

EDN: PWKCXI

УДК 630*439(571.51/.52)

Fire-Induced Transformation of Organic Matter in Scots Pine Stand in Siberia

Olga A. Shapchenkova* and **Elena A. Kukavskaya**

*V. N. Sukachev Institute of Forest SB RAS – separate subdivision
of the Federal Research Center “Krasnoyarsk Science Center SB RAS”
Krasnoyarsk, Russian Federation*

Received 06.08.2022, received in revised form 29.08.2023, accepted 02.10.2023

Abstract. In forest fires, considerable amounts of carbon are released to the atmosphere, yet part of the biomass is converted to pyrogenic organic matter (PyOM). Little is known about the amount and properties of PyOM in Siberian forests. We studied PyOM generated by a low to moderate severity wildfire in a Scots pine stand in Siberia using thermogravimetry (TG) and differential scanning calorimetry (DSC). DSC and TG of visibly completely charred (blackened) samples of the forest floor (litter layer L), down wood ($d < 1$ cm) and outer bark were carried out in an oxidative atmosphere. The PyOM samples showed a significant loss of thermolabile components and enrichment in thermally recalcitrant aromatic compounds, as well as higher values of activation energy and enthalpy (H) of thermal degradation compared to unburned samples. Thermal characteristics of PyOM derived from various fuel types differed substantially. The litter PyOM was the most thermolabile, i.e. showed the lowest recalcitrance. The down wood and bark PyOM had higher thermal stability due to a greater content of aromatic structures, which was reflected by the thermal recalcitrance indexes (R_{50} and Q_3). The litter PyOM had a low carbon sequestration potential and therefore was more susceptible to degradation compared to down wood and bark PyOM, which showed an intermediate carbon sequestration potential.

Keywords: forest fires, pyrogenic organic matter, thermal analysis.

Acknowledgements. The study was supported by the Russian Foundation for Basic Research, The Government of Krasnoyarsk Krai, the Krasnoyarsk Regional Foundation of Scientific and Scientific-Technical Support (grant #20–44–242004).

© Siberian Federal University. All rights reserved

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

* Corresponding author E-mail address: shapchenkova@mail.ru

ORCID: 0000-0002-1392-5171 (Shapchenkova O.); 0000-0002-2805-2588 (Kukavskaya E.)



Трансформация органического вещества в сосновом насаждении в Сибири под воздействием пожара

О. А. Шапченкова, Е. А. Кукавская

*Институт леса им. В. Н. Сукачева СО РАН – обособленное подразделение
Федерального научного центра «Красноярский научный центр СО РАН»
Российская Федерация, Красноярск*

Аннотация. При лесных пожарах в атмосферу выбрасывается значительное количество углерода, при этом часть биомассы преобразуется в пирогенное органическое вещество (ПОВ). О количестве и свойствах ПОВ в сибирских лесах известно мало. Мы изучили ПОВ, образовавшееся в результате лесного пожара от слабой до средней силы в сосновом насаждении Сибири, с использованием термогравиметрии (ТГ) и дифференциальной сканирующей калориметрии (ДСК). ДСК и ТГ визуально полностью обугленных образцов подстилки (подгоризонт L), веток на поверхности почвы ($d < 1$ см) и коры деревьев проводились в окислительной атмосфере. Образцы ПОВ показали значительную потерю термолабильных компонентов и обогащение термически устойчивыми ароматическими соединениями, а также более высокие значения энергии активации и энтальпии (ΔH) термодеструкции по сравнению с негоревшими образцами. Выявлены значительные различия в термических характеристиках ПОВ, образованного из различных горючих материалов. ПОВ подстилки было наиболее термолабильным, т.е. показало наименьшую устойчивость. ПОВ веток и коры имело более высокую термическую стабильность из-за большего содержания ароматических структур, что отразилось в индексах термической устойчивости (R_{50} и Q_3). ПОВ подстилки характеризовалось низким потенциалом секвестрации углерода и поэтому является более восприимчивым к деградации, чем ПОВ веток и коры, которое показало средний потенциал секвестрации углерода.

Ключевые слова: лесные пожары, пирогенное органическое вещество, термический анализ.

Благодарности. Исследование выполнено при поддержке Российского фонда фундаментальных исследований, Правительства Красноярского края, Красноярского краевого фонда научной и научно-технической поддержки (грант № 20–44–242004).

Introduction

Wildfires are a major disturbance factor in the boreal forests resulting in significant forest loss (Hansen et al., 2013). Huge areas of boreal forests burned by periodic wildfires are located in Siberia. Forest areas in Siberia account for approximately 605 million ha with 74 % being coniferous species (Danilin, Crow, 2008). In recent decades, elevated air temperatures in Siberia have led to more frequent wildfires and an increase in the burned areas. From 1999 to 2019, wildfires in Siberia resulted in a total of 200 million ha of burned area with forests accounting for 60 % (Kharuk et al., 2021). While 2020 was not the largest fire year in Siberia, it was exceptional in terms of substantial increase in fire activity above the Arctic Circle (Talucci et al., 2022) due to rising temperatures (Descals et al., 2022). Approximately 50 % of the total burned area in Siberia is caused by extremely large fires (> 2000 ha). Large-scale forest fires (area > 200 ha) account for ~ 30 % of total occurrences and ~ 90 % of total burned area. Most forest fires in Siberia (80–90 %) are surface fires that spread through the forest floor, burning vegetation litter and lower levels of vegetation (Korovin, 1996; Kharuk et al., 2021).

Wildfires release large amounts of carbon dioxide and other gases into the atmosphere and simultaneously convert part of the burned biomass into pyrogenic organic matter (also referred to as black carbon, pyrogenic carbon, charcoal) (Santín et al., 2015b). Pyrogenic organic matter (PyOM) production rate is closely related to vegetation type and climate. Thus, bio-climatic zones determine the rate of fuel accumulation and the fire return interval. This is an important factor, as increased dry fuel accumulation per unit area provides greater combustion, heat release, and flame temperatures under otherwise equal conditions (Bowring et al., 2022). The intensity of charring or the integral of the duration and maximum temperature reached during combustion of fuel and high diversity of fuel

materials at the soil surface influence formation of charcoals which may differ widely in their chemical, physical, and structural properties (Nguyen et al., 2010; Bird et al., 2015; Pyle et al., 2017; Santín et al., 2015b, 2016a; Abney, Berhe, 2018; Belcher et al., 2018; Gao et al., 2022).

