POLISH POLAR RESEARCH
vol. 39, no. 4, pp. 481–503, 2018 doi: 10.24425/118757

Molecular composition of humic substances isolated from permafrost peat soils of the eastern European Arctic

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Abstract: Humification plays an important role in stabilization of organic matter in soils of the cryolithic zone. In this context, the degree of organic matter stabilization has been assessed, using instrumental methods, for permafrost peat soils of the eastern European Arctic, based on selected plots from within the Komi Republic (Russian Federation). Humic substances (HSs) isolated from the mire permafrost peats of the forest-tundra subzone of the European Arctic have been characterized in terms of molecular composition. This was accomplished using elemental and amino acid fragments (AAFs) composition. Solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy was utilized to identify the structure of HSs. Changes in the molar $x(H) : x(C)$ ratio, ratio of aromatic to paraffin fragments and ratio of hydroxy AAFs to heterocyclic AAFs along the peat profiles have been revealed. They are due to the activation of cryogenic processes in the upper part of the seasonally thawing layer, the natural selection of condensed humic molecules, the botanical composition and degree of degradation of peat, which reflect the climatic features of the area in the Holocene. Humic acids and fulvic acids of the peat soils showed the prevalence of compounds with a low degree of condensation and a low portion of aromatic fragments. The aromaticity degree showed the trend to increase within the depth. Changes of quantitative and qualitative parameters of specific organic compounds occur at the permafrost boundary of peatlands, which can serve as an indicator of recent climate changes in environments from the high latitudes. The presented data can be useful in the evaluation of soil organic matter stabilization degree in the active layer and below the permafrost table.

Key words: Arctic, forest-tundra, Histosols, humic and fulvic acids, ^{13}C NMR, elemental and amino acid composition.

Introduction

Soils of boreal and polar environments have been currently considered as key components of the global carbon cycle (Yu *et al*. 2014; Bruun *et al*. 2015; Peng *et al*. 2015; Wasak and Drewnik 2015; Szymański *et al*. 2016). This is especially important for Arctic soils, because they contain maximum stocks of soil organic matter (SOM) within the whole pedosphere (McGuire *et al*. 2009; Oliva *et al*. 2014; Zubrzycki *et al*. 2014; Fritz *et al*. 2015; Ping *et al*. 2015). Northern polar wetland and tundra areas have significant amounts of carbon stored in their soil organic matter (Christensen *et al*. 1999). Current estimations of soil organic carbon (SOC) stocks are *ca*. 1307 Pg throughout the northern circumpolar region (Hugelius *et al*. 2014). These amounts surpass previous estimates (Tarnocai *et al*. 2009) and largely exceed the total carbon contained in the world vegetation biomass (460–650 Pg) or in the atmosphere (589 Pg). However, above-mentioned SOM/SOC stock assessments are still poorly constrained. The main cause of uncertainty is the fact that such estimates have been calculated from observations which are highly spatially clustered (Hugelius *et al*. 2014), whereas extensive land areas still remain uncharacterised due to logistic difficulties to reach these sites.

Stability and biodegradability of SOM are the key features of organic matter which should be taken into account for precise estimation of modern and future carbon stock and organic matter quality dynamics. The stabilization rate has been related to the humification degree, as more advanced stages in the humification process imply a depletion of the labile molecules as well as an increase in the bulk aromaticity, which provides a higher stability of SOM (Klavinš *et al*. 2012).

The stability of the stored carbon under changing climatic conditions is the subject of the concern due to the expected climate warming, which is predicted to be the most pronounced in northern continental regions (Schuur *et al*. 2015). Thawing and degradation of the permafrost release carbon compounds that have been immobilized and transferred to adjacent systems. Permafrost degradation in the peatland ecosystems affects global and regional carbon balances (Schuur *et al*. 2015). Climate change and further risks related to intensive exploration of the Arctic sector of Russia are resulting in alterations to the hydrology of Arctic permafrost peat soils and irreversible changes in the peat layers. This results in degradation and thawing of the permafrost and uncontrolled greenhouse gas emission. Assessment of the transformations is therefore needed to estimate the role of peat soils in the global and regional stabilization of this organic material.

Peat profiles can serve as "archives" indicating conditions in past environments. Peat reserves play a major role in the carbon biogeochemical cycling. Peat humic acids are of key importance in the context of the ongoing process of climate change. The ratio of aromatic to aliphatic humic acids (HAs) components is related to the type of peat material and content of oxygen-containing carboxylic

and phenolic groups. This ratio also reflects the degree of humification (Purmališ and Klavinš 2012). Conditions of the permafrost affect soil formation and, together with low microbiological activity in forest-tundra, lead to cryogenic denaturation and the transformation of highly dispersed HAs. Thawing-freezing cycles result in intensive changes in the composition of humus and its colloidal physicochemical properties. These changes are manifested in increased HA mobility because of increased polydispersity of the molecules (Dergacheva and Dedkov 1977). Thus, short- and long-term climatic changes could affect the quality of HAs. The alteration should be most pronounced in the supra-permafrost layers. The degree of organic matter stabilization of mineral and peat soils is considered as more important than amount of organic matter stored in the pedosphere, in terms of permafrost soils ecosystem services and regulation of biogeochemical pathways.

In order to evaluate the quality and stabilization of organic matter of the mire peatlands from the eastern European Arctic, the following objectives were formulated for the present study: (i) to investigate the molecular composition of HSs from permafrost peat soils; (ii) to evaluate the structural composition of HSs molecules within the soil depth; and (iii) to analyze the composition of amino acids as an important structural part of the HAs.

Materials and methods

Study area and soil morphology. — The investigated peatlands are located in the north forest-tundra subzone (the basin of the Seida River, a part of the Pechora River basin), Vorkuta district, Komi Republic, Russian Federation (Fig. 1A). The permafrost in this region is extensive. The climate is cold, subarctic and moderately continental (Kaverin *et al*. 2016). The annual mean air temperature is -4.0°C, the average sum of positive temperature values varies from 1150 to 1380°C, and the annual precipitation is *ca*. 550–600 mm. The evaporative power of the territory is 250 mm (Bratsev and Bratsev 1997).

Two peat soils, Hemic Folic Cryic Histosol and Hemic Folic Cryic Histosol (Turbic) (see FAO and IUSS 2015), have been studied within a peat plateau-thermokarst complex located west of the Ural Mountains (Fig. 1). These peat soils differ in their active layer thickness and thermal regime. In the summer season, the permafrost table is fixed at a depth of *ca*. 40–60 cm. The peat material of the studied soils was dark brown and deeply decomposed. The material on the peatland surface is not continuous, and is altered by wind corrosion and the cryogenic mass exchange effect. The total area of altered bare spots is about 8% of the total areas of peatland polypedons. Sampling was conducted to a depth of 2.0 m in three replications from the peatland polypedon.

