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SOIL CHEMISTRY

Comparison of the Methods for Determining Pyrogenically Modified Carbon Compounds

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Abstract—The soil organic matter (SOM) is searched for the biomarkers and specific features associated with the effect of wildfires by the case study of peat soil, Rheic Hemic Histosol (Lignic), in the south of the middle taiga of the Komi Republic. It is shown that fires considerably influence the peat organic matter. Pyrogenic activity is assessed according to the content of charcoal particles. SOM is examined using solid-state ^{13}C-NMR spectroscopy to determine the concentrations of polycyclic aromatic hydrocarbons (PAHs) and benzene polycarboxylic acids (BPCAs). The used methods allow for diagnosing the effects of wildfires on the SOM composition. In the horizons with the signs of pyrogenesis, the share of carbon represented by aromatic fragments increases as well as the PAH concentration, mainly at the expense of naphthalene, phenanthrene, and chrysene. The carbon stock of pyrogenically modified compounds, amounting to 4.4 kg/m^2, is for the first time assessed in the European north based on the BPCA content. The characteristics of pyrogenically changed organic compounds and their fragments obtained by different methods correlate well: the Pearson coefficient for the correlation of the carbon content in aromatic compounds (Caryl) with total BPCA content is $R = 0.84$ ($p < 0.05$) and with individual BPCAs, $R = 0.81$–0.90 ($p < 0.05$).

Keywords: PyC, peat, wildfires, Histosols, NMR, PAHs, BPCAs

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INTRODUCTION

Wildfires are among the major factors that change the terrestrial ecosystems of the globe [28, 32, 34, 57]. The ecosystems of northern latitudes contain considerable reserve of materials potentially subjected to fire [11, 23, 53]. Forest litter, peat, ground vegetation, and tree canopy are the first to be affected by wildfire. The pyrogenic activity in boreal forests during the Holocene was different. Depending on the mean annual air temperature and amount of precipitation, the intensity and frequency of wildfires differed between individual stages of the Holocene [4, 12, 14, 30, 35].

Currently, the carbon of pyrogenically modified organic compounds (PyC) is regarded as one of the most stable pools of soil carbon resistant to microbiological decomposition [10, 54, 55]. As is believed, PyC can persist in soil to several thousand years [49]. That is why, PyC in many recent studies is regarded as an important pool of the carbon sequestered from the atmosphere [38, 39]. Many researchers believe that PyC is promising for the leveling of the effect of increasing carbon dioxide concentration in the atmosphere. Although the PyC importance in ecosystems is generally accepted, any unified approaches to its notification in soil are still absent [45]. The earlier studies has shown that the content of polycyclic aromatic hydrocarbons (PAHs) increase manifold during wildfires [24, 26, 47]. Part of researchers relates the PyC content with the aromatic fractions in the region of 110–165 ppm on NMR spectra [50].

The interest in the bog ecosystems and different aspects in their function is ever increasing [9]. As has been shown, peats contain considerable amounts of carbon, including PyC [50]. Peat fires have catastrophic consequences [7, 8, 58]. Peatlands occupy about 10% of the territory of the Komi Republic [22]. The geobotanical composition [5], morphology, and some chemical properties of the peat soils in the plain part of the Komi Republic have been so far studied in sufficient detail and the composition of peat organic matter in the northern regions has been comprehensively described [21, 51, 56]. However, the effects of wildfires on the chemical properties of peat soils in the European north are absent.

The goal of the work was to assess the applicability of different modern methods to assaying the carbon content in pyrogenically modified organic compounds by the case study of peat soil.

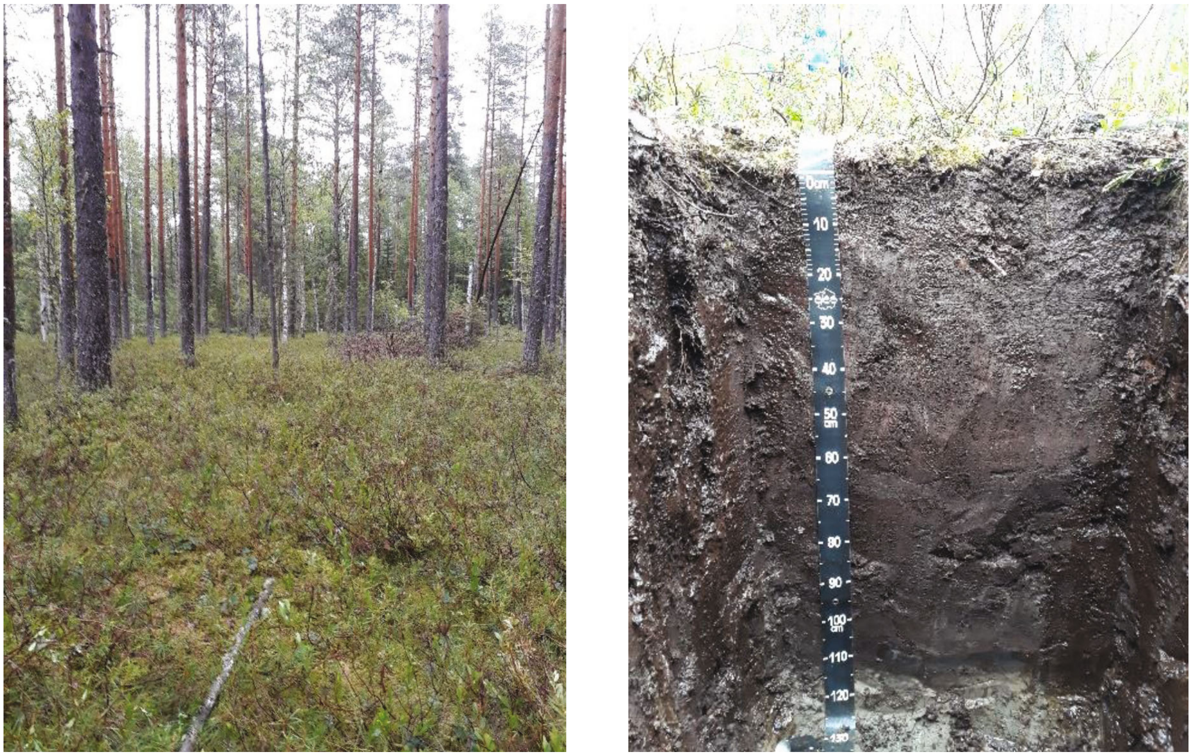

Fig. 1. Landscape and horizonation of soil profile.