Pyrogenic material is not a homogenous organic C pool and is considered as “combustion continuum”: from slightly charred biomass of low aromaticity and high reactivity, generated at low temperatures, to particulate black carbon and a range of individual pyrogenic molecules with high aromaticity and low reactivity, formed at high temperatures (Bird, Ascough, 2012). The charcoal derived from vegetation fires represents the major source of PyOM in soils, while soot is formed as a secondary combustion product by condensation of volatiles into polycyclic aromatic hydrocarbons (Knicker, 2011).

High-severity fires result in higher PyOM production than low-severity fires mainly due to larger amounts of fuel affected by fire (Santín et al., 2015a). At the same time, Doerr et al. (2018) found that a low-intensity experimental fire resulted in higher PyOM production rate than a high-intensity fire, which was reflected in the percentage of pyrogenic carbon in wood samples. This indicates that more intense fires release a greater proportion of carbon into the atmosphere than is converted into PyOM for a given amount of fuel exposed to burning. Higher temperatures and extended periods of heating produce PyOM with a greater degree of aromatic condensation and therefore higher resistance to biological degradation (Nguyen et al., 2010; Santín et al., 2016b). The degree to which pyrogenic material is susceptible to abiotic and biotic degradation processes depends on its characteristics and local environmental conditions such as soil type, land use, temperature, moisture (Bird et al., 2015).

Despite the fact that PyOM has been addressed in numerous environmental research,

neither the chemical structure of PyOM nor the processes involved in its formation or degradation are well understood (Knicker, 2011; Ascough et al., 2020). Various methods have been used to describe PyOM, including thermal analysis such as thermogravimetry (TG) and differential scanning calorimetry (DSC) (Leifeld, 2007; De la Rosa et al., 2008; Mastrolonardo et al., 2014; Santín et al., 2017, 2020; Doerr et al., 2018). Although research interest in PyOM has significantly increased over recent decades worldwide, there is a considerable lack of information on its properties, resistance to degradation in particular, with respect to Siberian forest ecosystems. Thus, the aim of the present paper was to determine the characteristics of PyOM generated by a surface fire in a Scots pine forest in Siberia by thermal analysis methods.

Materials and methods

Study area and sampling procedure

The study was carried out in mature pure Scots pine stands (*Pinus sylvestris* L.) with feather

moss (*Pleurozium schreberi*), *Vaccinium vitis-idaea*, and grasses (*Calamagrostis* sp., *Pyrola rotundifolia*, *Carex macroura*) as dominant ground vegetation. The study sites were located in the subtaiga zone on the left bank of the Yenisey River in Krasnoyarsk Krai (56°26'N; 93°39'E). The climate of the region is sharply continental, with the annual average temperature of +0.6 °C. The total precipitation over the warm season is 330–350 mm and over the cold season – 110–120 mm (<http://www.meteo.ru>). Two study plots, one burned and the other unburned (control), were laid out on soddy-podzolic soils (Shishov et al., 2004) adjacent to each other (Fig. 1). Soddy-podzolic soils correspond to retisols in the world reference base for soil resources (Anjos et al., 2015).

A fast-moving surface fire occurred in May 2021. The severity of the wildfire was classified as low to moderate based on the average char heights on the trees (Kurbatsky, 1962) and the completeness of combustion of ground fuels (Rosleskhov derective, 1998). Mainly the upper



Fig. 1. Location of the study area and views of unburned (a) and burned (b) plots in a Scots pine forest

layer of the forest floor was burned. Trees were slightly damaged by the fire as indicated by burned bark in the bottom part of tree stems. Sampling was performed one day after the fire. There was no rain after the fire before the collection of samples. We sampled the litter layer (L) in 5 replicates at the burned plot and in 3 replicates at the unburned plot. The litter consisted of undecomposed needles, small pieces of bark, withered grass and small shrubs deposited on top of the duff layer. At the burned plot, we sorted the collected samples by eye into charred (blackened) plant material and uncharred plant residues. The charred material was used for thermal analysis. Additionally, the samples of small dead/down wood pieces $d < 1$ cm lying on the surface (typical wildfire fuel) and outer bark from Scots pine trees were collected at burned and control plots in 3–5 replicates.

Laboratory analysis

All samples were air-dried, ground, and sieved in the laboratory. The 0.3–0.5 mm size fraction was used for thermal analysis. Thermal analysis consists in gradual heating of the samples in order to measure the mass loss (TG) and the amount of energy released or absorbed in the form of heat (DSC). A different degree of resistance to thermal degradation (combustion) allows to distinguish labile and recalcitrant forms of organic matter (De la Rosa et al., 2019).

Thermogravimetry was carried out using a TG 209 F1 thermal analyzer (Netzsch, Germany) in an air atmosphere with the gas flow of 20 mL/min from 25 to 850 °C, at the heating rate of 10 °C/min in a platinum crucible. Differential scanning calorimetry was performed using a DSC 204 F1 thermal analyzer (Netzsch, Germany) in an air atmosphere at the temperature ranging from 25 to 590 °C, gas flow of 40 mL/min, heating rate of 10 °C/min, in an aluminum pan with a pierced lid. Data analysis

was performed using the Netzsch *Proteus*® Software. The stages of thermal degradation of the samples were determined by the number of peaks in derivative thermogravimetric (DTG) curves. DTG provides information on the onset, peak, and offset temperatures for each stage. The mass loss at each stage and the residual mass were obtained from TG curves. The enthalpy (ΔH , total heat content) was obtained from DSC curves by integrating the area of the reaction peak and the interpolated baseline between the start and the end of the reaction (Jiang, Drummer, 2020).

To evaluate the non-isothermal kinetic parameters from the thermogravimetry data, we used the Broido method (Broido, 1969). The activation energy for thermal (or thermo-oxidative) degradation of the samples was estimated using the equation:

$$\ln \left[\ln \left(\frac{1}{y} \right) \right] = -\frac{E_a}{RT} + C$$

where y is the mass of the sample not yet degraded (obtained from the TG data), E_a is the activation energy, R is the universal gas constant, T is the temperature, and C is a constant. The plot $\ln(\ln(1/y))$ versus $1000/T$ resulted in a straight line with a slope of $-E_a/R$. Activation energy was calculated from the slope of this plot.

To estimate the contribution of thermolabile and recalcitrant compounds in the organic matter composition before and after fire, the ratio (Z) of mass loss in the low-temperature region (< 400 °C) to high-temperature region (> 400 °C) was calculated (Chernikov et al., 1979; Uskova et al., 2018; Krylov, Mamontov, 2022).

