

## **What happens to peat during bog fires? Thermal transformation processes of peat organic matter**

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**Abstract.** Bog fires are a serious natural phenomena. Major increase in the number of fires has happened during the last decades due to bog transformation into agricultural lands, accidents and human activities. During bog fires the peat is exposed to high temperatures due to which chemical transformation and even mineralisation of peat can occur. The aim of the study was to analyse the impacts of the bog fires on the bog as an ecosystem, advance the understanding and knowledge of fire impact on peat and humic matter properties and application possibilities. As the material for the study peat samples from burnt sites and thermally treated peat were used. To reveal peat transformation during bog fires, thermogravimetric analysis of peat samples were done, where amounts of bitumens, humic acids and mineral matter were estimated. During bog fires thermal modification of peat properties takes place, resulting in full mineralisation of peat and release of mineral substances. Bog fires lead to development of peat char, bitumens and significant changes in structure and properties of peat humic acids. However, from perspective of application of peat as a substrate and from perspective of impacts on the bog ecosystems, the effects are negligible.

**Key words:** bog fires, humic substances, peat, recultivation, torrefication.

### **INTRODUCTION**

Bog fires can be considered as serious natural event, considering their significant dimensions (from local scale fires, to regional), significant increase during last decades due to bog transformation to agricultural lands, climate change, accidents and human activities. Bog fires has raised attention at first due to resulting air pollution and adverse impacts on human health. Fires has happened in Europe (Shvidenko et al., 2011), South East Asia (Usup et al., 2004; Hayasaka et al., 2014), South America (Aragão et al., 2018) and elsewhere (Turetsky et al., 2015). Bog fires contribute at the global warming as huge amounts of greenhouse gasses are emitted (Page et al., 2002). While peatlands can burn with open fire, smouldering peatland fires are wildfires with the largest fuel consumption in the world. Peatland fires cause large-scale accumulation of smoke at low altitudes in the atmosphere, which results in the decrease of air quality (Hu et al., 2017). Large smouldering peatland wildfires are very rare events at the local scale, but when they happen, they severely affect peatlands, producing physical, chemical and biological

changes to peat (Rein et al., 2008). However not only air pollution is of importance, but the manifestation of fires on bogs and adjacent territories are of equivalent significance. Locally bog fires results in destruction of valuable and unique ecosystems, landscapes, change of hydrological regime in bogs, threats to forest and other ecosystems (Turetsky et al., 2015). All these aspects urge to take actions to protect bogs from accidental fires. However, bog fires changes peat chemical and physical properties. During fires the peat is subjected to high temperature transformation of the peat organic matter, finally to mineralization of peat. It can be supposed that peat after bog fires have significantly different properties than original peat and thus can influence the peat supporting capacity to life on bogs, peat revegetation after bog fires and, of course, can influence the quality of peat if it is mined and used for production of growing media.

It is a very simple question: What happens to peat during bog fires? However, the answer is by far not so easy as very few studies are dedicated to the studies of peat transformation during bog fires. There are studies of soil organic matter transformation during forest fires (González-Pérez et al., 2004; De la Rosa et al., 2012), peat properties during recultivation activities (Rosenburgh et al., 2013) as well as water retention capacity of peat after fires (Thompson & Waddington, 2013). Prolonged heating and the large loss of the peat mass change functional properties of peat humic substances. It is believed that 1 h under the temperature that exceeds 300 °C leads to 90% of mass loss of burnt peat layers and complete peat sterilization (Rein et al., 2008). Specifically impact of bog fires on major group of peat organic substances – humic substances has been studied (Kihara et al., 2015).

Peatland fires in natural peatlands with unaffected groundwater level are extremely rare, while in peatlands with peat excavation sites, deforestation and forest degradation, that all are linked to peatland drainage, they are very common, especially in summer seasons with low rainfall. Moisture content controls peat ignition, dry peat ignites very easily and can burn for months, smouldering underground and re-emerge away from the initial source (Rein et al., 2008). Smouldering peatland fires are more likely to appear in raised bogs than in fens and these fires are highly unpredictable and uncontrollable and thus difficult to extinguish (Svensen et al., 2003). Still the existing studies cover only a minor part of the knowledge needed to understand the impacts of the bog fires on the peat properties.

