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Soils and soil organic matter transformations during the two years after a low-intensity surface fire (Subpolar Ural, Russia)

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ABSTRACT

With an rise in temperature in the circumpolar region, an increase in the frequency of fires can be expected. We studied the effects of fire in larch (Lárix sibírica Lebed.) forests on the organic matter composition of topsoils of Leptosols in the Subpolar Ural Mountains (northern taiga, Komi Republic, Russian Federation). We compared topsoils before the fire (BF), during the low-intensity surface fire (DF), one (1AF) and two years (2AF) after the fire. The low intensity surface fire burnt only the upper part of the organic horizon, leading to the formation of a thin pyrogenic horizon. The soil alteration included alkalization of the solution by three pH units, threefold increase in the content of exchangeable forms of cations, a nine times increase in the specific surface area of the solid phase, increase in total carbon and nitrogen contents, and a five-fold increase in the aromaticity of the organic matter. The latter is mirrored by a strong increase in benzene polycarboxylic acids (BPCAs) as marker for pyrogenic carbon (PyC), representing 82 to 97 mg BPCA C g^{-1}C. Two years after the fire, arrival of fresh litter, intensified water regime and soil acidification led to a decline of the surface area of organic horizons. Thus, it was revealed that two years after a low-intensity fire, the soils differed from the initial ones in a total carbon and nitrogen contents, the organic matter aromaticity and the BPCA contents. The content of aromatic fragments in pyrogenic horizon evaluated according ^{13}C NMR spectroscopy decreased after two years after fire, but at the same time, the PyC concentration, estimated on the carbon of BPCAs, remains stable. This indicates that periodically repeating low-intensity fires in boreal northern forests can contribute to the accumulation of stable forms of PyC in soils.

1. Introduction

Wildfire is one of the most widespread processes on the planet affecting ecosystems (Doerr and Santın, 2016). Forest fires alter the morphological and physicochemical properties of soils (Tarasov et al., 2011; Bento-Goncalves et al., 2012; Abakumov et al., 2017), and lead to complete or partial degradation of organic horizons and the formation of so called pyrogenic horizons (Krasnoshchekov and Cherednikova, 2012; Certini, 2014; Dymov et al., 2017, 2018). Depending on the the quality and quantity of the fuel type of forest, the ignition season the climatic features of the summer and type of fire (Certini, 2014; Dymov et al., 2018), fires are having a pronounced effect on soils and soil organic matter (SOM). A number of studies have shown that fires in the boreal forests of Russia lead to a translocation of carbon from organic into mineral horizons (Bezkorovainaya et al., 2007; Dymov et al., 2014). In addition, fires in forests and steppes lead to a change in the SOM composition, being associated with an increase in aromaticity (González-Pérez et al., 2004; Knicker, 2007; Vasilyeva et al., 2011). After fire, the proportion of aromatic molecular fragments and polycyclic aromatic hydrocarbons (PAH) in SOM increases significantly in the pyrogenic horizons as compared to the intact organic layers (Dymov and Gabov, 2015; Wiedemeier et al., 2015; Dymov et al., 2017).

Vegetation fires lead to the formation of pyrogenic carbon (PyC) and its involvement in the biogeochemical cycle (Soucemarianadin et al., 2014; Myers-Pigg et al., 2015; Jones et al., 2019). According to various estimates (Forbes et al., 2006; Krasilnikov, 2015; Reisser et al., 2016), its contribution to total soil organic carbon varies from 1.6 to 60%. PyC can persist in soils and sediments for a long time. Based on model

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experiments, the decomposition period of PyC was identified to vary from decades (Singh et al., 2012) to several thousand years (Kuzyakov et al., 2014). Hence, it is considered as one of the most stable carbon pools and contributes to carbon sequestration from the atmosphere (Walker et al., 2019). The annual PyC input to soils of boreal forests is estimated from 7 to 17 Tg (Preston and Schmidt, 2006) to 100 Tg (Santin et al., 2020).

Large areas of forest ecosystems are affected by fires. However, the question of the contribution of PyC in the SOM of soils of high latitude boreal forests currently not studied. Natural abundance of stable carbon (C) and nitrogen (N) isotopes in soils and biological materials expressed in delta notation $\delta^{13}C$ and $\delta^{15}N$, are widely accepted as fingerprints to identify ecosystem processes (Ehleringer et al., 2000; West et al., 2006; Stephan et al., 2015). So, $\delta^{13}C$ and $\delta^{15}N$ ratios can be used to address decomposition processes of organic substances in peats and soils (Bird and Ascough, 2012; Drollinger et al., 2019). According to Bird and Ascough (2012), pyrogenesis can change the carbon and nitrogen isotopic composition. But data on the long-term effect of pyrogenesis on the isotopic composition of carbon and nitrogen have not been found in the literature.

Because of climatic warming and drought spells in recent times, fires in the European part of Russia spread more to the north, affecting large areas that are usually less frequently exposed to pyrogenesis events. In particular, in 2017 fires covered a significant territory of the northern taiga of European Russia. At the same time, the number of fires in the more southern regions was significantly lower. To date, there are practically no estimates of the effect of fires on the soils of the northern taiga.

The aim of this work was to assess the impact of fires on soil and SOM in a larch forest in the Subpolar Ural mountains of northern European Russia. Specifically, the objectives of this study were (i) to track changes in soils and their SOM during the first two years after a fire, and (ii) to determine the production and fate of pyrogenic carbon in the soils. To do so, we took advantage of a naturally occurring forest fire at a research site, where soil has been sampled before the fire as a control. Further soil samples have been taken immediately as well as one and two years after the fire.

2. Materials and methods

2.1. Site description and soil sampling

The study was conducted in the Yugyd va national park in the northern part of the subpolar Urals with natural, undisturbed ecosystems (Patova, 2010). The study area is located on the southern limit of continuous permafrost in the European subarctic region (Oberman, 1998). Climate is strongly continental, with the site-specific conditions depending on the local orographic features. The mean annual temperature varies from −3 to −7°C, and the annual precipitation is 800–1000 mm, with the highest amounts falling in May–October (Taskaev, 1997). The parent materials are carbonate rocks. Soil cover is characterized by high diversity including Podzols, Umbrisols and Cryosols (Dymov et al., 2015; Startsev et al., 2020). The field diagnostics of the studied soils and the determination of their classification position were performed according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015).