To characterize the pyrogenic organic matter, we applied the thermal recalcitrance indexes (R_{50} , Q_1 , Q_2 and Q_3) calculated using TG and DSC data (Merino et al., 2014, 2015; Campo, Merino, 2016; Santín et al., 2017, 2020). We calculated the R_{50} index according to Harvey et al. (2012):

$$R_{50,x} = T_{50,x}/T_{50,\text{graphite}}$$

where $T_{50,x}$ and $T_{50,\text{graphite}}$ are the temperature values corresponding to 50 % mass loss in the x sample and graphite, respectively.

The values of $T_{50,x}$ were obtained directly from the TG thermograms in the temperature range from 170 to 850 °C where the thermal degradation of samples occurred after the loss of hygroscopic water. For graphite, we used the data obtained by Santín et al. (2020). $T_{50,\text{graphite}}$ was 823 °C. We classified the samples into recalcitrance/C sequestration potential classes according to Harvey et al. (2012): Class A ($R_{50} > 0.70$), Class B ($0.50 \leq R_{50} < 0.70$), Class C ($R_{50} < 0.50$). PyOM of Class A and Class C has recalcitrance and carbon sequestration potentials comparable to soot/graphite and uncharred plant biomass, respectively, whereas PyOM of Class B has an intermediate recalcitrance and carbon sequestration potential (Harvey et al., 2012).

For each DSC thermogram, we divided the area under the DSC curve between 150 and 590 °C into three temperature regions which represent different levels of organic matter resistance to thermo-oxidation: labile organic matter ($150 < T_1 < 375$ °C), mainly polysaccharides and other aliphatic compounds; recalcitrant organic matter ($375 < T_2 < 475$ °C), such as lignin or other polyphenols; and highly recalcitrant organic matter ($475 < T_3 < 550$ °C), such as polycondensed aromatic forms (Campo, Merino, 2016). We calculated the partial heats of thermal degradation of organic matter from the DSC thermograms using the Netzsch *Proteus*® Software. Partial heat was defined as the percentage of heat released within a certain temperature range out of the total amount of heat. The resulting partial heats representing these three regions were designated as Q_1 , Q_2 and Q_3 , respectively. The index Q_3 can be used as an indicator of thermally recalcitrant organic matter which has also proven to be more resistant

to microbial degradation than the material falling into regions Q_1 and Q_2 (Campo, Merino, 2016; Santín et al., 2020).

The mean and standard deviation of the parameters were calculated using Microsoft Excel.

Results and discussion

Differential scanning calorimetry

DSC provides information about all reactions with heat transfer effects during thermal degradation of a sample. Thermolabile components of plant material, such as hemicelluloses and cellulose, decompose within the temperature ranges from 225 to 325 °C and from 305 to 375 °C, respectively (Shen et al., 2009; Barros et al., 2011). The aromatic polymer lignin undergoes thermal degradation at a higher temperature than polysaccharides (hemicelluloses and cellulose). The polymer structure in lignin slowly starts to decompose at 200–275 °C, but the main process occurs around 400 °C (Brebu, Vasile, 2010).

DSC thermograms of unburned samples revealed an endothermic effect due to loss of hygroscopic water and an exothermic effect attributed to thermal degradation of organic matter (Fig. 2). The endothermic peak in DSC curves of unburned samples was observed at 59–66 °C. The enthalpy values of evaporation ranged from 163 to 192 J/g (Table 1). The thermal degradation of organic matter consisted of two stages. The first stage (exothermic peak at 345–349 °C) was associated with the decomposition of polysaccharides and production of charcoal residue. For unburned bark, the peak of polysaccharides is reduced to a shoulder due to their lower content compared to down wood and litter (Fig. 2). The second stage (exothermic peak at 407–458 °C) occurred due to thermal degradation of lignin and charcoal generated at the earlier stage. The enthalpy values of

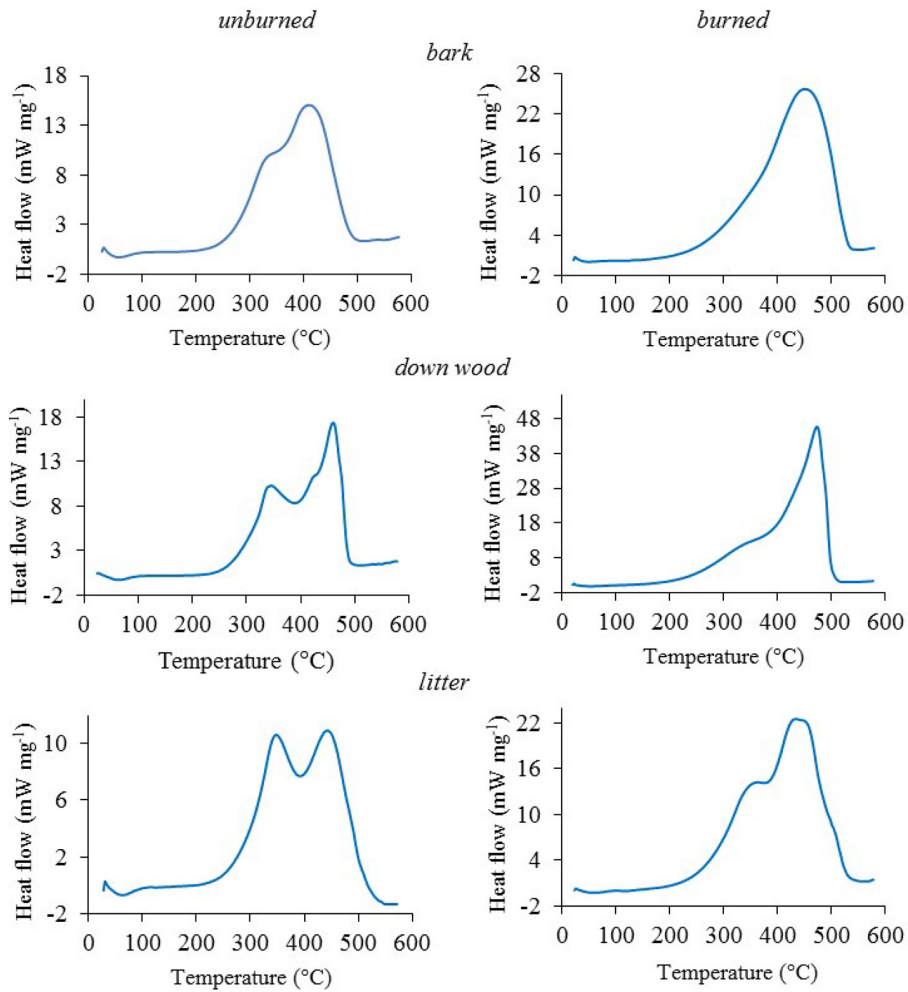


Fig. 2. DSC thermograms of unburned and burned (PyOM) samples in an air atmosphere at a heating rate 10 °/min

