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## ORIGINAL ARTICLE

# $^{13}$C-NMR, PAHs, WSOC and water repellence of fire-affected soils (Albic Podzols) in lichen pine forests, Russia

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**Abstract** Soil organic matter (SOM) in boreal forest ecosystems can be strongly transformed by fires which, in turn, can affect soil physical and biological properties such as water repellency and nutrient cycling. The article contains the results of a study on SOM content in fire-affected lichen pine forests of the middle taiga subzone of the European part of Russia (Komi Republic). Soils which survived surface fires 2, 10, 16 years ago and unburned area were studied. We investigated changes in SOM composition using $^{13}$C NMR spectroscopy, and we measured water-soluble organic carbon (WSOC) content, polycyclic aromatic hydrocarbons (PAHs) concentrations, and contact angles of water droplets on soils. Forest fires increased pyrogenic organic carbon content and also largely transformed SOM composition. $^{13}$C NMR spectroscopy showed that the SOM composition of densimetric fractions in pyrogenic and unburned soil greatly differs. Fires increased the aromatic content in SOM composition of light fractions. The highest amount of aromatic carbon probably pyrogenic origin accumulated in fractions of free and occluded organic matter. According to $^{13}$C NMR spectroscopy, the aromatic component of organic matter increased in the pyrogenic horizons. The strongest PAHs concentrations occurred in the fractions of free particulate

and occluded organic matter, in reference and fire-affected soils. The presence of PAHs in light densimetric fractions may serve as markers of past fire and fire intensity. In the initial years after fire, there was a decrease in the content of WSOC compounds; however, the WSOC content recovered with the recovery of ground vegetation. Our results showed that the greatest changes of contact angles were in upper pyrogenic soil horizons, whereas fires did not modify the contact angle value of lower mineral horizons.

## Introduction

Fires in the boreal zone are one of the most important historical disturbance factors and can transform forest ecosystems (Certini 2005; Bond-Lamberty et al. 2007; Egli et al. 2012; Santín and Doerr 2016). Fire intensity and area burned largely depend on climate conditions and often vary substantially from year to year. Previous studies have shown changes in the morphological and physicochemical properties of postpyrogenic soils (Dymov et al. 2014; Dymov and Gabov 2015). Pyrogenic changes are observed in the forest litter and upper mineral horizons. Special features of pyrogenic soils are diagnosed in the first years after the fires. Differences in the soil properties of pyrogenic soils are manifested in changing the acidity of the soil horizons, increasing the degree of base saturation, reducing the C:N ratio compared with the soils of undisturbed forests. The mineral soil horizons in the burnt area become enriched in the most mobile amphiphilic fractions of the organic matter, which is seen from the increase in the

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absolute and relative contents of the hydrophilic fractions, which might be represented by the products of combustion of fresh plant remains and litter.

Soils of the boreal zone contain up to 30% of planetary soil organic carbon (SOC) (Scharlemann et al. 2014). Fires transform SOM in litters and so form a thin pyrogenic horizon which is characterized by specific properties (Badia et al. 2014). Fires modify SOM composition (Knicker 2011; Santín et al. 2013; Soucemarianadin et al. 2014), with the response of various types of SOM compounds reacting differently to fire (González-Pérez et al. 2004; Knicker 2007; Krasilnikov 2015). For example, low-intensity fires have been shown to increase the contribution of aromatic compounds in SOM (Alexis et al. 2010; Vergnoux et al. 2011; Dymov et al. 2015) and affect the biological properties of soils (Maksimova et al. 2017). SOM composition can also influence the physical properties of soils. For example, it can change SOM hydrophilic and hydrophobic properties (Doerr et al. 2000; Dlapa et al. 2008; Atanassova and Doerr 2011). However, changes to SOM resulting from the impact of fire in forests of North Eurasia are largely understudied (Bodi et al. 2014).

In the European North of Russia and the Komi Republic, fires are common in pine forests which occur on well-drained sandy soils. Low- and medium-intensity running surface fires normally dominate. The aims of this study were to (1) investigate SOM composition after surface fires by $^{13}$C-NMR spectroscopy; (2) identify differences in SOM composition (densimetric fractions) differences of fire-affected soils; (3) assess changes in water-soluble organic carbon (WSOC); and (4) study amphiphilous properties of fire-affected soils using contact angle of wetting.

## Materials and methods

The studied plots are located at middle taiga subzone of European part of Russian Federation (Komi Republic Russia). The average annual temperature is approximately 0 °C, annual precipitation varies from 500 to 600 mm, absolute altitude ranges between 100 and 150 m asl, and the parent material consists of sandy deposits (Taskaev 1997). A detailed description and location of the study location was given by us earlier (Dymov and Gabov 2015). The brief

characterization of the study plots and description of soil profiles can be found in Table 1. The soil samples were taken according to soil genetic horizons in fivefold repetition within each study site. Classification status of the investigated soils was determined according to the World Reference Base for Soil Resources (IUSS Working Group 2014). Fire characterization, morphological and physicochemical properties of soil under consideration areas have been described earlier (Dymov and Gabov 2015). Densimetric fractionation was performed according to Cerli et al. (2012) and Grunewald et al. (2006). The free particulate organic matter (FPOM) fraction was isolated using a solution with a density of $1.60 \pm 0.03$ g cm$^{-3}$. The occluded particulate organic matter (OPOM) was separated using a solution of the same density after ultrasonic treatment at 150 J cm$^{-3}$. Organic–mineral complexes prevail in heavy fraction (HF) with a density more than $1.60 \pm 0.03$ g cm$^{-3}$.