OBJECTS AND METHODS

The field studies were conducted in August of 2019. A peatland under a Ledum–sphagnum pine stand near the Koigorodsky National Park was selected as the object of the study. The national park occupies the offshoots of the Northern Uvaly, dividing the basins of the Volga and the Northern Dvina Rivers [2]. According to the soil - geographic zoning [19], this territory is at the boundary between the middle taiga Luza-Sysol'sky region of podzol and bog-podzol soils and the southern taiga Letka region of soddy-podzolic soils. The mean annual air temperature there is 1–2°C, and precipitation, 800 mm (400–500 mm in the summer season) [1]. Figure 1 shows the landscape and general appearance of soil profiles of the area. The soil profile comprises a peat layer with underlying mineral G horizon. According to the Russian classification, the soil belongs to a peat oligotrophic type [20] and according to the WRB, to Rheic Hemic Histosol (Lignic). The soil profile comprises TO1 (0–10 cm)–T2pyr (10–15 cm)–T3 (15–30 cm)–T4 (30–50 cm)–T5 (50–70 cm)–T6 (70–90 cm)–T7pyr (90–105 cm)–T8pyr (105–115 cm)–G (115–130 cm) horizons. The organic part of the profile consists of plant residues at different stages of decomposition: from fresh moss mat (degree of decomposition, 5–10%) to moderately and well decomposed lower moss horizons (25–30% of decomposition to a depth of 70 cm). The peat color varies from yellow-brown through brown to dark brown, respectively. Carbon-bearing inclusions, suggesting a wildfire, are observed in the T2pyr horizon at a depth of 10–15 cm. Starting from the depth of 70 cm, the peat layer is represented by organomineral depositions with a high humus content. Presumably, peat accumulation started there with waterlogging after a wildfire. The bulk density of the horizon was determined in triplicate using an auger of 50 cm^3.

The quantitative chemical analyses of soils were performed in the certified ecoanalytic laboratory and in the Department of Soil Science, Institute of Biology, Komi Scientific Center, Russian Academy of Sciences (certificate no. RU.0001.511257 of September 2019). The total organic carbon and nitrogen contents were determined in an EA-1100 (Carlo Erba) elemental analyzer; pH, in an Edge HI2002-02 (Hanna Instruments, Romania) pH-meter with a digital electrode (±0.01 pH) at a soil to solution ratio of 1 : 25 for litter and 1 : 2.5 for mineral horizons. The exchangeable cations were extracted using a mechanical programmed extractor with subsequent detection of cations in solution (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) by inductively coupled plasma atomic emission spectroscopy [60]. The age of the sediments was determined by radiocarbon dating of peat samples at the Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch, Russian Academy of Sciences by liquid scintillation method in a Quantulus spectrometer-radiometer (Joint Access Tomographic Center, Siberian Branch, Russian Academy of Sciences). The carbon dating was calibrated to a real age using Calib Rev 7.10 [25]. The contents of stable ^{13}C and ^{15}N isotopes were determined at the Institute of Soil Science, Leibniz Universität (Hannover, Germany).

The charcoal particles in peat were counted according to the classical protocol [12, 52]. Peat (1 cm^3) was sampled each 2 cm; the sample was supplemented with 5% NaOCl water solution and kept at a room temperature for 24 h, washed with distilled water on a sieve (mesh 125 μm), and placed into a Petri dish. Then, the charcoal macroparticles were counted using a stereomicroscope (multiplication, ×40). The counts of particles were recorded in an Excel table to further analyze using Clam and Char Analysis in the R programming environment [46].

In the Clam program, the depths of the taken samples were interpolated to age to compute the model of the rate of increase in the vertical peat layer to obtain the median values. The obtained information was then compared to the concentration of charcoal macroparticles and input to Char Analysis to get the data on charcoal accumulation rate and reliable wildfire events. To distinguish the fires of a local level, the program computes the data and suggests the background and threshold levels of the black carbon accumulation rate. The background values are the low-frequency oscillations of charcoal accumulation rate, which to a greater degree reflect a regional signal of wildfire dynamics as well as a number of parameters, such as possible inaccuracies in sample preparation and analysis, the factor of decomposition of burnt residues within the peat column, and redeposition of earlier sedimented charcoal particles. The threshold value implies that the "noises" (Signal-to-Noise Index) follow a Gaussian distribution of admixtures within a specified time window. A window of 1000 years was used to unify the statistical functions; 95th percentile was set as the threshold for noise distribution. If the determined values of charcoal particles accumulation rate were higher than the threshold, this was regarded as a reliable local fire event.

Determination of PAH content. The system of an accelerated extraction with the ASE-350 (Dionex Corporation, United States) solvents was used for a complete extraction of PAHs from soil. A peat sample (1 g) was placed into an extraction cell and extracted three times with a mixture of methylene chloride and acetone (1 : 1) at a temperature of 100°C. The extracts were concentrated in a Kuderna–Danish apparatus in a thermostat at 70°C, and the solvent was replaced with hexane. The resulting concentrate of the sample (volume, 3 cm^3) was purified from organic impurities by column chromatography using aluminum oxide (Brockmann activity II) and 30 cm^3 of hexane and methylene chloride mixture (4 : 1) as an eluent. The eluate was concentrated in a Kuderna–Danish apparatus in a thermostat at a temperature of 85°C to a volume of 5 cm^3, supplemented with 3 cm^3 of acetonitrile, and boiled down at a temperature of 90°C to the complete the removal of hexane. The contents of 15 individual PAHs were determined. The degree of PAH carcinogenicity was assessed by reducing all studied polyarenes to the carcinogenicity of benzo(*a*)pyrene (BaP equivalent), which was calculated according to the index of toxicity and the content of polyarenes in soils [15].

Water-soluble organic matter (WOM). The contents of carbon (C_{WOM}) and nitrogen (N_{WOM}) of water-soluble organic compounds were determined in a TOC-VCPN (Shimadzu, Japan) with a TNM-1 unit. The water-soluble substances were extracted with deionized water (ELGA LabWater, United Kingdom) at a room temperature (20–23°C), at soil to water ratio of 1 : 50 for the mineral horizons and 1 : 100 for the organic horizons in BIOFIL tubes and filtered through quartz filters (MN, Germany; mesh, 0.4 μm) immediately after shaking in a Millipore device.

