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

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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, South East Asia, South America and elsewhere . 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. 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, peat properties during recultivation activities as well as water retention capacity of peat after fires. 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. Specifically impact of bog fires on major group of peat organic substances – humic substances has been studied.

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. Upper layer of the peat (further – coked peat) with evident impact of the bog fire (presence of black particles of peat char) were studied. For further analysis the coked peat was dried (105 °C) and homogenized.
- **Peat thermal treatment**
  Typical raised bog samples were chosen to study changes in peat properties after bog fires. wet peat by volume was packed in a cast iron capsule and charred in 4 temperatures – 150 °C; 225 °C; 300 °C and 375 °C.
- **Scanning electron microscopy (SEM)**
- **Characterization of peat**
  waxes and bitumens was calculated
  pH, total dissolved solids and conductivity were measured.
- **Extraction of humic substances from peat**
- **Excitation-Emission Matrix Fluorescence Spectroscopy**
  The excitation-emission matrix spectrum was taken using a 1 cm glass cuvette using distilled water as blank.
- **Thermogravimetrical analysis (TGA)**
  5 mg of peat samples was heated with a constant heating rate 20 °C/min to 900 °C in inert atmosphere with nitrogen gas flow of 100 mL/min and oxygen during last 5 minutes. Moisture, volatile, fixed carbon and ash content was detected. Data of weight loss (w%) and derivative weight loss was recorded (w%/°C) during whole TG analysis.
- **Peat mineralisation**
  Peat sample was heated one more time at 900 °C. Na; Ca; Mg and K were analysed. Sulphate ions in filtered water phase were measured. Peat water extract was titrated with 0.02M $AgNO_3$ using potassium chromate as an indicator to determine chloride ions.

RESULTS AND DISCUSSION

Changes of peat properties during bog fires – experimental study

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 (Figure1). 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.

In chemical composition of dried natural peat, the main chemical element is oxygen reaching approximately 61 to 69% and it does not vary significantly with the heating temperatures. From other elements determined predominantly only carbon fluctuates from 27 to 37%. In the chemical composition of charred peat oxygen varied from 61 to 68% and decrease of carbon was observed. There were other elements (Si, K, Al, N, Br) determined, however in small quantities.

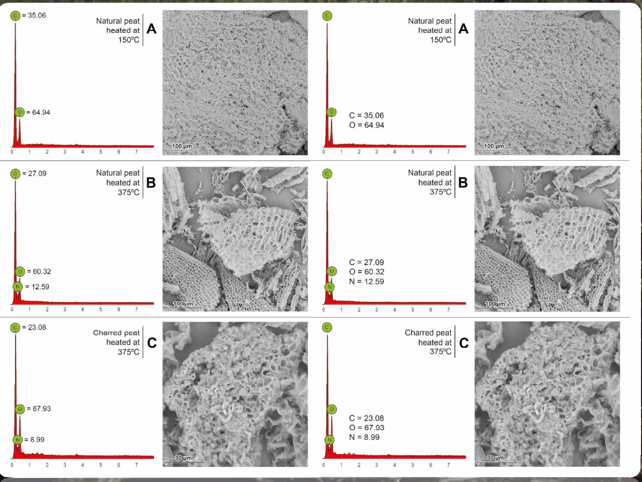

Figure 1. Scanning electron microscopy images of natural peat heated at 150 °C (A); at 375 °C (B) and coked peat heated at 375 °C (C) as well as elemental composition of corresponding peat samples obtained using energy dispersive spectroscopy

The first stage of peat thermal transformation – removal of constitutionally bound water, happens at 110 °C (Figure 2). At higher temperatures (200–300 °C) the destruction takes place of less condensed components. The stage of destructive drying or torrefication is entered around 200 °C. As it is showed by earlier studies, 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.

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. The TGA analysis do not reveal significant differences between natural peat and coked (charred) peat (Figure 2 A, C) as well as natural peat and coked peat after thermal treatment (torrefication) (Figure 2 B, D).

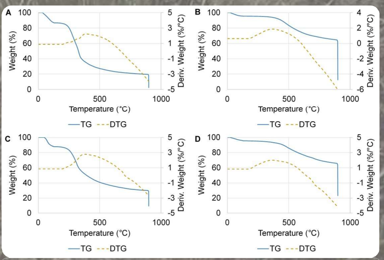

Figure 2. Thermogravimetrical analysis of peat sample thermal decomposition: A - natural peat; B - natural peat torrefied at 375 °C; C - coked peat; D - coked peat torrefied at 375 °C

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 a 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 (Figure 3). 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 torrefication: 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 Figure 3., this process involves crosslinking reactions producing significant amounts of fixed carbon.

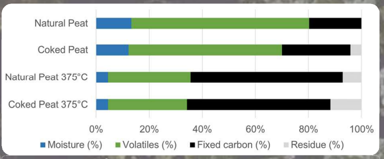

Figure 3. Proximate analysis of peat, coked peat and natural and coked peat after treatment at 375 °C

The excitation-emission matrices of peat humic substances suggests the presence of complex structural components with high relative degree of aromatic condensation and high relative number of conjugated fluorophores (Figure 5).

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.

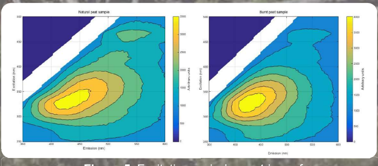

Figure 5. Excitation-emission matrices of Sphagnum moss peat humic substances in natural settings and after a smouldering peatland fire

Thermal treatment of the peat significantly reduces the amount of humic substances available in the peat (Figure 4). The yields of humic substances in coked peat is significantly lower (~ 25%) than in natural 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.

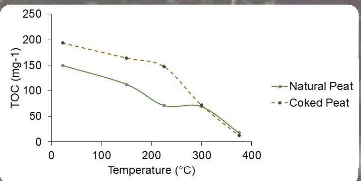

Figure 4. Changes of concentration of humic substances (expressed as total organic carbon concentration) in peat (natural and coked) depending on the temperature of the following thermal treatment

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.

Peat sample	pH	TDS, ppm	σ, µS/cm	TOC, mg/g	W_{HA}, %	$W_{FA, TOC}$, %	W_{lipids}, %
Coked Peat	4.50	55.9	110.0	193.7	79.1	20.9	1.23
Natural Peat	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

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

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. A 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 proves 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.

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REFERENCES

Hu, Y.; Fernandez-Anez, N.; Smith, T.E.L.; Rein, G. 2017. Review of emissions from smouldering peat fires and their contribution to regional haze episodes. International Journal of Wildland Fire 27(5), 293–312. https://doi.org/10.1071/WF17084

Page, S.E., Siegert, F., Rieley, J.O., Boehm, H.D.V., Jaya, A., & Limin, S. 2002. The amount of carbon released from peat and forest fires in Indonesia during 1997. Nature 420(6911), 61.

Rein, G., Cleaver, N., Ashton, C., Pironi, P., Torero, J.L. 2008. The severity of smouldering peat fires and damage to the forest soil. Catena 74(3), 304–309. https://doi.org/10.1016/j.catena.2008.05.008

Svensen, H.; Dysthe, D.K.; Bandlien, E.H.; Sacko, S.; Coulibaly, H. & Planke, S. (2003) Subsurface combustion in Mali: Refutation of the active volcanism hypothesis in West Africa. Geology, 31(7), 581-584. https://doi.org/10.1130/0091-7613(2003)031<0581:SCIMRO>2.0.CO;2