Hemic Folic Cryic Histosols are typical of permafrost peatland with vegetation cover (vegetated peat areas). The plot in question (67°03’ N, 62°56’ E)

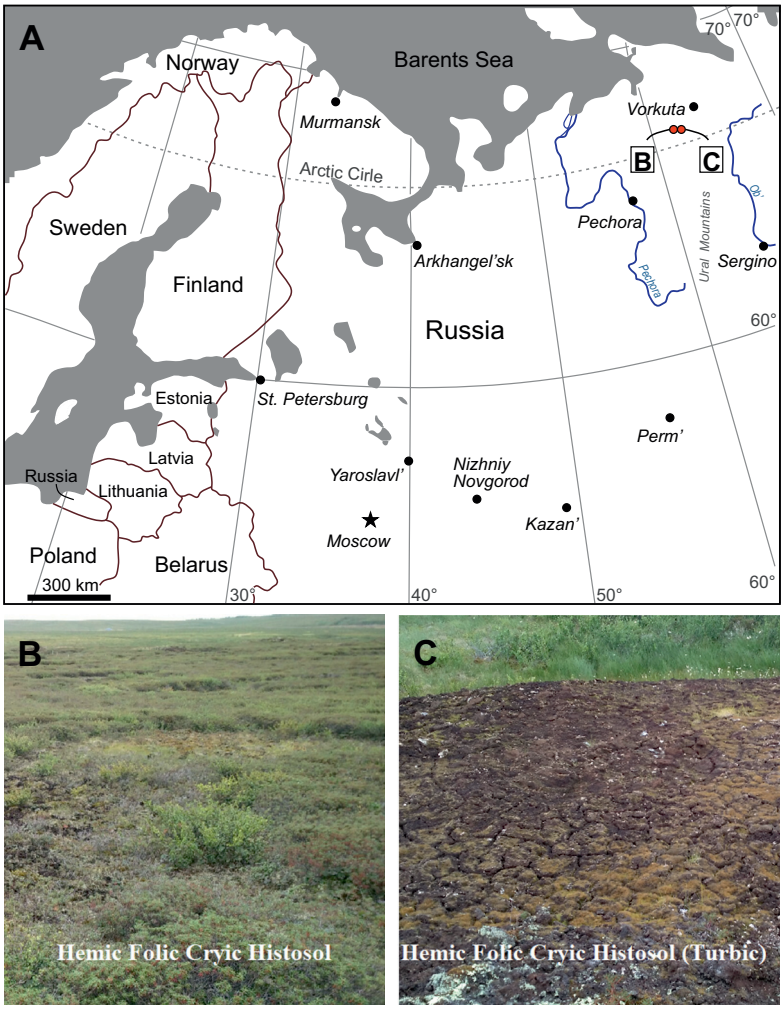

Fig. 1. Sampling location and study sites.

is located 7 km southwest of the railway station Seida. The landform is moraine lowland, and the diameter of the hillock is *ca*. 12 m. The upper limit of the permafrost is at a depth of 40 cm. The vegetation cover is formed by *Cladonia* spp., *Polytrichum commune*, *Empetrum hermaphroditum*, *Vaccinium vitis-idaea*, *Rubus chamaemorus*, *Vaccinium uliginosum*, and *Betula nana* along the edges of the hillock (Fig. 1B). Hemic Folic Cryic Histosols (Turbic) are typical of permafrost peatland without vegetation cover (bare peat spots). The diameter of the polypedon in question (67°03' N, 62°56' E) is *ca*. 5 m. The upper limit of the permafrost is at a depth of 60 cm. Cryogenic crack formation was evident for bare sites (Fig. 1C).

The analysis of the temperature regimes of the studied soils showed that during the summer, soil with bare spots was heated and insolated more intensively than the soil with vegetated plots. This is exemplified by the heating difference (Σt > 0°C) being 2–5 times higher at depth >10 cm than that of soils from vegetated plots. The soils of bare peat spots have a lower sum of negative temperatures during the autumn-winter periods (-1160°C·days at a depth of 10 cm; -1099°C·days at 20 cm). This is due to the absence of a thermo-insulating moss layer, compared to vegetated peat areas (-522°C·days at a depth of 10 cm; -455°C·days at 20 cm).

Data on the composition, and physical and chemical properties of peat soils (Table 1) showed that the lowest pH values (3.5–3.9) are typical of topsoil material and indicate strong acidity that is typical of oligotrophic peat soils. The lowest horizons showed enrichment in the exchangeable fractions of Ca and Mg, providing higher pH values, up to 5.5 in the middle part of the strata, and increased content of Fe, Al, and Ca. The highest C/N ratios were registered in superficial layers, while the lowest occurred in permafrost horizons. This indicated the greatest degree of OM alteration with depth. The fractional and group compositions of the SOM show a prevalence of HAs vs. fulvic acids (FAs).

Extraction of humic substances. — Samples from the active permafrost-free layers of peat soils were taken from open pits from the seasonally thawed layer in increments of 10 cm. Samples from permafrost layer of peat soils were cored using steel pipes that were drilled into the ground in 20-cm increments, and intact frozen cores were retrieved between the drillings. Air-dried peat samples were homogenized and sieved though a 1-mm sieve. The powders of HAs and FAs were extracted from the peat material samples by double-extractions with 0.1 mol/dm^3 NaOH according to the IHSS recommendations (Swift 1996). The HAs were desalinated by dialysis. The FAs were purified on activated carbon AG-3 according to Forsyth (1947) and desalinated on cation exchanger KU-2 (H^+ form). The powders of HAs and FAs were obtained by heating at 35°C in the drying chamber.

Elemental analyses. — Humic acids were characterized for their elemental composition (C, N and H) using a EA-1110 analyzer. Water content was measured by the gravimetric method, while ash content was evaluated based of ignition loss. Data were corrected for water and ash content. Oxygen content was calculated by difference, considering the general content of C, N, H, O as 100%. The elemental ratios (C/N, H/C and O/C) reported in this paper are based on molar percentages. The H/C and O/C ratios were also cross-plotted in the form of a van Krevelen diagram.

Table 1

Properties of peat soils.