Chromatographic fractionation of labile (alkali-soluble matter) was performed according to Milanovsky [13] on a 1 × 10 cm column filled with hydrophobized agarose gel (Octyl Sepharose CL-4B, Pharmacia) using a BioLogic LP (Bio-Rad, United States) chromatography system. The alkaline extracts (0.1 M NaOH) at a soil to solution ratio of 1 : 10 were assayed (see [13] for the detailed protocol). The carbon content in alkaline extracts was determined by wet combustion with a chromic mixture. The extinction coefficients were calculated at two wavelengths, 465 and 650 nm, in a KFK3 photocolorimeter [16].

NMR spectroscopy. The composition of organic matter was determined by solid-state ^{13}C-NMR spectroscopy; the ^{13}C-NMR spectra were recorded in a Bruker Avance III 400 WB (Bruker, Germany) spectrometer with an operating frequency of 100.53 MHz using CP-MAS (cross polarization magic angle spinning) at the Research Park of St. Petersburg State University, resource center "Magnetic Resonance Methods" (sample spinning frequency, 12.5 kHz; contact time, 2 ms; and relaxation time, 2 s). The chemical shifts are shown relative to tetramethylsilane with a shift of 0 ppm; the peak of adamantane was used as a standard. The samples were preliminaryly treated with 10% hydrofluoric acid to remove the paramagnetic admixtures of iron isotopes [43, 59]. Numerical integration over the regions corresponding to the positions of functional groups and molecular fragments was used for semi-quantitative processing (TopSpin 3.2 software package; Bruker, Germany).

The content of aromatic structures (AR) was determined according to the summed areas of the signals at 110–145 and 145–165 ppm and of aliphatic structures (AL), according to the summed areas of the signals at 0–110, and 165–185 ppm. The degree of organic matter decomposition was assessed according to the ratio of alkyl (0–45 ppm) to O,N-alkyl (45–110 ppm) [27].

Determination of BPCA content. The concentrations of BPCAs in soil samples were determined according to the data by Brodowski et al. [31] at the Institute of Soil Science, Leibniz Universität (Hannover, Germany). To remove the polyvalent metals, a soil sample (~1 g) was treated with 10 mL of 4 M trifluoroacetic acid at 105°C for 4 h. After cooling, the residue was several times washed with deionized water via filtration through a Whatman GF/F glass fiber filter and dried at 40°C for 3 h. The residue was then transferred to reactors, supplemented with 4 mL of 65% HNO_3, and combusted at 170°C for 8 h in a high-pressure reactor. The mixture was quantitatively transferred and filtered through a Whatman 1450–055 cellulose filter into 25-cm^3 calibrated flasks. Then, a 4-cm^3 aliquot was diluted with deionized water and supplemented with 100 μL of citric acid as the first internal standard. The solution was passed through cation exchange resin (Dowex 50 WX8; mesh, 200–400); the water samples were freeze-dried and dissolved in methanol. 2,2'-Biphenyl dicarboxylic acid (100 μL) in methanol was added as the second internal standard. After drying in the atmosphere of nitrogen, the samples were derivatized for 2 h at 90°C using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and N-trimethylsilyl iodide (TMSI) at a ratio of 49 : 1 [29]. The BPCAs were identified in an HP 6890 (Agilent Technologies, United States) gas chromatograph with a flame ionization detector. Six BPCAs were used as standards [42]. In total, the contents of eight BPCAs were determined. It is recommended to use the acids carrying more than four carboxyl groups when calculating the PyC content since the acids with a smaller number of carboxyl groups may be of a biotic origin [41, 44]. Ba4 was calculated as the sum of pyromellitic, mellophanic, and prehnitic acids. The Ba4/Ba6 and Ba5/Ba6 ratios were used (Ba5 is the carbon content in benzene pentacarboxylic acid and Ba6, in mellitic acid).

RESULTS AND DISCUSSION

The age of the studied peatland is about 9000 years. Note that this peatland repeatedly experienced wildfires both during the Holocene and in modern times. The content of charcoal particles suggests that the most active wildfires in this peatland took place in the Atlantic and Subboreal periods (Fig. 2). Presumably, large peaks suggest that the upper organic horizon was under fire. A well-pronounced pyrogenic horizon at a depth of 10–15 cm suggests a strong wildfire event approximately 140 years ago. The time since the last fire was assessed according to the age of the forest stand. The flattened parts of the plot most likely reflect the combustion of the forests adjacent to the examined plot.

Table 1 lists the physicochemical soil properties. The peat oligotrophic soil is strongly acidic (pH_{KCl} 3.0–3.9). The upper oligotrophic peat horizon has the maximum acidity, while the acidity of the lower peat horizons is somewhat lower. The distribution of acidity along the soil profile is uniformly eluvial. The ash content in the soil peat horizons is 2.6–9.5%. An increase (to 4.5%) in the ash residues is observed in the pyrogenic T2pyr horizon.

The content of exchangeable bases is nonuniformly distributed along the soil profile. The content of calcium cations is maximal and is somewhat lower for the magnesium, potassium, and sodium cations. The Ca^{2+} content in peat horizons varied from 2.1–4.5 cmol(equiv)/kg and in the mineral horizon it was 1.5 cmol(equiv)/kg. The highest content was observed in the TO1 upper horizon.

The distribution of carbon and nitrogen along the soil profile was uniform with a drastic decrease in the mineral horizons. The carbon content in the studied soil varies from 568 g/kg in the organic and organomineral horizons to 11.5 g/kg in mineral horizon G. The nitrogen concentration in peat horizons is 5.5–15.0 g/kg in the peat horizons and 0.71 g/kg in the mineral horizon. The carbon to nitrogen ratio varies from 22 to 70 in organic horizons and to 19 in the mineral horizon. In general, the distribution of C/N ratio along the soil profiles expectedly decreases.

Analysis of the carbon (C_{WOM}) and nitrogen (N_{WOM}) contents in the water-soluble organic compounds demonstrates that their maximums are observed in the upper organic horizons, represented by fresh moss mats. The WOM uniformly decreases along the soil profile. The C_{WOM} content downward the profile changes from 3.51 g/kg in the upper organic horizon to 0.21 g/kg in the mineral horizon.