Table 1. DSC characteristics for unburned and burned (PyOM) samples (mean±standart deviation)

| Sample | Endothermic region | | Exothermic region | | | Thermal recalcitrance indexes, % | | |
|----------------------|-----------------------------------|------------------------------|-----------------------------------|-----------------------------------|-------------------------------|----------------------------------|--------|-------|
| | $T_{\text{peak}}, ^\circ\text{C}$ | $\Delta\text{H}, \text{J/g}$ | $T_{\text{peak}}, ^\circ\text{C}$ | $T_{\text{peak}}, ^\circ\text{C}$ | $\Delta\text{H}, \text{kJ/g}$ | Q_1 | Q_2 | Q_3 |
| Unburned plot | | | | | | | | |
| Bark | 60±4 | 163±21 | shoulder | 407±4 | -11.6±0.2 | 42±1 | 55±2 | 3±2 |
| Down wood | 59±7 | 192±74 | 345±1 | 458±3 | -9.6±1.5 | 36±0.5 | 60±0.4 | 4±1 |
| Litter | 66±3 | 172±35 | 349±2 | 444±9 | -11.0±1.2 | 39±2 | 50±2 | 10±1 |
| Burned plot | | | | | | | | |
| Bark PyOM | 48±2 | 70±17 | – | 459±12 | -22.8±2.4 | 22±1 | 58±1 | 20±1 |
| Down wood PyOM | 52±4 | 170±37 | shoulder | 469±7 | -24.7±3.2 | 22±7 | 65±11 | 13±4 |
| Litter PyOM | 58±3 | 113±45 | shoulder | 431±3; 452±5 | -19.5±2.3 | 35±2 | 55±2 | 10±2 |

Note. n=3–5; T_{peak} – peak temperature; ΔH – the enthalpy

thermal degradation for unburned samples varied from -9.6 to -11.6 kJ/g (Table 1).

Fire had a significant effect on the properties of litter, down wood, and bark. The enthalpy values of water evaporation were lower for PyOM samples with bark PyOM giving the lowest value. The peak temperature of water evaporation significantly decreased for bark PyOM compared to unburned bark (Table 1).

A slight shoulder of residual polysaccharides can be seen in the DSC curve of down wood PyOM while it is completely absent in the DSC curve of bark PyOM, indicating the loss of polysaccharides. The DSC curves of bark and down wood PyOM showed only one exothermic peak that occurred at higher temperatures (459 and 469 °C) due to formation of more heat-resistant aromatic compounds. The litter PyOM showed a well-defined shoulder of residual polysaccharides in the DSC curve and no increase in the temperature of the second exothermic peak. This testifies that the litter layer is subjected to fire-induced alteration to a smaller degree compared to down wood and bark PyOM. We observed the same shape of the DSC curve for down wood PyOM as the DSC curve obtained by Santín et al. (2020) for small down wood charcoal pieces.

The enthalpy values of thermal degradation for the PyOM samples were 1.8–2.6 times greater than for unburned samples due to enrichment in aromatic compounds (Table 1). Down wood and bark PyOM demonstrated higher values of the enthalpy than litter PyOM, indicating greater proportion of aromatic structures. This is confirmed by higher thermal recalcitrance indexes (Q_2 , Q_3 , Table 1) and thermogravimetry data (Table 2).

Calculation of partial heats revealed that the largest fraction in all studied samples was Q_2 (recalcitrant compounds), which made up 50–60 % and 55–65 % of total combustion heat

for unburned and PyOM samples, respectively (Table 1). The Q_1 attributed to the most easily degradable compounds was 36–42 % for unburned samples and decreased up to 22–35 % for PyOM samples. Down wood and bark PyOM showed significantly higher Q_3 values compared to unburned samples due to greater proportions of highly recalcitrant compounds. In contrast, litter PyOM revealed Q_3 similar to unburned litter, indicating substantially lesser alteration of the litter layer by fire. The obtained indexes for unburned samples are consistent with those found by Campo and Merino (2016) for litterfall and forest floor in tropical forests of the Yucatan Peninsula. Our results are in agreement with the earlier observations by Santín et al. (2017) who found that down wood charcoal had a higher Q_3 (22 %, maximum temperature 796 °C) compared to forest floor charcoals (11–17 %, maximum temperature 550–950 °C) after an experimental high-severity crown fire in pine (*Pinus banksiana*) stands. However, in our study down wood PyOM showed a markedly lower (13 % vs. 22 %) Q_3 value compared to the data obtained by Santín et al. (2017), probably due to the lower fire severity.

Thermogravimetry

TG provides information on the number of mass loss stages during thermal degradation of organic matter. The thermograms of the samples revealed substantial differences in the shape of DTG curves, the temperature of DTG peaks, and mass loss before and after fire (Fig. 3). From 25 up to 120 °C (Stage I), the unburned samples showed similar mass losses due to the dehydration process (5.51–5.77 %) (Table 2). Thermal degradation of polysaccharides and lignin occurred in the temperature ranges from 170(180) to 350(375) °C (Stage II) and from 350(375) to 500(540) °C (Stage III), respectively. The narrow shape of the peaks in the DTG curves reflects rapid thermal degradation of plant constituents. Bark