Depth, cm	Peat layer	Calibrated age, median (cal yr BP)	Peat type	Dominant botanical species	Degree of decomposition, %	pH H_2O	C/N
Hemic Folic Cryic Histosol							
0–10	T1	1357	Raised	*Polytrichum*	20–25	3.75	30.1
10–20	T2	n.d.	Raised	Subshrub	35–40	3.70	24.5
20–40	T3	3754	Fen	*Carex*, *Eriophorum*	30–40	3.74	21.4
40–60	T4	6011	Fen, frozen	*Betula* sp., wood	30–35	4.34	32.0
60–80	T5	6473	Fen, frozen	*Menyanthes*, *Carex*	30–35	4.86	22.4
80–100	T6	6508	Fen, frozen	*Betula* sp., wood, *Carex*	35–40	4.94	26.8
100–150	T7	7022	Fen, frozen	*Betula* sp., wood, *Carex*	30–40	4.95	22.2
150–175	T8	n.d.	Fen, frozen	*Betula* sp., wood, *Carex*	35–40	5.37	22.0
175–200	T9	7984	Fen, frozen	*Betula* sp., *icea*, wood, grass	50	5.33	17.2
Hemic Folic Cryic Histosol (Turbic)							
0–5	T1	1231	Raised	*Polytrichum*	20–25	3.61	28.7
5–20	T2	n.d.	Transitional	Subshrub, *Eriophorum*	40–45	3.42	25.5
20–40	T3	5457	Fen	*Carex*	30–35	3.66	26.6
40–60	T4	6062	Fen	*Hypnaceous*, *Carex*	30–50	4.24	23.6
60–80	T5	n.d.	Fen, frozen	Subshrub, *Carex*	35–40	5.05	25.0
80–100	T6	n.d.	Fen, frozen	*Carex*	35	5.00	24.1
100–150	T7	n.d.	Fen, frozen	*Betula* sp., *Picea*, wood, *Carex*	35–40	5.47	23.4
150–175	T8	n.d.	Fen, frozen	*Betula* sp., *Picea*, wood, *Carex*	40–45	5.32	21.0
175–200	T9	n.d.	Fen, frozen	*Equisetum*, *Betula* sp., *Picea*, wood, *Carex*	> 50	5.51	18.6

Note:
[1] n.d. – not determined.

Amino acid measurements. — The amino acid composition of the 6 mol/dm^3 HCl extract of HAs and FAs was studied by liquid chromatography on ion exchange resins (AAA 339 amino acid analyzer). The amino acid mixture was separated into components on a chromatographic column filled with the Ostion ion exchanger. The content of each amino acid in the eluate was determined photometrically from the absorption of the yellow compound formed in the postcolumn reaction between the amino acid and ninhydrin at λ = 520 nm.

^{13}C NMR measurements. — Measurements were carried out using a JNM-ECA 400 (JEOL) NMR spectrometer (100.53 MHz for ^{13}C). Solid-phase samples were placed in a 4-mm zirconium oxide rotor and spun at a frequency of 6 kHz at the magic angle. The cross-polarization sequence of excitation pulses was used for the registration of ^{13}C spectra (CP/MAS). The contact time was 5 ms, the delay time was 5 s, and the number of scans was 13000. Chemical shifts were referenced to low field signal of adamantane at 38.48 ppm.

Statistics. — Bivariate correlation analyses were conducted using the Pearson product-moment correlation coefficient (r), and its statistical significance was assessed via Neyman-Pearson (NP) approach. Technically, the observed value of the coefficient (based on n pairs) was compared against the critical value (r_{cr}) for a two-tailed test and significance level (α) of 0.05.

Results and interpretation

Elemental composition. — The content of carbon in HAs and FAs from Hemic Folic Cryic Histosol (Turbic) is 50.1–60.8% and 45.8–49.6%, respectively. The corresponding values for HSs from Hemic Folic Cryic Histosol are 52.2–60.8% and 41.1–48.8%, respectively (Table 2). The values are comparable with those in other permafrost-affected soils (Lodygin *et al*. 2014). The analysis of the van Krevelen diagram (Fig. 2) revealed similar atomic x(O) : x(C) ratios for HA preparations confined to the upper and central peat layers (Fig. 2, region II). The position of HSs in the diagram relates the differences between HA and FA preparations to the different development of their aliphatic chains and their degrees of condensation (Chukov *et al*. 2015). Significant differences in the x(H) : x(C) ratio of HA and FA preparations are observed between peat layers. HA preparations occupy a peculiar diagram region at the boundary of permafrost (region III) and lower horizons (region I). The decarboxylation and dehydration of HA molecules occur at the transition from region II to region I; their demethylation occurs between region II and region III. HAs from the lower layers consist of reduced molecules with a low content of oxygen-containing functional groups.

Table 2

Elemental composition of HAs and FAs.

Plot	Depth, cm	Mass fraction, %				Molar ratios[1]			Degree of oxidation, ω^2
		C	N	H	O	H:C	O:C	C:N	
Humic acids									
Hemic Folic Cryic Histosol	0–10	53.1 ± 1.7[3]	3.45±0.23	5.2±0.5	38.3±1.8	1.16±0.12	0.54±0.11	18.0±1.3	-0.08
	10–20	52.9±1.7	3.30±0.22	4.9±0.4	38.9±1.8	1.10±0.11	0.55±0.11	18.7±1.4	-0.00
	20–40	53.7±1.7	3.38±0.23	4.8±0.4	38.1±1.8	1.07±0.11	0.53±0.11	18.5±1.4	-0.00
	40–60	52.6±1.7	3.18±0.21	4.7±0.4	39.5±1.8	1.06±0.10	0.56±0.10	19.3±1.4	0.07
	60–80	52.2±1.7	2.98±0.20	4.3±0.4	40.6±1.7	0.98±0.10	0.58±0.10	20.4±1.5	0.19
	80–100	59.3±1.9	3.51±0.24	4.5±0.4	32.7±2.0	0.92±0.09	0.41±0.09	19.7±1.5	-0.09
	100–150	60.8±2.0	3.90±0.26	4.6±0.4	32.7±2.0	0.90±0.09	0.38±0.09	18.2±1.4	-0.15
	150–175	56.3±1.8	3.17±0.21	4.4±0.4	36.1±1.9	0.94±0.09	0.48±0.10	20.7±1.5	0.02
	175–200	55.8±1.8	3.44±0.23	4.5±0.4	36.2±1.9	0.98±0.10	0.49±0.10	18.9±1.4	-0.01
Hemic Folic Cryic Histosol (Turbic)	0–5	54.1±1.7	3.48±0.23	4.7±0.4	37.7±1.8	1.05±0.10	0.52±0.10	18.1±1.3	-0.00
	5–20	52.0±1.7	3.15±0.21	4.4±0.4	40.5±1.7	1.01±0.10	0.59±0.10	19.2±1.4	0.16
	20–40	52.2±1.7	2.2±0.4	3.6±0.3	42.0±1.8	0.82±0.08	0.60±0.09	28.1±2.1	0.38
	40–60	50.1±1.6	2.2±0.4	3.5±0.3	44.2±1.7	0.83±0.08	0.66±0.09	26.7±2.0	0.49
	60–80	51.1±1.6	2.93±0.20	4.0±0.4	42.0±1.7	0.93±0.09	0.62±0.09	20.3±1.5	0.30
	80–100	60.8±2.0	3.78±0.25	4.7±0.4	30.7±2.0	0.93±0.09	0.38±0.09	18.8±1.4	-0.17
	100–150	60.6±1.9	3.64±0.24	4.6±0.4	31.2±2.0	0.91±0.09	0.39±0.09	19.4±1.4	-0.14
	150–175	57.1±1.8	3.63±0.24	4.4±0.4	34.9±1.9	0.92±0.09	0.46±0.09	18.4±1.4	0.00
	175–200	56.3±1.8	3.56±0.24	4.3±0.4	35.8±1.9	0.92±0.09	0.48±0.09	18.5±1.4	0.03