Chromatography of the hydrophobic interaction makes it possible to separate the mixture of alkali-soluble substances into five fractions differing in the amphiphilic properties. The hydrophilic fractions are represented by the fragments of aliphatic structure. The first fraction correlates in a statistically significant manner with the aliphatic compounds of the O-alkyl group ($R = 0.76$, $p < 0.05$) and di-O,N-aliphatic fragments with doubly substituted heteroatoms ($R = 0.82$, $p < 0.05$). Presumably, the cellulose and hemicellulose extraction products are prevalent in this fraction. The sum of hydrophilic fractions (first and second fractions) amounted to 17–54%. The content of the first hydrophilic fraction in the soil profile varied from 8.6 to 45.6% and of the second fraction, from 5.9 to 11.8%. The maximum content was observed in the TO1 horizon, represented by a fresh moss mat. The distribution of alkali-soluble hydrophilic compounds in general follows the WOM distribution in the soil profile. The correlation coefficient between the first fraction and C_{WOM} is $R = 0.72$ ($p < 0.05$) and with N_{WOM}, $R = 0.73$ ($p < 0.05$). The share of hydrophilic compounds decreases with depth. Chromatography fractionation demonstrates a high content of the fractions of the alkali-soluble organic matter associated with lignin- and cellulose-like compounds [13], belonging to the hydrophobic fractions

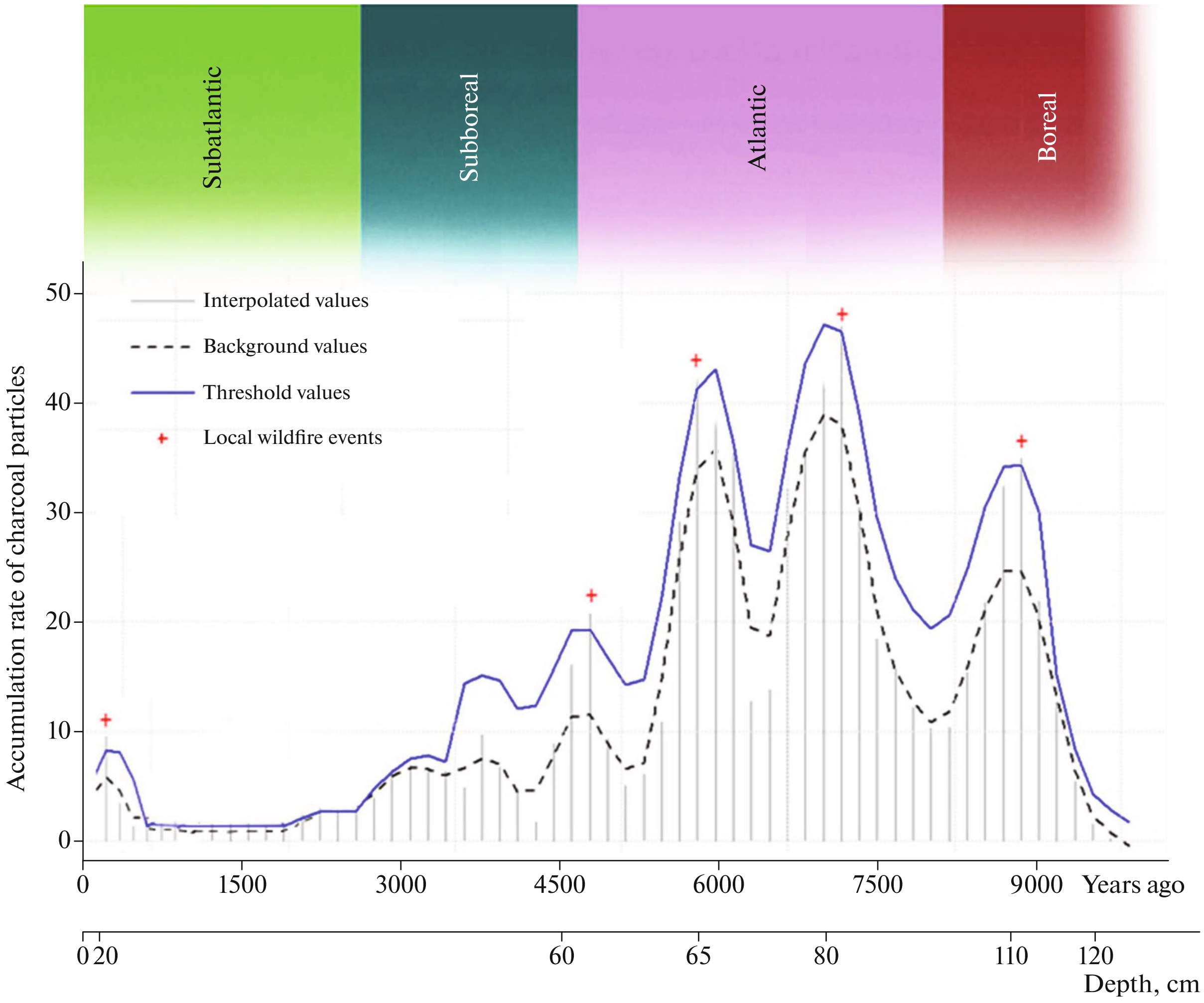

Fig. 2. Charcoal particles content (number of particles/cm^2 yr) in studied soil.

(third and fourth fractions) in the studied soil profile (Table 2). The third fraction varied in the profile from 16.1 to 51.3%; the fourth, from 28.0 to 40.3%; and the content of the fifth fraction was insignificant (0.9–3.0%). Note that the role of carbon content in the water-soluble compounds and individual amphiphilic fractions is less important as an indicator when studying the effects of the wildfires of the past as compared with the current wildfires in the forest ecosystems on mineral soils [6].

Hydrophilic organic compounds mainly belong to the mobile SOM components, which readily dissolve and migrate in soil profile. Under stagnant moistening in bog ecosystems, hydrophilic fractions accumulate only in the upper horizon of peat soils. The middle and low peat horizons are rich in hydrophobic fractions (46–83%), represented by the biopolymers from plant residues with different degrees of decomposition. Presumably, an increase in the content of hydrophobic fractions, represented by high-molecular weight structural components, including those of aromatic nature, can indirectly reflect a pyrogenic influence. The E_{465}/E_{650} ratio is minimal in the T2pyr horizon and maximal in the horizon of fresh moss mat at a depth of 0–10 cm. As for the remaining peat horizons, the values vary from 4.6 to 6.3. However, any significant effect of pyrogenesis on the composition of alkali-soluble organic matter and the content of amphiphilic fractions is unobservable.