The study was carried out on the left bank of the river Kozhim, about 3 km southeast of the estuary Limbekay river and 1 km from “Pereprava” point (Fig. 1). The study site is located on top of a gentle slope (steepness of about 3–7°). At the end of July 2017, a low intensity surface fire occurred, affecting an area of about 487 ha at the Verkhne-Kozhimsky forestry department of the Yugyd va national park. The fire was exposed to a mixed-age larch green-moss forest (*Larix sibirica* Ledeb.) with spruce (*Picea abies* (L.) Karst.) in the undergrowth. The shrub and herbaceous layer vegetation included *Betula nana* L., *Vaccinium vitis-idaea* L., *Empetrum nigrum* subsp. *hermaphroditum* (Hagerup) Böcher, *Hylocomium splendens* (Hedw.) Schimp, *Pleurozium schreberi* (Willd. ex Brid.) Mitt, *Equisetum sylvaticum* L., *Deschampsia cespitosa* (L.) P. Beauv., *Chamaenerion angustifolium* L., *Peltigera s.p.* and *Persicaria bistorta* (L.) Samp.

Soils of the control site before fire impact are classified as primarily Histic Leptosols and some occasional Entic Podzols formed on thin clay loams deposits underlain by carbonate rock. Larch and spruce forests growing in these areas provide with their litter fall well burning fuel, which enable fast and low-intense fire affecting the morphological properties of the organic horizon Oi. During the fire, the dry Oi horizon serves as fuel, burns out and forms a thin Qpyr horizon in its place, where the main products of partial pyrolysis of the organic matter (OM)

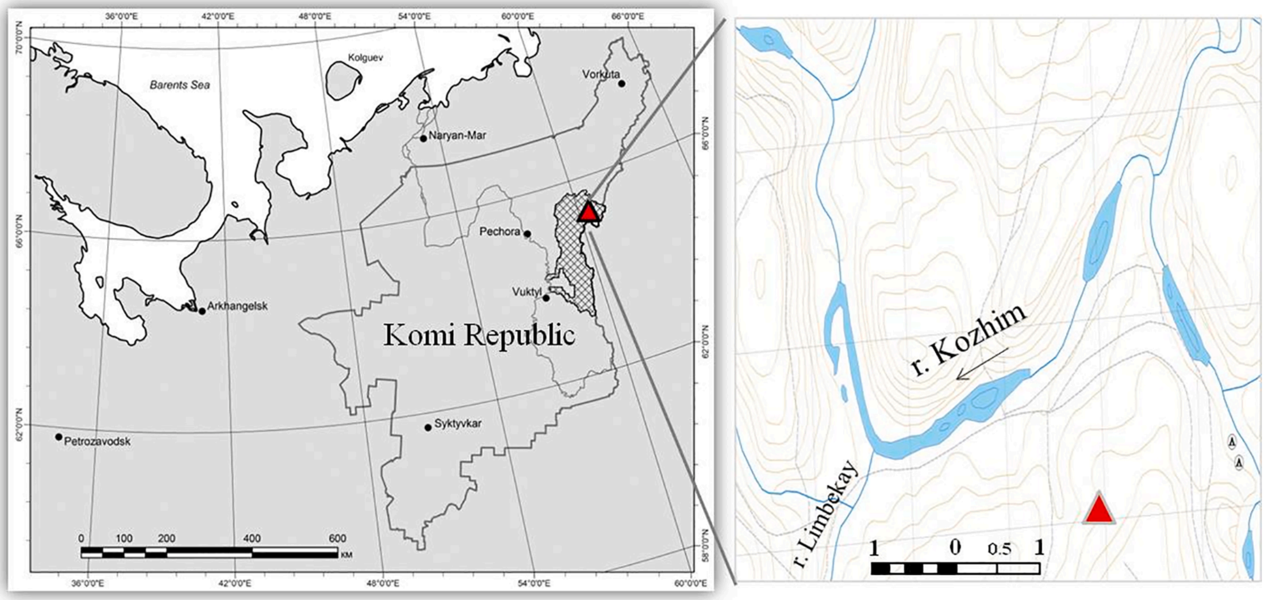

Fig. 1. Location of study site.

was concentrated (Fig. 2).

Soil sampling was carried out before the fire (BF), during the fire in late July (DF), one year after the fire in July 2018 (1AF), and two years after the fire in July 2019 (2AF). Only the upper part of the organic horizon (Oi) was burned and charred to fire and transformed to a pyrogenic horizon (Qpyr) with a thickness of 1–2 cm on the soil surface. The middle (Oe) and lower organo-mineral horizons (Ah) were not burned to fire. Fig. 2 shows the study site at the different sampling times, and the upper layers of a soil sampled at 2AF as example.

At all sampling campaigns, the samples were taken at random from five points from the same place within a radius of 10 m, and bulked. Samples were air-dried and living visible roots and all particles with a diameter greater than 2 mm were removed by dry-sieving as a preparation for analysis. Organic layer samples were ground with a sample grinder WCG75 (Pro Prep, Torrington, USA).

2.2. General soil analysis

Chemical analyses of the soils were performed in the certified Ecoanalit laboratory of the Institute of Biology (Komi Science Center, Urals Branch of the Russian Academy of Sciences) (certificate ROSS RU.0001.511257 from September 2019). Soil pH was determined by potentiometric titration with an Anion-4100 ionometer (Anion, Novosibirsk, Russian Federation) at a soil:water ratio of 1(m):2.5(v) for Ah horizons and 1(m):25(v) for organic and pyrogenic horizons, respectively. Total C and N were determined by dry combustion on an EA-1100 analyzer (Carlo Erba, Milano, Italy). Due to low pH and negligible contents of mineral N in the forest floor, total C and N were considered to represent organic C and N. δ^{13}C and δ^{15}N ratios of soil samples were determined at the Institute of Soil Science of Leibniz Universität Hannover (Germany) on an Elementar IsoPrime 100 IRMS (IsoPrime Ltd., Cheadle Hulme, UK) coupled to an Elementar Vario MICRO cube EA C/N analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

Fig. 2. Photos of study sites: I – before fire (BF), II – during fire (DF), III – pyrogenic horizon (Qpyr), IV – one year after fire (1AF), V – two years after fire (2AF), VI – soil profile, two years after fire.

Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) were extracted with 1 M CH_3COONH_4 on the a mechanical extractor (Sampletek, Mavco Industries Inc., Lawrenceburg, USA) according to (Van Reeuwijk, 2002). The cation concentrations were detected by inductively coupled plasma atomic emission spectroscopy (ICP Spectro Ciros CCD, Spectro Al, Kleve, Germany). The cation exchange capacity (CEC) was determined according to (Van Reeuwijk, 2002). Base saturation (BS) was defined as the ratio of the sum of exchangeable cations to CEC (%). Alkaline soluble organic matter was extracted with 0.1 M NaOH at a soil:solute ratio of 1 (m):10(v). The alkaline extract was separated from insoluble residues by centrifugation (20 min, 8000 rpm) and filtration through a membrane filter (0.45 μm Whatman Grade 589/3, GE Healthcare UK Limited, Little Chalfont, United Kingdom) (Ponomariova and Plotnikova, 1980; Vergnoux et al., 2011). Organic carbon in a pre-evaporated aliquot (10–15 cm^3) of an alkaline extract was determined according to titrometric version of Tyurin's method (Orlov and Grisina, 1981). The method is based on the oxidation of organic matter carbon (with heating at boiling point for exactly 5 min) of the soil with potassium dichromate in the presence of sulfuric acid, accompanied by the reduction of Cr^{6+} to Cr^{3+}.

2.3. ^{13}C NMR and pyrolysis GC–MS

The composition of the organic matter was determined by solid-state cross polarization magic angle spinning nuclear magnetic resonance (CP-MAS ^{13}C NMR) and pyrolysis gas chromatography-mass spectrometry (Pyr GC–MS). Solid-state ^{13}C NMR spectra of the two upper soil horizons were recorded on a 100.53 MHz Bruker Avance III 400WB (Bruker, Ettlingen, Germany) with rotor size 4 mm, material ZrO, a rotation frequency of 12.5 kHz, a contact time of 5 ms, and a 2-s recycle delay at the resource center of the research park “Magnetic Resonance Research Methods” of Saint-Petersburg State University, Russia. Before analysis, the samples were treated with 10% hydrofluoric acid to remove paramagnetic iron according to Goncalves et al. (2003). 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 total content of aryl C was calculated as the sum of the signals at 110–165 ppm fields. Signals from alkyl C were recorded in the 0–110 ppm range. The degree of aromaticity (fa) was determined as proportion of total content of aryl C components (110–145 and 145–165 ppm) on total C (excluding the contribution in the range of 165–220 ppm).

The same samples were also analyzed by Pyr GC–MS using a multi-shot EGA / PY-3030D pyrolyzer (Frontier Lab Ltd., Fukushima, Japan) connected to a QP2010 Ultra GC–MS (Shimadzu, Kyoto, Japan) at Dokuchaev Soil Science Institute (Moscow, Russia). A sample (4 mg) in a small crucible was introduced into a furnace preheated to 500 °C, where it was kept for one minute. The evolved gases separated in the chromatographic capillary column GsBP-5MS (30 m × 0.25 mm, film thickness 0.25 μm; GS-Tek Inc., Newark, DE, USA). The initial temperature was set to 40 °C (held for 1.5 min) followed by an increase to 300 °C at a rate of 5 °C min^{-1}. Helium was used as the carrier gas. The gas flow rate was 1 cm^3 min^{-1}. The temperature of the ion source was 250 °C. Chromatograms were processed using GC–MS LabSolution software (Shimadzu, Kyoto, Japan). Compounds were identified by comparing the obtained mass spectra with data from the NIST 11 (Gaithersburg, Maryland, USA).

2.4. Determination of benzene polycarboxylic acids in soils

The concentrations of benzene polycarboxylic acids (BPCAs) in the soil samples were determined according to Glaser et al. (1998) and Brodowski et al. (2005). Briefly, to eliminate polyvalent metals, about 1 g of the soil was digested in 10 cm^3 of 4 M trifluoroacetic acid (TFA) at 105 °C for 4 h. After cooling, the residue was rinsed several times with deionized water by filtration through a glass fiber filter (Whatman GF/F, GE Healthcare UK Limited, Little Chalfont, United Kingdom) and dried at 40 °C for 3 h. The residue was then transferred to teflon bombs, to which 4 cm^3 of 65% HNO_3 was added and reacted at 170 °C for 8 h in a high pressure digestion apparatus. The mixture was quantitatively transferred and filtered with a cellulose filter (Whatman 1450–055, GE Healthcare UK Limited, Little Chalfont, United Kingdom) into 25 cm^3 volumetric flasks. Then, 4 cm^3 aliquot was diluted 5 times with 10 cm^3 of deionized water, and 100 mm^3 of citric acid as the first internal standard was added. The solution was treated using cation exchange resin (Dowex 50 WX8, 200–400 mesh, SERVA Electrophoresis GmbH, Heidelberg, Germany). The treated aqueous samples were freeze-dried and re-dissolved in methanol, and 100 mm^3 of 2,2′-biphenyldicarboxylic acid in methanol was added as the second internal standard. After drying in a nitrogen atmosphere, the samples were derivatized. The derivatisation was done at 90 °C for 2 h with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA; Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and N-trimethylsilyl iodide (TMSI; Sigma-Aldrich Produktions GmbH, Steinheim, Germany) at a ratio of 49:1 (Birk et al. 2012), and analysis was performed by GC-FID on an Agilent, 7890A GC System with a 5975C quadrupole mass selective detector (Agilent, Santa Clara, CA, USA). Six BPCAs were used as external standards: 1,2,3-benzenetricarboxylic acid hydrate, 1,2,4-benzenetricarboxylic acid, 1,2,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, benzenepentacarboxylic acid and benzenehexacarboxylic (mellitic) acids (all Sigma-Aldrich Produktions GmbH, Steinheim, Germany, except of 1,2,5-benzenetricarboxylic acid which was from Alfa Aesar GmbH & Co KG, Karlsruhe, Germany. 1,2,3,4-benzene-tetracarboxylic (prehnitic) and 1,2,3,5-benzenetetracarboxylic acids (mellophanic) acid were not accessible commercially. For calculations, the response factor of the recovery standard 1,2,4,5-benzenetetracarboxylic acid (pyromellitic) acid was used (Glaser et al., 1998).

2.5. Specific surface area by N_2 gas adsorption

Specific surface area (SSA) of the samples was determined on a surface area analyzer (Sorbtometr-M, Katakon, Russia) with N_2 as the adsorbate gas at the Faculty of Soil Science, Lomonosov Moscow State University (Moscow, Russia). The principle of operation of the device is based on the nitrogen thermal desorption from the surface of the samples under dynamic conditions. Sorption was carried out at a boiling point of liquid nitrogen of 77 K and a relative pressure $P / Po = 0.20$ (single-point method). Surface area was calculated using the BET model (Brunauer et al., 1938). To remove hygroscopic moisture, all samples were kept in a vacuum chamber at 105 °C for at least 24 h before analysis. Before starting the measurement, the sample was heated (30 min) in a helium stream at a temperature of 100 °C to remove absorbed gases and vapors from its surface.

2.6. Statistics

Correlation analysis was used to determine the relationship between the obtained data. Correlation coefficients (r-Pearson) were calculated using the STATISTICA 10.0 (Stat. Soft Inc, Tusla, USA); differences were considered significant at the significance level $p < 0.05$.