Fulvic acids									
Hemic Folic Cryic Histosol	0–10	45.2±1.4	2.2±0.4	5.0±0.5	47.7±1.6	1.32±0.13	0.79±0.13	24.1±1.8	0.26
	10–20	42.5±1.4	1.9±0.3	4.8±0.4	50.8±1.5	1.35±0.13	0.90±0.13	26.5±2.0	0.44
	20–40	44.1±1.4	2.2±0.4	5.1±0.5	48.6±1.5	1.38±0.14	0.83±0.14	23.2±1.7	0.27
	40–60	41.1±1.3	2.2±0.4	4.3±0.4	52.4±1.4	1.26±0.12	0.96±0.12	21.7±1.6	0.66
	60–80	47.1±1.5	2.7±0.5	4.5±0.4	45.7±1.6	1.15±0.11	0.73±0.11	20.5±1.5	0.31
	80–100	48.8±1.6	2.0±0.4	4.6±0.4	44.6±1.7	1.14±0.11	0.69±0.11	28.1±2.1	0.23
	100–150	47.9±1.5	2.3±0.4	4.3±0.4	45.5±1.6	1.07±0.11	0.71±0.11	24.3±1.8	0.35
	150–175	–	–	–	–	–	–	–	–
	175–200	45.8±1.5	3.0±0.5	4.2±0.4	47.0±1.6	1.11±0.11	0.77±0.11	18.1±1.3	0.43
Hemic Folic Cryic Histosol (Turbic)	0–5	45.8±1.5	2.7±0.5	4.5±0.4	47.0±1.6	1.18±0.12	0.77±0.12	19.5±1.4	0.35
	5–20	47.8±1.5	2.4±0.4	4.3±0.4	45.5±1.6	1.08±0.11	0.71±0.11	23.6±1.8	0.35
	20–40	48.9±1.6	1.30±0.23	3.6±0.3	46.1±1.6	0.89±0.09	0.71±0.09	44±3	0.52
	40–60	47.2±1.5	1.38±0.25	4.0±0.4	47.4±1.6	1.02±0.10	0.75±0.10	40±3	0.49
	60–80	48.0±1.5	1.40±0.25	3.8±0.4	46.8±1.6	0.95±0.09	0.73±0.10	40±3	0.51
	80–100	49.0±1.6	2.0±0.4	4.3±0.4	44.6±1.7	1.05±0.10	0.68±0.11	28.8±2.1	0.31
	100–150	49.6±1.6	2.3±0.4	4.5±0.4	43.6±1.7	1.09±0.11	0.66±0.11	24.7±1.8	0.23
	150–175	48.7±1.6	2.4±0.4	3.9±0.4	45.0±1.7	0.96±0.09	0.69±0.10	24.1±1.8	0.43
	175–200	47.8±1.5	2.5±0.4	4.5±0.4	45.3±1.6	1.12±0.11	0.71±0.11	22.5±1.7	0.30

Notes:
[1] H:C = x(H) : x(C), O:C = x(O) : x(C), C:N = x(C) : x(N).
[2] $\omega = (2 \cdot x(O) - x(H)) : x(C)$.
[3] ± D – denotes the absolute error limits at the confidence level of 0.95.

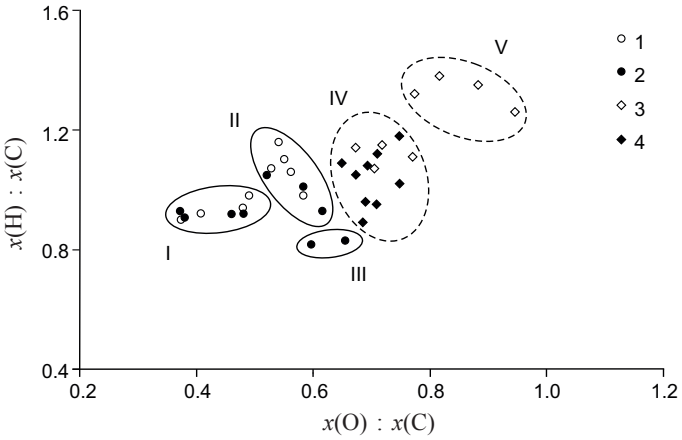

Fig. 2. The joint distribution of x(H) : x(C) and x(O) : x(C) molar ratios in HA (1, 2) and FA (3, 4) preparations from Hemic Folic Cryic Histosol (1, 3) and Hemic Folic Cryic Histosol (Turbic) (2, 4). Clusters I–V are discussed in text.

The x(H) : x(C) ratio characterizes the degrees of condensation and maturity of HS molecules. This index can be used as a value for assessment the HAs stabilization rate. A decrease in the x(H) : x(C) ratio of HAs is revealed down the profile – from 1.05 to 0.82 in bare spots and from 1.16 to 0.90 in vegetated peat areas, which is due to the natural selection of biothermodynamically stable molecular structures and determines the high degree of organic matter humification in lower peat layers (Table 2). The degree of peat degradation increases down the profile from 20% for moss peats in the upper part of the profile to 35–40% for sedge and trefoil–sedge species in the central part and to 35–50% for wood-sedge peat in the lower layers. A reliable relationship is observed between the x(C) : x(H) ratio in HAs and the degree of humus degradation (n = 18, r = 0.578, r_{cr} = 0.468).

The regular decrease in the x(H) : x(C) atomic ratio along the profile is considered to be related to the changes in the botanical composition of peat: the increase in the share of herbaceous plants deeper than 60 cm and woody plants in the lower peat horizons. It is suggested that lignin components largely determine the degree of benzoidicity of HSs (Kovaleva and Kovalev 2015). According to Orlov (1995), the content of lignin in dry ash-free lichens and mosses (8–10%) is lower than in grasses (15–20%), and shrubs and trees (20–30%). This results in a lower incorporation of phenylpropane lignin units into the nuclear fragments of HS molecules from moss and sedge peats than those from woody and woody-sedge peats confined to the central and lower parts of soil profile.