Note that the studied soil contains rather large amount of total carbon (184 kg C/m^2) and nitrogen (4.6 kg N/m^2). These values are significantly higher as compared with the estimates for the soils of the region based on the data for the unforested bogs with the calculated density values and not the field data [17]. Most likely, the high values are associated with the periodical wildfires, which result not only in the input of partially charred particles with a high carbon content, but also in an increase in the bulk density of peat. An increase in density in the pyrogenic horizons has been earlier described for the soils of Central Siberia [7].

Table 1. Physicochemical properties of the studied soils

Horizon	Depth, cm	pH		C	N	C/N	Ca^{2+}	Mg^{2+}	K^+	Na^+	Σ	CEC	BS	Ash	C_{WOM}	N_{WOM}	ρ	$\delta^{13}C$, ‰ PDB	$\delta^{15}N$, ‰ Air
		KCl	H_2O	g/kg			cmol(+)/kg						%		g/kg		g/cm^3		
TO1	0–10	3.0	4.4	485 ± 17	13.9 ± 1.5	41	4.5	2.8	2.97	0.18	10.4	90	12	2.6	3.51	0.29	0.08 ± 0.03	–30.16	–0.71
T2pyr	10–15	3.1	4.1	568 ± 20	9.5 ± 1.0	70	4.1	1.3	0.40	0.09	5.9	111	5	4.5	1.32	0.08	0.19 ± 0.02	–26.88	1.68
T3	15–30	3.2	4.5	541 ± 19	15.0 ± 1.6	42	2.2	0.7	0.08	0.07	3.0	42	7	2.6	1.35	0.09	0.19 ± 0.02	–28.06	0.74
T4	30–50	3.8	4.5	491 ± 17	11.3 ± 1.2	51	2.0	0.6	0.05	0.07	2.7	89	3	2.7	1.07	0.08	0.21 ± 0.01	–28.46	1.97
T5	50–70	3.3	4.5	541 ± 19	14.1 ± 1.6	45	2.9	0.9	0.04	0.07	3.9	103	4	2.8	1.40	0.09	0.23 ± 0.01	–29.11	1.35
T6	70–90	3.5	4.8	555 ± 19	13.0 ± 1.4	50	2.9	1.0	0.04	0.09	4.0	99	4	3.6	1.20	0.09	0.26 ± 0.01	–29.31	1.42
T7pyr	90–105	3.7	4.6	529 ± 19	12.0 ± 1.3	51	3.2	1.1	0.06	0.08	4.5	97	5	9.5	0.80	0.07	0.94 ± 0.08	–29.65	0.67
T8pyr	105–115	3.9	4.7	102 ± 10	5.5 ± 1.1	22	2.1	0.8	0.20	0.07	3.2	36	9	75.4	0.70	0.04	0.94 ± 0.08	–29.22	–0.62
G	115–130	3.8	4.9	11.5 ± 2.7	0.71 ± 0.14	19	1.5	1.0	0.18	0.04	2.6	13	20	95.4	0.21	0.01	Not determined		

Table 2. Relative content of amphiphilic fractions in SOM (%), content of alkali-soluble organic matter, and ratio of extinction coefficients

Horizon	Depth, cm	ω(C) 0.1 M NaOH, %	C_{alk}, % of C_{tot}	E_{465}/E_{650}	Number of chromatography fraction					Dh*
					1	2	3	4	5	
TO1	0–10	5.51 ± 0.04	11.4	8.1	45.6	8.6	16.1	28.0	1.7	1.18
T2pyr	10–15	8.69 ± 0.05	17.9	4.3	17.6	8.1	34.0	38.7	1.5	0.35
T3	15–30	14.2 ± 0.3	29.3	5.5	12.2	11.8	51.3	23.7	1.1	0.32
T4	30–50	13.85 ± 0.07	28.6	5.5	12.6	9.2	44.4	32.5	1.3	0.28
T5	50–70	16.7 ± 0.05	34.4	5.2	9.8	6.5	44.4	36.3	3.0	0.20
T6	70–90	18.43 ± 0.23	35.8	4.9	8.6	8.3	45.9	36.0	1.3	0.20
T7pyr	90–105	4.01 ± 0.06	38.0	6.3	12.1	5.9	40.8	40.3	0.90	0.22
T8pyr	105–115	0.235 ± 0.001	8.3	5.9	29.7	8.0	33.6	28.7	Not detected	0.61

* Dh—degree of hydrophily, the ratio of the sum of hydrophilic (first and second) fractions to the sum of hydrophobic (third–fifth) fractions.

Table 3. Relative content (%) of molecular fragments in SOM according to CP-MAS ^{13}C-NMR spectroscopy

Horizon	Depth, cm	Alkyl C	O-Alkyl C			Aryl C		Carboxyl C/ amide/ester		Alkyl/ O,N-alkyl	AR/AL	Caryl, %*
		$C_{Alk\text{-}H}$	$C_{CH_3\text{-}O}$	$C_{Alk\text{-}O}$	$C_{O\text{-}Alk\text{-}O}$	$C_{Ar\text{-}H(H)}$	$C_{Ar\text{-}O,N}$	$C_{COOH(R)}$	$C_{C=0}$			
		0–45	45–60	60–95	95–110	110–145	145–165	165–185	185–220			
TO1	0–10	16.0	7.0	45.4	11.6	11.3	4.6	3.9	0.1	0.2	0.2	7.7
T2pyr	10–15	19.1	5.9	18.0	6.8	36.4	8.0	5.0	0.9	0.6	0.9	25.2
T3	15–30	39.2	7.4	21.4	6.3	14.5	5.3	4.7	1.1	1.1	0.3	10.7
T4	30–50	38.3	7.2	20.4	6.3	15.9	5.7	4.7	1.4	1.1	0.3	10.6
T5	50–70	36.3	7.2	18.7	6.4	17.9	6.8	5.2	1.5	1.1	0.4	13.4
T6	70–90	42.5	7.1	14.7	5.6	18.5	6.6	4.6	0.4	1.5	0.4	13.9
T7pyr	90–105	44.2	6.4	12.0	4.2	18.7	6.8	5.6	2.2	2.0	0.4	13.5
T8pyr	105–115	34.0	6.9	13.9	6.0	24.4	7.9	7.0	–	1.3	0.5	3.3

* Calculated taking into account the carbon content in individual horizon; hereinafter, dash denotes the amount below the determination limit.

