*Вестник Томского государственного университета. Биология. 2019. № 47. С. 6–21*

# АГРОХИМИЯ И ПОЧВОВЕДЕНИЕ

UDC 631.41
doi: 10.17223/19988591/47/1

**Vyacheslav I. Polyakov[1, 2, 3],**
**Nadezhda A. Chegodaeva[1], Evgeny V. Abakumov[1]**

*[1] St. Petersburg State University, St. Petersburg, Russian Federation*
*[2] Saint-Petersburg State Agrarian University, Pushkin, Russian Federation*
*[3] Arctic and Antarctic Research Institute, St. Petersburg, Russian Federation*

## Molecular and elemental composition of humic acids isolated from selected soils of the Russian Arctic

*Humic substances, isolated from selected soils of the Russian Arctic, were investigated in terms of molecular composition and stabilization rate. The degree of polar soil organic matter stabilization was assessed with the use of modern instrumental spectroscopy methods. The analysis of humic acid (HAs) preparations showed that aliphatic fragments prevail in the organic matter isolated in polar soils. The predominance of aliphatic fragments was revealed in HAs from soils located in the coastal zone, which could be caused by regular refreshment of organic matter during sin-lithogenic process and processes of hydrogenation in HAs. Breaking of the C-C bonds and formation of chains with a high hydrogen content, which leads to the formation of aliphatic fragments in HAs, were noted. Data on the calculated atomic ratios of the elements in HAs are given and graphs show the main regularities in the formation of HAs and their properties. The integrated indicators of the molecular composition of humic acids of soils of the Russian Arctic are presented.*

*The paper contains 4 Tables, 4 Figures and 44 References.*

**Key words:** CP/MAS $^{13}$C-NMR; humic acids; organic matter; permafrost-affected soils; Cryosol.

**Funding:** This work was supported by the Grant of Saint-Petersburg State University “Urbanized ecosystems of the Russian Arctic: Dynamics, state and sustainable development.”

*The authors declare no conflict of interest.*

## Introduction

In the territories located at high latitudes of northern Europe, Greenland, Canada, Alaska and Russia, soils were formed during the Quaternary period, the diversity of which is mainly associated with the cryogenic processes within the pedosphere [1-2]. The area occupied by permafrost-affected soils is more than 8.6 million km$^2$, which represents about 27% of the entire territory of the north

[3]. According to the latest data, organic matter accumulated in the soil of the Arctic up to 1024 Pg (1 Pg = $10^{15}$g) stored in the upper 3 m of soil [1, 2, 4-8].

In the Arctic, the formation of soil and organic matter is influenced by cryogenic processes such as cryogenic mass exchange cracking, frost formation, soil swelling, cryogenic solifluction, thermokarst, etc. In permafrost-affected soils occupying about 65% of the territory of Russia, biogeochemical processes take place within the active layer of soil, the depth of the active layer depends on landscape position, the type of vegetation, and organogenic horizons [1, 6, 9]. Moreover, essential amounts of organic matter are stabilized within the frozen ground below the permafrost table. A common feature of the soil cover of the Arctic is its complexity associated with the permafrost processes in various bioclimatic and geological and geomorphological conditions. For arctic soils, as a rule, a high water content is typical, especially near the permafrost table, which appears to be a water barrier. As a result, gray color and redoxymorphic conditions appear associated with the gleying process, which is most pronounced on loamy and well-structured soils [10].

The soils in the cryolithozone are considered as carbon storages. The accumulation of organic carbon in the profile of arctic soils is associated with processes of permafrost retinization, processes of cryogenic mass exchange, with the formation of organic matter *in situ* from plant residues, as well as inheritance from a soil-forming rock [11-13]. For the soils of watershed positions of the Arctic and Subarctic regions, the formation of superficial humus enriched layer is typical with a weak intensity of decomposition of organic residues and humification processes.

Low average temperatures and a short vegetation season in permafrost areas cause organic matter to accumulate throughout the Quaternary period [2]. Biomass forms during a short growing season and initially accumulates in the upper layer of soil, thus creating an annual accumulation of organic matter, during which alluvial sedimentation of organic residues is also involved [2, 14-15].

Cryoturbation also leads to redistribution of organic matter into deeper soil horizons. Another process is the movement of organic matter in a dissolved state and its accumulation at the boundary with permafrost [2, 16-18]. During cryoturbation, fine fragments of organic material, separated from the lower parts of the surface horizons under the influence of ice, move inside the profile, mixing with the mineral matter of the underlying horizons; the result of this movement of organic masses along the profile is its compaction, homogenization and decomposition of plant residues [19]. As a result of slope processes, organogenic horizons are often buried under material that has fallen here as a result of solifluction. In contrast to cryoturbated material, buried organogenic horizons are characterized by high porosity, absence of excessive overcompaction, and plant residues are destroyed much less [19].

Nowadays, the use of modern physicochemical research methods has made it possible to study the structure of HAs molecules in more detail without resorting to their destruction. The methods of infrared (IR), nuclear magnetic resonance (NMR) and electron paramagnetic resonance (ERS) spectroscopy can provide information not only about the qualitative set of the most important atomic groups and types of bonds, but also about the specific location of individual functional groups and molecular fragments. Among organic substances, humic acids are distinguished by the greatest biochemical resistance [20]. However, their composition and structure are variable and reflect the conditions of humus formation. The use of $^{13}$C-NMR spectroscopy allows the quantitative determination of structural and functional parameters of HAs, and, therefore, this method is used to evaluate their transformation under the influence of various factors, including man-made [19, 21-22].

$^{13}$C-NMR spectroscopy also allows to obtain detailed and reliable information about the number of structural fragments and functional groups of HAs, which appear in the corresponding spectral ranges in the form of resonant signals of carbon atoms characterizing typical structural features: the presence of aliphatic, aromatic fragments and functional groups: -C=O) - aldehydes, ketones and quinoid structures; (-COOH), (-$NH_2$), (-$OCH_3$), (-OH) - alcohols, carbohydrates and phenols [9, 17, 19, 23-24]. Studies of the principles of HAs structure, deciphering the intramolecular “state” allow going to the quantitative level of the description of the bound “structure - molecular weight”.

Thus, the main aim of this study was to determine the molecular composition of organic matter in selected soils of the Russian Arctic using CP/MAS (Cross-Polarization/Magic Angle Spinning) $^{13}$C-NMR spectroscopy.