The climatic features of the formation period of peat layers determine not only the qualitative composition of the main peat-forming substances, but also

the degree of degradation of organic biopolymers, including the depolymerization of the polyphenolic basis of lignin structures and the decomposition of proteins and polysaccharides under the effect of fungi and bacteria (Dobrovol'skaya *et al*. 2014). These processes directly depend on the climatic parameters of the environment, which were more favorable during the Holocene optimum. This determines, along with the above-mentioned factors, the high degree of humification of organic material during the initial period of peat formation.

The degree of humification of organic matter is more closely related to the thermic conditions of soils during the warm season. Hemic Folic Cryic Histosols are less heated in summer because of the buffer effect of moss litter. This can be a reason for the lower degree of condensation of HA and FA molecules in the peat horizons down to the permafrost table. It is known that the degree of organic matter humification is largely determined by biologically active temperatures (>10°C) (Dergacheva *et al*. 2012). According to some authors, the formation of cryogenic spots is a recurrent process (Luoto *et al*. 2004). The seasonally thawing layer of permafrost peatlands represents the current transformation stage of organic matter, which is subjected to alteration (most actively pronounced for the profiles of bare spots under the effect of biochemical processes). The sums of positive and biologically active temperatures in Hemic Folic Cryic Histosol (Turbic) practically simulate the current climate warming, which causes an essential transformation of high-molecular-weight organic compounds and appears as changes in structural and functional parameters of HSs.

The accumulation of biothermodynamically stable fragments caused by low x(H) : x(C) ratios for HAs at a depth of 20–60 cm and FAs at a depth of 20–40 cm in Hemic Folic Cryic Histosols (Turbic) is presumably due to dynamic thawing–freezing processes at the permafrost boundary. The absence of heat-insulating moss cover on Hemic Folic Cryic Histosols (Turbic) favors a steeper temperature gradient in the early meteorological winter and summer. According to some authors, these dynamic processes result in the detachment of the least condensed molecular fragments from HA and FA molecules, which increases the share of FAs in the fractional and group composition of humus (Dergacheva and Dedkov 1977).

From a depth of 80 cm, the x(H) : x(C), x(O) : x(C), and x(C) : x(N) ratios of HAs are almost similar for two profiles and indicate the relict character of humus, which is a result of diagenesis of the Atlantic period with warmer climate conditions. The similarity of these ratios is due to the high linear velocity of peat accumulation, when the peat-forming layers cover the lower layers and thus cut-off conditions for the biodegradation of plant residues and the humification of organic material in the lower peat horizons. In the peat layer at a depth of 80–150 cm, the most humified HS preparations correspond to the Holocene optimum 7022–6508 Cya (IGRAN 4644, 4645) and reflect the warmest climatic period of humus formation.

Comparison of the content of oxygen and the degree of HS oxidation in peat mounds with the data for mineral soils of the tundra zone (Lodygin *et al*. 2014) showed that HAs and FAs of peatlands consist of more reductive molecules. The anaerobic pedogenesis conditions in peat mounds also result in the lower content of oxygen and x(O) : x(C) ratio in FAs. The x(O) : x(C) atomic ratios for FAs of peat mounds are significantly lower than in mineral soils of the Bolshezemel'skaya tundra (0.85–1.71).

Amino acid composition. — Amino acid accumulation in HSs composition along peat profile is of a bimodal character. Amino acid weight fraction in dry part of HAs decreases downward soil profile from 8.6 to 5.5% (at a depth of 60–80 cm) and increases to 8.8% in low peat. For FAs, it also decreases from 4.9 to 1.6% (60–80 cm) and increases up to 4.0% in low soil part. The data on amino acid concentration in hydrolysable HSs in peat soils of the forest-tundra zone agree with the results on HSs elemental composition. Together, these data indicate that oligo- and polypeptide molecular fragments decrease in total nitrogen and nitrogen content.

Simultaneous processes such as mineralization of labile amino acid fragments (AAFs), whereby they serve as available nitrogen for microorganisms, as well as interaction of the concerned fragments with phenol groups of nuclear molecular part, start redistribution of hydrolysable nitrogen in HS composition which means its transformation into hydrophobic HS component. In the seasonally thawed layer, mineralization gradually decreases labile AAFs content down to the upper border of frozen soil layer. The decreasing weight fraction of nitrogen against total nitrogen is also associated with formation of heterocyclic nitrogenous bases which cannot serve for nutrition of microorganisms and plants which, in turn, are highly important for formation of HAs and FAs molecules. The high portion of AAFs in HSs from low peat layers seams to relate to two major factors such as organic matter humification and peat formation during the Holocene epoch.

Low peat normally includes grass and tree remnants. About 2000–2500 years ago, it was conserved by permafrost, and therefore isolated from further organic matter transformation processes. Amino acid weight fraction in composition of tree vegetation considerably exceeds that in grasses and mossy-lichen vegetation (Vasilevich *et al*. 2015), which is responsible for distribution of hydrolysable amino acid fragments in HS composition.

Hydrolysable humic acids are dominated by neutral amino acids (glycine, alanine, threonine etc.) whose relative mole fraction makes 66.5–71.1%. Neutral amino acids are thought to be highly stable. At bare spots, dicarboxylic AAFs take 19.3–24.8%, diamino AAFs – 5.7–11.4%, and aromatic AAFs – 4.2–7.0% of HAs. At bare spots dicarboxylic AAFs take 21.9–23.6%, diamino AAFs – 10.1–11.4%, and aromatic AAFs – 5.7–6.4% of HAs (Table 3). Mole fraction of aromatic and diamino AAFs in HA composition decreases downward peat profile

and that of dicarboxylic amino acids increases in low peat. These dynamics indicate carboxylation as one of the principal HA transformation processes.

FAs are characterized by a high content of dicarboxylic (24.5–34.4%) and low content of diamino (5.4–10.7%) AAFs, which agrees well with their more acidic nature. By the analysis of the obtained data, neutral AAFs of humic and fulvic acids are similar by quantitative composition. This may be associated by cryogenic transformation of HAs into FAs.

One of the principal humification features is a relative accumulation of cyclic amino acids which are involved into condensation reactions (Orlov 1995). The most interesting is distribution of stable heterocyclic AAFs into HAs which reflects the degree of organic matter humification and has three extremes downward peat profile. The first extreme occurs in the upper part of seasonally thawed layer with active organic matter humification processes, the second extreme – in its central part (40–80 cm deep), which was possibly affected by a local temperature maximum of the Early Sub-boreal Period. The third extreme develops in the low peat part, which was formed at the Holocene climatically optimum period. There exists a significant correlation between the relative mole fraction of heterocyclic amino acids and the aromaticity degree of HAs (n = 18, r = 0.47, r_{cr} = 0.47). The mole fraction ratio of hydroxy AAFs to heterocyclic AAFs indicates the soil biological activity level and can serve as a humification degree marker (Vasilevich *et al*. 2015). The lowest values of the ratio also occur in the low soil part and so indicate favorable climatic conditions of the Holocene.