The aim of the study is to analyse the impacts of the bog fires on example of thermal treatment of peat, on the peat and especially humic matter properties to advance the understanding of the bog fire impacts on the peat properties and bog ecosystem functioning.

## MATERIALS AND METHODS

### Peat sampling

Peat samples after bog fires were sampled in Saukas bog (Lat: 56,374520; Lon: 25,311041) where recently (July 2019) fire have happened. For further studies upper layer of the peat (further – coked peat) with evident impact of the bog fire (presence of black particles of peat char) were sampled (altogether 24 samples, each 1 kg – dry weight). For further analysis the coked peat was dried (105 °C) and homogenized.

### **Peat thermal treatment**

To study changes of peat properties during bog fires peat from Saukas bog were chosen – typical raised bog as in details described in previous studies (Klavins et al., 2009). Samples were finely ground and homogenised. Each sample was moistened in demineralised water, and excess water was pressed out to reproduce real life wet peat in a bog. Approximately 100 mL of wet peat by volume was densely packed in a separate cast iron capsule and charred in a muffle furnace (Nabertherm B180). Each sample was charred in 4 temperatures – 150 °C; 225 °C; 300 °C and 375 °C for 2 hours with a temperature rise of 5 °C min<sup>-1</sup>. After charring samples were cooled and packed for further analysis.

### **Scanning electron microscopy (SEM)**

Peat samples from Sauka Bog with low decomposition degree – natural peat and charred at 150 °C, 225 °C, 300 °C and 375 °C for 2 hours as described earlier were used. Each sample was analysed by taking 2 to 5 images with up to 10 points for each sample. For each point chemical data graph was obtained. Electronic microscopy analysis was done using scanning electron microscope Phenom ProX. Images for viewing and morphology evaluation were based on 10 kV mode. Images used for chemical analysis have a 15 kV powerful electron beam and often a point intensity to more accurately transmit the beam, thereby achieving X-ray emission from the material. Energy dispersive spectroscopy (EDS) were done at resolution 132 eV (for manganese K-alpha peak) using ultra-thin silicon nitride (Si<sub>3</sub>N<sub>4</sub>) drift detector with active surface 25 mm<sup>2</sup>. The EDS resolution was 132 eV (for manganese K-alpha peak). Maximum reception of emitted X-rays were 300,000 signals per second.

### **Characterization of peat**

1.00 g of sample (natural, heated or coked peat) was extracted 10 mL of CHCl<sub>3</sub>. After 24 hours the extract was filtered through paper in pre-weighted Petri dish. After drying in air and at 40 °C the dried lipids on Petri dish were weighed and the difference in weight between an empty, dry Petri dish and dried Petri dish containing waxes and bitumens was calculated by subtracting and expressed in percent.

The pH of peat is measured in an aliquot of sample and a reagent with the mass ratio of 1:5. The solution is prepared from 1-part of peat and 5 parts of a reagent, whether it be a 0.01M CaCl<sub>2</sub> or deionized water. 10 g of dry peat is weighed into an Erlenmeyer flask and 50 mL of deionized water is added to it. The sample is then put in an orbital shaker for 1 hour and then filtered through a filter paper and the pH of the sample is measured with a pH meter. Total dissolved solids (TDS) and conductivity ( $\sigma$ ) were measured in an aliquot of filtrated sample. They show the combined content of organic and inorganic substances in a liquid.

### **Extraction of humic substances from peat**

Approximately 1 gram of each peat sample was weighed in a 100 mL glass screwcap bottle and 50 mL of 4% NaOH was added to each sample. Samples were placed in an orbital shaker (Biosan PSU-20i) and shaken for 24 hours. After shaking samples were filtered through a filter paper. 1 mL of each sample was transferred to a 100 mL volumetric flask and diluted 100 times with distilled water. Total organic carbon in humic substance solutions were analysed with a total organic carbon analyser

(Shimadzu TOCV-CSN). 20 mL of each charred peat extract was acidified to pH of 2 with concentrated sulfuric acid to precipitate humic acids from fulvic acids. Precipitated humic acids were separated from fulvic acids by filtration. Each fulvic acid solution was diluted 10 times and analysed with a total organic carbon analyser.