3. Results

3.1. General soil properties, and carbon and nitrogen contents

The initial soil before the fire was acidic with a pH_{H2O} of 4.4–4.5 in the organic horizons and 5.4 at Ah horizon (Table 1). The CEC was greatest in the Oe horizon, and was about half in the Ah horizon. The composition of the exchangeable cations was dominated by Ca^{2+} with 20.3 cmol kg^{-1} in the Oi horizon to 32.6 cmol kg^{-1} in the Ah horizon. The concentration of exchangeable Mg^{2+} was between 12.0 and 10.0

Table 1
Chemical and physical properties of studied soils.

Horizons	Depth, cm	pH		Exchangeable cations				CEC	BS	$C_{tot.}$	N_{tot}.	C/N	$\delta^{13}C$	$\delta^{15}N$	Alkali-soluble carbon	SSA
		Water	KCl	Ca^{2+}	Mg^{2+}	K^+	Na^+									
				cmol kg^{-1}					%	g*kg^{-1}			[‰]		mg C_{alk} g^{-1} $C_{tot.}$	g m^{-2}
Unburnt soil (BF)																
Oi	0–5	4.5	4.0	20.3	12.0	7.0	0.8	70.8	56.7	438 ± 15	10.4 ± 1.1	49.1	−29.87	−1.99	224	0.48 ± 0.05
Oe	5–17	4.4	3.8	25.6	10.4	3.2	0.7	84.8	47.1	453 ± 16	13.9 ± 1.5	38.0	−29.40	−0.02	245	0.40 ± 0.02
Ah	17–30	5.4	5.0	32.6	10.1	0.2	0.1	41.9	102.6	60 ± 6	2.8 ± 0.6	25.0	−26.53	4.77	280	2.94 ± 0.07
During fire (DF)																
Qpyr	0–2	8.0	7.0	67.4	36.5	25.8	0.6	53.3	244.3	537 ± 19	20.5 ± 2.3	30.6	−30.07	−0.78	17	3.91 ± 0.18
Oe	2–17	4.1	3.1	14.8	6.1	3.4	0.3	87.7	28.1	473 ± 17	14.1 ± 1.6	39.1	−28.90	1.27	252	0.58 ± 0.03
Ah	17–30	5.6	5.2	28.6	9.7	0.2	0.1	40.2	96.0	51 ± 5	2.5 ± 0.5	23.8	−26.16	5.04	373	3.18 ± 0.03
Year after fire (1AF)																
Qpyr	0–1	5.5	5.0	38.7	5.7	2.8	0.1	72.9	65.1	574 ± 20	21.3 ± 2.3	31.4	−29.64	−1.04	74	0.98 ± 0.21
Oe	1–10	4.2	3.3	12.5	7.1	2.7	0.1	90.4	24.8	489 ± 17	15.8 ± 1.7	36.1	−29.47	−0.19	225	0.48 ± 0.06
Ah	10–25	5.4	5.2	41.9	13.4	0.3	0.1	60.0	92.6	118 ± 12	6.8 ± 0.8	20.2	−25.28	4.73	343	1.1 ± 0.10
Two years after fire (2AF)																
Qpyr	0–1	5.4	4.8	28.0	7.3	2.3	0.2	87.1	43.5	495 ± 17	23.7 ± 2.6	24.4	−29.92	0.79	43	1.93 ± 0.06
Oe	1–10	4.4	3.6	19.7	9.7	1.6	0.2	81.1	38.6	451 ± 16	15 ± 1.6	35.1	−29.12	1.46	167	0.54 ± 0.03
Ah	10–25	6.7	6.5	28.2	9.6	0.1	0.1	33.5	113.7	49 ± 7	2.4 ± 0.5	23.8	−20.96	5.60	479	3.25 ± 0.07

CEC – cation exchange capacity, BS – base saturation, SSA – specific surface area.

cmol kg^{-1}. Exchangeable K^+ amounted to 7.0 cmol kg^{-1} in the Oi horizon and gradually decreased to 0.2 cmol kg^{-1} in the Ah horizon. The BS increased from 56.6 in the Oi horizon to 102.6% in the Ah horizon. Before the fire, the organic layers had $C_{tot.}$ content of 438–453 g kg^{-1} and an $N_{tot.}$ content of 10.4 to 13.9 g kg^{-1}. The proportion of alkali-soluble carbon in the background soil is from 224 to 245 mg C_{alk} g^{-1} C_{tot}. The $\delta^{13}C$ ratio of the OM was increased from −29.9‰ in the upper horizon to −26.5‰ in the Ah horizon. Concurrently, the $\delta\ ^{15}N$ ratio increased from −2.0‰ to 4.8‰.

In the newly formed Qpyr horizon consisting of partial combustion products and ash, the pH value was three units higher as in the Oi horizon before burning. This went along with a threefold increase in the exchangeable forms of Ca^{2+}, Mg^{2+} and K^+ and a significant increase in the BS, whereas the CEC values decreased to 53.3 cmol kg^{-1} (Table 1). Compared to the Oi horizon before the fire, the Qpyr horizon showed larger C_{tot} and N_{tot} contents of up to 537 and 20.5 g kg^{-1}, respectively, while the OC contents in the Oe horizon remained unchanged. The increasing N_{tot} content in the Qpyr horizon resulting in a significant decrease in the C:N ratio. Fire led to a significant decrease in the solubility of OM in alkaline solution to 17 mg C_{alk} g^{-1} $C_{tot.}$ in the Qpyr horizon. The concentration C_{alk} in the Oe horizon did not change compared to the same horizon at BF site. Fire also did not affect the $\delta^{13}C$ ratio, while it increased the $\delta^{15}N$ ratio.

Two years after the fire, the organic layer acidified again with addition of new organic acids originating from litter fall and organic matter decomposition and with the leaching of alkaline and earth alkaline cations, i.e. Ca^{2+}, Mg^{2+}, and K^+. The C_{tot} and N_{tot} contents in Oe horizons did not change within two years after the fire. During this period, there was a tendency to an increase in N_{tot} in the pyrogenic horizon during succession changes. The most sensitive effect of pyrogenesis was detected by the C/N ratio, while there were no significant changes in the $\delta^{13}C$ ratios during a two-year period. At the same time, a slight increase of 0.8‰ was observed for $\delta\ ^{15}N$ in the Opyr horizon (Table 1).