Structural molecular composition (^{13}C NMR). — Analyses of the ^{13}C NMR spectra of the majority of HSs revealed that the most expressed intensity of the signals was diapason at 0–47 ppm, which is related to aliphatic carbon. The high portion of aliphatic carbon is related to the accumulation of organic precursors derived from organic remnants, such as long aliphatic chains from wax resins, fatty acids, cutin, and cell-wall phospholipids (Winkler *et al*. 2005; Jager *et al*. 2016).

The quantitative compositions of ^{13}C NMR spectra revealed a high portion of unoxidized aliphatic fragments in the HAs molecules. The lowest intensities of the signal at 0–47 ppm were fixed for the HAs for Hemic Folic Cryic Histosols (Turbic) from the depths of 20–40 cm and 40–60 cm on the border solum with the permafrost table. The highest concentration was in the HAs from superficial layers. Lower in the soil profile, the contribution of branched aliphatic structures decreases, especially for the HAs extracted from the permafrost layers from bare spots.

Quantitative analyses of the structural components of the HAs revealed a low portion of aromatic carbon in the HAs and FAs (15.2–36.3% and 1.6–12.8%, respectively). The content of functional groups was different in seasonally thawed

Table 3

Relative mole fraction of HA and FA amino acids, %.

Plot	Depth, cm	Group of amino acid fragments									(Hydroxy AAs)/ (hetero cyclic AAs)
		Neutral			Dicar-boxylic[3]	Diamino acids[4]	Hydroxy acids[5]	Cyclic			
		Polar[1]	Non-polar[2]	Total				Aro-matic[6]	Hetero-cyclic[7]	Total	
Humic acids											
Hemic Folic Cryic Histosol	0–10	17.41	50.19	67.60	21.94	10.46	15.07	6.18	6.94	13.12	2.17
	10–20	16.79	50.21	67.00	22.19	10.81	14.48	6.05	7.20	13.25	2.01
	20–35	17.07	50.15	67.22	22.38	10.40	14.71	6.13	6.94	13.07	2.12
	40–60	16.43	50.03	66.47	22.09	11.44	14.23	6.39	7.27	13.67	1.96
	60–80	15.45	52.19	67.64	22.22	10.14	13.38	5.68	8.58	14.26	1.56
	80–100	17.18	52.92	70.10	22.05	7.85	14.67	5.53	6.07	11.59	2.42
	100–150	17.00	51.56	68.55	24.01	7.43	14.99	4.55	5.38	9.93	2.78
	150–175	15.05	52.28	67.33	24.07	8.60	12.97	5.05	8.55	13.60	1.52
	175–200	14.64	52.45	67.08	23.58	9.33	12.78	4.71	7.64	12.35	1.67
Hemic Folic Cryic Histosol (Turbic)	0–5	16.26	50.68	66.94	21.69	11.37	13.93	6.07	6.73	12.80	2.07
	5–20	17.71	52.77	70.48	19.29	10.23	14.80	6.96	5.87	12.84	2.52
	20–40	15.11	56.07	71.19	20.70	8.11	13.60	3.82	8.56	12.39	1.59
	40–60	15.76	53.31	69.07	23.35	7.58	13.30	4.84	6.62	11.46	2.01
	60–80	16.64	53.77	70.42	21.10	8.48	13.93	6.14	6.45	12.59	2.16
	80–100	15.14	53.81	68.96	22.77	8.27	13.17	5.00	6.50	11.49	2.03
	100–150	16.12	53.04	69.16	22.60	8.24	14.16	4.67	6.39	11.06	2.22
	150–175	13.34	54.16	67.49	24.84	7.67	11.96	3.71	6.99	10.70	1.71
	175–200	14.56	54.32	68.88	24.35	6.78	12.78	3.89	7.56	11.45	1.69

Fulvic acids											
Hemic Folic Cryic Histosol	0–10	17.35	46.74	64.09	25.89	10.01	14.40	6.29	7.72	14.01	1.86
	10–20	16.26	44.51	60.77	32.31	6.93	13.69	5.82	6.28	12.11	2.18
	20–35	19.02	46.63	65.65	25.71	8.63	16.19	6.76	6.95	13.71	2.33
	40–60	16.3	47.03	63.34	27.06	9.60	14.56	4.35	5.72	10.06	2.55
	60–80	15.9	48.94	64.84	25.36	9.80	13.12	7.14	6.32	13.46	2.08
	80–100	17.85	48.09	65.94	29.78	4.28	15.37	4.41	4.31	8.72	3.57
	100–150	16.64	50.75	67.39	27.04	5.58	13.84	5.61	5.50	11.11	2.52
	150–175	–	–	–	–	–	–	–	–	–	–
	175–200	12.79	49.72	62.50	28.93	8.57	11.69	3.07	4.52	7.59	2.59
Hemic Folic Cryic Histosol (Turbic)	0–5	17.88	46.85	64.73	24.54	10.73	14.78	6.75	5.92	12.67	2.50
	5–20	17.01	47.08	64.09	26.79	9.12	13.94	5.27	6.29	11.56	2.22
	20–40	17.16	49.99	67.15	27.01	5.84	15.41	4.14	4.63	8.78	3.33
	40–60	16.36	50.35	66.71	27.05	6.25	13.98	6.72	4.04	10.77	3.46
	60–80	13.52	46.69	60.2	34.38	5.42	11.87	3.91	5.67	9.58	2.09
	80–100	14.89	50.25	65.14	29.81	5.04	12.04	5.70	5.41	11.11	2.23
	100–150	18.43	49.06	67.49	27.47	5.04	15.66	4.90	5.77	10.67	2.71
	150–175	14.56	54.32	68.88	24.35	6.78	12.78	3.89	7.56	11.45	1.69
	175–200	13.13	48.34	61.47	29.64	8.89	11.91	2.69	3.32	6.01	3.59

Notes:
[1] Sum of threonine, serine, tyrosine.
[2] Sum of proline, glycine, alanine, valine, isoleucine, leucine, phenylalanine.
[3] Sum of aspartic acid, glutamic acid.
[4] Sum of histidine, lysine, arginine.
[5] Sum of threonine, serine.
[6] Sum of tyrosine, phenylalanine.
[7] Sum of proline, histidine.

layers and permafrost layers. Specifically, the aromatic fragments and methoxy groups show increasing trends, and paraffin groups show decreasing trends with respect to depth (Table 4). This directly reflects the interrelationships between the structural composition of the HAs and climatic conditions of the Holocene period, and it could be related to periods of warm climate.