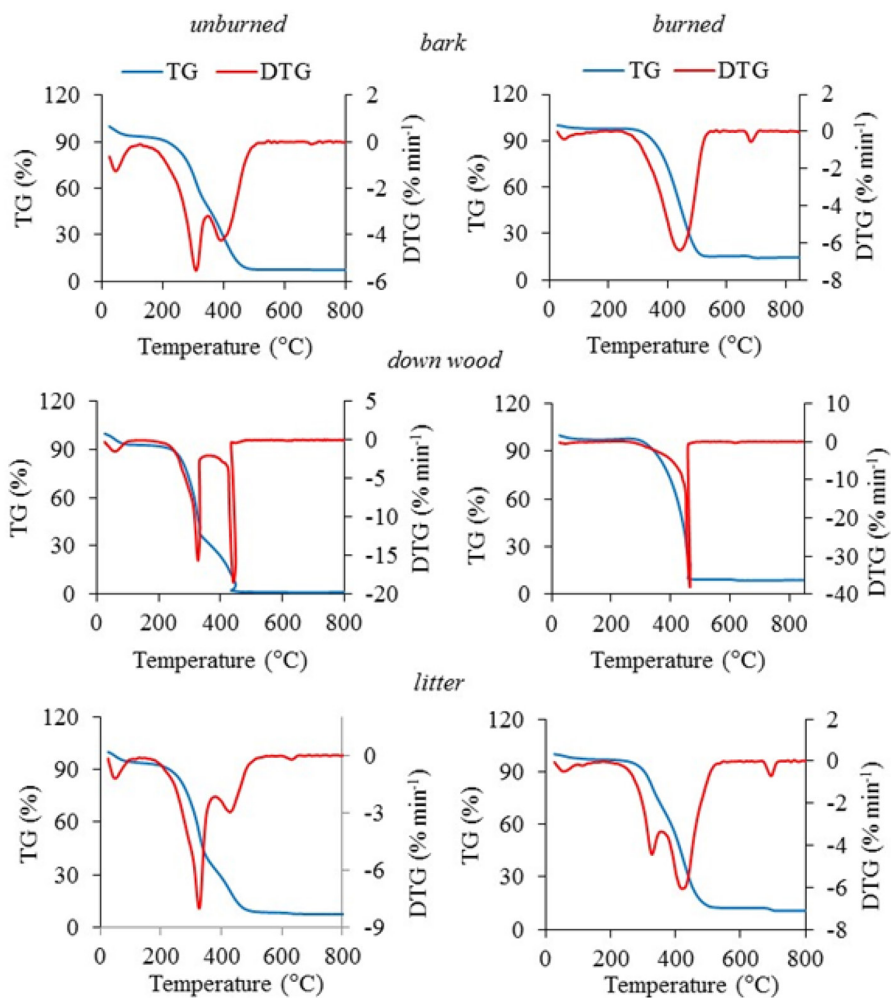


Fig. 3. TG/DTG curves of unburned and burned (PyOM) samples in an air atmosphere at a heating rate 10 °/min

showed the lowest mass loss related to thermal decomposition of polysaccharides and the greatest mass loss related to lignin (40.78 %). Down wood was characterized by the highest mass loss of polysaccharides (62.25 %). Litter showed the lowest mass loss (25.62 %) related to lignin (Table 2). Our thermogravimetry results agree with literature data on chemical composition of wood, bark, and needles of Scots pine trees (Johansson, 1995; Valentín et al., 2010; Dönmez et al., 2013). The fourth small peak (Stage IV) in the DTG curves of litter and bark associated with minor mass losses in the TG curves might be related to thermal degradation of the highly recalcitrant

charcoal formed previously. The Z ratio varied from 1.10 to 2.20, indicating predominance of thermolabile components over thermally stable aromatic structures in the chemical composition of unburned samples. The residual mass at 850 °C represents ash content. Litter and bark showed significantly greater residual masses compared to down wood (Table 2).

The TG results for PyOM samples indicated that mass loss due to water evaporation significantly decreased, which can be explained by high hydrophobicity of the freshly charred plant residues (Knicker, 2011). After hygroscopic water loss, the degradation of PyOM started at

Table 2. Thermal degradation parameters (TG/DTG) for unburned and burned (PyOM) samples (mean±standart deviation)

| Sample | Stage I | | Stage II | | Stage III | | Stage IV | | Residual mass at 850 °C, % | Z | T ₅₀ | R ₅₀ |
|----------------------|-------------------------|----------------------------|-------------------------|----------------------------|-------------------------|----------------------------|-------------------------|----------------------------|----------------------------|------|-----------------|-----------------|
| | Tpeak ₁ , °C | Mass loss ₁ , % | Tpeak ₂ , °C | Mass loss ₂ , % | Tpeak ₃ , °C | Mass loss ₃ , % | Tpeak ₄ , °C | Mass loss ₄ , % | | | | |
| Unburned plot | | | | | | | | | | | | |
| Bark | 50±4 | 5.51±0.68 | 309±1 | 45.01±0.15 | 396±2 | 40.78±0.92 | 629** | 0.16 | 7.41±0.01 | 1.10 | 345±2 | 0.42 |
| Down wood | 58±3 | 5.77±1.69 | 327±2 | 62.25±0.09 | 445±2 | 30.25±0.49 | – | – | 1.46±0.64 | 2.06 | 329±1 | 0.40 |
| Litter | 53±3 | 5.67±0.35 | 326±1 | 58.34±1.25 | 427±2 | 25.62±0.63 | 637±7 | 0.84±0.09 | 7.61±3.37 | 2.20 | 331±1 | 0.40 |
| Burned plot | | | | | | | | | | | | |
| Bark PyOM | 47±4 | 2.51±1.07 | – | 7.28±0.17* | 445±5 | 76.01±1.39 | 656±38 | 1.01±0.21 | 12.72±2.64 | 0.09 | 432±1 | 0.52 |
| Down wood PyOM | 45±1 | 2.58±0.51 | – | 12.06±2.42* | 455±11 | 75.58±1.08 | – | – | 9.00±0.14 | 0.16 | 431±3 | 0.52 |
| Litter PyOM | 51±2 | 2.82±0.93 | 325±3 | 23.82±4.51 | 420±3 | 57.87±5.03 | 692±4 | 1.34±0.38 | 12.68±2.31 | 0.40 | 396±7 | 0.48 |

Note: n=3-5; Tpeak – the temperature of DTG peak; * – since there was no DTG peak₂ for down wood and bark PyOM, the mass loss is shown in the same temperature range as for their unburned samples; ** – DTG peak₄ was observed for only one sample

higher temperatures (200–260 °C) compared to the unburned samples (170–180 °C) (Fig. 3). The peak related to thermolabile compounds tremendously decreased for litter PyOM and disappeared for bark and down wood PyOM. This indicates degradation of polysaccharides in the fire. The PyOM samples showed a significant decrease in mass loss of thermolabile compounds compared to unburned samples (Table 2). As the passing fireline heats surface and ground fuels, polysaccharides degrade more rapidly than lignin (Belcher et al., 2018).

A major mass loss of PyOM occurred within the temperature range from 339(370) to 520(540) °C. The peak temperature and mass loss attributed to thermal degradation of aromatic compounds significantly increased for down wood and bark PyOM compared to unburned samples (Table 2). A broad peak for bark PyOM at 445 °C indicates its slow thermal degradation. In contrast, thermal degradation of down wood PyOM occurred very quickly at 455 °C, probably due to a more homogeneous chemical composition. The litter PyOM also showed a higher proportion of aromatic compounds but the peak temperature slightly decreased (Table 2). This indicates that the litter layer was affected by fire to a lesser extent and the aromatic compounds formed had thermal stability similar to lignin in unburned litter. It could be explained by a higher moisture content in the forest floor compared to down wood and bark.