#### **Excitation-Emission Matrix Fluorescence Spectroscopy**

Humic solutions were prepared at concentrations of 80–90 mg L<sup>-1</sup>. The excitation-emission matrix spectrum of the prepared samples on an AQUALOG fluorometer was taken using a 1 cm glass cuvette. The laboratory reagent blank was distilled water. The fluorescence signals were normalised to the spectrometer lamp reference intensity, with spectral corrections applied by the instrument software. The emission spectra were scanned from 250 to 600 nm and from 250 to 600 nm in excitation wavelength in 5 nm steps. The spectra obtained were analyzed by PARAFAC, using MATLAB R2014a v. 5.3.0.532 software. Matrices obtained in the excitation-emission matrix fluorescence spectroscopy were corrected and treated with the parallel factor analysis on *MATLAB R2014a v. 5.3.0.532* software with *drEEM* toolbox (Krumins, 2018). Data were corrected for the inner filter effects with the subtraction of the blanks, but the fluorescence intensity was converted to Raman units (Lawaetz & Stedmon, 2009; Kothawala et al., 2013). Following the procedure of parallel factor analysis, the excitation-emission matrices of peat humic substances were disassembled into independent components (Murphy et al., 2013).

#### **Thermogravimetical analysis**

TA Instruments – Waters LLC SDT Q600 was used to conduct thermal analysis – thermogravimetry (TG) and differential thermogravimetry (DTG). Sample of peat (5 mg) was heated in a small crucible. Pyrolysis process were ensured in inert atmosphere with nitrogen gas flow of 100 mL min<sup>-1</sup>. Constant heating rate 20 °C min<sup>-1</sup> was used during TG process. Samples were heated from room temperature to 105 °C, kept isothermal for 5 minutes to detect amount of moisture and then heated to 900 °C, where samples were held isothermal for 5 minutes in oxygen atmosphere to detect fixed carbon and ash content. Data of weight loss (w%) and derivative weight loss was recorded (w%/°C) during whole TG analysis.

#### **Peat mineralisation**

Peat sample was pre-treated in different conditions in a muffle furnace (Nabertherm B180) – dry peat; charred peat at 375 °C; dry peat charred at 900 °C; peat charred at 375 °C one more time at 900 °C. Both fresh peat and ash were macerated in 100 mL of distilled water and shaken in an orbital shaker (BioSan PSU-20i) at 200 rpm for 24 hours. After shaking the samples were filtered through a filter paper. Na; Ca; Mg and K were analysed in the filtered water phase with an ICP-OES (Thermo Scientific iCAP 7000 series). Sulphate ions in filtered water phase were measured turbidimetrically with a spectrophotometer (Hach-Lange DR 2800) at 610 nm wavelength. Peat water extract was titrated with 0.02M AgNO<sub>3</sub> using potassium chromate as an indicator to determine chloride ions.

## RESULTS AND DISCUSSION

### **Bog fires and their occurrence in Latvia**

Extended periods of dry, hot and windy weather promote increase of frequency of bog fires. It is expected that also in Latvia incidence of fires in territories of bogs will significantly increase both in pristine mires and peat harvesting sites due to climate change, including increase of average air temperature and prolonged dry periods. Peatlands are significantly different in respect to the way fire spreads in peat - it is determined by peat properties (Huang & Rein, 2018).

Most of the bog fire events nowadays are directly connected with human activity (Aragão et al., 2018). Analysis of peat geological sections indicate that even during the Stone Age when human activity was insignificant in the territory of current Latvia periodical burning of peatlands did naturally occur. Before human inhabitation, larger areas of forests and mires were affected by wildfire of natural origin. Gradually human activity has changed the pattern of fire events thus influencing ecological conditions and natural processes (Suveizda, 2016). Impact of bog fires caused by human activity on local ecosystem is much greater than naturally occurring wildfire.

Data from 2011 to 2018 show that there have been more than 40 cases of peatland burnings in Latvia. In most cases territories affected by fire are not significant – up to 1ha - due to the fact that fire is quickly noticed and extinguished before spreading further. However, in hard to access places fire spreads rapidly and affected territories are extensive, for example, in 2018 conflagration in Stikli Mire complex affected 529 ha of both pristine mire and peat harvesting site. More than 21 peatland burnings were reported in 2018.