## Materials and methods

The study area is located around the islands of the Russian Arctic, and include Vaigach and Kolguev islands in the Kara sea (70°00'04.3"N 59°40'22.4"E and 69°07'36.8"N 49°30'53.7"E), Andrey island in the Laptev sea and Kurungnakh island in the Lena River Delta (76°46'46.0"N 110°47'11.6"E and 72°21'46.7"N 126°08'23.3"E) and Sosnowiec island in the White sea (66°29'21.9"N 40°40'57.8"E) (Fig. 1).

The article presents single plot areas, confirming the statement about the diversity of soils in the Arctic, which is associated with the differentiation of climatic conditions in the latitudinal and meridional direction, and with a large variety of soil-forming rocks and topographic situations. Vaigach Island, which is located in the Western part of the Russian Arctic between the Barents and Kara Seas, has more humid climatic conditions than Kolguev Island, located in the Barents Sea. The annual precipitations of these islands are 250-350 mm and 210-250 mm, respectively [25]. The thermal conditions are also different, for Vaigach Island (one latitude with the island of Sosnowiec), the average temperature of the warmest month is 5.8 °C, while for Andrey Island it is 2°C. Soil-forming rocks are represented either by sea loams of ancient sea terraces, or by skeletal deluvium of sandy and loamy composition. In the landscape, there is a pronounced microrelief associated with heaving mounds, the presence of structured soils, and also places of solifluction deformations.

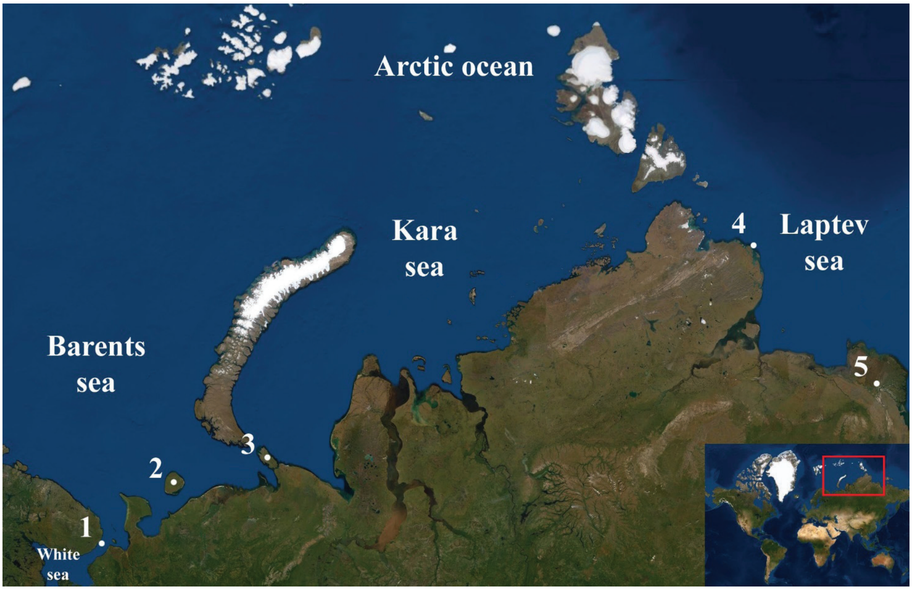


**Fig. 1.** Location of the study area and the studied soils. 1 - Sosnowiec island; 2 - Kolguev island; 3 - Vaigach island; 4 - Andrey island; 5 - Kurungnakh island. Source: ESRI

The vegetation of the islands is represented mainly by arctic tundra communities with fragmented grass and shrub cover with the predominance of moss and lichen. Soils of the Lena River Delta form in strong Arctic weather conditions, mean annual air temperature is – (-13°C), mean air temperature of the warmest month (July) is – 6.5°C, and of the coldest month (January) is – (-32°C). The thickness of snow is 23 cm, the annual amount of precipitations is 323 mm (in summer it is 125 mm). Parent materials of the Lena Delta are presented by fresh alluvial material and loamy and sandy loamy sediments.

Soil samples are represented by upper horizons of Cryosol, mainly humus weak developed horizons (W) or gray humus horizons – AY (Umbric horizons). In most cases, these horizons are replaced by the horizon of CR, a horizon with pronounced signs of cryogenic mass exchange.

Samples of soil were selected mostly in a polygonal tundra. Soil samples from surface horizons were collected during the summer of 2014-2015 during the Sea Expedition organized by the Arctic and Antarctic Research Institute. The soil description is presented in Table 1. The soils were identified according to WRB [26].

Table 1

**Description of the studied surface soil samples**

| Island | Sample № | Soil | Description of the studied surface soil horizons<br>Soil description of the upper horizon | pH | Color index |
|---|---|---|---|---|---|
| Sosnowiec | 1 | Histic Cryosol | Moss-lichen tundra, near residential buildings, peat horizon up to 30 cm, including sawdust. Vegetation: moss with lichens cover. Sample 2 is repetition of Sample 1 | 4.47 | 10 YR 4/3 |
| | 2 | Histic Cryosol | | 4.84 | 10 YR 4/3 |
| Vaigach | 3 | Folic Cryosol | The profile is located on a hill composed of eluvial-deluvial deposits of Silurian limestone, moss cover. Carbonates are found in the soil, the highest content of carbonates is noted in the upper horizons. Vegetation: *Stereocaulon* sp. Hoffm. and *Silene acaulis* (L.) Jacq. Clay loam class | 6.31 | 10 YR 6/3 |
| | 5 | Folic Cryosol | | 7.11 | 10 YR 6/3 |
| | 6 | Histosol | | 7.53 | 10 YR 4/3 |
| Kolguev | 7 | Histic Cryosol | Soils are formed on loose Quaternary sediments, sedge-cereal associations dominate with a significant proportion of green moss in the soil cover. Polygonal tundra. Loam class | 4.55 | 10 YR 4/2 |
| | 8 | Reductaquic Cryosol | | 6.03 | 7.5 YR 7/4 |
| | 9 | Histic Cryosol | | 4.61 | 10 YR 4/4 |
| Andrey | 11 | Reductaquic Cryosol | Permafrost table up to 40 cm, thixotropy, in the upper part pronounced processes of gleying, cryoturbation processes are less intense. Polygonal tundra. Vegetation: moss with lichens cover. Silt loam class | 4.82 | 7,5YR 7/4 |
| | 12 | Reductaquic Cryosol | Permafrost table up to 38 cm, thixotropy, in the upper part pronounced processes of gleying, cryoturbation processes are less intense. Polygonal tundra. Vegetation: moss with lichens cover. Silt loam class | 5.58 | 7,5YR 7/4 |
| | 13 | Reductaquic Cryosol | Soil is associated with the accumulation of iron and aluminum at the contact border with permafrost, this type is characterized by a reddish color forming under oxidative conditions. Polygonal tundra. Vegetation: *Salix glauca* L., *S. reptans* Rupr., *S. lanata* L., *Equisetum* sp. L. Loam class | 7.08 | 7,5 YR 6/3 |

