

Stabilization of organic material from soils and soil-like bodies in the Lena River Delta (¹³C-NMR spectroscopy analysis)

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Estabilización de la materia orgánica de suelos y cuerpos similares al suelo en el Delta del Río Lena (Análisis de espectroscopía ¹³C-NMR)
Estabilização da matéria orgânica do solo e corpos semelhantes ao solo no Delta do Rio Lena (Análise por espectroscopia ¹³C-NMR)

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ABSTRACT

The Arctic ecosystem has a huge reservoir of soil organic carbon stored in permafrost-affected soils and biosediments. During the short vegetation season, humification and mineralization processes in the active soil layer result in the formation of specific soil organic substances – humic substances. Humic acids are high molecular, specific, thermodynamically stable macromolecules. The study was conducted in the Lena River Delta, the largest river delta located in the Arctic. Cryosol-type soils on alluvial deposits of the river form an area of about 45 thousand km² under permafrost conditions. The vegetation cover is represented by moss-lichen communities with the presence of *Salix glauca* in the flooded areas, as well as *Betula nana* in the areas not subject to flooding. The paper presents the elemental and molecular composition of humic acids isolated from soils, integral indicators of humification (stabilization) of organic matter in the soils of the Lena River Delta. The study was conducted using the ¹³C (CP/MAS) NMR spectroscopy method. In the work, it was revealed that up to 33% of aromatic and up to 15% COOR fragments are accumulated in humic acids. The AR/AL ratio ranged from 0.69 to 0.89. The studied soils are variants of modern soil formation (not subjected to alluvial processes) and soil-like bodies that melted from the IC of the river delta. A relatively high degree of condensation of humic acid macromolecules in comparison with other polar regions of the Arctic and Antarctic was noted.

RESUMEN

*El ecosistema ártico constituye una enorme reserva de carbono orgánico que se encuentra almacenado en suelos afectados por permafrost y biosedimentos. Durante la corta estación vegetativa, los procesos de humificación y mineralización en la capa activa del suelo dan lugar a la formación de sustancias orgánicas específicas en el suelo, las sustancias húmicas. Los ácidos húmicos son macromoléculas de alto peso molecular, específicas y termodinámicamente estables. Este estudio se llevó a cabo en el Delta del Río Lena, el mayor delta de río situado en el Ártico. Allí se encuentran Criosoles formados sobre depósitos aluviales de río que ocupan un área aproximada de 45.000 km² bajo condiciones de permafrost. La cobertura vegetal está representada por comunidades de líquenes y musgos con la presencia de *Salix glauca* en las zonas inundadas, así como *Betula nana* en las zonas no inundadas. Este trabajo presenta la composición elemental y molecular de los ácidos húmicos aislados de los suelos, indicadores integrales de*

la humificación (estabilización) de la materia orgánica en los suelos del Delta del río Lena. El estudio fue realizado mediante el método de espectroscopía ¹³C (CP/MAS) NMR. Así, se obtuvo que en los ácidos húmicos se acumulaban hasta un 33% de fragmentos aromáticos y un 15% de fragmentos COOR. La relación AR/AL osciló entre 0,69 y 0,89. Los suelos estudiados son variantes de la formación de suelos modernos (no sometidos a procesos aluviales) y cuerpos similares al suelo que se derritieron a partir del Complejo de Hielo (IC) del delta del río. Se observó un grado relativamente alto de condensación de macromoléculas de ácidos húmicos en comparación con otras regiones polares del Ártico y Antártico.

RESUMO

O ecossistema Ártico é uma enorme reserva de carbono orgânico, que está armazenado em solos afetados por permafrost e em biosedimentos. Durante a curta estação vegetativa, os processos de humificação e mineralização na camada ativa do solo dão origem à formação de substâncias orgânicas específicas do solo – as substâncias húmicas. Os ácidos húmicos são macromoléculas de elevada massa molecular, específicas e estáveis em termos termodinâmicos. Este estudo foi realizado no Delta do Rio Lena, o maior delta fluvial localizado no Ártico. Numa área de aproximadamente 45 000 km², ocorrem Criossolos formados a partir de depósitos aluviais do rio Lena em condições de permafrost. A cobertura vegetal é representada por comunidades de líquenes e musgos com a presença de Salix glauca nas zonas inundadas, bem como Betula nana nas zonas não inundadas. O artigo apresenta a composição elementar e molecular dos ácidos húmicos isolados dos solos, indicadores integrais da humificação (estabilização) da matéria orgânica nos solos do Delta do Rio Lena. O estudo foi realizado utilizando o método de espectroscopia ¹³C (CP/MAS) NMR. Nos ácidos húmicos acumulam-se até 33% dos fragmentos aromáticos e 15% dos fragmentos de COOR. A relação AR/AL variou entre 0,69 e 0,89. Os solos estudados são variantes da formação moderna dos solos (não sujeitos a processos aluviais) e corpos semelhantes a solo que resultaram da fusão do Complexo de Gelo (IC) do delta do rio. Foi observado um grau relativamente elevado de condensação de macromoléculas de ácidos húmicos em comparação com outras regiões polares do Ártico e do Antártico.

KEYS WORDS

Permafrost soils, SOM, Arctica, CP/MAS, humic acids.

PALABRAS

CLAVE

Suelos del permafrost, SOM, Arctica, CP/MAS, ácidos húmicos.

PALAVRAS-

CHAVE

Solos de permafrost, SOM, Ártica, CP/MAS, ácidos húmicos.

1. Introduction

Soil organic carbon (SOC) is a product that accumulates in the soil after the partial decomposition of diverse types of materials, derived from microorganisms and plant remnants. This constitutes a key element of the global carbon cycle through the atmosphere, vegetation, soils, rivers and the ocean (Davis 2001; Dutta et al. 2006; Schimel 1995). The soil organic matter (SOM) supports the key functions of the soil and ecosystem services, as it is crucial for stabilizing the structure of the soil, retaining, releasing nutrients for plants, and for ensuring the penetration of water and its storage in the soil. Loss of SOC indicates a degree of soil dehumification and degradation. Soils represent the largest surface reservoir of organic carbon in the Earth. Due to the local geogenic features, climatic conditions and land use, and management (among other environmental factors), soils retain differing amounts of SOC (Boike et al. 2013; Dai et al. 2002; Kutzbach et al. 2004). It is estimated that the largest amount of SOC is stored in the northern permafrost region with over 1024 Pg (1 Pg = 10¹³ kg) of organic carbon in the soil in a layer of up to 3 m, as well as 34 Pg of nitrogen (Jones et al. 2010; Zubrzycki et al. 2013; Zubrzycki et al. 2014) mainly in peat soil. The permafrost-affected zone occupies an area of more than 8.6 million km², which is about 27% of all land areas above 50°N. They accumulate in themselves a huge amount of organic carbon, so they are considered one of the most important elements of the cryosphere. There, carbon accumulates in soils in huge quantities due to low temperatures, leading to low

biological activity and slow decomposition of SOM (Cauwet and Sidorov 1996; Ejarque and Abakumov 2016). The corresponding soil type is called Histosol (IUSS Working Group WRB 2015) and is characterized by SOC content of 12 to 50%. The presence of permafrost and long-term freezing of soils has a strong influence on the processes of ion exchange, the water-physical regime, the solubility of nutrients and their availability for plants, and on bioproductivity in general. The loss of SOC negatively affects not only soil health and food production, but also exacerbates climate change. When SOM decomposes, carbon-based greenhouse gases are released into the atmosphere. If this happens too fast, soils can contribute to the warming of our planet. On the other hand, many soils have the potential to increase SOC reserves, thus mitigating climate change by reducing atmospheric CO₂ (Knoblauch et al. 2013; Lara et al. 1998).