$^{13}$C-NMR spectra of soils and densimetric fractions were recorded on a JNM-ECA 400 spectrometer (JEOL, Japan) (100.53 MHz), with a rotation frequency of 6 kHz, a contact time of 5 ms, and a 5-s recycle delay. Chemical shifts of fractions were determined relative to a tetramethylsilane shift (0 ppm). The contribution of main carbon forms to the total spectral intensity was determined by integration of the corresponding chemical shift regions according to (Mastrolonardo et al. 2015; Miesel et al. 2015). The relative contribution of chemical shift regions is given in Table 2. The total content of aromatic structures (AR) was calculated as the sum of the signals at 110–165 and 185–220 ppm fields. Signals from aliphatic structures (AL) were recorded in the 0–110 and 165–185 ppm fields. The aromaticity values (AV) were identified according to $100 \times AR/(AR + AL)$ (Liang et al. 1996). Soil organic matter structural–functional properties were assessed only in organic horizons and in free and occluded organic matter fractions. Heavy fractions were not analyzed because of low carbon content.

The concentrations of polycyclic aromatic hydrocarbons (PAHs) in the soil samples were determined according to EPA method 8310 (US EPA 1986) and (PND F 2007). Extraction was done with dichloromethane/acetone mixture = 1/1 at 100 °C and pressure of 1500 psi on the Thermo Scientific Dionex ASE 350 Accelerated Solvent Extractor system. The qualitative and quantitative

**Table 1** Characteristics of the study plots

| Abbreviation | Location WGS84 | Forest type before fire and its composition | Fire characteristics | Fire year/time gone after fire accident |
|---|---|---|---|---|
| 1L | 61°21́30, 5́N 50°51́05, 2́E | Lichen pine, 10P | – | Unburned |
| 2L | 61°21́31, 6́N 50°50́42, 7́E | Lichen pine, 10P | Surface, high intensity | 2011/2 years |
| 3L | 62°07́25, 0́N 50°26́53.9́E | Lichen pine, 10P | Surface running, medium intensity | 2003/10 years |
| 4L | 62°06́17.4́N 50°26́10.4́E | Lichen pine, 10P | Surface running, medium intensity | 1997/16 years |

**Table 2** Percentage distribution (%) of signal intensity between selected chemical shift regions (ppm) of $^{13}$CPMAS NMR spectra of bulk soil and densimetric fractions

| Sample | Alkyl C | O-Alkyl C | | | Aryl C | | Carboxyl C/Amide/Ester | | Aromaticity values (AV) |
|---|---|---|---|---|---|---|---|---|---|
| | | Methoxyl/ N-alkyl | O-Alkyl | Di-O-Alkyl | Aromatic | Phenolic | Carboxyl/ amide | Aldehyde/ ketone | |
| | 0–45 | 45–60 | 60–95 | 95–110 | 110–145 | 145–165 | 165–185 | 185–220 | |
| Unburnt soil (1L) | | | | | | | | | |
| Oi | 37.9 | 7.5 | 40.5 | 7.3 | 2.8 | 1.6 | 2.3 | 0.1 | 4.4 |
| Oea | 16.6 | 2.7 | 66.2 | 12.4 | 0.0 | 0.1 | 2.0 | 0.0 | 0.1 |
| E (FPOM) | 58.0 | 6.3 | 11.7 | 1.0 | 18.6 | 1.0 | 2.5 | 0.9 | 20.6 |
| E (OPOM) | 44.2 | 7.8 | 19.4 | 4.1 | 17.8 | 2.2 | 2.0 | 2.4 | 22.4 |
| Burnt soil (2L) | | | | | | | | | |
| Oi | 40.3 | 6.6 | 40.7 | 5.5 | 3.9 | 0.4 | 2.7 | 0.0 | 4.3 |
| Qpyr | 27.5 | 7.5 | 26.1 | 5.2 | 23.8 | 2.0 | 1.3 | 6.7 | 32.4 |
| Q pyr (FPOM) | 24.2 | 8.0 | 14.2 | 7.4 | 37.8 | 3.7 | 0.8 | 3.9 | 45.4 |
| Qpyr (OPOM) | 69.7 | 5.2 | 14.3 | 1.4 | 4.4 | 2.8 | 1.7 | 0.4 | 7.6 |
| Burnt soil (3L) | | | | | | | | | |
| Oi | 56.1 | 7.4 | 30.1 | 3.0 | 0.0 | 0.2 | 3.0 | 0.1 | 0.3 |
| Qpyr | 59.6 | 7.4 | 22.2 | 2.3 | 4.7 | 0.7 | 2.1 | 0.9 | 6.3 |
| Qpyr (FPOM) | 40.5 | 6.5 | 17.9 | 14.8 | 16.6 | 1.8 | 1.0 | 0.9 | 19.3 |
| Qpyr (OPOM) | 48.0 | 7.6 | 17.6 | 3.5 | 17.6 | 1.9 | 1.8 | 2.0 | 21.4 |
| Burnt soil (4L) | | | | | | | | | |
| Qpyr | na | na | na | na | na | na | na | na | na |
| Qpyr (FPOM) | 43.8 | 6.6 | 17.4 | 4.4 | 22.6 | 3.0 | 1.3 | 1.0 | 26.6 |
| Qpyr (OPOM) | 53.4 | 6.6 | 14.4 | 1.9 | 18.4 | 1.2 | 2.3 | 1.8 | 21.4 |