The increase in soil density here is associated with the input of ash ($R = 0.98$, $p < 0.05$).

Figure 3 shows NMR spectra of the organic matter in the horizons of studied profile and Table 3 lists the integration results. The contents of fragments in SOM primarily depend on the composition of plants having accumulated in the peatland. In particular, characteristic of the upper peat horizons, mainly represented by mosses and weakly decomposed residues, is the prevalence of polysaccharides on the background of a small share of aromatic components. The composition of organic matter at depths of 15–105 cm remains sufficiently stable, with the aliphatic fragments accounting for 39–44%. The cellulose-like substances account for 12 to 21%; the share of methoxyl fragments is rather low, amounting to approximately 6–7%; and the share of hemicellulose ($C_{O\text{-}Alk\text{-}O}$) does not exceed 7%. The content of aromatic components (the characteristic frequently related to the effect of pyrogenesis) considerably increases in the T2pyr (10–15 cm) and T8pyr (105–115 cm) horizons, which carry rather large amount of black carbon. The share of aryl fragments, represented by the compounds at 110–145 and 145–165 ppm, elevates in these horizons to 32.3–44.4%.

Analysis of the stable isotopes in organic matter shows a certain increase in the ^{13}C and ^{15}N, thus displaying a heavier isotopic composition, in the pyrogenic horizon at the depth of 10–15 cm as compared with the higher and lower peat horizons. Statistically significant correlations with the content of C_{4-6} BPCAs ($R = 0.87$, $p < 0.05$) are observed.

The PAH content is frequently used in diagnostics and assessment of the effects of wildfires on SOM composition [6, 61, 62]. The PAH concentrations in the studied soil horizons are considerably different

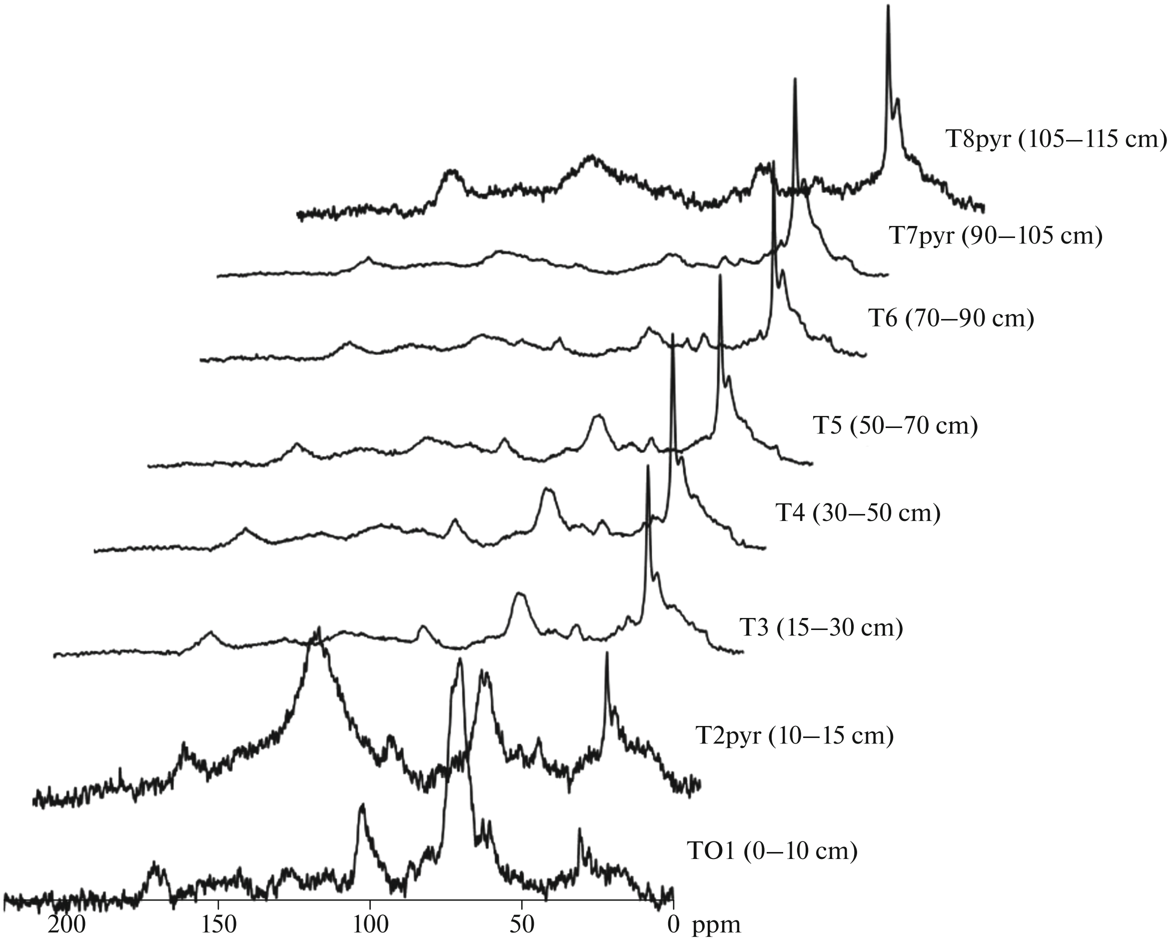

Fig. 3. NMR spectra of the studied soil horizons.

(Table 4). The horizons with pronounced pyrogenic signs display a considerable increase in both the total PAH content and the contents of individual compounds. Presumably, a pyrogenic origin is characteristic of naphthalene, phenanthrene, fluoranthene, and chrysene. As has been shown, these compounds are the main contributors to an increase in the PAH content in the postpyrogenic automorphic boreal soils [6, 36]. A considerable increase in the share of heavy 5-ring PAHs is observable in the lower horizons (90–105 cm). The concentrations of benzo(*k*)fluoranthene and dibenzo(*a,h*)anthracene are rather high, which is explainable with a biogenic factor [40]. The total PAH stock in the considered soil is 4.7 g/m^2.