During this period the fires in peatlands have occurred from February until November. Most of them took place during hot summer months – July and August. Although rare, but occasional repeated ignition and burning of peat occurs, usually during or after smoldering (after longer period of time).

Naturally occurring wildfires in boreal zone emphasizes the need for successful monitoring of conflagration and wildfire and reduce of adverse effects on environment. It can be achieved by research, analysing and understanding combustibility, flammability, fire spreading and burning and peat properties itself. Peat properties are quite different in both in the region of the Baltic States in comparison with other regions, like Ireland, the Netherlands, as well as peat properties are different even in nearby locates sites. Therefore, it is very important to carry out peat studies in details to understand how to protect peatlands from fires and how to use peat more effectively with added value.

### **Changes of peat properties during bog fires – experimental study**

In the thermally treated peat samples and in the samples from naturally burnt sites a number of parameters has been determined, such as amount of water soluble substances, tars and bitumens, trace elements, humic substances and others. Besides to that, the visual appearance of peat was studied using Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA).

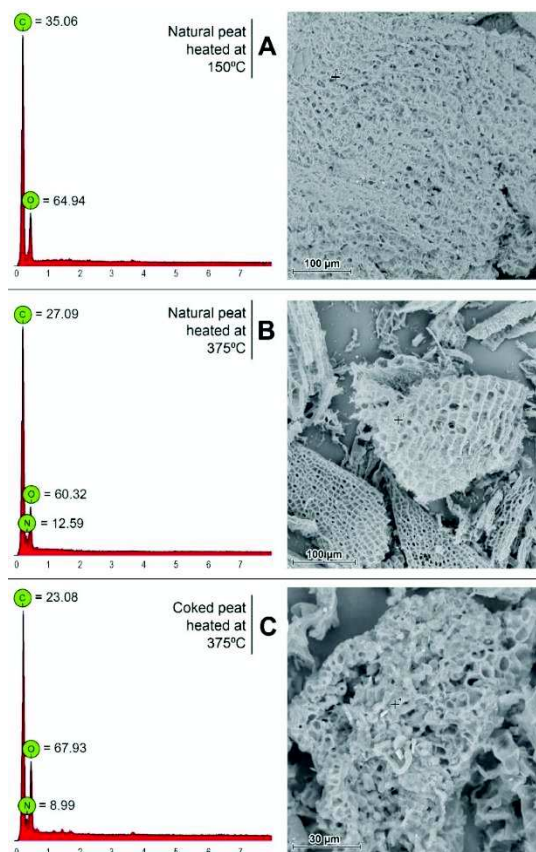
Obtained SEM images and data of chemical composition revealed in graphs show gradual changes in both peat structure and chemical composition. Results of dry natural and dry charred peat samples heated at 150 °C and 375 °C are shown in Fig. 1. and Fig. 2. and discussed in details.

Both analysed peat samples are represented by low decomposed raised bog type *Sphagnum* peat and in their botanical composition *Sphagnum fuscum* dominates up to 90% among moss remains forming peat. *Sphagnum* leaves have structure with pores resulting soak up water like a sponge. These large, clear, structural, dead cells of leaves have the large water-holding capacity, which may hold 16 to 26 times as much water as their dry weight (Klavins et al., 2009). Particularly these *Sphagnum* leaf structure properties are also preserved as the *Sphagnum* dies and forms peat and determines that natural peat moisture content is 90–96%. As shown in the obtained images, even at 150 °C heating, the structure and pores of the *Sphagnum* leaves are still well preserved. The pores are still partially retained heated at 375 °C while leaves are torn by heating.

In charred *Sphagnum* peat, both the structure and pores of the *Sphagnum* leaves are damaged before heating and there is increasing heating effect observed along the increase of heating temperature. The leaf structure becomes shapeless and the pores are compressed. More expressed changes happened also because of chemical processes in charred sample, while in dry and only heated sample changes are not significant.