3.2. CPMAS ^{13}C NMR and Pyr GC–MS

CPMAS ^{13}C NMR spectra of the Oi horizon before the fire showed strong signal intensities at 60–95 ppm, 0–45 ppm, and 95–110 ppm in the O, N-alkyl-C, alkyl C and di-O-alkyl regions respectively (Fig. 3). Integration of the C-species revealed close similarity between Oi and Oe horizons (Table 2). The OM of surface horizons contained 47.5–57.1% O, N-alkyl-C, while alkyl C represented 70.7–67.8%, and aryl-C and O-aryl-C amounted to 11.5–13.1% and 5.9–5.5%, respectively. This translates to a low alkyl-C/O, N-alkyl-C ratio of 0.2–0.4, and a low degree of aromaticity (fa) of 18.7–19.9%.

The OM of the newly Qpyr horizon was characterized by a significant increase in the proportion of aryl C to 70.3% as compared to the OM before the fire, while its share declined only to 62.6% two years after the fire. In contrast, the share of O, N-alkyl C, predominantly represented by cellulose C, decreased to 38.7%, the share of di-O-alkyl, probably attributable to hemicelluloses, decreased by 5.9%. The proportion of methoxyl C (45–60 ppm), probably associated with lignins, decreased to 2.5%. The composition of the OM in the Oe horizons was quite unaffected by the fire and was characterized by a high proportion of O-alkyl C (35–37%), followed by alkyl C (19–20%), aryl C (13–14%) and Di-O-alkyl C (10–11%).

Pyrolysis GC–MS could separate 54 compounds (examples of chromatograms from the Oi (BF) and Qpyr (DF) horizon using Pyr GC–MS are shown in Fig. S1 and the list of determined substances is presented in Table S1 in the supplementary information). These were divided into the following groups according to their probable origin and similar chemical structure: alkanes (Alk), aromatic compounds (Ar), fatty acids (Fa), phenolic compounds (Phe), nitrogen-containing compounds (N-cont), polysaccharides (PS). These substances showed different patterns in the Oi(e) and Ah horizons site at different times before, during and after the fire. In the pre-fire samples, the proportions of polysaccharides decreased from the Oi(e) to the Ah horizon, while that of hardly decomposable wax components, being represented by alkanes, and of

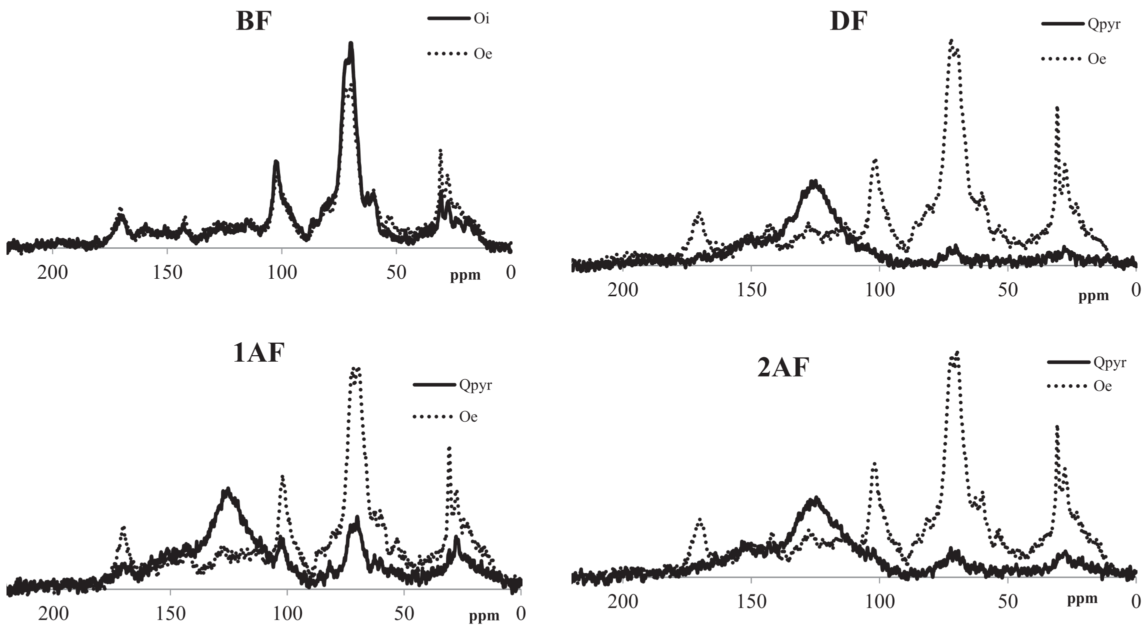

Fig. 3. ^{13}C CPMAS NMR spectra of organic horizons of studied soils. Abbreviations: BF – before fire, DF – during fire, 1AF – one year after fire, 2AF – two years after fire. Oi, Qpyr, Oe – horizons of the studied soils.

Table 2
Percentage distribution (%) of signal intensity between selected chemical shift regions (ppm) of ^{13}C CP-MAS NMR spectra.

Sample	Alkyl C	O-Alkyl C			Aryl C		Carboxyl C / Amide/Ester		Alkyl/ O,N-alkyl	fa	AR/AL
	0–45	Methoxyl/N-alkyl 45–60	O-Alkyl 60–95	Di-O-Alkyl 95–110	Aromatic 110–145	Phenolic 145–165	Carboxyl/Amide 165–185	Aldehyde/Ketone 185–220			
Unburnt soil (BF)											
Oi	13.6	4.7	44.8	12.3	11.5	5.9	5.1	2.2	0.2	18.7	0.2
Oe	20.3	7.2	36.9	10.6	13.1	5.5	5.2	1.2	0.4	19.9	0.2
During fire (DF)											
Qpyr	9.0	2.2	6.1	6.4	58.0	12.3	3.8	2.2	0.6	74.8	3.0
Oe	19.3	6.4	37.1	10.6	13.5	5.5	5.5	2.3	0.4	20.6	0.3
Year after fire (1AF)											
Qpyr	15.1	4.4	16.5	8.5	38.9	10.0	4.8	1.8	0.5	52.4	1.1
Oe	21.1	7.1	35.7	10.4	13.4	5.6	5.3	1.4	0.4	20.4	0.3
Two years after fire (2AF)											
Qpyr	11.7	2.6	9.5	8.0	49.2	13.4	4.5	1.1	0.6	66.3	2.0
Oe	20.4	6.7	35.5	10.6	13.9	5.9	5.5	1.5	0.4	21.3	0.3

fa - degree of aromaticity; AR - total content of aromatic structures (110–165 ppm); AL - total content of aliphatic structures (0–110 ppm).

aromatic and nitrogen-containing compounds produced by pyrolysis increased (Table 3). During the fire, the relative content of aromatic compounds in the pyrolysis products of the pyrogenic horizon increased. One year after the fire (1AF), the content of aromatic fragments decreased by 18.3%, and after two years (2AF) it increased again to 39.9%. The decrease in aromatic components after one year (1AF) was probably associated with an increase in the proportion of freshly fallen needles and, accordingly, in the proportion of polysaccharides in the composition of the upper pyrogenic horizon.