At the temperatures above 520(540) °C, mass loss for bark and litter PyOM may be indicative of the presence of highly recalcitrant pyrogenic forms such as polycondensed aromatic carbon (De la Rosa et al., 2008; Mastrolonardo et al., 2014). In comparison with unburned samples, all PyOM samples revealed a significantly lower Z ratio ranging from 0.09 to 0.40. This indicates the prevalence of thermally stable aromatic structures over thermolabile components. The

PyOM samples showed a higher ash content than unburned samples due to fire-induced loss of organic matter (Table 2).

A substantial increase in thermal recalcitrance of organic matter is also evidenced by the T_{50} value. T_{50} increased by 65 °C for litter PyOM, by 87 °C for bark PyOM, and by 102 °C for down wood PyOM compared to T_{50} for unburned samples (Table 2). The T_{50} values for bark and down wood PyOM were significantly higher than for litter PyOM. Harvey et al. (2012) reported that pyrogenic materials dominated by a larger proportion of C–C, single bonded structures, would have a lower thermal stability than those dominated by C=C, conjugated and aromatic structures.

We also estimated carbon sequestration potential of PyOM (Table 2). All PyOM samples showed higher R_{50} indexes compared to unburned samples. According to the classification by Harvey et al. (2012), litter PyOM is characterized by a low carbon sequestration potential (Class C, $R_{50} < 0.50$). Down wood and bark PyOM fit into class B ($0.50 \leq R_{50} < 0.70$), indicating enhanced chemical recalcitrance and an intermediate carbon sequestration potential. Harvey et al. (2012) observed the highest R_{50} values in biochars with the highest carbon contents, suggesting that the influence of formation conditions on the degree of biochars carbonization/aromatization was a major factor driving their thermal recalcitrance. Santín et al. (2017) demonstrated that forest floor charcoals formed at the maximum temperatures of 550 and 683 °C had $R_{50} < 0.50$, while dead wood and forest floor charcoals generated at 796 °C and 950 °C, respectively, had $R_{50} \geq 0.50$.

Kinetic analysis

We calculated the activation energy by the Broido method from TG curves in the temperature interval of 170–520 °C. An example of the Broido

graphs for major stages of degradation of litter PyOM is shown in Fig. 4. A plot of $\ln[-\ln(1-\alpha)]$ versus $1000/T(K^{-1})$ shows a good approximation of TG data to a straight line, as evidenced by the high values of regression coefficients.

The unburned samples showed the E_a values of 76.22–97.90 kJ/mol and 106.46–161.67 kJ/mol for thermal degradation of polysaccharides and lignin, respectively (Table 3). It suggests that more energy is required to break the bonds in lignin compared to polysaccharides.

As mentioned above, thermal degradation of PyOM samples began at higher temperatures, thus requiring more energy for thermal degradation compared to unburned samples. Gorshkov et al. (2021) reported that an increased degree of coalification affected biochar reactivity and caused an increase in the initial temperature of intense oxidation. All PyOM samples showed higher values of E_a compared to unburned samples. This implies cleavage of stronger bonds. The highest E_a value was observed for

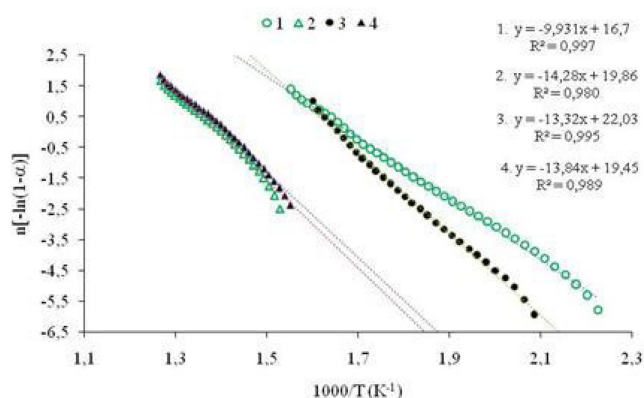


Fig. 4. Broido graphs for unburned (1, 2) and PyOM (3, 4) litter. 1, 3 and 2, 4 – E_a calculation for the thermal degradation of polysaccharides and aromatic complex, respectively

Table 3. The values of activation energy of thermal degradation for unburned and burned (PyOM) samples

| Sample | Temperature range, °C | Activation energy, kJ/mol | Coefficient of determination (R^2) |
|---------------------|-----------------------|---------------------------|--|
| Control plot | | | |
| Bark | 176–346 | 76.22±0.35 | 0.993–0.994 |
| | 356–506 | 106.46±2.44 | 0.981–0.987 |
| Down wood | 176–366 | 97.90±0.25 | 0.930–0.995 |
| | 371–506 | 161.67±5.41 | 0.986–0.998 |
| Litter | 176–371 | 79.44±3.10 | 0.995–0.998 |
| | 376–516 | 123.83±5.98 | 0.980–0.998 |
| Burned plot | | | |
| Bark PyOM | 267–517 | 107.85±3.45 | 0.986–0.987 |
| Down wood PyOM | 256–508 | 122.72±3.06 | 0.966–0.987 |
| Litter PyOM | 207–337 | 109.41±4.98 | 0.995–0.997 |
| | 347–517 | 106.40±6.10 | 0.972–0.997 |

down wood PyOM. The litter PyOM showed similar E_a values in both temperature ranges, thus indicating similar thermal degradation reactivity. The obtained E_a values of thermal degradation for PyOM samples are comparable with those of 97–240 kJ/mol reported by Gil et al. (2010) for coal/biomass blends combustion. Farrokh et al. (2019) recorded an activation energy of 154.37–183.61 kJ/mol for lignin char combustion. Fan et al. (2017) and Gorshkov et al. (2021) found an activation energy of 49–91 kJ/mol for combustion of macadamia and nut shells biochars. The differences in E_a values observed in literature can be related to the fact that kinetic characteristics of thermo-oxidative degradation (combustion) depend on the physicochemical properties of pyrogenic materials and the kinetic models used.