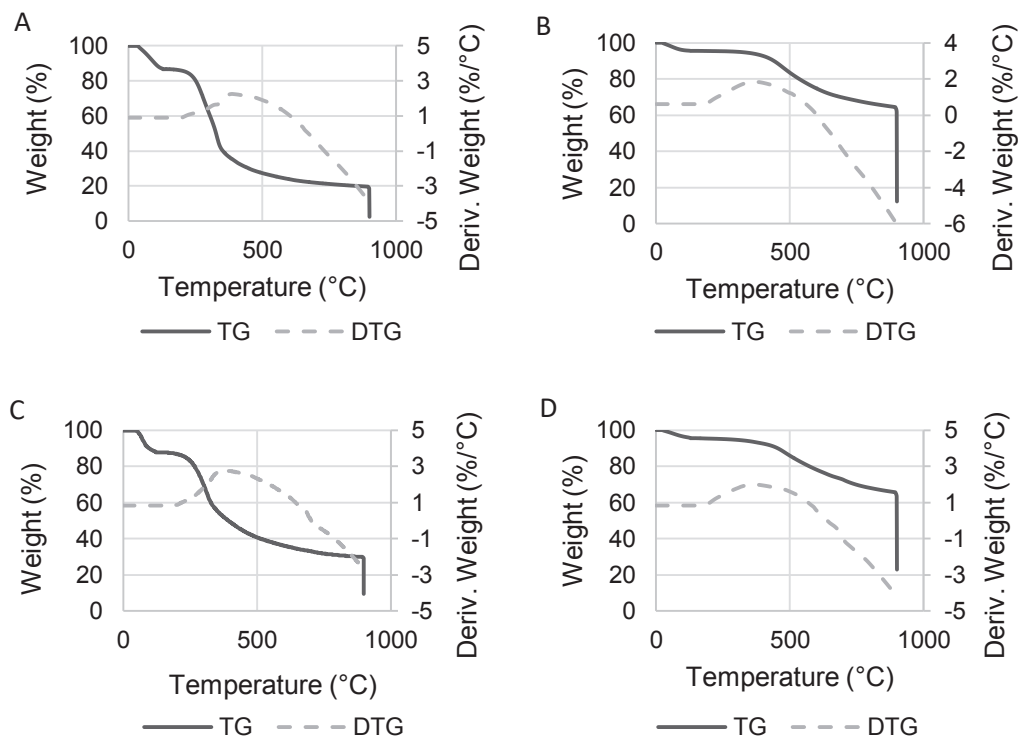
Chemical composition of both analysed samples is different. In chemical composition of dried natural peat the main chemical element is oxygen reaching approximately 61–69% and it does not vary significantly with the heating temperatures. From other elements determined predominantly only carbon, the amount of which is fluctuating 27–37%. In the chemical composition of charred peat oxygen varied from 61 to 68%, and decrease of carbon, but there more other elements (Si, K, Al, N, Br) are determined, however in small quantities.

The thermogravimetric analysis of the natural peat, peat obtained from sites after bog fires provides the information of the processes going on during bog fires – transformation of peat organic matter, torrefication or charring ending up in formation of peat char in presence of limited amounts of oxygen or full mineralization of peat



**Figure 1.** Scanning electron microscopy images of natural peat heated at 150 °C (A); at 375 °C (B) and coked peat, heated at 375 °C as well as elemental composition of corresponding peat samples obtained using energy dispersive spectroscopy (EDS).

(Fig. 2). The first stage of peat thermal transformation – removal of constitutionally bound water happening at 110 °C. At somewhat higher temperatures (200–300 °C), the destruction takes place of less condensed components, such as polysaccharides or of a part of humic substances. The stage of destructive drying or torrefication is entered around 200 °C. As it is showed by earlier studies (Klavins & Porshnov 2011; Klavins & Porshnov, 2013), destructive drying significantly changes water uptake properties of peat by increasing its hydrophobicity due to removal of hydrophilic hydroxyl and carboxyl functional groups from the surface of the material.

