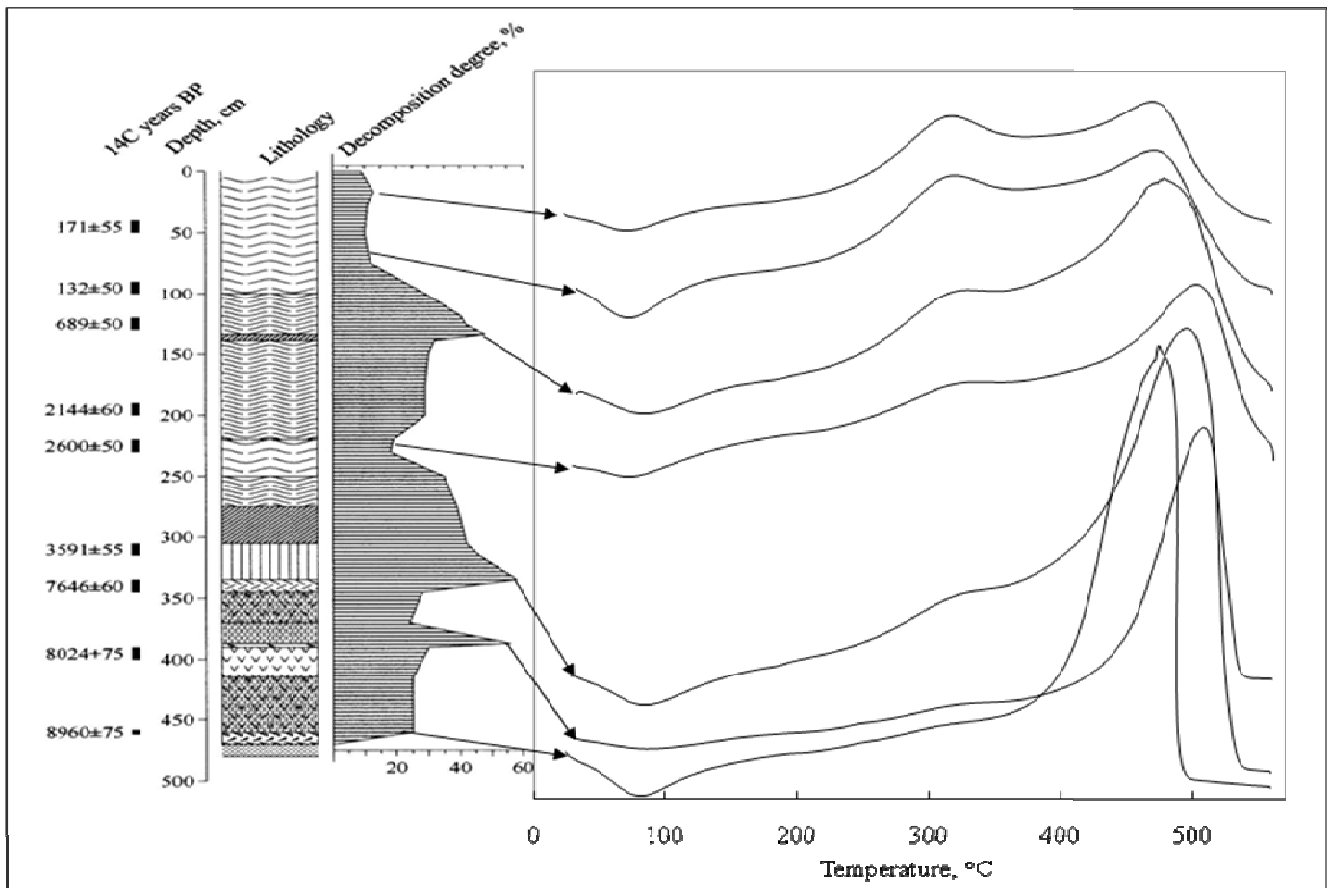


Fig.5. Differential thermal analysis (DTA) curves of humic acids isolated from the Eipurs Bog peat profile