Cryoturbation and cryogenic mass exchange lead to the translocation and further accumulation of organic matter into deeper soil horizons. Another process is the movement of organic matter in a dissolved state and its accumulation on the border with the permafrost table (Dutta et al. 2006; Schimel 1995). During to cryoturbation processes, small fragments of organic matter separate from the lower parts of the surface horizons under the influence of ice penetration, move inside the profile, and mix with the mineral part of the underlying horizons. Such movement of organic masses along the profile leads to its compaction, homogenization, and destruction of plant remnants (Davidson and Janssens 2006).

The Lena River has a great influence on the biogeochemistry of the Arctic Ocean. Arctic rivers are the main suppliers of organic and inorganic carbon and largely determines the organic carbon cycle in the Arctic basin (Boike et al. 2013; Dobrovolsky 2005; Kutzbach et al. 2004). The soils of the Lena River Delta are formed in conditions of seasonal freezing/thawing processes and annual flooding. The annual supply of nutrients by the river and a mild climate cause a high level of microbiological processes in the soil, which contributes to the relatively high rate of humification of organic matter in the soil (Bolshiyarov et al. 2013).

The SOM of Arctic soils is very specific in comparison with soils are not affected by permafrost, and modern instrumental methods and approaches are needed to study it. The intensity of mineralization and humification of soil organic matter is extremely low due to the long duration of the frozen state of soils and the small sum of positive temperatures (Ejarque and Abakumov 2016; Lodygin et al. 2017; Lodygin and Beznosikov 2010). The soils of the Lena Delta are characterized by humus and peat soils, and there are also buried organic residues associated with both cryogenic processes and the specifics of sedimentation in the deltas of large rivers (Polyakov et al. 2018). Due to the widespread development of the lake system, silty particles and organic residues are deposited at the bottom of the lakes due to permafrost lateral mass transfer (Boike et al. 2013; Bolshiyarov et al. 2013).

For specific conditions of soil formation, in particular humus accumulation, in addition to traditional methods for the analysis of organic matter, the recent method of the study of organic matter based on its molecular composition has an advantage. The content of molecular fragments of HAs determined by CP/MAS ¹³C-NMR spectroscopy contributes to the understanding of the fundamental processes of humus formation and the composition of natural high-molecular weight HAs in soils subjected to the influence of cryogenesis (Chukov et al. 2015; Dai et al. 2002; Ejarque and Abakumov 2016; Lodygin et al. 2014; Lupachev et al. 2017).

The advantage of the nuclear magnetic resonance spectroscopy method is the ability to quantify the content of groups of individual and structural fragments in humic acid (HAs) molecules. This method is also used to assess changes in SOM during decomposition and humification. So far, studies of the quality of SOM from polar environments have revealed a generalized, slightly degraded nature of organic molecules that retain most of the chemical nature of their precursor material due to the low progress of humification (Abakumov et al. 2015; Davidson and Janssens 2006; Dziadowiec et al. 1994).

Arctic soils, according to studies by various scientists, have a high proportion of aliphatic compounds in the composition of the HAs

(Abakumov et al. 2015; Chukov et al. 2015; Lodygin et al. 2017; Polyakov et al. 2019b; Vasilevich et al. 2018; Vasilevich et al. 2019). The low content of aromatic compounds of HAs is primarily associated with vegetation (the precursors of humification), as well as soil-climatic conditions, a low degree of aeration, cryogenic processes, and low microbiological activity that lead to soil mineralization and store of organic matter in permafrost. Russian scientists have well studied permafrost peat soils in north-west Russia, where they note a low proportion of aromatic compounds. Upon transition from the Arctic zone to the boreal zone, an increase in the proportion of aromatic compounds occurs, which is associated with an increase in microbiological activity and a change in plant communities.

The vegetation cover of the Arctic ecosystem is represented mainly by moss-lichen communities. The content of aromatic hydrocarbons in them, in particular lignin, tannin, and flavonoids, is rather low or close to zero. The content of proteins and nitrogen-containing fragments is also extremely low at 2-10%. Thus, the composition of precursors plays a key role in the composition of HAs. The predominantly aliphatic character of the HAs is associated with a high proportion of carbohydrates among the humification precursors (Orlov 1990). Antarctic soil-like bodies are also similar in relation to the aliphatic and aromatic fragments in the composition of the HAs by ^{13}C (CP/MAS) NMR and ^1H - ^{13}C HETCORE NMR spectroscopy. The spectra obtained are very homogeneous, due to the low diversity of the vegetation cover (Abakumov et al. 2015; Abakumov et al. 2019; Lodygin et al. 2017; Lodygin and Beznosikov 2010; Lodygin et al. 2014; Lupachev et al. 2017).

Humic acids are heterogeneous systems of high-molecular condensed compounds formed from the decay of plant and animal remnants in terrestrial and aquatic ecosystems. Climatic parameters, precursors of humification, and local position in the landscape determine the diversity of the composition and properties of HAs (Chukov et al. 2015; Ejarque and Abakumov 2016; Lodygin et al. 2014). The stabilization of organic material is defined as the transformation of organic matter into a state inaccessible

to soil microorganisms, and the stabilization property itself is a characteristic stage of carbon dynamics (Semenov et al. 2009). Using ^{13}C -NMR spectroscopy we identify the proportion of aromatic compounds in the composition of HAs, to assess the stabilization of organic matter in soils.

This work is the continuation of a long-term study of the molecular composition of Arctic soils, using the example of alluvial soils of the Lena River Delta. Thus, the aim of this work is to study HAs by ^{13}C -NMR spectroscopy of permafrost soils of the Lena River Delta, buried organic matter, and melted soil-like bodies from the Ice Complex of the delta. To achieve aim of work, the following objectives were set:

1. to find out the molecular composition of HAs from study soils
2. to investigate elemental composition of HAs
3. to determine the stabilization rates of HAs isolated from study soils

2. Materials and Methods

2.1. The study sites

The Lena River Delta, the largest northern delta in the world, is located in the Arctic zone and has an area of about 29,630 km². Due to such a huge area and location, it has a significant impact on the hydrological regime of the Arctic Ocean, since a large amount of fresh water flows from the delta into the least salty ocean of our planet. The delta was formed as a result of river activity: sediment removal, erosion, and abrasion under the influence of sea level fluctuations and the movement of the Earth's crust (Bolshiyarov et al. 2013) (**Figure 1**).