*na* data not available

determination of PAHs in the soils was performed by liquid chromatography on Lyumakhrom chromatograph (Lumex, Russia).

Water-soluble organic carbon (WSOC) was extracted with deionized water (ELGA Lab Water, England) at room temperature at a ratio of 1:50 (soil/water) for mineral horizons and 1:100 for organic and pyrogenic horizons in BIOFIL test tubes. Suspensions were shaken for an hour using the Heidolph Multi Reax shaker (acceleration 6×) at room temperature. Filtration was done immediately after shaking and utilized Millipore devices with quartz filters (MN, Germany, pore size 0.4 μm). Each sample was measured for total volume of filtrate. Total carbon and inorganic carbon (TC and IC) were assessed using the TOC-VCPN analyzer (Shimadzu, Japan) with TNM-1 module. Total organic carbon (TOC) was assessed by difference between TC and IC. The obtained results were recalculated on a dry soil mass basis.

To measure water repellence of soil, we used the contact angle approach. This method determines the contact angle water drop on soil surface by the static sessile drop method on a Kruss DSA 100 goniometer equipped with a micro-video camera and software for the analysis of drop shape. Samples for contact angle determination were prepared according to published recommendations (Bachmann et al. 2000; Wu 2001; Shang et al. 2008; Bachmann and McHale 2009). To measure a soil sample, a double-faced tape 1.5 × 1.0 cm in size was glued to a glass slide for microscopy. The soil sample was triturated, passed through a 0.25 mm sieve, and applied onto the upper surface of the tape. The soil material was pressed down by another glass slide with a force of about 100 g; the unattached particles were carefully shaken off, and the soil was pressed down again with the slide. The procedure was repeated one or two times more for a complete and uniform filling of the surface. Immediately before the measurement, the slide with the sample was dried at 40 °C for 3 h and cooled at ambient temperature; the contact angle was then measured according to the recommendations for clay minerals (Shang et al. 2008).

## Results and discussion

### $^{13}$C-NMR analysis of organic horizons

Structural and functional changes in litters of Albic Podzols under lichen pine forests and in pyrogenic horizons

**Fig. 1** Peak discharges of conifer needles after running surface fire at Pine forest
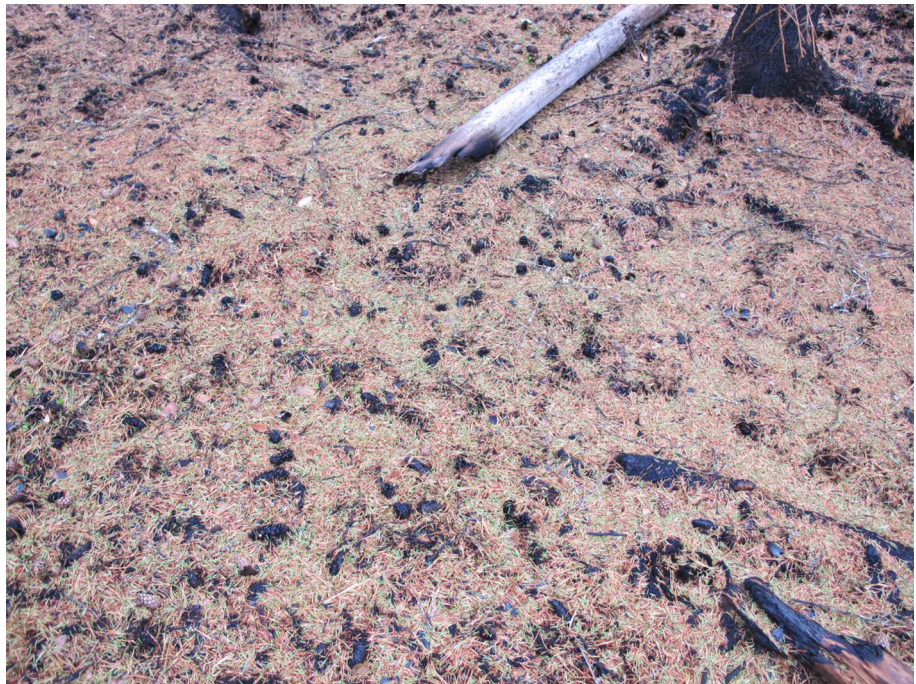