Table 1 (end)

| Island | Sample № | Soil | Description of the studied surface soil horizons<br>Soil description of the upper horizon | pH | Color index |
|---|---|---|---|---|---|
| Kurungnakh | 14 | Folic Reductaquic Cryosol | Soil develops under conditions of over humidification, occupying local meso- and micro-depressions. Characterized by the presence of a Folic horizon underlain by the Cryic horizon. Polygonal tundra. Vegetation: *S. glauca*, *S. reptans*, *Alopecurus alpinus* L. Sandy loam class | 6.95 | 10YR 3/2 |
| | 15 | Umbric Reductaquic Cryosol | Soil develops under the influence of several processes: the alluvial and zonal processes of soil formation (peat formation, gleying and cryogenesis). Polygonal tundra. Vegetation: *Hylocomium splendens* (Hedw.) Schimp., *Timmia austriaca* Hedwig. Sandy loam class | 7.65 | 7,5 YR 7/3 |
| | 16 | Turbic Reductaquic Cryosol | Soil develops on well-drained territories, but there are also signs of gley in contact with permafrost. Polygonal tundra. Vegetation: *H. splendens, T. austriaca, Dryas punctate* Juz., *Polygonum viviparum* L. Loam class | 6.61 | 10 YR 4/3 |
| | 17 | Reductaquic Cryosol | Soil develops on the drained positions, characterized by the presence of a surface Folic horizon of different composition, which is underlain by permafrost-affected soils. Polygonal tundra. Vegetation: *H. splendens, T. austriaca, Climacium dendroides* (Hedw.) Web. et Mohr. Sandy loam class | 6.14 | 7,5YR 7/3 |

Soil samples were air-dried (24 hours, 20°C), grounded, and passed through a 2 mm sieve. Soil chemical routine analyses were performed using classical methods: C, H and N content was determined using an element analyzer (Euro EA3028-HT Analyser). Data were corrected for water and ash content. Oxygen content was calculated by difference of whole samples of mass and gravimetric concentration of C, N, H and ash. pH in water and in salt (soil-dissolvent ratios 1:2.5 in case of mineral horizons and 1:25 in case of organo-mineral horizons) suspensions was detected using a pH meter (pH-150 M).

Humic acids (HAs) were extracted from each sample according to a published IHSS protocol [27]. The soil or cryoconite samples were treated with 0.1 M NaOH (soil/solution mass ratio of 1:10) under nitrogen gas. After 24 hours of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at 1.516 × g for 20 minutes and then acidified to pH 1 with 6 M HCl to precipitate the HAs. The supernatant, which contained fulvic acids, was separated from the precipitate by centrifugation at 1.516 × g for 15 minutes. The HAs were then dissolved in 0.1 M NaOH and shaken for four hours under nitrogen gas before the suspended solids were removed by centrifugation. The resulting supernatant was acidified again with 6 M HCl to pH 1 and the HAs were again isolated by centrifugation and demineralized by shaking overnight in 0.1 M HCl/0.3 M HF (soil/solution ratio of 1:1). Next, the samples were repeatedly washed with deionized water until pH 3 was reached and then finally freeze-dried. HAs extraction yields were calculated as the percentage of carbon recovered from the original soil sample [28]. Solid-state CP/MAS $^{13}C$-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in a 3.2-mm $ZrO_2$ rotor. The magic angle spinning speed was 20 kHz in all cases and the nutation frequency for cross polarization was u1/2p 1/4 62.5 kHz. Repetition delay and the number of scans were 3 seconds. HAs extraction yields were calculated as the percentage of carbon recovered from the original soil sample.

## Results and Discussion

### *Elemental composition of HAs*

In general, the elemental composition of HAs is comparable with the previous data for soils of the polar zone [6, 18, 23, 29-31]. The elemental composition of HAs is the most important indicator determining the progress of humification, oxidation and degree of condensation of HAs [30-31].

The obtained data on HAs elemental composition, atomic ratios and degree of oxidation (W) are presented in Table 2.

Table 2

**Elemental composition of the studied humic acids from surface soil horizons. Gravimetric concentrations are given for C, H, O and N content. C/N, H/C, O/C, H/Cmod and W were calculated from mole fraction of C,H,O and N content. H/C mod is the number of substituted hydrogen atoms in the humic acids; (H/C) mod = (H/C) + 2 (O/C) x 0.67; H/C and W indexes were calculated according to Orlov [43]. Sample numbers correspond to Table 1. SD±0.05 for N, H and C content**

| Sample, № | Island | N, % | C, % | H, % | O, % | C/N | H/C | O/C | H/Cmod | W |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Sosnowiec | 1.70 | 52.17 | 5.05 | 36.08 | 35.7 | 1.15 | 0.52 | 1.8 | -0.1 |
| 2 | | 1.74 | 51.77 | 4.91 | 36.58 | 34.67 | 1.13 | 0.53 | 1.8 | -0.1 |
| 3 | Vaigach | 5.01 | 48.47 | 5.78 | 35.75 | 11.29 | 1.42 | 0.55 | 2.2 | -0.3 |
| 5 | | 3.14 | 49.52 | 5 | 37.34 | 18.4 | 1.2 | 0.57 | 1.9 | -0.1 |
| 6 | | 3.36 | 46.05 | 4.96 | 40.63 | 15.98 | 1.28 | 0.66 | 2.2 | 0.1 |
| 7 | Kolguev | 3.74 | 48.43 | 5.78 | 37.05 | 15.11 | 1.42 | 0.57 | 2.2 | -0.3 |
| 8 | | 1.42 | 26.49 | 2.86 | 64.23 | 21.7 | 1.28 | 1.82 | 3.7 | 2.3 |
| 9 | | 2.83 | 38.11 | 4.53 | 49.53 | 15.68 | 1.41 | 0.98 | 2.7 | 0.5 |
| 11 | Andrey | 4.26 | 47.54 | 5.64 | 37.55 | 13.01 | 1.41 | 0.59 | 2.2 | -0.2 |
| 12 | | 3.05 | 34.23 | 4.77 | 52.95 | 13.1 | 1.66 | 1.16 | 3.2 | 0.7 |