The Lena River Delta is located in the area with an Arctic continental climate. The climatic characteristics of the area are presented in **Table 1**.



Figure 1. The Lena River Delta. Study area. Sample numbers correspond to Table 2.

Table 1. Climate parameters of the study region (Data obtained from the station «Samoylov Island»)

| Climate parameters | Lena River Delta |
|---|------------------|
| Mean annual air temperature (°C) | -13 |
| Mean air temperature (°C): | |
| of the warmest month (July) | 6.5 |
| of the coldest month (January) | -32 |
| Number of days with mean daily Air temperature: | |
| above 0 °C | 73 |
| above 5 °C | 35 |
| above 10 °C | 11 |
| Freezing depth (cm) | 30-50 |
| Snow thickness (cm) | 23 |
| Annual precipitation (mm) | 323 |
| In summer (mm) | 125 |

Most of the land is characterized by the presence of a permafrost table at a depth of about 1 meter. The depth of the active layer varies: on loamy soils it can reach 30 cm at the end of August, and on sand soils it can reach 1 meter.

The Lena River Delta is covered with various types of tundra vegetation. The main components are lichens, mosses, grasses (cereals and sedges) and some types of shrubs. Here,

cereal-sedge-moss coenoses predominate in relief depressions of the-hypno-sedge polygonal swamps (Table 2). The vegetation cover has a mosaic character ("spotted tundra"). The Lena River Delta is represented by the dominance of moss-lichen vegetation. Moss groups predominate on loam and lichen predominates on rocks. In addition, often near the thermokarst lakes, moss-lichen vegetation is replaced by sedge-cannon fodder. On the warm southern slopes on well-drained sandy soils and in the river valley there are areas with grassy vegetation (tundra meadows and floodplain meadows) (Boike et al. 2013; Kutzbach et al. 2004; Schneider et al. 2009).

2.2. Ice complex (IC)

The issue of the origin of the Ice Complex (IC) of rocks has not yet been resolved. There are several hypotheses that explain the

accumulation of sand-silt sediments and their simultaneous freezing. Some researchers associate this process with aeolian transport and the deposition of a huge amount of mineral material from the atmosphere, and there is also a theory about the formation of IC as a result of alluvial accumulation. Another point of view on the formation of IC is that in front of the ice sheet on the shelf of the Laptev Sea there was a stagnant reservoir in which accumulation of sediments of the IC occurred (Bolshiyarov et al. 2013).

We studied sample №9, a soil-like body extracted from the IC of the Lena River Delta. The results obtained during its processing differ from the soils investigated in this work. The carbon content in this sample is quite low and more similar in composition to fulvic acid. Apparently, during the long-term storage of organic matter in IC, the carbon content decreases with an increase in the oxygen fraction in HAs macromolecules.

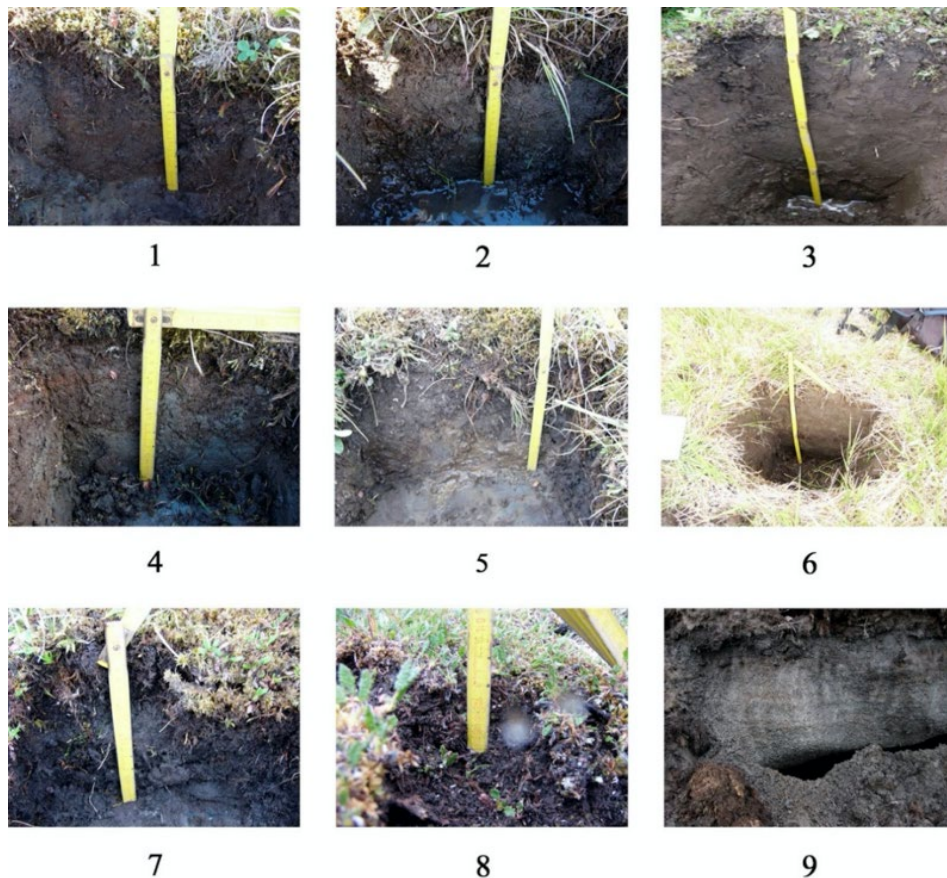


Figure 2. Morphological diversity of study soils. Sample numbers correspond to Table 2.

Table 2. Description of the studied soil and soil-like bodies

| Site | Sample | Description of the studied soil horizons Coordinates | Color index* | Vegetation | Soil name** |
|-------------------------------|--|---|--------------|--|-------------------------|
| Kurungnah isl. | 1 | Dark material, roots, iron spots, sandy loam, cryogenic mass exchange, permafrost table from 27 cm. Top of alas. N72.28920 E126.18025. | 10 YR 6/1 | Cetraria nivalis, Sphagnum, Carex aquatilis. | Turbic Cryosol (Siltic) |
| | 2 | Dark material, roots, gleyic processes, sandy loam, water table from 25 cm, permafrost table 29 cm. Bottom of alas. N72.29042 E126.18191. | 10 YR 6/1 | Cetraria nivalis, Sphagnum sp., Carex aquatilis. | Turbic Cryosol (Loamic) |
| | 3 | Roots, sandy loam, water table from 65 cm, permafrost table from 70 cm. Middle of alas. N72.29039 E126.18125. | 10 YR 6/1 | Sphagnum sp., Carex aquatilis, Salix glauca | Turbic Cryosol (Siltic) |
| | 4 | Organic material. Polygon rim. N72.29063 E126.18423. | 10 YR 4/3 | Cetraria nivalis, Sphagnum sp., | Turbic Cryosol (Loamic) |
| | 5 | Organic material. Inside of alas. N72.29143 E126.18628. | 10 YR 4/3 | Cetraria nivalis, Sphagnum, Carex aquatilis. | Turbic Cryosol (Loamic) |
| | 6 | Buried organic material. Young alas (~100-200 years). N72.32162 E126.25303. | 10 YR 3/2 | Trisetum, Phragmites. | Folic Cryosol |
| Interfluve (Kharaulakh ridge) | 7 | Organo-mineral material, thixotropy, loamy sand, rocks. Top of ridge. N72.39439 E126.76143. | 10 YR 3/2 | Cetraria nivalis, Sphagnum, Leptogium lichenoides, Dactylina arctica | Skeletal Cryosol |
| | 8 | Organo-mineral material, thixotropy, loamy sand, rocks. Top of ridge. N72.392723 E126.78203. | 10 YR 3/2 | Cetraria nivalis, Sphagnum, Leptogium lichenoides, Dactylina arctica | Soil-like body |
| 9 | Organo-mineral material from IC. N72.392402 E125.648261 (~34,299 ± 500 years BP)** * | 10 YR 3/2 | - | Soil-like body | |

*Munsell Color (Firm) 2010); **Soil name by WRB classification (IUSS Working Group WRB 2015); *** (Schirmer et al. 2003).