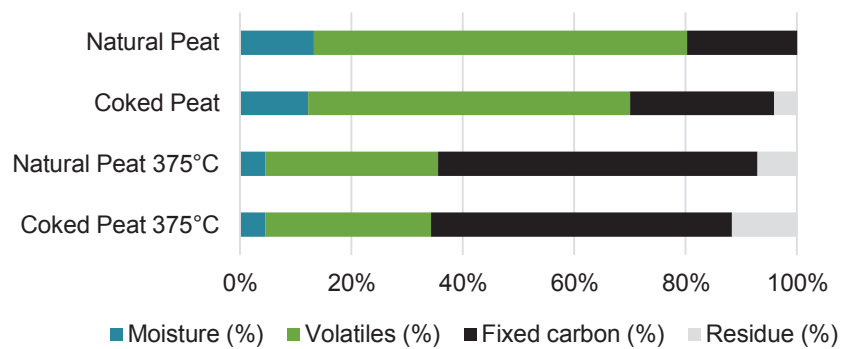


**Figure 2.** Thermogravimetric analysis of peat sample decomposition: A – natural peat; B – natural peat torrefied at 375 °C; C – coked peat; D – coked peat torrefied at 375 °C.

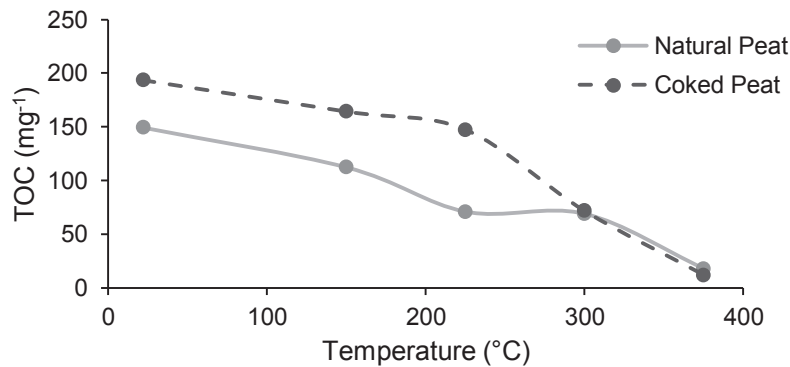
As it is showed on Fig. 2. water uptake decreases more than two times after the thermal treatment this fact undoubtedly plays significant role considering biological as well as chemical processes after the fire. Finally, at about 350–500 °C thermal effects are attributed to the pyrolysis of the more condensed materials, such as aromatic compounds of lignin and remaining humic acids (Almendros et al.; 1982). The TGA analysis do not reveal significant differences between natural peat and coked (charred) peat (Fig. 2, A, C) as well as natural peat and coked peat after thermal treatment (torrefication) (Fig. 2, B, D).

Thus, a conclusion can be drawn that despite the visually seen differences in the peat appearance (presence of small carbonaceous particles in coked peat) the actual differences in the major part of the peat mass after peat fires are not so significant. However, if the thermal transformation is deeper such as in case of the torrefication

resulting in the total transformation of peat mass in carbonaceous mass, the TGA demonstrates significantly differing the behaviour (Vitazek et al., 2019). Results of experimental thermal treatment of peat obtained from bog fire sites provides understanding of chemical processes taking place during bog fire in the layer of peat. Contrary to the upper layer where complete mineralisation of material take place, processes in the deeper layers differ significantly and must be characterised as pyrolytic decomposition or as torrefaction: depending on temperature experienced by material during the fire. The next stage of the thermal decomposition: pyrolysis (decomposition of polymeric chains) takes place at temperatures higher than 350 °C, as we see in Fig. 3, this process involves crosslinking reactions producing significant amounts of fixed carbon.



**Figure 3.** Proximate analysis of peat, coked peat and natural and coked peat after treatment at 375 °C.



**Figure 4.** Changes of concentration of humic substances (expressed as total organic carbon concentration) in peat (natural and coked) depending on the temperature of the following thermal treatment.

Thermal treatment of the peat significantly reduces the amount of humic substances available in the peat (Fig. 4). The yields of humic substances in coked peat is significantly lower (~ 25%) than in natural peat and the yield of humic substances depends on the temperature of the thermal treatment of the peat. Such changes can be related to the condensation of peat organic matter and related decrease of solubility. The



humic substances in the peat can affect the ability of peat to support development of vegetation on bogs and thus the reduction of the availability of the humic substances on the intensity of the thermal treatment (temperature) shows the impacts of bog fires on the peat properties and following application possibilities.