Table 2 (end)

| Sample, № | Island | N, % | C, % | H, % | O, % | C/N | H/C | O/C | H/Cmod | W |
|---|---|---|---|---|---|---|---|---|---|---|
| 13 | Ku-rungnakh | 3.43 | 50.13 | 4.85 | 36.6 | 17.07 | 1.15 | 0.55 | 1.9 | -0.1 |
| 14 | | 3.52 | 42.83 | 4.55 | 44.11 | 14.19 | 1.26 | 0.77 | 2.3 | 0.3 |
| 15 | | 3.13 | 42.94 | 4.88 | 44.06 | 16.00 | 1.35 | 0.77 | 2.4 | 0.2 |
| 16 | | 2.95 | 53.39 | 6.14 | 32.53 | 21.15 | 1.37 | 0.46 | 1.9 | -0.4 |
| 17 | | 3.44 | 44.59 | 4.84 | 42.15 | 15.14 | 1.29 | 0.71 | 2.2 | 0.1 |

The carbon content in the studied samples varies over a wide range from 26 to 52%. The studied HAs can be divided into two groups by carbon content, less than 37% and more than 37%. The first group includes samples from Kolguyev and Andrey islands, they are less charred, which is due to leaching of low carbon molecules from the organogeneous horizon. Samples from other islands have a higher carbon content and have a high degree of carbonization associated with humification processes.

The nitrogen content in all studied HAs is 4% lower. This is due to the low accumulation of nitrogen-containing compounds in plant residues and in preparations of humic substances.

The oxygen content in the studied soils also varied in a wide range from 33 to 64%. The highest oxygen values correspond to the preparations from Kolguev and Andrey islands in those samples where a low carbon content is observed. The high oxygen content is due to the better solubility of oxygen-enriched hydrophilic humic acid molecules and their migration to the underlying mineral horizons [32-36].

The calculation of the degree of oxidation showed that most of the studied samples were in reduction conditions (from -0.1 to -0.4). The exceptions were the samples from Kolguev and Andrey islands, where the degree of oxidation reaches +2.3 and 0.7, respectively. This causes the migration of oxidized HAs down the profile. The weak reductions of preparations of HAs of organogenius horizons is determined by the produce of fresh organic residues and their weak humification in the specific bioclimatic conditions of the North.

One of the most widely used methods is a numerical description of the structure of humic acids in order to identify the patterns of their formation and transformation in the construction of Kleinhempel diagrams [37]. The method is based on a graphical representation of the data in the coordinates H/Cmod - O/C and serves a convenient technique for demonstrating the contribution of oxidation and condensation processes to changes in the elemental composition of HAs.

Based on Kleinhempel diagram (Fig. 2), it was found that in most of the studied soils the value of H/Cmod and O/C is relatively low, which indicates a low content of oxygen-containing groups in humic acids and their low migration ability. Samples from Kolguev and Andrey islands have relatively high values of H/C mod and O/C, which indicates that they have a high degree of hydromorphism due to low microbiological activity, which promotes a better preservation of carbohydrate and amino acid fragments in the structure of HAs. Relatively low values of H/Cmod indicate accumulation of aromatic fragments in the composition of humic acids.

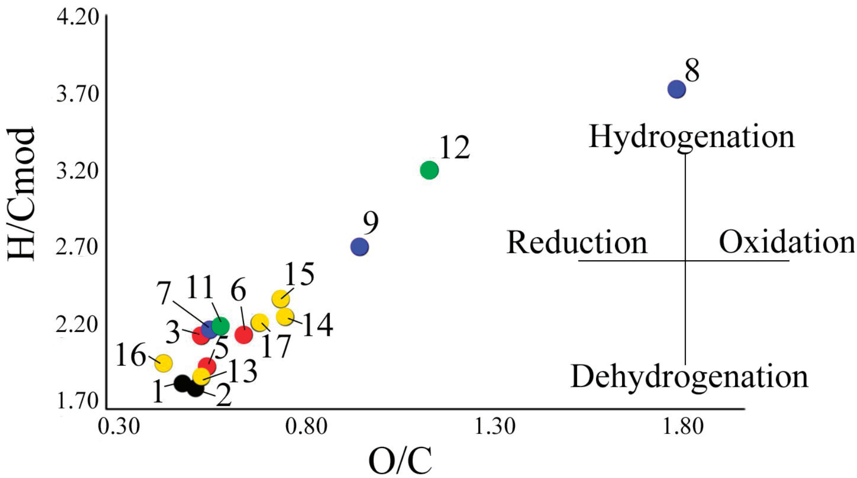


**Fig. 2.** Elemental composition of the studied humic acids isolated from surface soil horizons. Gravimetric concentrations are given for carbon, hydrogen, oxygen and nitrogen content. sH/C mod - The number of substituted hydrogen atoms in the humic acids; (H/C) mod = (H/C) + 2 (O/C) x 0.67; Sample numbers correspond to Table 1.

The values of the H/Cmod and O/C ratios decrease, i.e. accompanied by an increase in the proportion of aromatic structures in humic acid molecules [33, 36, 38].

***Characterisation of HAs by $^{13}$C-NMR spectroscopy***

Spectra of the CP/MAS $^{13}$C-NMR are given in Fig 3. Various molecular fragments were identified by CP/MAS $^{13}$C-NMR spectroscopy (Table 3): carboxyl (-SOOR); carbonyl (-C = O); $CH_3$-, $CH_2$-, CH-aliphatic; -C-OR alcohols, esters and carbohydrates; phenolic (Ar-OH); quinone (Ar=O); aromatic (Ar-), which indicates a great complexity of the structure of HAs and the polyfunctional properties that cause their active participation in soil processes [23].

The chemical shifts are shown in Table 4. The aromatic group is calculated from the sum of the shifts of 110-185 ppm. Aliphatic fragments are calculated from the sum of the shifts of 0-110 ppm, 180-200 ppm, Al h, r + Ar h, r (total number of unoxidized carbon atoms) – The signals were summed over the regions 0-46 and 110-160 ppm, C, H-Al / O, N-Al. Signals from C, H-alkyls were summed in the range of 0-47 ppm. O, N-alkyl at regions 46-60 and 60-110 ppm [23]. The presence of all peaks of the carbon species which are required for identification of the studied substances as humic acids was revealed.

Aliphatic fragments of HAs were predominant up to 74% in the studied samples. In the studied soils, mineralization processes predominate. The low content of aromatic fragments due to low microbiological activity leads to accumulation of organic matter in the soil [18-19, 39]. The low content of carboxyl fragments (160-185 ppm) indicates that humic substances have low migration activity and are less enriched in oxygen-containing compounds, which is confirmed by elemental analysis data of HAs. To standardize the quantitative characteristics of HAs macromolecules, the following parameters were used: the ratio of carbon of aromatic structures to carbon of aliphatic chains – Ar/Al, the degree of decomposition of organic matter (C, H-alkyl/O, N-alkyl) and the integral indicator of hydrophobicity of HAs (Al h, r + Ar h, r). The integral indicator of hydrophobicity is shown in Figure 4.