2.3. Sampling procedure

Samples of soils were collected in various elements of the landforms («Old» alas, «young» alas (buried material), organo-mineral material from IC and interfluve (Kharaulakh ridge)), soil

description are presented in **Table 2**. Soil pits are presented in **Figure 2**.

Kurungnah Island, located at the central part of the delta, has a connection with the Olenek Channel from the west and consists of sediment

from the IC and the underlying sand from the surface. It is built from the surface by deposits of the IC and the underlying sand. The thickness is composed of two packs of rocks. The lower part is composed of fine-grained, sorted quartz sands. Horizontal layering is inherent in it, and it is rarely wavy. In the lower part there are lenticular layers of plant residues with sand. The entire stratum was formed in the middle of the Late Neopleistocene (Bolshiyarov et al. 2013). Interfluvial (Kharaulakh ridge) consist of ultra-fine or fine calcarenite and dolarenite (with minor siliciclastic material) and sandstone. The lithite-quartz-feldspar sandstone contains minor dolomite and limey clasts and is intercalated with calcarenite, mudstone, calcareous mudstone, and silty mudstone, with intraclasts and breccia suggesting occasional landslides (Izokh and Yazikov 2017).

2.4. Soil analysis, ^{13}C NMR spectroscopy and elemental analysis procedure of HAs

Soil samples were air-dried (24 hours, 20 °C), ground, and passed through 2 mm sieve. Routine chemical analyses were performed using classical methods: C and N content were determined using an element analyzer (EA3028-HT EuroVector, Pravia PV, Italy) and pH in water and in salt suspension (soil-dissolvent ratios 1:2.5 in case of mineral horizons and 1:25 in case of organo-mineral horizons) suspensions using a pH meter (pH-150M Teplopribor, Moscow, Russia).

Humic acids were extracted from each sample according to a published IHSS protocol (Swift 1996). HAs extraction yields were calculated as the percentage of carbon recovered from the original soil sample (Vasilevich et al. 2018). 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 frequency was 20 kHz in all cases and the nutation frequency for cross polarization was $u1/2p\ 1/4\ 62.5$ kHz. Repetition delay were 3 seconds. The number of scans was 6500-32000. Contact time is 0.2 us.

The elemental composition of HAs represents the percentage of C, H, N, O elements in them. The high variability of the elemental composition of HAs among different soils is explained by the varying degree of accumulation of elements in the HAs. The highest C content is normally typical of Chernozems with a well-developed mollic layer and high degree of organic matter humification. In the soils of the Arctic zone, the carbon content is much lower. This peculiarity is explained by the effect of increased acidity and humidity. A reduced nitrogen content in soils of the arctic environment is also observed, which is associated with its low content in peat and an increase in hydrogen content. Information on the elemental composition of organic substance provides significant information on the general principles of molecular construction and some of their properties (Orlov 1990). To conduct a graphical analysis of the elemental composition, we used the van Krevelen diagram (van Krevelen 1950), using the H/C-O/C ratios to identify the direction of the transformation processes of various organic compounds in natural conditions. Thus, we can evaluate the processes of oxidation/reduction and hydration/dehydration in HA macromolecules. Elemental compositions were corrected for gravimetric water and ash content. Oxygen content was calculated by difference of whole samples mass and gravimetric concentration of C, N, H and ash.

3. Results and Discussion

3.1. Elemental composition of humic acids isolated from study soils

The elemental composition of HAs is the most important indicator determining the progress of humification, oxidation and degree of condensation of HAs (Abakumov et al. 2015; Beznosikov and Lodygin 2010). Characteristic features of HAs formed in cold conditions, and especially in permafrost-affected soils, are a relatively high H content and a reduced O content compared to boreal and sub-boreal soils (Lupachev et al. 2017).

The obtained data on HAs elemental composition, atomic ratios and degree of oxidation (W) are presented in **Table 3**.

From the obtained data, the carbon content in the study samples confined to modern soil formation is quite small and in a narrow range (41-45%), while the carbon content in the sample

Table 3. Elemental composition of the studied HAs from soils. Gravimetric concentration is 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/Cmod is the number of substituted hydrogen atoms in HAs; $H/C_{mod} = H/C + 2 (O/C) \cdot 0.67$; H/C and W indexes were calculated according to (Orlov 1985). Sample numbers correspond to **Table 2**. SD \pm 0.05 for N, H and C content

| Site | Sample | N, % | C, % | H, % | O, % | C/N | H/C | O/C | H/C mod | W |
|-------------------------------|--------|---------------|------------|---------------|------|-------|------|------|---------|-------|
| Kurungnah isl. | 1 | 3.0 \pm 0.1 | 41 \pm 2 | 5.0 \pm 0.2 | 45 | 13.81 | 1.50 | 0.82 | 2.60 | 0.15 |
| | 2 | 4.0 \pm 0.2 | 44 \pm 2 | 5.0 \pm 0.2 | 42 | 13.91 | 1.43 | 0.71 | 2.38 | -0.01 |
| | 3 | 3.0 \pm 0.1 | 44 \pm 2 | 5.0 \pm 0.2 | 42 | 15.16 | 1.43 | 0.73 | 2.40 | 0.03 |
| | 4 | 3.0 \pm 0.1 | 43 \pm 2 | 5.0 \pm 0.2 | 43 | 15.18 | 1.44 | 0.76 | 2.45 | 0.07 |
| | 5 | 3.0 \pm 0.1 | 44 \pm 2 | 5.0 \pm 0.2 | 42 | 16.82 | 1.38 | 0.72 | 2.35 | 0.06 |
| | 6 | 3.0 \pm 0.1 | 45 \pm 2 | 5.0 \pm 0.2 | 42 | 15.78 | 1.37 | 0.70 | 2.32 | 0.03 |
| Interfluve (Kharaulakh ridge) | 9 | 3.0 \pm 0.1 | 36 \pm 1 | 5.0 \pm 0.2 | 51 | 13.93 | 1.59 | 1.05 | 3.00 | 0.52 |
| | 7 | 3.0 \pm 0.1 | 44 \pm 2 | 5.0 \pm 0.2 | 42 | 15.16 | 1.42 | 0.71 | 2.37 | 0.01 |
| | 8 | 4.0 \pm 0.2 | 42 \pm 2 | 5.0 \pm 0.2 | 44 | 12.65 | 1.46 | 0.80 | 2.53 | 0.13 |