The thermal treatment of peat results in increase of the pH as well as in the concentrations of dissolved substances (as indicated by the changes of TDS and conductivity of the aqueous extracts of the peat) (Table 1). Also, slight increase in concentrations of inorganic ions, representing the mineral matter of peat can be observed in coked peat in comparison with natural peat as well as in the peat depending on the temperature of the thermal treatment. As the re-vegetation of peatlands after bog fires, depends on availability of nutrients, this finding illustrates the impacts of bog fires on the peatlands.

**Table 1.** Changes of composition of peat water soluble components and peat humic substances

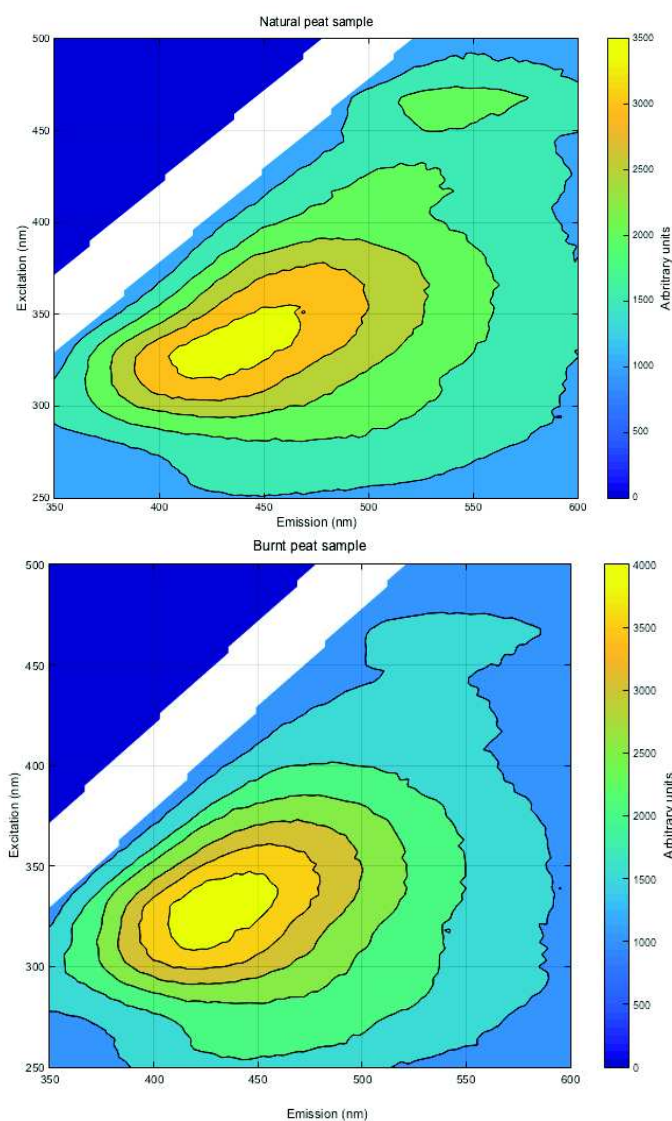
Peat sample	pH	TDS, ppm	$\sigma$ , $\mu\text{S cm}^{-1}$	TOC, $\text{mg g}^{-1}$	$W_{\text{HA}}$ , %	$W_{\text{FA, TOC}}$ , %	$W_{\text{lipids}}$ , %
Coked Peat (CP)	4.50	55.9	110.0	193.7	79.1	20.9	1.23
Natural Peat (NP)	4.97	43.8	86.9	149.4	70.2	29.8	1.15
NP 150 °C	5.10	25.6	51.3	112.3	60.8	39.2	1.33
NP 225 °C	5.00	38.3	72.2	70.9	60.2	39.8	1.85
NP 300 °C	5.06	34.6	70.6	68.9	52.8	47.2	2.30
NP 375 °C	6.28	15.2	31.4	17.8	52.4	47.6	1.95
CP 150 °C	4.56	50.9	101.2	164.5	75.0	25.0	1.45
CP 225 °C	4.58	60.4	111.4	147.5	71.1	28.9	2.50
CP 300 °C	5.28	27.6	63.4	71.8	48.7	51.3	3.20
CP 375 °C	5.37	17.0	35.0	12.1	47.9	52.1	2.80

On the other hand also the total amount of humic substances (as indicated by the total organic carbon in peat extracts with 0.1 N NaOH) is decreasing depending on the temperature of the thermal treatment of the peat as well as in peat after bog fires in comparison with unaffected peat. The increase of the temperature of the thermic treatment reduces the amounts of humic acids and increases the percentage of fulvic acids (more soluble part of the humic matter pool).