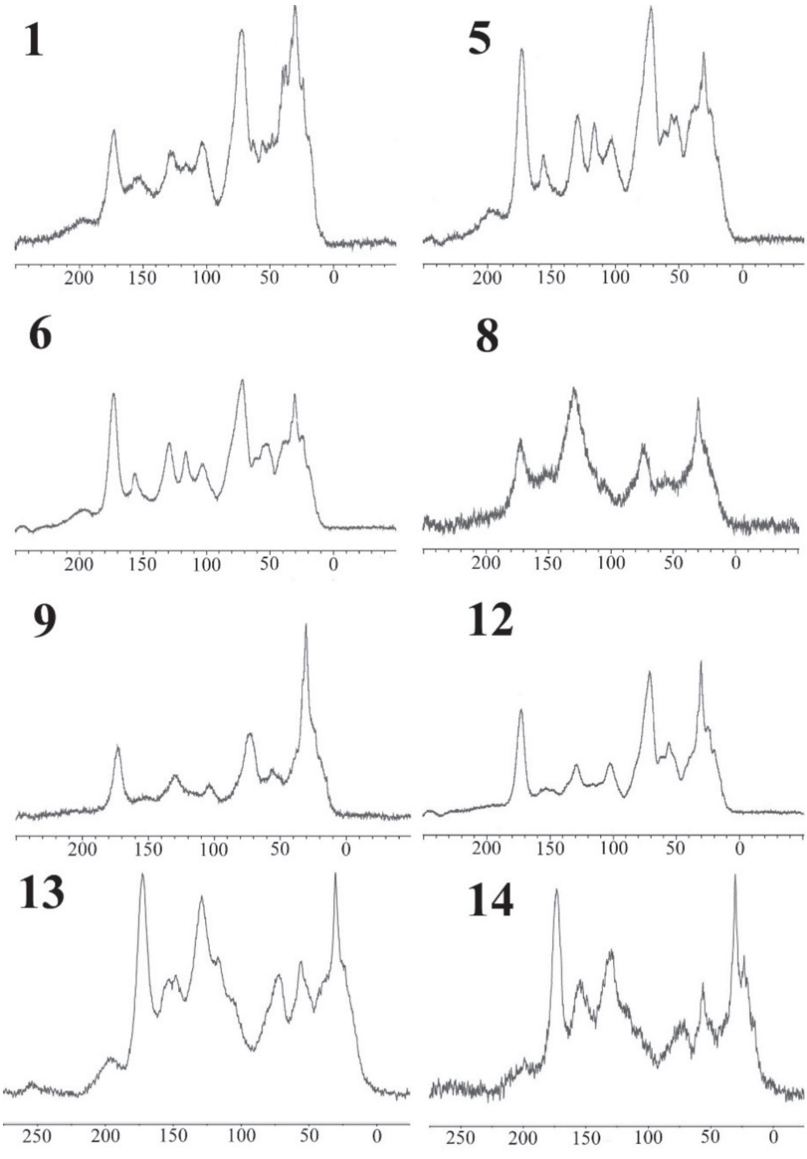


**Fig. 3.** CP/MAS $^{13}C$-NMR spectra of HAs from soils of the Russian Arctic. Number corresponds to Table 1; on the X-axis - Chemical shift, ppm; on the Y-axis Vaxis - Relative intensity, dimensionless

Table 3

**Chemical shifts of atoms of the $^{13}C$ molecular fragments of humic acids**

| Chemical shift. ppm | The type of molecular fragments |
|---|---|
| 0-46 | C, H-substituted aliphatic fragments |
| 46-60 | Methoxy and O, N-substituted aliphatic fragments |
| 60-110 | Aliphatic fragments doubly substituted by heteroatoms (including carbohydrate) and methine carbon of ethers and esters |
| 110-160 | C, H-substituted aromatic fragments; O, N-substituted aromatic fragments |
| 160-185 | Carboxyl groups, esters, amides and their derivatives |
| 185-200 | Quinone groups; Groups of aldehydes and ketones |

Table 4

**Percentage of carbon in the main structural fragments of humic acids from the studied surface soil horizons (according to CP/MAS $^{13}C$-NMR data). Sample numbers correspond to Table 1; Ar - aromatic fraction; Al-aliphatic fraction; $Al_{h,r}$ + $Ar_{h,r}$ % - hydrophobicity degree; C, H-Al / O, N-Al - the degree of decomposition of organic matter. SD±0.05**

| № | Island | Chemical shifts. ppm | | | | | | | *Ar* | *Al* | *Ar/Al* | *Al h,r + Ar h,r, %* | *C,H - Al/ O,N - Al* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0-46 | 46-60 | 60-110 | 110-144 | 144-160 | 160-185 | 185-210 | | | | | |
| 1 | Sos-nowiec | 33 | 6 | 33 | 13 | 6 | 7 | 2 | 26 | 74 | 0.35 | 51.80 | 0.85 |
| 2 | | 27 | 7 | 30 | 13 | 13 | 6 | 4 | 33 | 67 | 0.49 | 53.89 | 0.73 |
| 3 | Vaigach | 23 | 8 | 37 | 12 | 7 | 11 | 2 | 29 | 71 | 0.42 | 42.05 | 0.52 |
| 5 | | 24 | 6 | 34 | 11 | 14 | 9 | 2 | 34 | 66 | 0.52 | 48.77 | 0.60 |
| 6 | | 24 | 8 | 31 | 12 | 13 | 8 | 4 | 33 | 67 | 0.48 | 47.81 | 0.60 |
| 7 | Kolguev | 23 | 10 | 39 | 9 | 11 | 7 | 1 | 27 | 73 | 0.36 | 42.28 | 0.47 |
| 8 | | 21 | 9 | 19 | 23 | 20 | 7 | 1 | 50 | 50 | 1 | 64.23 | 0.75 |
| 9 | | 36 | 7 | 27 | 9 | 10 | 7 | 4 | 27 | 73 | 0.36 | 55.61 | 1.08 |
| 11 | Andrey | 28 | 7 | 34 | 10 | 7 | 10 | 4 | 27 | 73 | 0.38 | 46.09 | 0.70 |
| 12 | | 27 | 2 | 40 | 15 | 5 | 7 | 4 | 27 | 73 | 0.37 | 46.47 | 0.64 |
| 13 | Ku-rungnakh | 21 | 8 | 20 | 23 | 11 | 12 | 5 | 46 | 54 | 0.85 | 55.00 | 0.75 |
| 14 | | 24 | 7 | 17 | 23 | 13 | 15 | 1 | 51 | 49 | 1.04 | 60.00 | 1.00 |
| 15 | | 23 | 9 | 21 | 24 | 9 | 13 | 1 | 46 | 54 | 0.85 | 56.00 | 0.77 |
| 16 | | 45 | 7 | 12 | 20 | 7 | 9 | 0 | 36 | 64 | 0.56 | 72.00 | 2.37 |
| 17 | | 23 | 9 | 18 | 24 | 11 | 14 | 1 | 49 | 51 | 0.96 | 58.00 | 0.85 |