from the frozen soil of the IC is noticeably lower (36%). This may indicate that less organic residue reached the IC during its formation. The C/N ratio varies from 12 to 16, indicating a low enrichment of carbon by nitrogen. It is associated with a nitrogen reservoir in the Arctic systems where the processes of nitrogen fixation and ammonification are low due to the low microbiological activity. Moreover, the oxygen content in the studied samples is comparable with the carbon content; there is a high oxygen content in the sample from the IC (51%). The high oxygen content is due to the better solubility of oxygen-enriched hydrophilic HAs molecules and their migration ability (Lodygin et al. 2014). The H/C ratio is an indicator of the stability of HAs in soils. The lower this indicator, the higher the process of condensation of monomers in high-molecular substances. From the obtained data, it can be seen that the sample from the IC has the highest H/C ratio, which is the result of a low level of molecular condensation in the absence of a relationship with the upper horizons of the soils. In samples from «old» alas (№ 1-5), depending on the landscape position, the accumulation of high-molecular compounds from the top of the alas to its

bottom also occurs. In buried soils of «young» alas (№ 6), the lowest H/C ratio was observed, which indicates that selective degradation of condensed structures occurs with depth inside the profile and an increase in the proportion of herbaceous vegetation, which is the reason for the condensation of high molecular weight compounds (Hatcher et al. 1981; Vasilevich et al. 2019).

From the W index, it follows that most of the study samples are in an oxidized state, only sample 2, located in the bottom of the «old» alas, has reducing conditions associated with a relatively high level of hydromorphism in the soil. Oxidative environmental conditions are associated with the ability of elements to migrate to the bottom of the profile, in particular, iron and aluminum ions, which actively migrate in weakly-acidic and acidic soil solutions. Weak reducing conditions are due to the production of fresh organic residues and the process of humification in the specific bioclimatic conditions of the river delta (Vasilevich et al. 2018).

One of the methods for graphical representation of the elemental composition of HAs from soils

in order to identify patterns of their formation is based on the method outlined by Kleinhempel (1970) and van Krevelen (1950). The method is based on constructing H/C_{mod} and O/C diagrams and serves as a technique to demonstrate the contribution of oxidation and condensation to changes in the elemental composition of HAs (Lodygin et al. 2014; Polyakov et al. 2019a).

Based on the obtained diagram (Figure 3), the H/C_{mod} and O/C integral indicator is relatively low in most of the studied HAs, which indicates a low content of oxygen-containing fragments in the HAs and a relatively low migration ability. As already mentioned above, a high value of H/C_{mod} and O/C is noted in the sample from the IC and indicates that the sample was formed in a

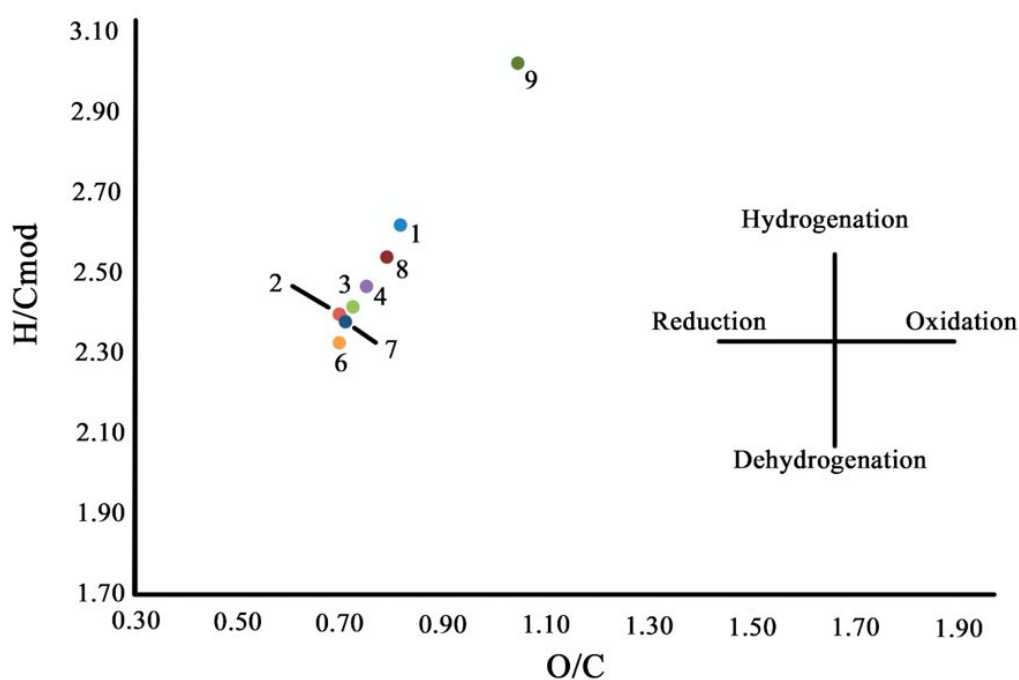


Figure 3. Elemental composition of the studied HAs isolated from study soil. H/C_{mod} – the number of substituted hydrogen atoms in the HA. Sample numbers correspond to Table 2.

environment with a high level of hydromorphism with a low level of microbiological activity, thereby contributing to better conservation of carbohydrate and amino acid HAs fragments. A decrease in H/C_{mod} indicates the accumulation of aromatic fragments in the composition of soil soils (Pengerud et al. 2017; Strebel et al. 2010).

The obtained data correspond to the previously published work by a numerous of scientists. The Arctic environment is characterized by low microbiological activity and the composition of the precursors of humification. The most characteristic distribution is from west to east of the country as the H/C ratio increases

and the proportion of aliphatic compounds grows. Freezing/thawing processes lead to the evolutionary selection of macromolecules of HAs, which is characteristic of the tundra and boreal zones (Abakumov et al. 2015; Beznosikov and Lodygin 2010; Lupachev et al. 2017; Polyakov et al. 2019b).

3.2. Characterization of HAs by ¹³C–NMR spectroscopy

Numerous molecular fragments were identified by CP/MAS ¹³C–NMR spectroscopy (Table 4): carboxyl (–COOR), carbonyl (–C=O); CH₃–,

CH₂-, CH-aliphatic, -C-OR alcohols, esters and carbohydrates, phenolic (Ar-OH), quinone (Ar = O) and aromatic (Ar-) groups, which indicates the great complexity of the structure

of HAs and the polyfunctional properties that cause their active participation in soil processes (Lodygin et al. 2014; Yao et al. 2019).

Table 4. Chemical shifts of atoms of the ¹³C molecular fragments of HAs

| 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 |

Six chemical groups in HAs were identified according to the ¹³C-NMR spectroscopy method. Signals from non-polar alkyls (0-46 ppm), N-alkyl/methoxyl (46-60 ppm), O-alkyl and anomeric (60-110 ppm), aromatics (110-160 ppm), carboxyl, esters, amides (160-185 ppm) and quinone (185-200 ppm).