were analyzed. The NMR analysis results are given in Table 2. The $^{13}C$ NMR spectra of litter at the control site attributed to O-alkyl structures, mainly cellulose and hemicelluloses, and also alkyl C. The contribution of signal in alkyl region was different at Oi and Oea horizons. The organic matter of the upper horizon mostly represented fresh litter; for example, the alkyl C content was high in the Oi subhorizon but significantly decreased in the Oea subhorizon, and the decrease was accompanied with an increase in the content of cellulose and hemicellulose fragments. Organic matter of the Oi and Oea subhorizons had an extremely low aromaticity value. Generally, the obtained results are similar to the previously published data on litter composition in forests of Canada (Santin et al. 2016) and of northern Minnesota, USA (Miesel et al. 2015). In contrast to soil types of Central Italy (Mastrolonardo et al. 2015), the soils in our study sites have lower aromaticity, as well as C-Aryl and carboxyl carbon content. Forest fires largely modified the content of structural–functional groups in organic horizons. Pyrogenic horizons underwent serious changes as they decreased in alkyl carbon, cellulose and hemicellulose components and increased in aromatic carbon content. The SOC aromaticity value also greatly increased (Table 2). Fires activate loss of needles by conifers (Fig. 1) which partly obscure pyrogenic changes. Pine needles form a new litter layer after fire (up to several cm thick) with a relatively chemical stable composition. The content of some fractions and the aromaticity value at the 2-year-old burnt plot are similar to those at the background plot. SOM of upper soil horizons is dominated by alkyl and O-alkyl carbon with a very low concentration of aromatic and phenol carbon.

The pyrogenic horizon of the 2-year-old fire plot best illustrates fire aftereffects. The structural–functional groups in SOM included practically equally dominant concentrations of aliphatic, O-alkyl and aromatic groups in the presence of very minor contribution from phenol, carboxylic, and aldehyde groups. Ten years after fire, the composition of Oi subhorizon becomes similar to the background site. For example, the contribution from aromatic groups largely decreases and aliphatic fragments increase. Although combustion products significantly affect SOM composition, peak discharges of pine needles also play an important role, for example, by increasing the contribution from aliphatic groups such as we observed in the site representing 10 years after fire. The major transformations in pyrogenic soils result from combustion products (Pereira et al. 2012) which can persist in soils for a long period of time.

## Changes of densimetric fractions identified by $^{13}C$-NMR

The upper horizons of studied soils differed in the content of densimetric fractions. It has been previously shown that an increase in FPOM and OPOM fractions can occur in soils affected by fires. Upper mineral soil horizons at burned sites had greatly changed carbon and nitrogen content. FPOM increased up to 3–8%, OPOM—1.8–2.4% wt, and heavy fractions (HF) decreased to 88–92% wt.
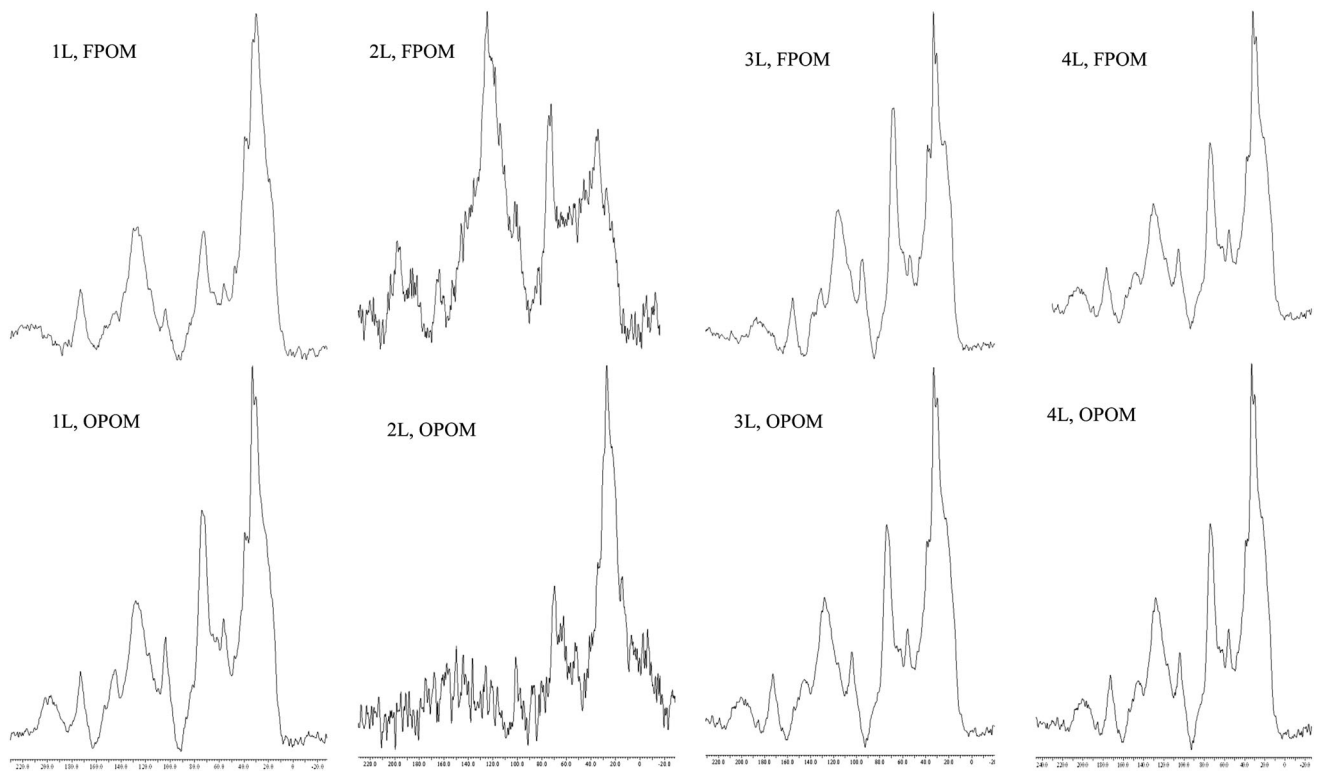
**Fig. 2** $^{13}$C CPMAS NMR spectra of densimetric fractions from upper mineral horizons of studied soils