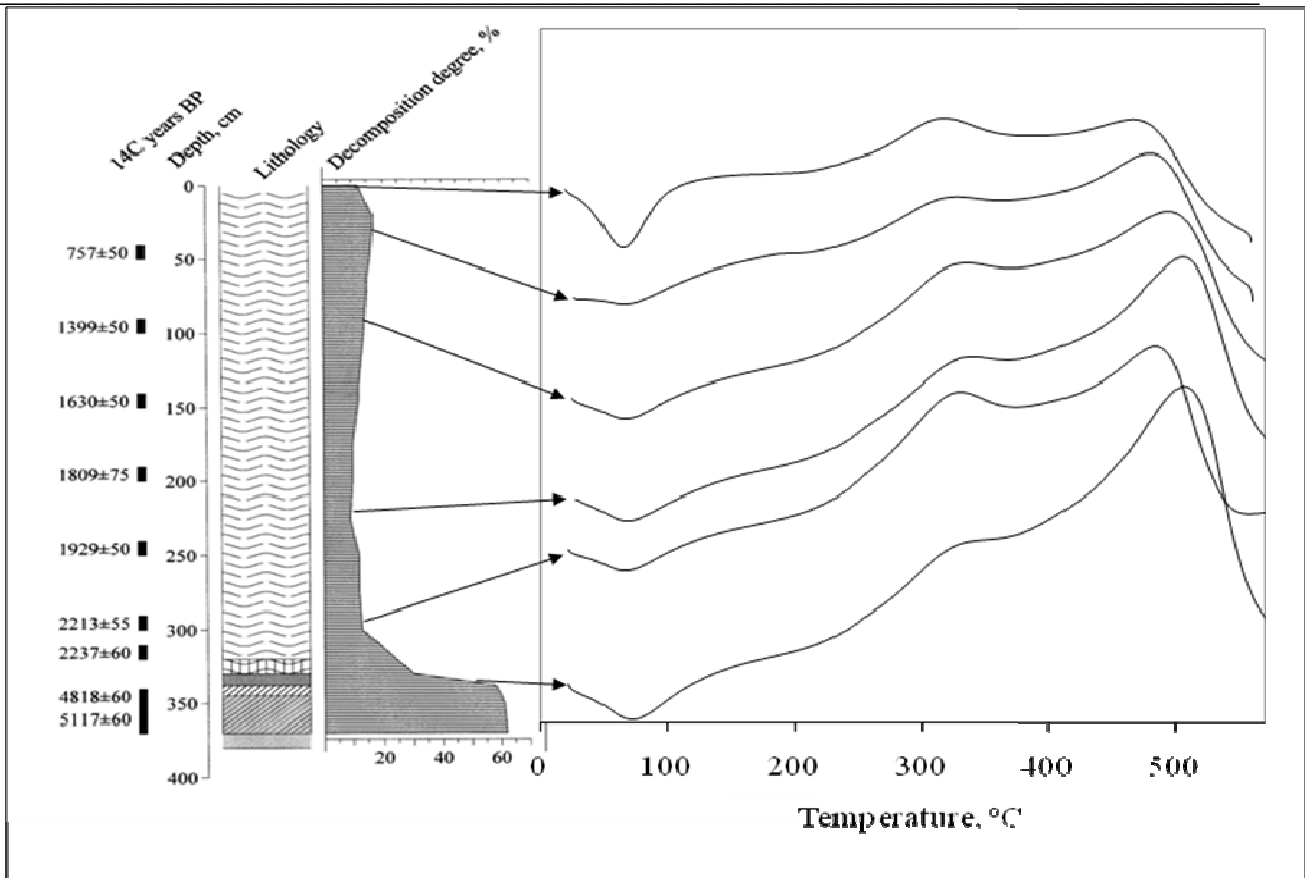


Fig.6. Differential thermal analysis (DTA) curves of humic acids isolated from the Dzelve Bog peat profile

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 <sup>14</sup>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 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 Bog peat and much less expressed intensity in peat from the Eipurs Bog, especially from the deeper, more decomposed peat layers). 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 profile in the molecules of peat humic acids.

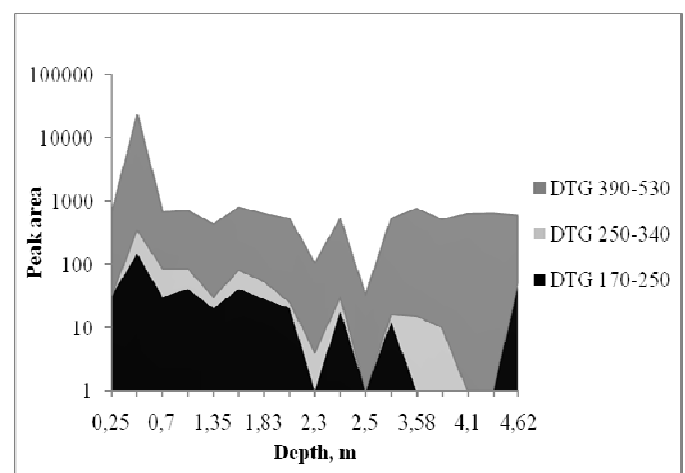


Fig.7. Eipurs bog peat humic acid thermal decomposition curves (DTG) peak area depending on the depth of the peat profile

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) and

by analyzing the changes in the peat decomposition peat area with the depth of the sample location it becomes possible to follow the structural changes into peat composition. Thermal treatment of peat can serve as a tool to increase peat hydrophobicity and thus oil sorption capacity to develop sorbents for oil removal (Figure 8).