The obtained spectra are presented in **Figure 4**. According to the obtained data, we can identify three main groups of fragments that accumulate in the delta soils, these are C,H-alkyl ((CH₂)_n/CH/C and CH₃), aromatic compounds (C-C/C-H, C-O) and OCH group (OCH/OCq). 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 0-47 ppm. O, N-alkyl at regions 46-60 and 60-110 ppm. The presence of all peaks of the carbon species which are required for identification of the studied substances as HAs has been revealed (Yao et al. 2019). Data of chemical shifts in the studied soil are presented in **Table 5**.

Aliphatic fragments of HAs (53-59%) dominate in the studied soils, which indicates the dominant mineralization process of organic matter in the soils of the Lena River Delta. The predominance

of aliphatic fragments indicates the scarcity of vascular plant remnants or the low maturation of humic substances in the terrestrial environment. The predominance of aliphatic structures is typical of humic substances formed under reducing conditions, including aquatic humic substances. The microbial and algal biomass consists of protein and membrane lipids, and sometimes carbohydrate. An aliphatic enhancement in humic substances often occurs when there is contribution of microbial biomass. At the same time, relative to other polar sectors of the Arctic (the Yamal Peninsula, a number of Russian northern islands in the Barents, Kara Seas and the Svalbard archipelago), a significant amount of aromatic fragments accumulate in soils (41-45%). This ratio is closer to the soils of the taiga zone (Abakumov et al. 2019; Lodygin et al. 2014; Polyakov et al. 2019b; Strebel et al. 2010). We previously studied a number of samples from the Lena Delta in recent works, where we noted that a significant amount of aromatic fragments accumulate in the delta in the alluvial soils of the first terrace of the river (annually flooded), as well as samples from the island of Kurungnah (typical permafrost soils). From the data obtained, it was seen that alluvial soils are more enriched in aromatic fragments, and the ratio of aliphatic to aromatic in some samples was more than one (Polyakov et al. 2018; Polyakov et al. 2019b).

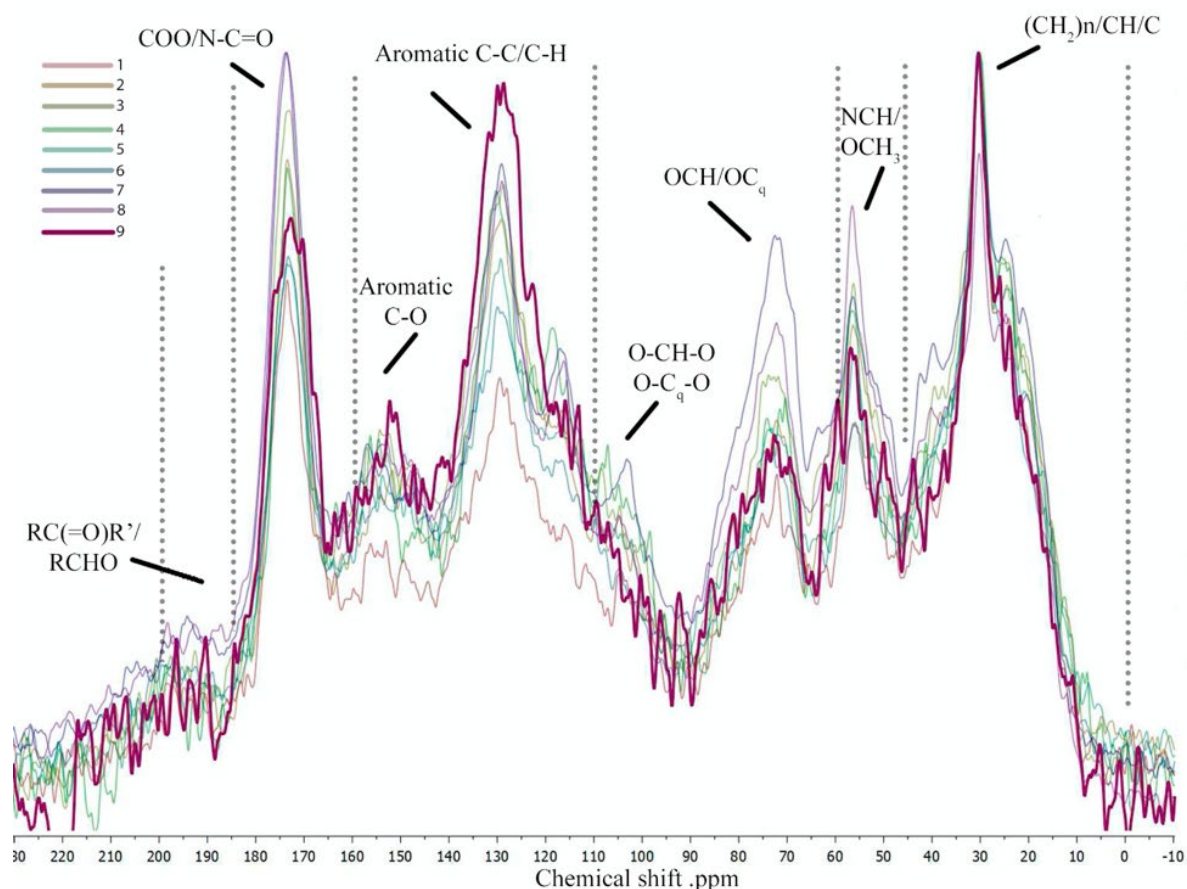


Figure 4. CP/MAS ^{13}C -NMR spectra of HAs from study soils. Number corresponds to Table 2.

Table 5. Percentage of carbon in the main structural fragments of HAs 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

| Sample | Chemical shifts, % of total C-13 signal | | | | | | AR | AL | AR/AL | AL h,r + AR h,r, % | C,H-AL/ O,N-AL |
|--------|---|-------|--------|---------|---------|---------|----|----|-------|-----------------------|-------------------|
| | 0-46 | 46-60 | 60-110 | 110-160 | 160-185 | 185-200 | | | | | |
| 1 | 28 | 8 | 21 | 27 | 14 | 2 | 41 | 59 | 0.69 | 76 | 0.97 |
| 2 | 26 | 8 | 20 | 30 | 13 | 3 | 43 | 57 | 0.75 | 76 | 0.93 |
| 3 | 24 | 8 | 21 | 30 | 14 | 3 | 44 | 56 | 0.79 | 75 | 0.83 |
| 4 | 25 | 7 | 22 | 30 | 13 | 3 | 43 | 57 | 0.75 | 77 | 0.86 |
| 5 | 25 | 7 | 22 | 29 | 13 | 4 | 42 | 58 | 0.72 | 76 | 0.86 |
| 6 | 25 | 7 | 20 | 31 | 14 | 3 | 45 | 55 | 0.80 | 77 | 0.96 |
| 7 | 24 | 8 | 24 | 28 | 14 | 2 | 42 | 58 | 0.72 | 76 | 0.75 |
| 8 | 21 | 9 | 22 | 30 | 15 | 3 | 45 | 55 | 0.82 | 73 | 0.68 |
| 9 | 22 | 7 | 21 | 33 | 14 | 3 | 47 | 53 | 0.89 | 76 | 0.79 |

3.3. Characterization of HAs from «old» alas (Kurungnah isl.)

In the «old» alas, depending on the position in the landscape, 5 soil pits were made (Figure 5).