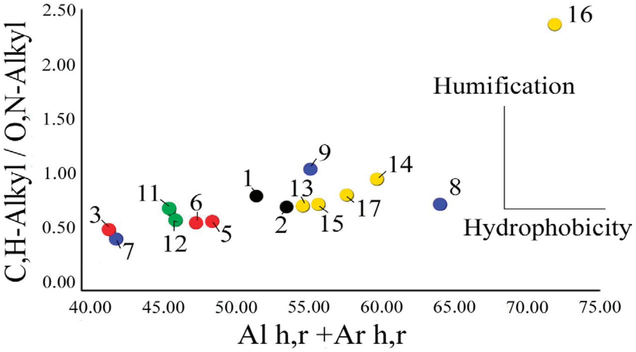


**Fig. 4.** The diagram of integrated indicators of the molecular composition of humic acids. Sample numbers correspond to Table 1; Al h,r + Ar h,r indicates the total number of unoxidized carbon atoms

In the studied soils, a significant amount of aliphatic fragments in the ranges of 0-46 and 110-144 ppm is accumulated, which is due to the increased humidity in the Arctic sector. A comparative analysis of humic substances from different sectors of the Russian Arctic shows that, depending on the region, soils can accumulate different amounts of aliphatic and aromatic fragments of humic substances [18]. The Ar/Al ratio ranges from 0.35 to 1.04, which is caused by different climatic parameters, as well as soil-forming processes and activity of cryogenic processes. Soils, forming on sandy loam and silt loam classes of parent materials, have a relatively high degree of humification due to natural drainage and low degree of cryogenic processes. In soils from the islands of Sosnowiec, Vaigach, Kolguev and Andrey, the molecular and elemental composition is similar and is confirmed by data from other researchers working in the Arctic [11, 17-18, 39-41]. Such soils develop according to the cryogenic type of soil formation. Soils from Kurungnakh island, located in the Lena River Delta, accumulate a relatively high content of aromatic fragments up to 51%, which is typical of the podzolic type of soil formation. Accumulation of aromatic fragments of HAs is associated with high microbiological activity, on the island of Kurunnakh, on sandy and loamy sandy soils and leads to favorable conditions for the microbiota [31].

A number of factors affect the qualitative composition of humic substances in soil, the leading features are hydromorphism and the quality of plant residues. The soils of the Arctic are mainly represented by moss-lichen communities, which are enriched with aliphatic compounds [42-44]. Under cryogenic processes, anaerobic conditions are formed in the soil, due to the nearness of permafrost table and excessive humidity. Such conditions decrease the microbiological activity, which decreases the rate of transformation of soil organic matter and promotes accumulation of paraffin fragments in the structure of humic substances. The processes of humification of plant residues in the soils of Kurungnakh Island, developing in the podzolic type of soil formation, proceed more intensively, contributing to the formation of aggressive humic substances enriched with oxygen-containing functional groups up to 15% and with a high content of aromatic fragments. Humic substances from the islands of Sosnowiec, Kolguev, Vaigach and Andrey have a lower degree of aromaticity and contain mainly non-oxidized aliphatic fragments up to 74% in their structure, which together with anaerobic conditions leads to the gleying process.

## Conclusions

Structural characteristics and elemental composition of humic acids in soils formed in different sectors of the Russian Arctic have been studied. The analysis of the elemental composition showed an increase in the degree of hydromorphism in the soils of the islands of Sosnowiec, Vaigach, Kolguev and Andrey and is accompanied by an increase in values (H/Cmod), which is determined by the lower microbiological activity of Cryosol, which leads to a conservation of carbohydrate and amino acid fragments in the structure of HAs. Soils from the island of Kurungnakh, the Lena River Delta, revealed relatively low ratios of the values (H/Cmod) in the soils, which indicates an increase in the proportion of aromatic fragments in the structure of HAs.

Analysis of the molecular composition of HAs showed that humic acid molecules from the island of Kurungnakh are enriched with aromatic fragments relative to the humidification of soils from the islands of Sosnowiec, Vaigach, Kolguev and Andrey where aliphatic chains and structures like carbohydrates and amino acids prevail in the carbon skeleton. The structurally functional composition of humic acids in tundra soils is less enriched with aromatic structures. Excessive humidity leads not only to accumulation of humic substances, but also affects their molecular composition, namely, causes accumulation of humic substances in the soils enriched with aliphatic structures.

Analysis of the integral indicator of the hydrophobicity of HAs (Al h, r + Ar h, r) showed that HAs in the Arctic zone are resistant to oxidation (including microbial). Relatively high rates of C, H-Al/O, N-Al are observed in soils from the island of Kurungnakh in the Lena River Delta, which indicates a more significant degree of humification compared to other studied soils of the Russian Arctic.