Free and occluded OM fractions of fire-affected soils were composed of carbon by 322–438 and of nitrogen by 6.7–12.2 g*kg$^{-1}$ (Dymov and Gabov 2015). The content of particular fractions greatly differed depending on fire characteristics and time since fire. At the background plot, free organic matter fractions consisted mainly of aliphatic carbon (58%) and aromatic carbon (Fig. 2). The composition of occluded organic matter fraction differed strongly from the FPOM fraction. In the OPOM fraction, O-alkyl groups dominated over alkyl carbon evidencing involvement of tree waste into the humification processes. Occluded organic matter largely consisted of aromatic compounds. At the pine forest plot burnt 2 years ago, the FPOM fraction seriously differed from background soil and was dominated by aromatic structures, phenol carbon and carboxylic groups (Table 2). Aliphatic structures decreased and aromaticity values increased at FPOM of soil 2L. For OPOM fraction of the 2L soil, aromaticity values decreased along with a high content of alkyl carbon. But FPOM and OPOM organic matter composition in 3L and 4L soils was similar to that of background soil with dominance of aliphatic and few aromatic fragments. OPOM composition at 10- and 16-year-old fire plots is not changed over time since fire. It is mainly alkyl carbon (48–53%) which increases during postpyrogenic succession. Our data agree with the earlier published data of Glaser et al. (2000).

Thus, fires largely change structural–functional properties of soil organic matter. The changes depend on fully or partly-burnt litter, incorporation of fresh plant waste and partly destructed plant waste components. Pyrogenic changes are well diagnosed on densimetric fractions, but they often become minimized by postpyrogenic vegetation succession.

## PAHs content in densimetric fractions

Earlier studies have shown that fires in boreal forests largely increase the content of PAHs in soils (Gennadiev and Tsibart 2013; Dymov et al. 2014; Tsibart et al. 2014, Dymov et al. 2015); however, their status in soil horizons is not always clear. Therefore, we assessed the content of PAHs in densimetric fractions. Concentration of particular PAHs in densimetric fractions is given in Table 3. Fractions of free and occluded organic matter had the highest concentrations of polyaromatic compounds equally in background and pyrogenic soils. Interestingly but FPOM (free organic matter) fraction of background plot had a high total concentration of PAHs which could possibly evidence previous fires. As the concentration of OPOM fraction in upper soil horizons was extremely low, we could not extract the required amount of fraction for analysis. The total PAH content in the heavy fraction of the background plot was also low (30 ng g$^{-1}$). It can be assumed that