Depending on the height, different amounts of aromatic and aliphatic HAs fragments accumulate in soils. First of all, this is due to the predominance of various types of vegetation; mosses and lichens, as precursors of humification, dominate on the windy top of alas

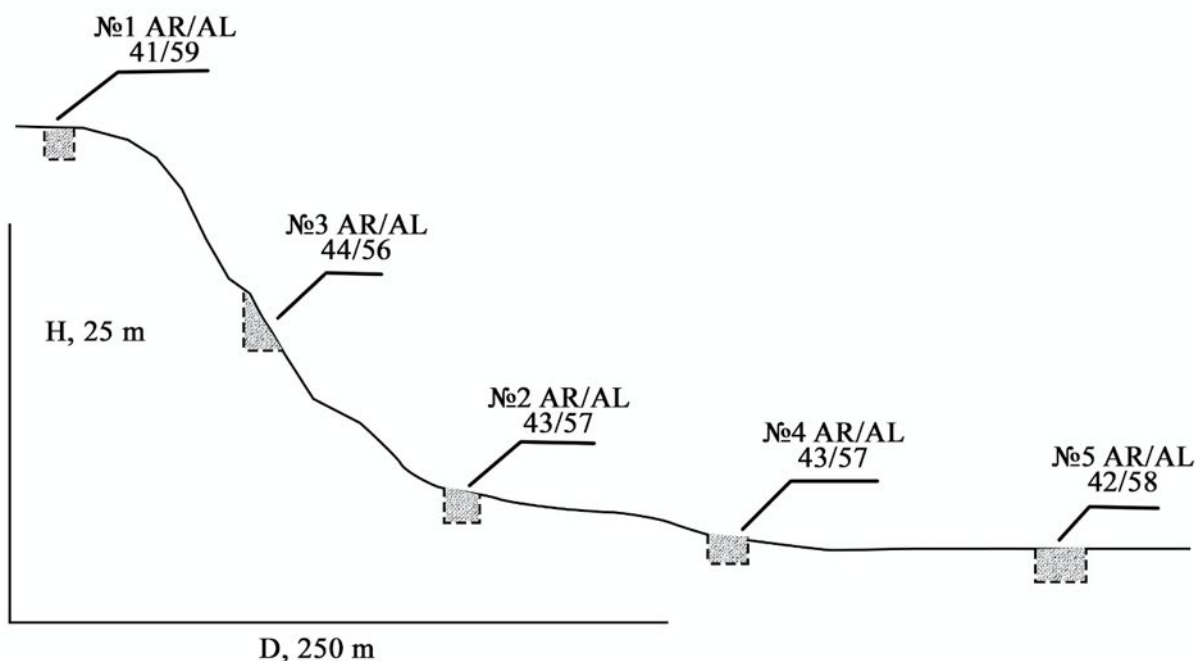


Figure 5. Soil catena of «old» alas in Kurungnah isl. AR/AL – aromatic to aliphatic compounds ratio; H – height of alas; D – distance from point 1 to point 5.

(№ 1); mosses and lichens are characterized by the presence of aliphatic constituents and lead to accumulation of aliphatic compounds in the composition of HAs. Sample № 3 is characterized by a higher content of aromatic fragments due to more favorable climatic parameters and the absence of stagnant moisture, the thickness of the active layer reaches 70 cm. This allows a greater number of shrubs to develop on the slope surface, and the southern exposure of the slope is more warmed up during the summer season, which allows the soil microbiota to transform the soil organic matter for a longer season. Sample № 2 (the bottom of the slope) is characterized by a slightly lower content of aromatic fragments. Permafrost processes are more active here, and together with a high permafrost table, stagnic conditions and the mosses and lichens prevailing in the vegetation cover, this leads to

accumulation of C,H-alkyl fragments in HAs. According to the composition of HAs, it is most similar to sample 1 and aliphatic fragments predominate the humic substances. Samples № 4 and 5, developed under conditions of excessive moisture and confined to the polygonal tundra, with increasing stagnification in the soil, and an increasing proportion of oxygen-containing fragments according to spectroscopy.

In general, the obtained spectra for this locality are characterized by a rather close position of the chemical shifts and the composition of the HAs, which indicates the homogeneity of the precursors of humification.

3.4. Characterization of HAs from «young» alas

«Young» alas landscapes and soils are about 200 years old and zonal cryoturbation processes here are not as clearly traced as in previous samples. About 200 years ago, there was a lake that began to dry out due to soil and coastal degradation. Today it represents a lowering with a several sporadic pingos, on the tops of which vegetation different from the typical tundra vegetation. The vegetation cover plays a rather important role in the formation of soil and its reserves of organic matter; in «young» alas, it is represented by perennial herbs. At that time, when there was a lake at the place of alas, a significant amount of organic residues accumulated in its bottom sediments, which, after drainage, began to actively interact with the atmosphere and already modern soils began to form in their place.

The SOM buried here turned out the most humified (45% AR) among the studied samples, as well as a high content of organic carbon. Relative to the studied soils, the highest indicator of the content of aromatic fragments (C–C/C–H, C–O) is here, this also confirms the thesis that selective degradation of condensed structures and condensation of high molecular compounds occur with depth. With an increase in the proportion of aromatic compounds, soil organic matter stabilizes, and so the soils buried here will not be subjected to active microbiological effects due to the complex structure of high molecular compounds. The vegetation cover of this site is characterized by a predominance of vascular plants with a developed root system. This results in an intensive input of lignin-derived compounds into soils. Herbaceous plants and their root system show accumulation rates of approximately 30% lignin compounds. These substances play an important role in the formation of HAs. Lignin is crucial component for formation of HAs macromolecules. Chemically, it is a three-dimensional polymer with highly branched molecule composed of phenol units with strong intramolecular bonding (Mišurcová et al. 2012). Lignin transformation ways in soils are presented both by decaying of monomers and by partial changes in the macromolecule. During lignin transformation, a decrease in the group of $-OCH_3$ fragments occurs. Demethylation is a characteristic elementary process of

humification, during the decomposition of lignin the accumulation of the COOH group occurs. Thus, an increase in the proportion of vascular plants and lignin may indicate the formation of macromolecules that are more resistant to microbial decomposition indicates the maturity of HAs. The vegetation cover of young alas is a mixture of perennial grasses with a predominance of cereals; annually, as a result of the growing season, straw forms here, which is enriched with nitrogen, carbohydrates, easily and hardly hydrolysable polysaccharides and lignin, during the transformation of which high-molecular compounds are condensed (Verkhoturova and Evstaf'ev 2016).