## *References*

1. Anisimov O, Arnalds Ö, Arnoldusen A, Bockheim J, Breuning-Madsen H, Broll G, Brown J, Desyatkin R, Goryachkin S, Jakobsen BH, Jones A, Konyushkov D, Mazhitova G, McCallum I, Montanarella L, Naumov E, Overduin PP, Nilsson S, Solbakken E, Ping CL, Ritz K, Spaargaren O, Stolbovoy V, Tarnocai C. Soil Atlas of the Northern Circumpolar Region: An initiative of the European Union to support the International Polar YearJRC European Commission. Institute for Environment. Jones A, Principal editor. Luxembourg: Publ. Office of the European Union, 144 p. doi: 10.2788/95795
2. Zubrzycki S, Kutzbach L, Pfeiffer E.-M. 2014. Permafrost-affected soils and their carbon pools with a focus on the Russian Arctic. *Solid Earth*. 2014;5:595-609. doi: 10.5194/se-5-595-2014
3. Schädel C, Schuur EAG, Bracho R, Elberling B, Knoblauch C, Lee H, Luo Y, Schimel DS. Terrestrial ecosystems and the carbon cycle. *Global Change Biology*. 1995;1:77-91. doi: 10.1111/gcb.12417
4. Schimel DS. Terrestrial ecosystems and the carbon cycle. *Global Change Biology*. 1995;1:77-91. doi: 10.1111/j.1365-2486.1995.tb00008.x
5. Davis TN. Permafrost: A Guide to Frozen Ground in Transition. Fairbanks, AK, U.S.A.: University of Alaska Press; 2001. 351 p.
6. Dutta K, Schuur AG, Neff JC, Zimov SA. Potential carbon release from permafrost soils of Northeastern Siberia. *Global Change Biology*. 2006;12:2336-2351. doi: 10.1111/j.1365-2486.2006.01259.x
7. Polyakov VI, Orlova KS, Abakumov EV. Evaluation of carbon stocks in the soils of Lena River Delta on the basis of application of "dry combustion" and Tyurin's methods of carbon determination. *Biological Communications*. 2017;62:67-72. doi: 10.21638/11701/spbu03.2017.202
8. Uchaev AP, Nekrasova OA. Mobile humic substances in the forest-tundra zone podzols. *BioClimLand*. 2013;1:58-66.

9. Okoneshnikova MV. Current state and prediction of changes in soils of the middle Lena valley (Central Yakutia). *Tomsk State University Journal of Biology.* 2013;3(23):7-18. doi: 10.17223/19988591/23/1 In Russian
10. Bölter M, Blume H-P, Wetzel H. Properties, formation, classification and ecology of soils: Results from the Tundra Northwest Expedition 1999 (Nunavut and Northwest Territories, Canada). *Polarforschung*. 2006;73:89-101.
11. Dai XY, Ping CL, Michaelson GJ. Characterizing soil organic matter in Arctic tundra soils by different analytical approaches. *Organic Geochemistry*. 2002;33:407-419. doi: 10.1111/j.1365-2389.2007.00908.
12. Kutzbach L, Wagner D, Pfeiffer E-M. Effect of microrelief and vegetation on methane emission from wet polygonal tundra. Lena Delta, Northern Siberia. *Biogeochemistry*. 2004;69:341-362. doi: 10.1023/B:BIOG.0000031053.81520.db
13. Boike J, Kattenstroth B, Abramova K, Bornemann N, Chetverova A, Fedorova I, Frob K, Grigoriev M, Grube RM, Kutzbach L, Langer M, Minke M, Muster S, Piel K, Pfeiffer E-M, Stoof G, Westermann S, Wischnewski K, Wille C, Hubberten H-W. Baseline characteristics of climate, permafrost and land cover from new permafrost observatory in the Lena River Delta, Siberia (1998-2011). *Biogeosciences*. 2013;10:2105-2128. doi: 10.5194/bg-10-2105-2013
14. Kirpotin SN. Western Siberia in a changing climate. *International J Environmental Studies*. 2014;71(5):591-594. doi: 10.1080/00207233.2014.945695
15. Cazzolla Gatti R, Callaghan TV, Rozhkova-Timina I, Dudko A, Lim A, Vorobyev SN, Kirpotin SN, Pokrovsky OS. The role of Eurasian beaver (Castor fiber) in the storage, emission and deposition of carbon in lakes and rivers of the River Ob flood plain, western Siberia. *Science of the Total Environment*. 2018;644:1371-1379. doi: 10.1016/j.scitotenv.2018.07.042
16. Lodygin ED, Beznosikov VA. The molecular structure and elemental composition of humic substances from Albeluvisols. *Chemistry and Ecology*. 2010;26:87-95. doi: 10.1080/02757540.2010.497759
17. Ejarque E, Abakumov E. Stability and biodegradability of organic matter from Arctic soils of Western Siberia: Insights from 13C-NMR spectroscopy and elemental analysis. *Solid Earth*. 2016;7:153-165. doi: 10.5194/se-7-153-2016
18. Lodygin E, Beznosikov V, Abakumov E. Humic substances elemental composition of selected taiga and tundra soils from Russian European North-East. *Polish Polar Research*. 2017;38:125-147. doi: 10.1515/popore-2017-0007
19. Lupachev A, Abakumov E, Gubin S. The influence of cryogenic mass exchange on the composition and stabilization rate of soil organic matter in cryosols of the Kolyma Lowland (North Yakutia. Russia). *Geosciences*. 2017;7:24. doi: 10.3390/geosciences7020024
20. Zharinova NY, Yamskih AA. Humus characteristics of alluvial dark-humus soils of Krasnoyarsk forest-steep. *Tomsk State University Journal of Biology.* 2011;1(13):5-10. In Russian
21. Chefetz B, Salloum MJ, Deshmukh AP, Hatcher PG. Structural components of humic acids as determined by chemical modifi cations and carbon - 13 NMR, pyrolysis and thermochemolysis-gas chromatography/mass spectrometry. *Soil Science Society of America Journal*. 2002;66:1159-1171. doi: 10.1016/S1001-0742(08)62285-8
22. Szymański W, Wojtuń B, Stolarczyk M, Siwek J, Waścińska J. Organic carbon and nutrients (N, P) in surface soil horizons in a non-glaciated catchment, SW Spitsbergen. *Polish Polar Research*. 2016;37:49-66. doi: 10.1515/popore-2016-000
23. Lodygin ED, Beznosikov VA, Vasilevich RS. Molecular composition of humic substances in tundra soils (13C-NMR spectroscopic study). *Eurasian Soil Science*. 2014;47:400-406. doi: 10.1134/S1064229314010074
24. Chukov SN, Abakumov EV, Tomashunas VM. Characterization of humic acids isolated from Antarctic soils by 13C NMR spectroscopy. *Eurasian Soil Science*. 2015;48:1207-1211. doi: 10.1134/S1064229315110046