The carcinogenic hazard of PAHs in the studied soils is most pronounced in the T2pyr, T7pyr, and T8pyr horizons (Table 4). The anthropogenic emission was assessed using the quantitative ratio of "technogenic" to "natural" PAHs, namely, (PYR + BaPYR)/(PHEN + CRY), where PYR, BaPYR, PHEN, and CRY are the modules of pyrene, benzo(*a*)pyrene, phenanthrene, and chrysene inputs, respectively. The value of this ratio exceeding unity suggests the presence of polyarenes from "pyrogenic" sources. According to our data, the pyrogenic component is the most pronounced in the T7pyr horizon (6.9), indicating that the polyarenes formed by combustion of organic substances are prevalent.

For the PAHs with a relative molecular weight of 178, the ratio of anthracene to the sum of anthracene and phenanthrene, ANT/(ANT + PHEN) or ANT/178, below 0.10 demonstrates an "oil" or natural origin of these compounds versus ANT/178 > 0.10, which indicates that the corresponding PAHs result from pyrogenesis [63]. This ratio is <0.10 in all examined horizons, suggesting a prevalently natural origin of the PAHs. Computation of the indicator PAH ratios that demonstrate the degree to which the observed association is "pyrogenic" or natural is not completely adequate for soils because the numerical values for the natural/technogenic boundary may significantly differ from the published data for other geographic regions.

One of the most widely used methods for assaying PyC is based on BPCAs; in particular, the current global PyC estimates were obtained with this method [48]. The content of BPCAs (Table 5) allows for quantifica-

Table 4. Contents of PAHs, ng/g

Hori-zon	Depth, cm	2-ring			3-ring		4-ring				5-ring				6-ring		ΣPAHs	I	II	III
		NAPH	ACE	FLU	PHEN	ANT	FLA	PYR	BaANT	CRY	BbFLA	BkFLA	BaPYR	DBahANT	BghiPER	IPYR				
TO1	0–10	90 ± 40	–	–	180 ± 40	2.9 ± 1.5	–	–	–	–	–	1.8 ± 0.9	1.3 ± 0.7	7 ± 3	8 ± 4	16 ± 7	335	0.01	0.02	10
T2pyr	10–15	650 ± 230	–	20 ± 8	260 ± 60	5.0 ± 2.5	26 ± 12	–	–	46 ± 24	–	15 ± 7	8 ± 4	60 ± 30	–	–	1102	0.03	0.02	71
T3	15–30	130 ± 70	–	10 ± 4	85 ± 19	1.9 ± 1.0	–	–	–	6 ± 3	–	2.4 ± 1.2	5.4 ± 2.7	11 ± 5	–	–	265	0.06	0.02	17
T4	30–50	209 ± 104	–	18 ± 7	111 ± 24	7 ± 4	–	–	–	10 ± 5	–	–	–	28 ± 13	–	–	400	0.00	0.06	29
T5	50–70	160 ± 80	–	16 ± 6	97 ± 21	4.9 ± 2.5	–	–	–	–	–	–	–	–	–	–	295	0.00	0.05	0
T6	70–90	110 ± 60	–	11 ± 4	70 ± 40	4.4 ± 2.2	–	–	–	–	–	–	–	–	10 ± 4	–	227	0.00	0.06	0
T7pyr	90–105	100 ± 50	–	–	70 ± 40	2.2 ± 1.1	–	–	–	55 ± 28	67 ± 28	19 ± 9	860 ± 210	260 ± 80	42000 ± 9000	–	43642	6.88	0.03	1549
T8pyr	105–115	44 ± 22	–	–	26 ± 13	1.3 ± 0.7	–	–	–	4.0 ± 2.1	–	–	2.9 ± 1.5	15 ± 7	8200 ± 1800	–	8356	0.10	0.05	100
G	115–130	28 ± 14	–	11 ± 4	80 ± 40	3.9 ± 2.0	–	–	–	–	–	–	–	–	–	–	138	0.00	0.05	0

(–) Below the detection limit (<6 for ACE, <6 for FLU, <20 for FLA, <20 for PYR, <6 for BaANT, <3 for CRY, <6 for BbFLA, <1 for BkFLA, <1 for BaPYR, <6 for DBahANT, <6 for BghiPER, and <6 for IPYR); NAPH, naphthalene; ACE, acenaphthene; FLU, fluorene; PHEN, phenanthrene; ANT, anthracene; FLA, fluoranthene; PYR, pyrene; BaANT, benzo(*a*)anthracene; CRY, chrysene; BbFLA, benzo(*b*)fluoranthene; BkFLA, benzo(*k*)fluoranthene; BaPYR, benzo(*a*)pyrene; DBahANT, dibenzo(*a,h*)anthracene; BghiPER, benzo(*ghi*)perylene; and IPYR, indeno(1,2,3-*cd*)pyrene. PAH ratios: I, (PYR + BaPYR)/(PHEN + CRY); II, ANT/(ANT + PHEN); and III.

Table 5. Contents of benzene polycarboxylic acids (BPCAs) in studied soil

Horizon	Depth, cm	Ba3*			Ba4			Ba5	Ba6	Sum, %	C1–6Ba	C4–6Ba	C_4Ba/C_6Ba	C_5Ba/C_6Ba	C_{BPCA}/C_{tot}, %	PyC stock	
		I	II	III	IV	V	VI	VII	VIII							$C_1–C_6$	$C_4–C_6$
		%														kg/m^2	
TO1	0–10	0.01	0.06	0.00	0.06	0.06	0.07	0.23	0.21	0.70	0.32	0.28	1.00	1.17	0.65	0.026	0.022
T2pyr	10–15	0.45	0.67	0.00	0.96	1.82	1.41	6.58	6.46	18.36	8.19	7.61	0.73	1.07	14.42	0.78	0.72
T3	15–30	0.01	0.10	0.00	0.09	0.10	0.11	0.67	0.57	1.65	0.74	0.68	0.60	1.22	1.36	0.21	0.19
T4	30–50	0.02	0.17	0.01	0.18	0.20	0.20	1.40	1.19	3.37	1.50	1.40	0.56	1.24	3.05	0.63	0.59
T5	50–70	0.02	0.08	0.01	0.11	0.16	0.13	0.53	0.63	1.67	0.74	0.69	0.70	0.89	1.37	0.34	0.32
T6	70–90	0.01	0.06	0.00	0.09	0.14	0.10	0.46	0.57	1.44	0.64	0.60	0.65	0.85	1.16	0.33	0.31
T7pyr	90–105	0.05	0.15	0.00	0.27	0.41	0.38	0.82	0.71	2.79	1.27	1.16	1.67	1.21	2.39	1.79	1.64
T8pyr	105–115	0.08	0.12	0.00	0.04	0.04	0.03	0.71	0.57	1.58	0.71	0.61	0.22	1.32	6.92	0.67	0.57
Total																4.78	4.36