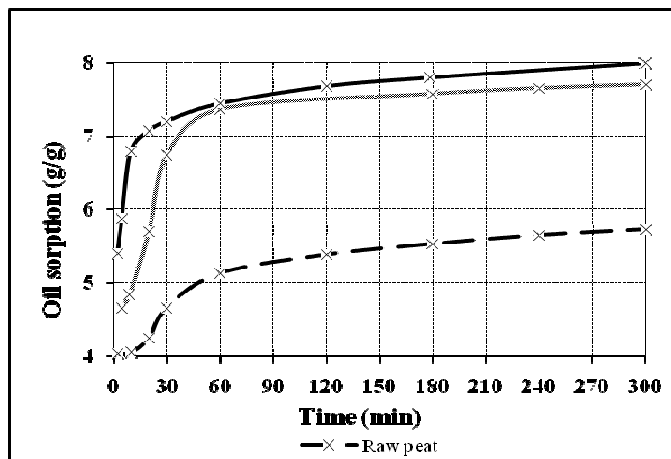


Fig.8. Oil sorption kinetics on raw and thermally treated peat

Thermal treatment allows to increase significantly oil sorption capacity and the speed of the oil sorption.

To test the factors influencing oil sorption and the role of thermal decomposition of humic acids, peat samples were treated (saturated) with humic acid solutions, and later heated (Figure 9).

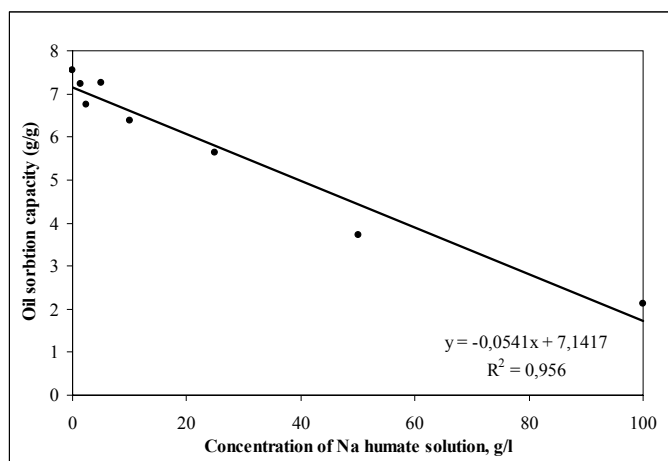


Fig.9: Oil sorption on thermally treated peats, enriched with humic acids

However treatment of peat with humic substances significantly reduced the oil sorption capacity and the reduction of the sorption capacity was dependent on the amount of humic substances added. Thus this finding also indicates the role of "other" ingredients of peat in their hydrophobicity and especially on the sorption capacity of oil after thermal treatment.

#### IV. CONCLUSIONS

Thermal analysis of peat profiles and corresponding humic acids allows to determining structural changes in the studied

material and improving understanding of the diagenesis of peat deposits and corresponding humic materials. Thermally treated peat can be considered as prospective sorbent for oil removal during spills.

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**Oskars Purmalis:** researcher, PhD student.  
University of Latvia, Faculty of Geography and Earth Sciences, Department of Environmental Sciences.  
Address: Raiņa bulv. 19, LV-1586, Riga, Latvia  
e-mail: [oskars.purmalis@lu.lv](mailto:oskars.purmalis@lu.lv)

**Dmitrijs Poršņovs:** laboratory assistant, student.  
University of Latvia, Faculty of Geography and Earth Sciences, Department of Environmental Sciences.  
Address: Raiņa bulv. 19, LV-1586, Riga, Latvia  
e-mail: [dmitrijs.porsnovs@lais.lv](mailto:dmitrijs.porsnovs@lais.lv)

**Māris Kļaviņš:** professor, dr.hab.chem.  
University of Latvia, Faculty of Geography and Earth Sciences, Department  
of Environmental Sciences.  
Address: Raiņa bulv. 19, LV-1586, Riga, Latvia