**Table 3** Content of PAHs in densimetric fraction and soils, ng g$^{-1}$

| Horizon | Sample | 2-Nuclear | | | 3-Nuclear | | 4-Nuclear | | | | 5-Nuclear | | | | 6-Nuclear | Sum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | NP | ACE | FL | PHE | ANT | FLA | PYR | BaA | CHR | BbF | BkF | BaP | DahA | BghiP | |
| 1L | | | | | | | | | | | | | | | | |
| E | BS | n.f. | n.f. | 41 ± 17 | 27 ± 13 | 1.2 ± 0.6 | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | 29 ± 13 | 98.2 |
| | FPOM | 410 ± 210 | 11 ± 4 | 580 ± 150 | 140 ± 30 | 12 ± 6 | 130 ± 50 | 120 ± 60 | 8 ± 4 | 130 ± 40 | 53 ± 22 | 14 ± 7 | 21 ± 11 | 9 ± 4 | 270 ± 60 | 1908.0 |
| | HF | n.f. | n.f. | 23 ± 9 | 7 ± 4 | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | 30.0 |
| 2L | | | | | | | | | | | | | | | | |
| Qpyr | BS | 63 ± 30 | n.f. | 84 ± 22 | 43 ± 22 | 2.1 ± 1.1 | n.f. | n.f. | n.f. | 4.4 ± 2.3 | 19 ± 8 | 1.8 ± 0.9 | 2.3 ± 1.2 | n.f. | 14 ± 6 | 233.6 |
| | FPOM | 740 ± 260 | 33 ± 13 | 1210 ± 220 | 610 ± 140 | 39 ± 9 | 220 ± 80 | 150 ± 70 | 6 ± 3 | 84 ± 29 | 340 ± 90 | 21 ± 10 | 39 ± 19 | 39 ± 19 | 47 ± 21 | 3578.0 |
| | OPOM | 1170 ± 190 | 51 ± 20 | 1700 ± 300 | 900 ± 200 | 44 ± 11 | 100 ± 40 | 70 ± 30 | 9 ± 4 | 90 ± 30 | 320 ± 80 | 22 ± 11 | 31 ± 15 | 31 ± 15 | 31 ± 13 | 4539.0 |
| | HF | 23 ± 11 | n.f. | 50 ± 20 | 27 ± 13 | 1.7 ± 0.9 | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | 1.1 ± 0.6 | n.f. | 6 ± 3 | 108.8 |
| 3L | | | | | | | | | | | | | | | | |
| Qpyr | BS | 150 ± 80 | n.f. | 170 ± 40 | 121 ± 27 | 6 ± 3 | 23 ± 11 | n.f. | n.f. | 19 ± 10 | 11 ± 4 | 4.3 ± 2.1 | 8 ± 4 | n.f. | 7 ± 3 | 519.3 |
| | FPOM | 450 ± 220 | 18 ± 7 | 660 ± 170 | 390 ± 80 | 25 ± 6 | 58 ± 27 | 30 ± 14 | 7 ± 3 | 70 ± 40 | 100 ± 26 | 9 ± 4 | 27 ± 14 | 9 ± 4 | 37 ± 16 | 1890.0 |
| | OPOM | 470 ± 230 | 18 ± 7 | 630 ± 160 | 410 ± 90 | 40 ± 10 | 100 ± 40 | 70 ± 30 | n.f. | 80 ± 40 | 60 ± 25 | 10 ± 5 | 26 ± 13 | 14 ± 7 | 98 ± 23 | 2026.0 |
| | HF | 50 ± 25 | n.f. | 110 ± 30 | 47 ± 23 | 2.3 ± 1.2 | n.f. | n.f. | n.f. | 3.1 ± 1.6 | n.f. | n.f. | 1.1 ± 0.6 | n.f. | n.f. | 213.5 |
| 4L | | | | | | | | | | | | | | | | |
| Qpyr | BS | 42 ± 21 | n.f. | 54 ± 21 | 34 ± 17 | 1.0 ± 0.5 | n.f. | n.f. | n.f. | 3.9 ± 2.0 | n.f. | n.f. | 1.3 ± 0.7 | n.f. | 9 ± 4 | 145.2 |
| | FPOM | 410 ± 210 | 15 ± 6 | 630 ± 160 | 480 ± 110 | 22 ± 5 | 67 ± 25 | 70 ± 30 | 36 ± 15 | 80 ± 40 | 113 ± 29 | 9 ± 5 | 29 ± 14 | 12 ± 6 | 28 ± 12 | 2001.0 |
| | OPOM | 400 ± 200 | 27 ± 11 | 740 ± 190 | 580 ± 130 | 26 ± 6 | 120 ± 50 | 70 ± 30 | 6 ± 3 | 90 ± 30 | 31 ± 13 | 12 ± 6 | 24 ± 12 | 24 ± 12 | 150 ± 40 | 2300.0 |
| | HF | n.f. | n.f. | 36 ± 14 | 16 ± 8 | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | n.f. | 12 ± 5 | 64.0 |

*NP* naphthalene, *ACE* acenaphthene, *FL* fluorene, *PHE* phenanthrene, *ANT* anthracene, *FLA* fluoranthene, *PYR* pyrene, *BaA* benzo[a]anthracene, *CHR* chrysene, *BbF* benzo[b]fluoranthene, *BkF* benzo[k]fluoranthene, *BaP* benzo[a]pyrene, *DahA* dibenzo[a,h]anthracene, *BghiP* benzo[g,h,i]perylene, *IcdP* indeno[1,2,3-c,d]pyrene, *n.f.* not found (the obtained result is under the below quantitative limit as for NP < 20, ACE < 6, FL < 6, PHE < 6, ANT < 1, FLA < 1, PYR < 20, BaA < 6, CHR < 3, BbF < 6, BkF < 6, BaP < 1, DahA < 6, BghiP < 6, IcdP < 6). *BS* balk soil

**Table 4** PAHs diagnostic ratios in soils and densimetric fractions of soils

| Horizon | Sample | ANT/(ANT + PHE) | FLA/(FLA + PYR) | BaA/(BaA + CHR) |
|---------|--------|-----------------|-----------------|-----------------|
| 1L | | | | |
| E | BS | 0.04 | – | – |
| | FPOM | 0.08 | 0.52 | 0.06 |
| | HF | – | – | – |
| 2L | | | | |
| Qpyr | BS | 0.05 | – | – |
| | FPOM | 0.06 | 0.59 | 0.07 |
| | OPOM | 0.05 | 0.59 | 0.09 |
| | HF | 0.06 | – | – |
| 3L | | | | |
| Qpyr | BS | 0.05 | – | – |
| | FPOM | 0.06 | 0.66 | 0.09 |
| | OPOM | 0.09 | 0.59 | – |
| | HF | 0.05 | – | – |
| 4L | | | | |
| Qpyr | BS | 0.03 | – | – |
| | FPOM | 0.04 | 0.49 | 0.31 |
| | OPOM | 0.04 | 0.63 | 0.06 |
| | HF | – | – | – |

wildfires are the main source of PAHs in these soils, including soils of the unburned background site.