25. Glazov MV, Goryachkin SV. Changes in natural zones of the Russian Arctic. *Priroda.* 1997;5:32-47. In Russian
26. *IUSS Working Group WRB World Reference Base for Soil Resources 2014, update 2015*. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. World Soil Resources Reports No. 106. Rome: FAO; 2015. 192 p.
27. Swift RS. Organic matter characterization. In: *Soil Science Society of America Book Series. No 5. Methods of soil analysis*. *Pt 3. Chemical methods*. Bigham JM, editor-in-chief SSSA. Madison, Wisconsin, USA: Soil Science Society of America Inc.; 1996. pp. 1011-1170. Electronic resource. Available at: https://www.waterboards.ca.gov/waterrights/water_issues/programs/bay_delta/california_waterfix/exhibits/docs/Islands/II_41.pdf (access 12.07.2019)
28. Vasilevich RS, Lodygin ED, Beznosikov VA, Abakumov EV. Molecular composition of raw peat and humic substances from permafrost peat soils of European Northeast Russia as climate change markers. *Science of ehe Total Environment*. 2018;615:1229-1238. doi: 10.1016/j.scitotenv.2017.10.053
29. Celi L, Schnitzer M, Nègre M. Analysis of carboxyl groups in soil humic acids by a wet chemical method. Fourier-transform infrared spectrophotometry, and solution state carbon-13 nuclear magnetic resonance. A comparative study. *Soil Science*. 1997;162:189-197. doi: 10.1097/00010694-199703000-00004
30. Beznosikov VA, Lodygin ED. High-molecular organic substances in soils. *Proceedings of the Komi Science Centre of the Ural Division of the Russian Academy of Sciences*. 2010;1:24-30. In Russian
31. Vasilevich RS, Lodygin ED, Beznosikov VA. Molecular-mass distribution of humus substances tundrain soils of the European north-east Russia. *Vestnik SPbSU. Biology*. 2015;4:103-111. In Russian
32. Baldock JA, Preston CM. Chemistry of carbon decomposition processes in forests as revealed by solid-state carbon-13 nuclear magnetic resonance. In: *Carbon Forms and Functions in Forest Soils*. Kelly JM and McFee WW, editor. Madison, Wisconsin, USA: Soil Science Society of America, Inc.; 1995. 89-117 p.
33. Panettieri M, Knicker H, Murillo JM, Madejón E, Hatcher PG. Soil organic matter degradation in an agricultural chronosequence under different tillage regimes evaluated by organic matter pools, enzymatic activities and CPMAS $^{13}$C NMR. *Soil Biology and Biochemistry*. 2014;78:170-181. doi: 10.1016/j.soilbio.2014.07.021
34. Dergacheva MI, Bazhina NL, Ondar EE, Ochur KO, Ryabova NN. Environmentally induced composition and properties of humic acids in soils of Western Tuva. *Vestnik Orenburg State University*. 2015;10(185):166-169. In Russian
35. Tsybenov YB, Chimitdorzhieva GD, Egorova RA, Gongal'skii KB. The pool of organic carbon and its isotopic composition in cryomorphic quasi-gley chernozems of the Trans-Baikal region. *Eurasian Soil Science*. 2016;49(1):8-14. doi: 10.1134/S106422931507011X
36. Xu J, Zhao B, Chu W, Mao J, Zhang J. Chemical nature of humic substances in two typical Chinese soils (upland vs paddy soil): A comparative advanced solid state NMR study. *Science of The Total Environment*. 2017;576:444-452. doi: 10.1016/j.scitotenv.2016.10.118
37. Kleinhempel D. Ein Beitrag zur Theorie des Huminstoffezustondes. *Albrecht-Thaer-Archiv*. 1970;14(1):3-14. In German
38. Abakumov EV, Trubetskoj O, Demin D, Celi L, Cerli C, Trubetskaya O. Humic acid characteristics in podzol soil chronosequence. *Chem. Ecol*. 2010;26:59-66. doi: 10.1080/02757540.2010.497758
39. Abakumov E, Lodygin E, Tomashunas V. 13C NMR and ESR Characterization of humic substances isolated from soils of two Siberian Arctic Islands. *International J Ecology*. 2015;e390591. doi: 10.1155/2015/390591
40. Abakumov E. Characterisation of humic acids isolated from selected subantarctic soils by 13C-NMR spectroscopy. *Czech Polar Reports*. 2017;7:1-10. doi: 10.5817/CPR2017-1-1

41. Mergelov N, Mueller CW, Prater I, Shorkunov I, Dolgikh A, Zazovskaya E, Shishkov V, Krupskaya V, Abrosimov K, Cherkinsky A, Goryachkin S. Alteration of rocks by endolithic organisms is one of the pathways for the beginning of soils on Earth. *Scientific Reports*. 2018;8:3367. doi: 10.1038/s41598-018-21682-6
42. Amelung W, Flach KW, Zech W. Climatic effects on soil organic matter composition in the great plains. *Soil Science Society of America Journal*. 1997;61:115-123. doi: 10.2136/sssaj1997.03615995006100010018x
43. Orlov DS. Soil Chemistry: A Textbook. Moscow: Moscow State University Publ.; 1985. 376 p. In Russian
44. Polyakov V, Zazovskaya E, Abakumov V. Molecular composition of humic substances isolated from selected soils and cryconite of the Grønfjorden area. Spitsbergen. *Polish Polar Research*. 2019;40(2):105-120. doi: 10.24425/ppr.2019.128369

*Received 9 July 2019; Revised 15 August 2019;*
*Accepted 11 September 2019; Published 27 September 2019*

**Author info:**
**Polyakov Vyacheslav I,** Master of Sci. (Biol.), Engineer, Department of Applied Ecology, Faculty of Biology, Saint Petersburg State University, 13B Universitetskaya Emb., St. Petersburg 199034, Russian Federation; Postgraduate Student, Department of Soil Science and Agrochemistry, Faculty of Agriculture, Saint-Petersburg State Agrarian University, 2 Petersburg Highway, Pushkin 196601, Russian Federation; Engineer, Department of Geography of Polar Region, Arctic and Antarctic Research Institute, 38 Bering Str., St. Petersburg 199397, Russian Federation.
ORCID iD: http://orcid.org/0000-0001-6171-3221
E-mail: slavon6985@gmail.com
**Chegodaeva Nadezhda A**, Master of Sci. (Biol.), Student, Department of Applied Ecology, Saint Petersburg State University, 13B Universitetskaya Emb., St. Petersburg 199034, Russian Federation.
ORCID iD: http://orcid.org/0000-0001-5547-7306
E-Mail: nadenka9517@mail.ru
**Abakumov Evgeny V,** Dr. Sci. (Biol.), Professor, Department of Applied Ecology, Saint Petersburg State University, 13B Universitetskaya Emb., St. Petersburg 199034, Russian Federation.
ORCID iD: http://orcid.org/0000-0002-5248-9018
E-mail: e_abakumov@mail.ru

**For citation:** Polyakov VI, Chegodaeva NA, Abakumov EV. Molecular and elemental composition of humic acids isolated from selected soils of the Russian Arctic. *Vestnik Tomskogo gosudarstvennogo universiteta. Biologiya = Tomsk State University Journal of Biology*. 2019;47:6-21. doi: 10.17223/19988591/47/1