3.3. *BPCA contents*

The total content of BPCA in soils before the fire (BF) was 3.1–5.4 mg BPCA g^{-1} soil or 3–23 mg BPCA-C g^{-1}C, and was dominated by mellitic and benzolpentacarboxylic acids (Table 4). In the newly formed pyrogenic horizon, the total BPCA content increased to 99 mg BPCA g^{-1} soil or 82 mg BPCA-C g^{-1}C. Most of this increase was due to mellitic and benzolpentacarboxylic acids, but also the contents of mellophanic, hemimellitic, trimillitic and pyromellitic acids increased. In contrast, the concentrations of BPCAs in the Oe and Ah horizons of the DF plot remained low and comparable with that of the respective horizons before the fire. Within two years after the fire, the total BPCA content in the Opyr horizon did not change with 107–108 mg BPCA g^{-1} soil or 83–97 mg BPCA-C g^{-1}C, respectively. In contrast, in the Oe horizons of the 1AF and 2AF plots, a two-fold increase in the total content of BPCA, predominantly due to mellitic and benzenpentacarboxylic acids, occurred.

3.4. *Surface area of soil samples*

The SSA as determined by low-temperature N_2 adsorption of the Oi horizon was small (0.48 m^2 g^{-1}) due to the dominance of quite intact litter, and increased to 0.4 m^2 g^{-1} in the Oe horizon to 2.9 m^2 g^{-1} in the Ah horizon (Table 1). After the fire, the newly formed Qpyr horizon had a 7-fold larger SSA of 3.41 m^2 g^{-1} than the Oi horizon from which it originated. Fire did not significantly affect the SSA of the Oe and Ah horizons. Considering all soil samples, there was a positive relationship between the OC contents and the SSA values in the Oe horizon ($OC = 21{,}809 * SSA + 33{,}817$, $R^2 = 0{,}938$), while there was a negative relationship in the Ah horizon ($OC = -2{,}6373 * SSA + 13{,}904$, $R^2 = 0{,}998$).

Table 3
Relative contents of the main groups of compounds according to Pyrolysis GC–MS chromatography.

Horizons	Alk	Ar	Fa	Phe	N-cont	Ps
Unburnt soil (BF)						
Oi	3.7	12.8	1.2	11.5	1.0	69.8
Oe	2.5	11.4	0.8	11.1	2.0	72.2
Ah	21.5	38.6	0.1	16.8	7.2	15.8
During fire (DF)						
Qpyr	23.0	39.0	0.1	23.8	2.9	11.2
Oe	3.2	10.6	1.9	10.7	0.7	72.9
Ah	17.6	40.1	–	15.7	8.6	18.0
One year after fire (1AF)						
Qpyr	5.8	20.1	3.7	18.3	6.4	45.7
Oe	3.4	10.7	1.6	10.4	1.4	72.5
Ah	18.5	35.9	0.2	15.6	7.7	22.1
Two years after fire (2AF)						
Qpyr	18.7	41.6	0.3	13.7	4.2	21.5
Oe	2.5	11.7	0.5	9	1.2	75.1
Ah	23.2	55.6	–	–	7.2	14.0

Alk – alkanes, Ar – aromatic compounds, Fa – fatty acids, Phe – phenolic compounds, N-cont – nitrogen-containing compounds, Ps – polysaccharides, – not found.

4. Discussion

4.1. Immediate and direct effects of fire

Fires in boreal forests affect large areas, but strong changes of soil properties are mostly restricted to the surface horizons (Dymov et al., 2018). Also our study shows that surface fires in larch forests led to burning and charring of the upper and driest part of the organic layer only. A pyrogenic horizon was formed from the Oi horizon, which is represented by partial combustion products of the organic surface layer and components of wood litter and plants of the ground cover (Fig. 2, III). The Oe and Ah horizons practically did not change their morphological properties due to the fire. Similar patterns in humus form modification by fires in more southern regions have been reported by Egli et al. (2012), Badia et al. (2014) and Cui et al. (2014). The formation of only a thin pyrogenic horizon and the conservation of the lower part of the organic layer likely are due to the high moisture of the latter. In contrast, in the more southern regions, the low thickness of the pyrogenic horizon is often due to the lack of combustible material (Maximova and Abakumov, 2017; Gabbasova et al., 2019).

The most pronounced soil transformation occurred in the upper 1–2 cm of the soil profile with the formation of char coal, soot, partially combusted plant debris and ash which largely determined the properties of the Qpyr horizon. In the organic topsoil, also a neutralization of acidity and a shift in pH values to a slightly alkaline region were observed along with an increase of exchangeable Ca^{2+}, Mg^{2+} and K^{+}. Probably, unusually high values of CEC and BS are associated with a high concentration of exchangeable forms in the ash. A significant role is played by the behavior of Na^{+}, which is used to determine the content of CEC. But at the same time, Na^{+} concentration in the Qpyr horizon practically does not change at DF plot and fire and during two years after fire. A CEC decrease in the soils after the fire was also noted for the forest soils of North America (Ulery et al., 2017).

Organic matter in boreal soils plays an important role in the global carbon cycle of the planet (Lal, 2005). However, so far pyrogenic components of the SOM are practically not taken into account. An increase in concentration of total carbon was detected in the Qpyr horizons of soils after fires (Santín et al., 2016; Dymov et al., 2018). This may be due to several factors. At first, the additional supply of carbonized plant residues including branches, needles and bark of wood contributes to an increase in concentration of total carbon in this horizon (Santin et al., 2020). Second, mineralization processes are slowed down from these partly charred materials due to its higher resistance against biotic decomposition as compared to the original organic material and also due to the destruction of soil biota by high temperatures on the surface (Bogorodskaya et al., 2010; Korobushkin et al., 2017). Third, the potential mobility of the OM, as estimated by alkali-soluble carbon was 13 times smaller in the Qpyr horizon as compared to the original Oi horizon of BF plot. We have described similar patterns for soils of boreal forests in the middle taiga of the European North of Russia (Dymov, 2020). In this case, a more significant increase in the nitrogen content and a decrease in the C/N ratio were observed in pyrogenic horizons. An almost threefold increase in nitrogen-containing compounds pyridine and hexadecanamide was revealed according to the results of Pyr GC–MS in the Qpyr horizon (Table 3). Similar data on the increase in the proportion of pyridine under the combustion of peat described earlier (Kosyakov et al., 2020). Their concentration during combustion is determined by the initial composition of substances and also the temperature and time of combustion, as well as the availability of oxygen. Probably, their formation is associated with cyclization of biogenic organic-N such as peptides and amino sugars (Knicker, 2010). We find similar increasing N_{tot} contents in soils after a prescribed fire because of the low temperatures reached that facilitate the incorporation of ashes rich in nitrogen (Úbeda et al., 2005). This went along with a slight increase in $\delta^{15}N$ values. Also, Huber et al. (2013) observed increasing $\delta^{15}N$ values as a result of a forest fire in Australia, and such observation can be probably due to a selective loss of ^{15}N with volatization and combustion that occurs during a fire (Johnson et al., 2011).