Conclusion

The characteristics of PyOM derived from different fuels during a low to moderate severity surface fire in a Scots pine forest in Siberia were

studied by the methods of thermal analysis (TG, DSC). The PyOM samples showed a significant loss of thermolabile components and enrichment in thermally recalcitrant aromatic compounds. PyOM formed from litter, down wood and bark had different thermal characteristics and resistance to thermal degradation. The major mass loss of PyOM occurred within the range from 339(370) to 520(540) °C. The values of activation energy and enthalpy (ΔH) of thermal degradation were higher for PyOM than for unburned samples. In comparison to litter PyOM, down wood and bark PyOM showed greater proportions of highly recalcitrant compounds (Q_3). The litter PyOM had a low carbon sequestration potential, while down wood and bark PyOM showed intermediate carbon sequestration potentials.

We found that the type of fuel substantially affected the properties of PyOM formed during fire. To better understand the role of PyOM in the carbon budget, more regional studies are required to account for a range of different ecosystem types and fire characteristics.

References

- Abney R. B., Berhe A. A. (2018) Pyrogenic carbon erosion: implications for stock and persistence of pyrogenic carbon in soil. *Frontiers in Earth Science*, 6: 26
- Anjos L., Gaistardo C., Deckers J., Dondeyne S., Eberhardt E., Gerasimova M., Harms B., Jones A., Krasilnikov P., Reinsch T., Vargas R., Zhang G. (2015) *World reference base for soil resources 2014 International soil classification system for naming soils and creating legends for soil maps*. Schad P., Van Huyssteen C., Micheli E. (eds.) FAO, Rome (Italy)
- Ascough P.L., Brock F., Collinson M.E., Painter J.D., Lane D.W., Bird M.I. (2020) Chemical characteristics of macroscopic pyrogenic carbon following millennial-scale environmental exposure. *Frontiers in Environmental Science*, 7: 203
- Barros N., Salgado J., Villanueva M., Rodriguez-Anon J., Proupin J., Feijoo S., Martin-Pastor M. (2011) Application of DSC-TG and NMR to study the soil organic matter. *Journal of Thermal Analysis and Calorimetry*, 104(1): 53–60
- Belcher C.M., New S.L., Santín C., Doerr S.H., Dewhirst R. A., Grosvenor M.J., Hudspith V.A. (2018) What can charcoal reflectance tell us about energy release in wildfires and the properties of pyrogenic carbon? *Frontiers in Earth Science*, 6: 169
- Bird M.I., Ascough P.L. (2012) Isotopes in pyrogenic carbon: A review. *Organic Geochemistry*, 42(12): 1529–1539

- Bird M.I., Wynn J.G., Saiz G., Wurster C.M., McBeath A. (2015) The pyrogenic carbon cycle. *Annual Review of Earth and Planetary Sciences*, 43: 273–298
- Bowring S.P. K., Jones M.W., Ciais P., Guenet B., Abiven S. (2022) Pyrogenic carbon decomposition critical to resolving fire's role in the Earth system. *Nature Geoscience*, 15: 135–142
- Brebu M., Vasile C. (2010) Thermal degradation of lignin – a review. *Cellulose Chemistry and Technology*, 44(9): 353–363
- Broido A. (1969) A simple, sensitive graphical method of treating thermogravimetric analysis data. *Journal of Polymer Science, Part A-2: Polymer Physics*, 7(10): 1761–1773
- Campo J., Merino A. (2016) Variations in soil carbon sequestration and their determinants along a precipitation gradient in seasonally dry tropical forest ecosystems. *Global Change Biology*, 22(5): 1942–1956
- Chernikov V.A., Kulchaev E.M., Konchits V.A. (1979) Derivative-graphical analysis of fulvic acids in virgin and cultivated chernozem and soddy-podzolic soils. *Izvestiya of Timiryazev Agricultural Academy [Izvestiya Timiryazevskoj sel'skohozyajstvennoj akademii]*, 2: 88–93 (in Russian)
- Danilin I.M., Crow T.R. (2008) The great Siberian forest: challenges and opportunities of scale. *Patterns and processes in forest landscapes*. Laforteza R., Sanesi G., Chen J., Crow T.R. (eds.) Dordrecht, Springer, p. 47–66
- De la Rosa J.M., Knicker H., López-Capel E., Manning D.A. C., González-Perez J. A., González-Vila F. J. (2008) Direct detection of black carbon in soils by Py-GC/MS, carbon-13 NMR spectroscopy and thermogravimetric techniques. *Soil Science Society of America Journal*, 72(1): 258–267
- De la Rosa J.M., Merino A., Jiménez Morillo N. T., Jiménez-González M. A., González-Pérez J. A., González-Vila F. J., Knicker H., Almendros G. (2019) Chapter 18. Unveiling the effects of fire on soil organic matter by spectroscopic and thermal degradation methods. *Fire effects in soil properties*. Pereira P., Mataix-Solera J., Úbeda X., Rein G., Cerdà A. (Eds.) CSIRO Publishing, Australia, p. 281–308
- Descals A., Gaveau D.L. A., Verger A., Sheil D., Naito D., Penuelas J. (2022) Unprecedented fire activity above the Arctic Circle linked to rising temperatures. *Science*, 378(6619): 532–537
- Doerr S.H., Santín C., Merino A., Belcher C.M., Baxter G. (2018) Fire as a removal mechanism of pyrogenic carbon from the environment: effects of fire and pyrogenic carbon characteristics. *Frontiers in Earth Science*, 6: 127
- Dönmez İ.E., Hafizoğlu H., Kılıç A. (2013) Effect of altitude on the main chemical composition of Scots pine (*Pinus sylvestris* L.). *International Caucasian Forestry Symposium*, Turkey, p. 866–869
- Fan F., Zheng Y., Huang Y., Lu Y., Wang Z., Chen B., Zheng Z. (2017) Combustion kinetics of biochar prepared by pyrolysis of macadamia shells. *BioResources*, 12(2): 3918–3932
- Farrokh N. T., Suopajarvi H., Sulasalmi P., Fabritius T. (2019) A thermogravimetric analysis of lignin char combustion. *Energy Procedia*, 158: 1241–1248
- Gao C., Cong J., Sun Y., Han D., Wang G. (2022) Variability in pyrogenic carbon properties generated by different burning temperatures and peatland plant litters: implication for identifying fire intensity and fuel types. *International Journal of Wildland Fire*, 31(4): 395–408
- Gil M.V., Casal D., Pevida C., Pis J.J., Rubiera F. (2010) Thermal behaviour and kinetics of coal/biomass blends during co-combustion. *Bioresour Technol*, 101(14): 5601–5608