**Oskars Purmalis, Dmitrijs Poršņovs, Māris Kļaviņš. Kūdras un tās humusvielu diferenciālā termiskā analīze.**

Pētījumā analizēts divu Latvijas augsto purvu kūdras profila un to humīnskābju termogravimetriskais raksturs. Kūdras termogravimetrisko sadalīšanās raksturu būtiski ietekmē kūdras sastāvs, vecums un tās izcelsme. Termogravimetrisko parametru analīze ļauj noteikt atšķirības ne tikai starp kūdrām un no tās izdalītajām humīnskābēm, bet arī starp tādiem kūdras raksturojošajiem parametriem kā kūdras vecums, sadalīšanās pakāpe, organisko vielu degradācijas raksturs un organisko vielu sastāvs. Tādējādi kūdras un to humusvielu termogravimetriskā analīze ir izmantojama to izcelsmes noskaidrošanai. Kūdras termiskā apstrāde ļauj paātrināt organisko vielu transformāciju un to īpašību izmaiņas, kas būtiski paaugstina to spēju saistīt naftas produktus. Pieaugot kūdras hidrofobumam, to termiski apstrādājot, pieaug arī to pielietojuma iespējas naftas produktu sorbcijai.

Kūdras paraugi tika ievākti purva centrālajā daļā ar urbi kūdras paraugu iegūšanai. Tiem tika veikta datēšana izmantojot <sup>14</sup>C, noteikta sadalīšanās pakāpe, botāniskais sastāvs, pelnainība, elementsastāvs un mikroelementu saturs. No kūdras paraugiem tika izdalītas humīnskābes, izmantojot Starptautiskās humusvielu pētnieku savienības rekomendētu metodi [12]. Termogravimetriskās analīzes tika veiktas, izmantojot termogravimetru SH EXSTAR 6300 TG/DTA. Paraugu iesvars termogravimetriskajai analīzei bija 20 mg kūdras vai kūdras humusvielu, tie tika karsēti temperatūrā intervālā 25–550 °C ar karsēšanas ātrumu 10 °C minūtē.

Naftas produktu sorbcijas palielināšanai, kūdra tika apstrādāta ar rūpnieciski ražotu humusvielu prepfrātu 1,5 – 100 g/l 0,1 M NaOH šķīdumā un karsēta laboratorijas žāvskapī 5 stundas 240-250 °C

Pētījuma mērķis – analizēt kūdras un kūdras humusvielu termogravimetrisko raksturu 2 augstajos purvos Latvijā, to atšķirības atkarībā no kūdras veida un izcelsmes, kā arī iespējas izmantot termiski apstrādātu kūdras naftas produktu sorbcijai.

**Оскарс Пурмалис, Дмитрий Поршнев, Марис Клявинш. Дифференциальный термальный анализ торфа и торфяных гуминовых кислот.**

В данной статье рассмотрен характер термического распада верхового торфа двух латвийских болот, и его гуминовых кислот. Результаты ДТА указывают на то, что характер разложения торфа зависит от его состава, возраста, и происхождения. Исследование параметров термического распада торфа помогает идентифицировать различия между торфом и содержащимися в нем гуминовыми веществами, также упомянутые параметры связаны с такими свойствами торфа, как степень разложения, характер разложения и состав органического вещества. Это означает, что ДТА гуминовых веществ возможно использовать для выяснения их происхождения. Термическая обработка торфа помогает ускорить трансформацию органического вещества, что значительно улучшает его гидрофобные и олеофильные свойства. В результате термической обработки торфа возрастают возможности его использования в качестве сорбента нефтепродуктов.

Образцы торфа получены в центральных частях болот, с помощью геологического бура. Произведена датировка образцов с помощью метода <sup>14</sup>C. Также определена степень разложения, ботанический состав, зольность, элементарный состав, и содержание микроэлементов. Из торфа, по методу IHSS [12], были выделены гуминовые кислоты. Термогравиметрический анализ произведен на дериватографе SH EXSTAR 6300 TG/DTA, с навеской образца 20 мг, в интервале температур 25-550 °C, со скоростью нагревания 10 °C/мин.

Для улучшения сорбции нефтепродуктов, торф был обработан раствором промышленно произведенных ГК в NaOH, в концентрациях 1,5-100 г/л. И подвергнут термической обработке в печи, при температуре 240-250 °C, в течение 5 часов.

Цель исследования: анализировать характер термического распада верхового торфа двух Латвийских болот, и его гуминовых кислот и различия в данном характере, в зависимости от вида и происхождения торфа. Также исследована возможность использования термически обработанного торфа в качестве сорбента нефтепродуктов.