Along with a general increase in the content of free and occluded matter fractions in pyrogenic soils (Table 3), there was an increase in PAH content in all fractions. The highest concentrations were identified for the FPOM and OPOM fractions at the 2-year-old burnt plot. In analogous fractions of 10- and 16-year-old fire plots, the PAH content was also high for every fraction. However, the PAH content in the fractions we investigated generally decreased with time since fire. Total PAH content also increased in heavy densimetric fractions at burnt plots, in contrast with analogous fractions of the background soil. Only an insignificant part of PAHs became involved into organic–mineral interactions and formed organic–mineral complexes in upper mineral horizons. In contrast with unburned soil, the increase in fire-affected soils associated with naphthalene, fluorene, and phenanthrene. We suggest that the PAH content in densimetric fractions (FPOM and OPOM) could be possibly applied as fire markers.

Numerous literature sources utilize PAH ratios (diagnostic criteria) in environmental media to obtain information on origin and sources of different PAHs. Table 4 includes most popular PAH ratios as FLA/(FLA + PYR), ANT/(ANT + PHE), BaA/(BaA + CHR) which could tell about the origin of study isomers (petrogenic or combustion). But applied to soils (densimetric fractions), PAH ratios depend on several parameters (soil type, moisture degree, sampling site, PAH resistance to degradation by microorganisms, etc.). For the study subzone, the earlier published PAH ratios do not unambiguously identify origin of polyarenes (Yunker et al. 2002) and need to be reworked.

## Water-soluble organic carbon

Fire-affected soils largely changed WSOC content. Upper litter and newly formed pyrogenic horizons were directly fire-impacted and therefore decreased in WSOC concentration. Soils at the 2-year-old burnt plot decreased in TC concentration by 2–4 times. This is probably due to the pyrogenic effect on ground cover plants, which play a significant role in the production of water-soluble organic compounds. At the 10- and 16-year-old plots, TC content is similar to the background site (Table 5), which we attribute to ground cover revegetation. Simultaneously, soil litters decreased whereby mineral soil part increased in TC. WSOC content changes in the study pyrogenic soils largely depended on fire intensity, as well as on revegetation processes as ground cover plants serve as the main producers of water-soluble organic matter. Similar data on WSOC changes were obtained for larch forests of Siberia (Prokushkin et al. 2008; Prokushkin et al. 2011; Masyagina et al. 2016). Postpyrogenic organic compounds may be transported to water bodies immediately

**Table 5** Content of water-soluble organic compounds at studied soils

| Site | Horizon | Depth (cm) | TC mg g$^{-1}$ soil | IC | TOC |
|------|---------|------------|---------------------|-----|-----|
| 1L | Oi | 0–1 | 5.42 ± 1.11 | 0.006 ± 0.0016 | 5.41 ± 1.12 |
| | Oea | 1–3 | 9.3 ± 1.8 | 0.015 ± 0.004 | 9.23 ± 1.8 |
| | E | 3–13 | 0.10 ± 0.02 | 0.001 ± 0.0002 | 0.10 ± 0.02 |
| | Bs | 13–45 | 0.01 ± 0.002 | 0.001 ± 0.0003 | 0.01 ± 0.002 |
| 2L | Oi | 0–1 | 2.42 ± 0.48 | 0.009 ± 0.002 | 2.408 ± 0.48 |
| | Qpyr | 0–6 (12) | 0.02 ± 0.004 | 0.002 ± 0.0005 | 0.019 ± 0.004 |
| | E | 12–15 | 0.090 ± 0.018 | 0.001 ± 0.0003 | 0.086 ± 0.017 |
| | Bs | 15–40 | 0.01 ± 0.002 | 0.001 ± 0.0003 | 0.012 ± 0.002 |
| 3L | Oi | 0–1 | 6.01 ± 1.2 | 0.018 ± 0.005 | 5.994 ± 1.2 |
| | Qpyr | 1–3 | 0.10 ± 0.02 | 0.002 ± 0.0005 | 0.100 ± 0.02 |
| | E | 3–7 | 0.11 ± 0.022 | 0.002 ± 0.0005 | 0.112 ± 0.02 |
| | Bs | 6–20 | 0.06 ± 0.012 | 0.002 ± 0.0005 | 0.055 ± 0.011 |
| 4L | Oi | 0–1 | 5.6 ± 1.1 | 0.013 ± 0.003 | 5.62 ± 1.12 |
| | Qpyr | 1–3 | 0.22 ± 0.04 | 0.001 ± 0.0003 | 0.215 ± 0.04 |
| | E | 3–8 | 0.09 ± 0.018 | 0.008 ± 0.002 | 0.079 ± 0.016 |
| | Bs | 8–25 | 0.06 ± 0.012 | 0.006 ± 0.0016 | 0.059 ± 0.012 |

after fire (Kawahigashi et al. 2011; Myers-Pigg et al. 2015).