- Gorshkov A., Berezikov N., Kaltaev A., Yankovsky S., Slyusarsky K., Tabakaev R., Larionov K. (2021) Analysis of the physicochemical characteristics of biochar obtained by slow pyrolysis of nut shells in a nitrogen atmosphere. *Energies*, 14(23): 8075
- Hansen M.C., Potapov P.V., Moore R., Hancher M., Turubanova S.A., Tyukavina A., Thau D., Stehman S.V., Goetz S.J., Loveland T.R., Kommareddy A., Egorov A., Chini L., Justice C.O., Townshend J.R. G. (2013) High-resolution global maps of 21st-century forest cover change. *Science*, 342(6160): 850–853
- Harvey O.R., Kuo L.J., Zimmerman A.R., Louchouart P., Amonette J.E., Herbert B.E. (2012) An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). *Environmental Science and Technology*, 46(3): 1415–1421
- Jiang F., Drummer D. (2020) Curing kinetic analysis of acrylate photopolymer for additive manufacturing by photo-DSC. *Polymers*, 12(5): 1080
- Johansson M.-B. (1995) The chemical composition of needle and leaf litter from Scots pine, Norway spruce and white birch in Scandinavian forests. *Forestry: An International Journal of Forest Research*, 68(1): 49–62
- Kharuk V.I., Ponomarev E.I., Ivanova G.A., Dvinskaya M.L., Coogan S.C.P., Flannigan M.D. (2021) Wildfires in the Siberian taiga. *Ambio*, 50(11): 1953–1974
- Knicker H. (2011) Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and survival in soil environments. *Quaternary International*, 243(2): 251–263
- Korovin G.N. (1996) Analysis of the distribution of forest fires in Russia. *Fire in ecosystems of boreal Eurasia*. Goldammer J.G., Furyaev V.V. (eds.) Kluwer Academic Publishers, Dordrecht/Boston/London, p. 112–128
- Krylov V.A., Mamontov V.G. (2022) The impact of different cenoses on the thermal characteristics of labile humic substances of typical chernozem in Kursk oblast. *Eurasian Soil Science*, 55(4): 452–459
- Kurbatsky N.P. (1962) *Forest fire suppression procedures and tactics*. Moscow, Goslesbumizdat, 154 p. (in Russian)
- Leifeld J. (2007) Thermal stability of black carbon characterised by oxidative differential scanning calorimetry. *Organic Geochemistry*, 38(1): 112–127
- Mastrolonardo G., Francioso O., Di Foggia M., Bonora S., Rumpel C., Certini G. (2014) Application of thermal and spectroscopic techniques to assess fire-induced changes to soil organic matter in a Mediterranean forest. *Journal of Geochemical Exploration*, 143: 174–182
- Merino A., Chávez-Vergara B., Salgado J., Fonturbel M.T., García-Oliva F., Vega J.A. (2015) Variability in the composition of charred litter generated by wildfire in different ecosystems. *Catena*, 133: 52–63
- Merino A., Ferreiro A., Salgado J., Fonturbel M.T., Barros N., Fernández C., Vega J.A. (2014) Use of thermal analysis and solid-state ¹³C CP-MAS NMR spectroscopy to diagnose organic matter quality in relation to burn severity in Atlantic soils. *Geoderma*, 226–227: 376–386
- Nguyen B.T., Lehmann J., Hockaday W.C., Joseph S., Masiello C.A. (2010) Temperature sensitivity of black carbon decomposition and oxidation. *Environmental Science & Technology*, 44(9): 3324–3331
- Pyle L.A., Magee K.L., Gallagher M.E., Hockaday W.C., Masiello C.A. (2017) Short-term changes in physical and chemical properties of soil charcoal support enhanced landscape mobility. *Journal of Geophysical Research: Biogeosciences*, 122(11): 3098–3107

Rosleskhoz directive (1998) *On approval of instructions for estimating damage caused by forest fires*. No. 5 from 03.04.98 (in Russian)

Santín C., Doerr S.H., Jones M.W., Merino A., Warneke C., Roberts J.M. (2020) The relevance of pyrogenic carbon for carbon budgets from fires: Insights from the FIREX experiment. *Global Biogeochemical Cycles*, 34(9): e2020GB006647

Santín C., Doerr S.H., Kane E.S., Masiello C.A., Ohlson M., de la Rosa J.M., Preston C.M., Dittmar T. (2016a) Towards a global assessment of pyrogenic carbon from vegetation fires. *Global Change Biology*, 22(1): 76–91

Santín C., Doerr S.H., Merino A., Bucheli T.D., Bryant R., Ascough P., Gao X., Masiello C.A. (2017) Carbon sequestration potential and physicochemical properties differ between wildfire charcoals and slow-pyrolysis biochars. *Scientific Reports*, 7: 11233

Santín C., Doerr S.H., Otero X.L., Chafer C.J. (2015a) Quantity, composition and water contamination potential of ash produced under different wildfire severities. *Environmental Research*, 142: 297–308

Santín C., Doerr S.H., Preston C.M., González-Rodríguez G. (2015b) Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle. *Global Change Biology*, 21(4): 1621–1633

Santín C., Doerr S.H., Merino A., Bryant R., Loader N.J. (2016b) Forest floor chemical transformations in a boreal forest fire and their correlations with temperature and heating duration. *Geoderma*, 264, Part A: 71–80

Shen D.K., Gu S., Luo K.H., Bridgwater A.V., Fang M.X. (2009) Kinetic study on thermal decomposition of woods in oxidative environment. *Fuel*, 88(6): 1024–1030

Shishov L.L., Tonkonogov V.D., Lebedeva I.I., Gerasimova M.I. (2004) *Classification and diagnosis of soils in Russia*. Smolensk, Oikumena, 342 p. (in Russian)

Talucci A.C., Loranty M.M., Alexander H.D. (2022) Siberian taiga and tundra fire regimes from 2001–2020. *Environmental Research Letters*, 17(2): 025001

Uskova N.V., Chernikov V.A., Belopukhov S.L. (2018) Agroecological estimation of long-term application effect of various fertilizer systems on humus condition of sod-podzolic soil. *Izvestiya of Timiryazev Agricultural Academy* [Izvestiya Timiryazevskoi sel'skokhozyaistvennoi akademii], 2: 18–33 (in Russian)

Valentín L., Kluczek-Turpeinen B., Willför S., Hemming J., Hatakka A., Steffen K., Tuomela M. (2010) Scots pine (*Pinus sylvestris*) bark composition and degradation by fungi: potential substrate for bioremediation. *Bioresource Technology*, 101(7): 2203–2209