The excitation-emission matrices of peat humic substances correspond to a system with a number of fluorescent components. Peak fluorescence for natural and charred peat humic substances is similar and locates around  $\lambda$  440 nm of emission wavelength with indication of electron-donating functional groups in the material. Fluorescence at this emission wavelength suggests the presence of complex structural components with high relative degree of aromatic condensation and high relative number of conjugated fluorophores (Enev et al., 2014).

The difference in the fluorescence between natural and charred humic substances emerges in the relative intensity, which in charred peat humic substances is higher, suggesting increase in aromaticity due to prolonged heat impact on peat. It is believed that peat fire induces increased production of benzene, which is least complex aromatic hydrocarbon.

Data suggests that smouldering peatland fire also affect humic substances in the fluorescence excitation region between  $\lambda$  450–500 nm with the emission of  $\lambda$  500–575 nm, functionalities at this range due to heat impact seems to collapse. Following the procedure of parallel factor analysis, a two-component model with 99.96% probability was generated and validated by the residual examination and split-half analysis. Simple two-component model reveals severe physical and chemical changes to peat humic substances due to peatland fire, especially a significant decrease in humic substance fluorescence intensity (more than 1,000 arbitrary units) in  $\lambda$  500–575 nm emission region.



**Figure 5.** Excitation-emission matrices of *Sphagnum* moss peat humic substances in a) natural settings and b) after a smouldering peatland fire.

### **Consequences of bog fires on peat properties and possible impacts of recovery of peatlands after bog fires**

The bog fires result in significant changes of peat properties. At first the development of peat char (biochar) particles is evident: after peat fires - everyone can observe black char on the surface of bogs. Peat char is much more stable in respect to degradation than peat and can remain in peat layers for thousands of years. Also, SEM figures prove the significant changes in the view of peat particles.

The structure and pores of the *Sphagnum* leaves from the dried natural peat is preserved even after heating, while the structure and pores of the burned peat are significantly deformed and do not change significantly when heated, suggesting that the peat has been exposed to really high temperatures during fire.

Irrespective of the heating temperature, the chemical composition of natural peat mainly is represented by the oxygen (61–69%) and carbon (27–37%), but the presence of other elements is small, however the mineral substances (inorganic ions) after bog fires can leak out from the peat.

The chemical composition of burnt peat is more variable than that of natural peat. Although the main elements are the same as in natural peat - oxygen and carbon - it still contains up to 12% silicon (Si), as well as other chemical elements (Br, Al, K, N) have been determined.

The structure of the charred peat is significantly and irreversibly affected, possibly resulting in loss of peat absorption properties.

## **CONCLUSIONS**

The peat thermal decomposition results in release of mineral substances (at first inorganic ions) from the peat as demonstrates the changes in pH, TDS as well as analysis of water-soluble substances. The ions, such as  $K^+$ ,  $Ca^{+2}$  and others in mineral matter poor peat can be considered as nutrients and they can greatly support burned peatland re-vegetation, however not with the indigenous *Sphagnum* species, but rather with higher plants.

Another major way of impacts of peat thermal transformation (burning) includes impacts on peat organic matter as demonstrated by changes of peat humic substances. The decrease of humic acid concentration and increase of fulvic acid (lower molecular mass, higher solubility directly can influence the drainage water composition from peatlands – their brownification as well as the increase of mineral substances in the drainage.

From perspective of peat mining – the admixtures of burnt peat will not have significant adverse effects on the plant development or rather even can be considered as beneficial at production of growth substrates. However, from perspective of recovery of native vegetation especially in raised bogs, peat fires can support development of higher vegetation.

Data suggests that due to prolonged heat impact on peat it is characteristic for aromatic and condensed molecules to increase in number, while more labile compounds collapse into smaller, more stable formations. It is believed that during peat fire high amounts of aromatic hydrocarbon is produced, which significantly increases the aromaticity of peat.

Only two major functional compounds can be traced in humic substances of both natural and charred peat, which means that severe physical and chemical changes have been made to peat material and due to prolonged heating, most functionalities have been destroyed.

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