In the active layers of bare spots, the portion of aromatic fragments of HA showed a substantial increase with depth. Dynamic thawing and freezing on the border of the permafrost results in increased aromaticity and a decreased portion of unoxidized aliphatic fragments. This is most pronounced on the border of permafrost. The indexes are correlated with the elemental composition data, which indicates a higher degree of condensation of the HA molecules.

Long periods of low temperatures lead to the destruction of the easily decomposable parts of molecules and to transformation of the main part of molecules. Nevertheless, peat from bare spots is more intensively heated during the summer period. This result in more raw peat decomposition in seasonally thawed layers. The index increases from 20–25% to 40–50% for superficial layers and layers bordering the permafrost, respectively. An increase of up to 55% was found in the portion of sedge remnants in the composition of peat-forming remnants. Soils formed under stable vegetation cover show lower degrees of peat decomposition: 20–25% in superficial layers and 30–35% in permafrost border layers. The deepest humification is precisely related to these indexes in soil from bare spots (Routh *et al*. 2014).

It should be emphasized that there are substantial structural differences in the HAs from the two soil types. Field data from Savelieva *et al*. (2010) indicate that the humification process is more active in sedge-type peats. These processes initiate in tissues of the sedges and can be established in the increase in signals from aromatic carbon species in the ^{13}C NMR spectra. This means that the active layer of the peat soils is present by the modern stage of OM transformation, and this process is more intensively pronounced in soil from bare spots. The higher indexes of the positive temperatures in soils from bare spots simulate the climate change and result in transformation of the structural parameters of humic acids. These transformations can be regarded as an intensification of diagenesis of the peat sediments. This involves carbonification accompanied by processes of dehydration and demethylation of HSs molecules, resulting in reductions of unoxidized paraffin fragments and probably resulting in the release of methane. In this regard, it is important to note that the formation of unvegetated peat spots is a modern process, which has probably occurred no earlier than 300–400 years ago (Routh *et al*. 2014).

The low differentiation of humic acids composition in peat layers under the permafrost table is caused by many periods of restratification of the peat materials on the border of the early and middle Holocene. Partial isolation of the peat materials determines the degree of peat destruction. The lower horizons

were partially buried and isolated with less pronounced intensity of the soil formation, which almost stopped with the formation of the permafrost layers in the Subboreal period (Chimitdorzhieva *et al*. 2008). For the relic peat sampled from depths of 150–175 cm, intense maximums of aromatic carbon were revealed for both HAs and FAs (Table 4). These peaks are related to the Holocene climatic optimum (Roland *et al*. 2015), which is dated at about 7000 cal BP (IG RAS 4645, 4646).

The content of the labile forms of humus is related to weak biological activity and reductive conditions in the peat layers. Partially isolated OM shows very slow transformation trends. The portion of labile carbohydrate fragments of the HAs decreases slowly with the soil depth. Similar data were obtained for peatlands in Latvia (Klavinš *et al*. 2012; Klavinš and Purmališ 2013). It is well known that bacteria play a more active part in the humification of OM of peat materials in comparison with micro fungi, saccharomyces, and actinomyces (Chimitdorzieva *et al*. 2008; Khabibullina *et al*. 2014).

FAs are more enriched by oxygen-containing fragments but have fewer of the paraffin structures (up to 24.2%). The similar content of carboxylic croups in HAs and FAs revealed in peat soils is unusual for mineral soils of taiga and tundra zones (Lodygin and Beznosikov 2010; Lodygin *et al*. 2014). The carboxylation process leads to an increase of – COOH groups with the soil depth and to a higher portion in the FAs of the lower layers. The high portion of carbohydrate fragments in FAs (up to 80.1%) results in increased bioavailability of the FA molecules in comparison with the HAs (up to 24.6%).

The main difference between FAs and HAs is expressed in the content of methoxy groups, amino acid fragments (shifts between 47–60 ppm), and aromatic and aliphatic carbonyl groups. The lower portion of groups associated with the shift at 47–60 ppm (up to 10.1% in FAs and 15.8% in HAs) is related to the lower portion of nitrogen of amino groups. Alteration of the structural composition of the FAs can be considered to be the most flexible for the soil formation conditions. Differentiation of alkyl, methoxy, and amino groups results from changes in the soil temperature regimes and types of botanical composition of peats during the different Holocene phases. The highest content of aromatic fragments in the FAs of the T4 layer is probably connected with sharp freezing-thawing cycles.

Statistical analysis. — The representative data array, including portion of the groups and fragments of HSs, the degree of peat decomposition, the calculated lignin content and botanical composition, obtained after statistical processing allowed us to analyze the main trends of humification. Methoxyl groups are associated with mostly phenilpropane fragments of lignin-type aromatic components. This was confirmed by the correlation of the methoxy group content with the portion of oxidized aromatic fragments in HAs and FAs

Table 4

Percentage of carbon in the main structural fragments of HAs and FAs (according to ^{13}C NMR).

Plot	Depth, cm	Chemical shift, ppm								Integrated indicators	
		0–47	47–60	60–108	108–144	144–164	164–183	183–190	190–204	AR/AL[1]	*fa*,[2] %
		Alkyl	O,N-Alkyl		Aromatic		Carboxyl, ester, amide	Quinone	Carbonyl		
Humic acids											
Hemic Folic Cryic Histosol	0–10	40.4	10.4	22.0	13.6	3.9	8.4	0.3	1.0	0.217	17.81
	10–20	46.6	10.5	20.3	11.2	3.8	7.4	0.2	0.1	0.180	15.22
	20–40	37.6	10.2	22.2	15.4	5.3	8.3	0.3	0.7	0.266	21.03
	40–60	35.5	10.4	23.2	16.9	4.9	7.7	0.7	0.7	0.290	22.49
	60–80	35.6	11.4	22.1	16.9	4.8	7.5	0.9	0.9	0.291	22.56
	80–100	30.4	14.5	20.4	19.4	5.3	7.8	1.1	1.0	0.349	25.85
	100–150	34.8	15.8	21.5	16.0	3.1	8.0	0.5	0.2	0.244	19.61
	150–175	32.1	11.9	19.9	20.7	5.9	8.8	0.2	0.6	0.365	26.71
	175–200	33.2	12.2	18.5	20.6	5.1	9.1	0.1	1.4	0.347	25.75
Hemic Folic Cryic Histosol (Turbic)	0–5	40.8	10.9	22.2	14.0	2.9	8.5	0.1	0.5	0.205	16.98
	5–20	36.1	12.6	24.0	14.9	4.7	7.5	0.1	0.2	0.246	19.71
	20–40	19.0	8.9	24.6	25.1	10.8	9.7	0.4	1.5	0.571	36.34
	40–60	20.7	12.6	23.5	25.1	7.5	8.7	0.9	1.1	0.502	33.44
	60–80	39.3	12.2	22.8	14.2	5.0	6.1	0.2	0.1	0.242	19.47
	80–100	38.4	12.6	18.0	17.0	3.5	8.0	0.9	1.6	0.272	21.39
	100–150	38.0	13.4	18.8	16.1	2.7	8.3	1.3	1.5	0.251	20.07
	150–175	27.7	9.4	17.2	25.3	9.2	10.8	0.0	0.4	0.526	34.46
	175–200	39.8	10.2	16.7	17.3	4.8	10.0	0.3	0.9	0.289	22.39