## Contact angle of studied soils

Assessment of the contact angle of wetting for pyrogenic soils allowed for some changes in amphiphilous surface properties of soil samples. The highest values of contact angles were found for soil litters (Oea) as with fresh plant waste. The values also did not sufficiently vary between the plots (contact angles values of about 120°–130°). By the contact angles values for Albic Podzols under lichen pine forests and pyrogenic plots burnt 2, 10, and 16 years ago (Fig. 3), the upper pyrogenic horizons (Qpyr) of upper soil layer had the majority of differences. They sufficiently increased in contact angle value relative to the E horizon of the background plot. But their contact angle value gradually decreased, which we attribute to vegetation succession. The hydrophobicity value of pyrogenic horizons decreased with time since fire. But we identified a gradual increase in contact angle value in E and Bs horizons at 10- and 16-year-old burnt plots. That could be associated not only with specificity of composition of mineral horizons but also with migration of hydrophobic components in water solutions. We hypothesize that some fire-produced hydrophobic components may have been slowly washed out of the pyrogenic horizons and were sorbed in the Bs horizon. Additionally, Bs horizons gradually increased in content

of oxalate- and dithionite-soluble iron and aluminum forms.

## Conclusions

Thus, fires affect soil and soil organic matter properties of Albic Podzols formed under pine forests in the middle taiga subzone of Eurasia. In the initial years after fire, we observed a decrease in the content of water-soluble organic compounds in soils. The content of water-soluble OM recovered over time, which we attribute to the recovery of ground vegetation cover, and at 10- and 16-year-old burnt plots, the values are similar to those at unburned plot. In the short term after fire, the organic matter of forest litters increased in aromatic components. However, abundant needle loss by conifers after these fires increases aliphatic fragments in SOM composition, thereby somewhat reversing the immediate effect of fire on SOM composition. The highest amount of pyrogenic carbon accumulated in fractions of free and occluded matter. The composition of these fractions undergoes changes during postfire succession and became similar to that of the background plot 10–16 years after fire. Densimetric fractions largely increased in PAH content. The strongest PAH rise occurred in fractions of free and occluded organic matter, and we suggest that the PAH content in densimetric fractions (FPOM and OPOM) possibly serves markers of fire. In general, our results suggest that the majority of PyC is not
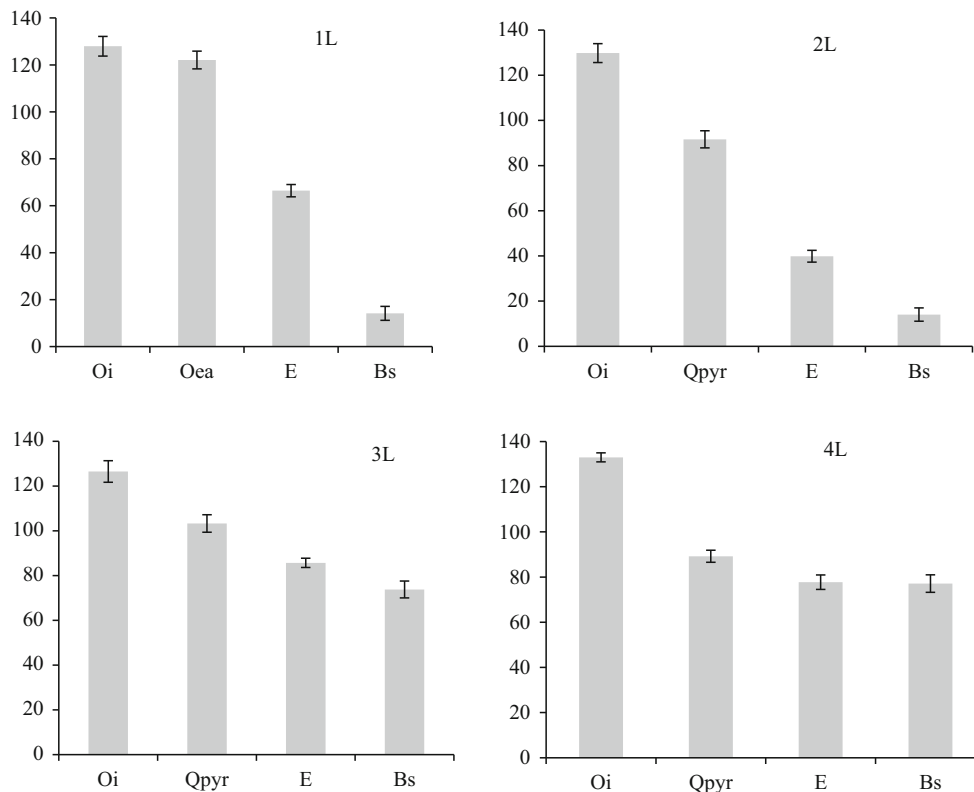
**Fig. 3** Contact angles of studied soils ($n = 10$)

chemically stable in burned lichen pine forests. PyC mainly accumulated in the upper 10-cm soil layers. Pyrogenic horizons were identified for increasing contact angle of wetting. Our study showed that the greatest changes occurred in upper soil horizons and that fires do not essentially modify the contact angle value of lower mineral horizons.

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