Table 4
The content of benzene polycarboxylic acids (BPCAs) in the studied soils, mg BPCA g^{-1} soil.

Horizons	Hemimellitic acid	Trimellitic acid	Trimesic acid	Pyromellitic acid	Mellophanic acid	Prehnitic acid	Benzolpenta carboxylic acid	Mellitic acid	Sum	BPCA-C	mg BPCA-C g^{-1}C
Unburnt soil (BF)											
Oi	0.1	0.5	–	0.3	0.4	–	0.8	1.1	3.2	1.5	3.3
Oe	0.1	0.5	–	0.3	0.5	–	1.1	2.8	5.4	2.4	5.3
Ah	0.1	0.2	–	0.2	0.4	–	0.9	1.3	3.1	1.4	22.7
During fire (DF)											
Qpyr	4.5	6.4	–	7.0	12.7	0.1	29.8	38.5	98.9	44.3	82.5
Oe	0.2	0.6	–	0.6	0.7	–	1.6	2.3	6.0	2.7	5.7
Ah	0.1	0.2	–	0.3	0.5	0.4	2.1	2.3	6.0	2.7	52.1
One year after fire (1AF)											
Qpyr	3.4	5.3	0.4	6.2	5.7	4.0	41.9	40.7	107.6	47.8	83.4
Oe	0.1	0.8	0.1	0.8	1.0	0.8	3.6	5.5	12.8	5.7	11.6
Ah	0.5	0.9	–	0.3	0.5	0.4	10.4	13.3	26.4	11.6	97.9
Two years after fire (2AF)											
Qpyr	1.3	8.7	0.6	8.9	5.9	4.1	38.1	40.1	107.8	48.1	97.3
Oe	0.5	0.7	0.1	0.9	1.5	1.3	5.5	4.2	14.6	6.6	14.5
Ah	0.1	0.1	–	0.2	0.3	0.2	1.2	1.4	3.6	1.6	32.4

– not found.

The direct effect of the surface fire was reflected only in the OM composition of the upper organic horizon (Qpyr). The largest pyrogenic changes in the OM composition caused by the fire impact was the decrease in the content of O-alkyl and di-O-alkyl C species from 57.1 to 12.5% in the ^{13}C NMR spectra. In contrast, the combustion processes resulted in an increase in the proportion of thermostable aromatic and phenolic compounds. According to ^{13}C NMR spectroscopy, the proportion of C species assigned to phenolic compounds in the Qpyr layer of DF were two times more than in the Oi horizon of BF. This is echoed by the results of the Pyr GC–MS, where fragments assigned to aromatic compounds were three times higher in the pyrogenic horizon while the proportion of phenols was two times higher. The changes in organic matter during incomplete combustion depend on the temperature burning (Bird et al., 2015). The temperature during surface fires, as it took place in the present study, can reach up to 700 °C (Santín et al., 2016), while the major losses of litter weight occur at 200–250 °C and at about 400 °C (Prokushkin et al., 2011). With heating, thermal destruction of hemicelluloses takes place first, followed by destruction of cellulose and lignin with further increasing temperature (Kosheleva and Trofimov, 2008). Aromatic structures are formed from biomass precursor between 250 and 350 °C (Matosziuk et al., 2019). So according to Patwardhan et al. (2011), phenols and biphenyls can be products of partial combustion of lignins. Further, polysaccharides are preferentially transformed to furans, puranones and benzofurans (Knicker, 2011) or oxidized completely during fires (Haddix et al., 2016).

One of the most important characteristics of charcoal is its specific surface area, which depends on the combustible material, temperature and combustion parameters (Bergeron et al., 2013). There was an increase in the SSA in the Qpyr horizon during the fire by more than 9 times in comparison with the Oi horizon before fire. Most likely this is due to the formation of nanosized pores with a high surface area on the surface of charred organic components of the litter (Bird et al., 2015). In the process of further development, the sorption capacity is saturated and the mobilization of PyC is possible. Probably, after saturation of the sorption capacity of a given surface, migration of dissolved PyC into water bodies can occur, since in the global estimates made by Jones et al., (2020), the fraction of dissolved black carbon has the highest values in rivers of high latitudes.

4.2. *Transformations during the two-years period after the fire*

As a general feature of fire, the easily diagnosable Qpyr horizon remained on the soil surface for the two years of observation. However, there occurred a decrease in the thickness of the Qpyr horizon (Fig. 2), which may be associated with surface runoff caused by an increase in hydrophobicity of the surface, as well as the filling of pores with combustion products and an increase in soil density (Efremova and Efremov, 2006). During this period of time a significant part of the larch stand collapsed (Fig. 2). Probably, this will be lead to mixing of soils, connection with the fall of trees with root systems.

Already within one year, an acidification of the upper horizons, including the pyrogenic horizon, by 2.5 pH units occurred. The dealkalinization is likely due to the dissolution and migration of alkaline and earth alkaline elements, as is indicated by the decrease in exchangeable Ca^{2+}, Mg^{2+} and K^{+} from the Qpyr horizon. At the same time, CEC is largely determined by OM, as evidenced by significant correlations with C_{tot} ($r = 0.8$, $p < 0.05$) and N_{tot} ($r = 0.7$, $p < 0.05$). Short-term changes in acidity after a fire due to ash input have been described previously (Bodí et al., 2014; Dymov et al., 2018). Further, during the first years after fire the intensity of litter fall is particularly high (Dymov et al., 2017), which also contributes to post-fire acidification of the forest floor. After two years after the fire (2AF), the chemical composition of the Oe horizon was similar compared to the Oe horizon before the fire.