Fulvic acids											
Hemic Folic Cryic Histosol	0–10	12.1	6.6	74.0	1.6	0.0	5.7	0.0	0.0	0.016	1.62
	10–20	7.1	4.5	80.1	2.3	0.1	5.7	0.0	0.1	0.024	2.34
	20–40	11.7	7.2	72.4	3.0	0.1	5.5	0.0	0.1	0.032	3.08
	40–60	9.8	5.0	64.7	10.2	2.2	6.7	0.5	1.0	0.147	12.83
	60–80	16.2	9.0	61.2	4.5	1.0	7.3	0.1	0.6	0.059	5.60
	80–100	10.7	5.0	70.8	3.4	0.2	9.6	0.0	0.2	0.038	3.63
	100–150	15.3	10.0	61.9	3.1	0.5	9.1	0.0	0.1	0.038	3.62
	150–175	14.5	7.7	55.0	9.2	2.2	11.1	0.0	0.2	0.129	11.42
	175–200	16.9	10.1	56.4	3.7	0.8	11.5	0.0	0.5	0.047	4.52
Hemic Folic Cryic Histosol (Turbic)	0–5	11.2	6.8	69.8	4.6	0.4	6.8	0.2	0.2	0.055	5.22
	5–20	17.2	8.6	59.0	4.6	1.1	8.7	0.1	0.7	0.061	5.78
	20–40	24.2	8.9	54.0	5.8	0.7	6.1	0.0	0.2	0.070	6.54
	40–60	18.2	7.9	61.1	2.5	1.3	8.1	0.0	0.9	0.040	3.82
	60–80	18.3	8.1	55.8	6.8	1.6	9.4	0.0	0.1	0.091	8.32
	80–100	15.0	7.9	57.9	3.4	1.2	12.4	0.5	1.8	0.053	5.07
	100–150	15.4	8.8	59.2	3.0	1.3	10.6	0.5	1.3	0.050	4.79
	150–175	17.9	9.8	47.4	8.4	1.4	14.3	0.0	0.8	0.108	9.75
	175–200	14.9	9.4	59.3	3.6	0.4	12.1	0.0	0.3	0.041	3.98

Notes:
[1] The signals from the aromatic structures (AR) were summed for the regions of 108–164 and 183–190 ppm; those from the aliphatic structures (AL) were summed for the regions of 0–108, 164–183, and 190–204 ppm.
[2] Aromaticity.

(n = 36, r = 0.50, r_{cr} = 0.33). The indexes of aromaticity and the portion of carboxylic groups of HAs are also correlated (n = 18, r = 0.64, r_{cr} = 0.47). This indicates the main trends of HA development during the humification process, *i.e.* carboxylization and saving the most stable groups. A significant negative correlation of unoxidized aromatic and aliphatic fragments was revealed (n = 18, r = -0.94, r_{cr} = 0.47). These results cannot be explained solely by the degradation of paraphinous structures as stochastic processes. This could be the result of the cyclization of aliphatic chains with subsequent dehydrogenation and the formation of aromatic fragments.

The degree of peat decomposition positively correlates with the methoxy groups (r = 0.47) and carboxylic (r = 0.61) groups of FAs (n = 18, r_{cr} = 0.47). There was also a negative correlation of this parameter with the portion of carbohydrate fragments of the HAs (r = -0.56). The calculated lignin content correlates with the portion of oxidized aromatic fragments (r = 0.49) and carboxylic group content in FAs (r = 0.52). The degree of condensation of HA molecules is not an indicator of peat decomposition in all cases, and is related to its botanical composition. The structure of the aromatic fragments of HAs is related to the portion of sedge remnants (r = 0.53, r_{cr} = 0.47), while the portion of paraffin fragments correlates with the composition of subshrubs (r = 0.53). The structure of aromatic fragments of FAs is related to the portion of wood remnants (r = 0.57), while carbohydrates show a correlation with the composition of subshrubs (r = 0.72) and mosses (r = 0.52). The portion of unoxidized aromatic fragments of HAs also demonstrates a correlation with the occurrence of plants such as *Carex aquatilis* (r = 0.54), *Carex cespitosa* (r = 0.47), and *Menyanthes* (r = 0.55) in the peat material. The occurrence of *Carex rostrata* (r = 0.63) and *Carex cespitosa* (r = 0.47) correlates with the portion of methoxy groups of HAs (r_{cr} = 0.47).

Conclusions

This study identified, for the first time, the molecular composition of HSs from permafrost-affected peats of the eastern European Arctic (Komi Republic, Russian Federation). It was shown that climatic conditions were the main driver of the formation of organic matter as well as the quality and degree of natural polymer destruction. These parameters are reflected in the functional groups and molecular compositions of the HSs studied in both relic and modern-formed peat layers. Changes in the molar x(H) : x(C) ratio along the peat profiles have been revealed, which are due to the activation of cryogenic processes in the upper part of the seasonally thawing layer, the natural selection of condensed humic molecules, and the botanical composition and degree of degradation of peat, which reflect the climatic features of the area in the Holocene. The content

of functional groups and molecular fragments in the HAs illustrated a trend of decreasing paraffin groups and the accumulation of aromatic species of HAs as well as carboxylic groups from FAs along the depth of the peat soils profile. The highest indexes of biological activity from bare spots indicate possible climate changes in cases of increased soil temperatures. The mole fraction ratio of hydroxy AAFs to heterocyclic AAFs indicates the soil biological activity level and can serve as a stabilization degree marker. The data on molecular composition of HSs can be used as an indicator of the degree of organic matter alteration in the sequence of vegetated and bare permafrost peat soils.

Acknowledgements. — The reported study was funded by Russian Federal budget (Institute of Biology Komi SC UB RAS) (No AAAA-A17-117122290011-5) and RFBR according to the research project № 18-05-60195 (No AAAA-A18-118062090029-0). The authors are grateful to the reviewers O. Bezuglova and J. Kostecki for their valuable comments that have improved this article.

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Received 5 July 2018
Accepted 12 September 2018