C_{BPCA} is carbon content in benzene polycarboxylic acids in a horizon taking into account the carbon in individual molecules. The stock is calculated taking into account the density and thickness of horizons. * Asterix denotes the number of carboxylic groups in BPCAs. Trivial (chemical) names are given: I, hemimellitic (benzene-1,2,3-tricarboxylic) acid; II, trimellitic (benzene-1,2,4-tricarboxylic) acid; III, trimesic (benzene-1,3,5-tricarboxylic) acid; IV, pyromellitic (1,2,4,5-benzene tetracarboxylic) acid; V, mellophanic (benzene-1,2,3,4-tetracarboxylic) acid; VI, prehnitic (1,2,3,4-benzene tetracarboxylic) acid; VII, 1,2,3,4,5-benzene pentacarboxylic acid; and VIII, mellitic (benzene-1,2,3,4,5,6-hexacarboxylic) acid.

Table 6. Pearson correlation coefficients for some of the studied parameters

Parameter	CAr-H(C)	AR	Caryl, %	NAPH	PHEN	FLA	CRY
Hemimellitic acid	0.93*	0.90*	0.76*	0.93*	0.73*	0.81*	0.61
Trimellitic acid	0.88*	0.85*	0.80*	0.96*	0.75*	0.83*	0.65
Trimesic acid	–0.22	–0.21	–0.03	–0.01	–0.07	0.04	–0.29
Pyromellitic acid	0.84*	0.81*	0.88*	0.96*	0.78*	0.83*	0.73*
Mellophanic acid	0.86*	0.83*	0.88*	0.96*	0.78*	0.83*	0.70
Prehnitic acid	0.85*	0.81*	0.88*	0.96*	0.78*	0.82*	0.73*
Benzene pentacarboxylic acid	0.88*	0.84*	0.82*	0.98*	0.77*	0.86*	0.60
Mellitic acid	0.88*	0.85*	0.84*	0.98*	0.78*	0.87*	0.59
Total, %	0.88*	0.84*	0.84*	0.98*	0.78*	0.86*	0.63
C_{BPCA}	0.88*	0.84*	0.84*	0.98*	0.78*	0.86*	0.63

* Significant at $p < 0.05$, $n = 8$.

tion of the share of pyrogenic carbon in SOM. In the studied soil, the total BPCA content varies from 0.7 to 18.4 wt % or 0.3 to 8.2% recalculated to carbon, which accounts for 0.6 to 14.4% of the total carbon content in soil horizons. The highest PyC content is observed in the pyrogenic horizon at the depth of 10–15 cm, most likely resulting from a wildfire that took place 140 years ago. The effect of the wildfires involved in the formation of this peatland and occurring about 9000 years ago enhanced PyC accumulation in the lower horizons at the amount of 2.4–6.9% of total carbon content. Recalculation of the PyC stock taking into account the bulk densities of individual horizons gave the PyC estimate of 4.78 kg/m^2 (considering all eight BPCAs) or 4.36 kg/m^2 considering only 4–6-ring acids. Note that only a few papers report the data on the BPCA content on the territory of Russia and mainly refer to the automorphic soils of Siberia. The data on the PyC content in peats are sparse. We have obtained somewhat higher values of the PyC stock and content as compared with the peat soils in the forest-tundra of the Krasnoyarsk krai (Russia) [44]. This is explainable by that the studied area is more southern and, correspondingly, more subject to wildfires both now and in different periods of the Holocene. The observed PyC content in the studied soil is considerably higher as compared with podzols [33].

Our results suggest that most of the used approaches make it possible to diagnose the pyrogenic signs in SOM. Moreover, many characteristics correlate well with one another. The most significant correlation coefficients are listed in Table 6. The total BPCA content significantly correlates with the concentrations of naphthalene ($R = 0.98$, $p < 0.05$), phenanthrene ($R = 0.78$, $p < 0.05$), fluoranthene ($R = 0.86$, $p < 0.05$), and the aromatic fragments ($C_{Ar\text{-}H(C)}$) identified with NMR spectroscopy ($R = 0.88$, $p < 0.05$). Note that the total PAH content correlates only with the total carbon content in a sample. The significant correlations with a high coefficient are observed for individual BPCAs and several PAHs. Except for trimesic acid, the correlation coefficients of individual BPCAs with naphthalene amount to 0.96–0.98 ($p < 0.05$); with phenanthrene, to 0.75–0.78 ($p < 0.05$); with fluoranthene, to 0.82–0.86 ($p < 0.05$); and with chrysene, to 0.73–0.74 ($p < 0.05$).

CONCLUSIONS

A comparison of the NMR spectroscopy data and PAH contents has shown that these methods make it possible to diagnose the input of pyrogenically modified organic compounds. The share of the carbon associated with benzene rings considerably increases in the SOM molecular fragments with pyrogenic signs. The concentrations of naphthalene, fluoranthene, phenanthrene, and chrysene, which have putative pyrogenic origin, are increased in the PAHs of the horizons. An increase in the content of molecular aromatic fragments and several individual PAHs can be used as markers of pyrogenesis. These parameters can indicate only the general trend of an increase in the degree of SOM aromaticity. The total PAH stock is extremely small and the PAH concentrations only partially characterize the total content of PyC and its stock in soils.

The method relying on BPCAs gives a more realistic data on the PyC stock in soils. A hard acid hydrolysis allows for extraction of a large amount of aromatic carbon from soil, which better reflects its concentration. Correspondingly, this method is more adequate for quantification of pyrogenic carbon.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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