Two years after the fire, a decrease in the C_{tot} content of the Qpyr horizon is observed, and stayed constant in the Oe and Ah horizons. A slight increase in the Ntot content in the Qpyr horizon led to a narrowing of the C/N ratio to 24 value. While the direct impact of fire affected only the upper few centimeters, all subsequent changes were associated with the movement of carbon compounds under the influence of water. A slight decrease in the C_{tot} during two years after fire in the pyrogenic horizon is probably associated with the leaching of the soluble pyrogenesis products from this horizon to deeper soil layers and finally to the hydrosphere (Jones et al., 2020). The renewal of ground cover plants and the influx of fresh litter also lead to an increase in the mobility of organic compounds in the Qpyr horizon, as is estimated by the concentration of alkali-soluble compounds.

The δ^{13}C ratio in the organic surface layers remained the same for two years after the fire. It can be assumed that during two years after the δ^{13}C ratio do not significantly changed. The δ^{15}N ratio increased slightly in the pyrogenic horizon during two years after fire. Similar results were found after fire at various ecosystems (Hogberg, 1997; Huber et al., 2013; López-Martín et al., 2017), and can likely be assigned to combustion of the upper δ^{15}N-depleted surface soil layer and enhanced nitrification are two widely-recognized mechanisms to explain the ^{15}N enrichment in organic soil (Liu et al., 2016)

Within the two years after fire, there were subtle changes in the composition of the OM in the Qpyr horizon as is indicated by CP MAS ^{13}C NMR spectroscopy and Pyr GC–MS. During the additional supply of fresh litter to the soil surface, the share of O-alkyl in the Qpyr horizon slightly increases, while the share of C-aryl remains quite high (62.6%). After two years, the Qpyr horizon showed a decrease in the degree of aromaticity, the AR/AL ratio. Similar patterns of changes in the composition of organic matter during two years after the fire were obtained using Pyr GC–MS (Fig. 4, Table 3). The incorporation of fresh litter contributes to an increase in the proportion of polysaccharides (Ps) and a decrease in the proportion of phenolic compounds, which diagnose the concentration of lignin.

The composition of the OM in the Oe horizon remained practically unchanged within the two years after fire. Probably, the decomposition processes at this climatic conditions are too slow to modify the composition of OM so much that it can be identified by NMR and Pyr GC–MS.

Estimation of the content of BPCAs during the recovery succession gives the most sensitive indication of the evolution of PyC with time. Concentration PyCat Qpyr horizon share even increased slightly up to 9.7% after two years, probably due to leaching of ash and soluble combustion products from this horizon. The persistence of high concentrations of benzolpentacarboxylic and mellitic acids in the Qpyr horizon for two years confirms the high stability of the polyaromatic PyC.

Within two years after the fire, sorption of water-soluble OM on the charred surfaces, as well as the intake from moss and needles led to a decrease in SSA to about one fourth to the value right after the fire. This may indicate a deactivation of the surface of the charcoal formed during the fire, both with organic matter and mineral components (ash) and changes in sorption capacity (Saidian et al. 2016). The surface values have high correlation coefficients with C_{tot} in Ah horizon, probably it can lead to organic blocking of pores on the surface of the mineral matrix.

Despite the difference in the method for assessing the composition of SOM between the results obtained using various approaches, fairly high correlation coefficients ($r = 0.86–0.98$, $p < 0.05$) was found between C-aryl determined by NMR and individual BPCAs with the exception of trimesic and prehnitic acids. The coefficient of correlation between O-alkyl and di-O-alkyl using ^{13}C NMR spectroscopy and polysaccharide content using Pyr GC–MS was $r = 0.92–0.95$ ($p < 0.05$).

5. Conclusions

The influence of a low-intensity fire in the larch forests of the Subpolar Urals led to the consumption of the upper part of the organic horizon. In the event of a fire, a number of parameters (pH, C/N, CEC,

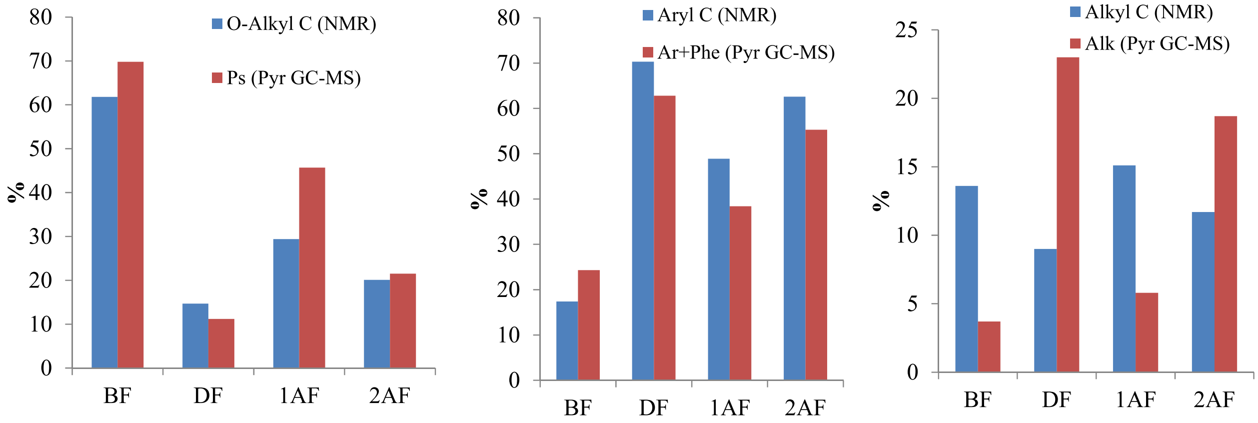

Fig. 4. Comparison of the main groups compound contents (molecular fragments) using ^{13}C NMR and Pyr GC–MS methods in the upper horizons of the studied soils (Oi - BF; Qpyr - DF, 1AF, 2AF).

BS, C mobility, SSA) changed in the upper subhorizon, including the production of Cpyr (coal, ash, soot). But within two years after the fire, most of the inorganic parameters returned to close to their original state.

Analyzing the composition of OM by CP MAS ^{13}C NMR spectroscopy and Pyr GC–MS chromatography indicated that forest surface fires, first of all, lead to pyrogenic destruction of polysaccharides. Concurrently, high proportions of compounds containing aromatic fragments were formed as a result of partial combustion and carbonization of the organic compounds in the litter layer. In the course of the subsequent two-year post-pyrogenic recovery, there was a slight decrease in the proportion of aromatic fragments, probably associated with the input of fresh litter and an increase in the proportion of polysaccharides. Our results generally show that surface fires do not have a critical impact on the carbon content of the studied soils. The products of incomplete combustion of the organic matter in the forest floor can be quite stable. With periodically occurring low-intensity surface fires soils may accumulate a certain amount of PyC. In the long term perspectives, PyC can be viewed as a reliable stabilization in northern soils.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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