3.5. Characterization of HAs from Interfluve (Kharaulakh ridge)

The soils formed here are zonal variant of soil formation and can be considered the baseline for this region, this site is not under the active influence of the river. Soils are formed here under continuously windy conditions, therefore, they are represented by low-developed profiles and soil formation takes place on stony rock including carbonates. Nevertheless, the organic matter that is formed here has relatively high levels of humification and up to 45% of aromatic fragments accumulate here; the content of aliphatic fragments is mainly in the C, H–alkyl and OCH group. The high content of aromatic fragments may be due to the lack of permafrost table in the soil, since the soil cover is formed directly on the rock, while the presence of many cracks in the stones prevents the accumulation of excess moisture here and the carbonates available (from the parent rock). The precursors component composition of humic substances depends fundamentally on the type of vegetation and the microbial biomass.

3.6. Characterization of HAs from soil-like body of IC

Annually, due to the action of the river coastal erosion and abrasion, the IC of the Lena River Delta is destroyed and a huge amount of organo-mineral substance enters the atmosphere from the frozen state (Figure 6). During the interaction of organomineral components with

the atmosphere, SOM is mineralized, and carbon dioxide, water and mineral salts are released. Due to the activation of microorganisms, an enhanced cleavage (mineralization) of the aliphatic structures occurs with an increase in the degree of benzoidicity (Orlov 1990). We have conducted an analysis of this organic matter. According to radiocarbon analysis, the age of these deposits is about $34,299 \pm 500$ years BP (Schirrneister et al. 2003). During the analysis, we found that this material was the most humified among the samples we studied. If we consider theories of the origins of the IC,

our data show that a reservoir could exist in place of the IC in which the accumulation and transformation of organic matter took place. Frozen organic matter from the IC is the most stable of all the samples we studied. It seems that as a result of the accumulation of various organic residues here and their long-term transformation during the selective degradation of condensed structures, condensation of high-molecular compounds occurred, which led to an increase in the aromaticity of HAs in the soil-like bodies of the IC.

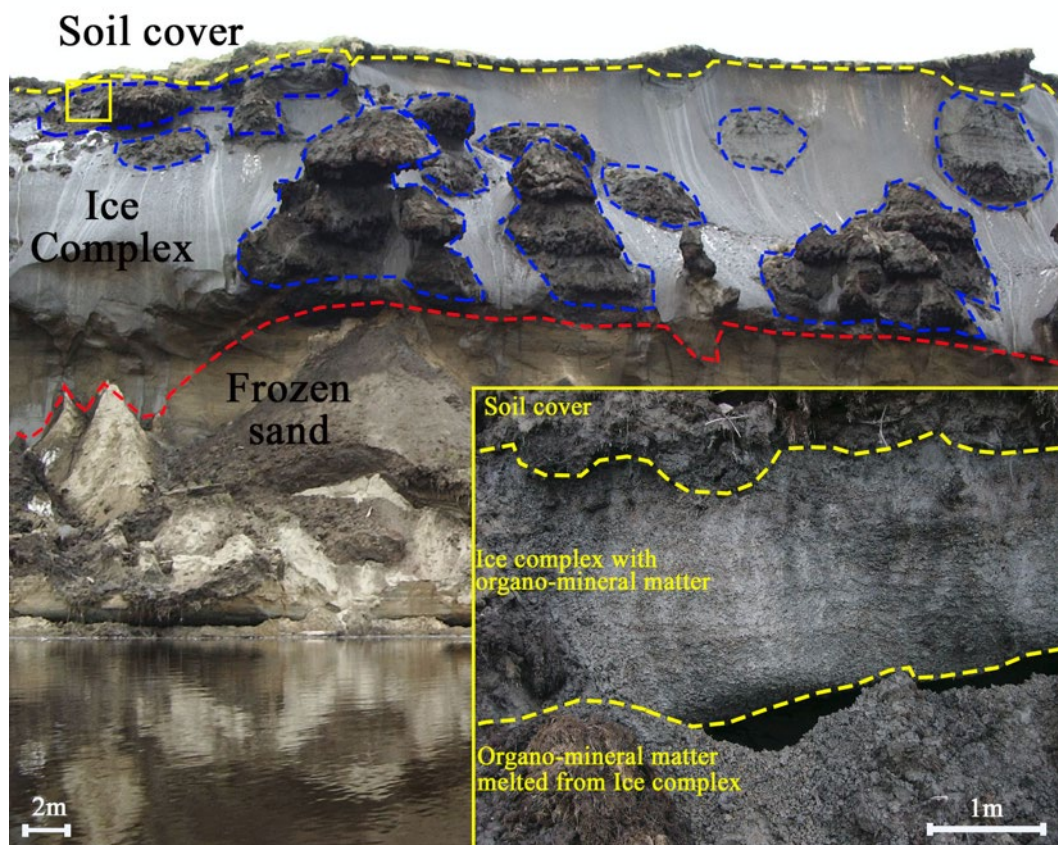


Figure 6. Structure of IC in the Lena River Delta.

3.7. Stabilization rate of organic matter from study soils

In the study samples up to 47% of aromatic compounds accumulate, which indicates the stabilization of organic matter in the soils of the Lena delta. However, aliphatic fragments

remain dominant and their accumulation is associated with the predominant mineralization process in soils. The decrease in the portion of aromatic fragments is primarily associated with low microbiological activity and precursors of humification. This ratio AR/AL in study samples leads to the accumulation of organic matter in

the soil. As a result of studying the composition of structural fragments of the studied soils, we can conclude the contribution of plant communities to the composition of HA. Thus, in sample № 6, which is formed under vascular plants with about 30% lignin, an increase in signals is observed in the interval of 110-160 ppm. Aromatic and carboxyl fragments in the structure of HA are formed around lignin transformations, which leads to increasing of the stability of HAs to biodegradation. The highest AR/AL ratio (0.89) was observed in the sample from the IC (№ 9). The aromatic fragments content is higher than in the sample formed under vascular plants (№ 6) AR/AL (0.8), this trend may be associated with cryogenic and thawing/freezing processes. The temperature amplitude in the Arctic environments can reach 90 °C. It was suggested that the humid season allows the formation of soluble precursors, and the dry season favors molecular condensation. In areas that are formed under conditions where the lignin content is minimal, under a moss-lichen cover, a decrease in aromatic fragments in the HA is noticeable due to the low content of aromatic precursors in the precursors of humification. Moreover, the

condensation of macromolecules is apparently associated with climatic features in this region. The Lena delta region is quite different from the continental part of Siberia; it has a much milder climate due to the proximity of the sea, and in the summer, the warm Lena waters with temperatures up to 18 °C also contribute to the heating of air, and, accordingly, soils. Thus, the influence of the river on this region is quite high, which favors the development of soils and the formation of HAs with a relatively high proportion of aromatic and carboxyl groups, which are more resistant to biodegradation, compared to other Arctic regions. At the same time, evolutionary selection of organic compounds takes place and high-molecular organic compounds condense at the permafrost table.

The following parameters were used to standardize the quantitative characteristics of HAs macromolecules: the ratio of carbon of aromatic structures to aliphatic, degree of decomposition of organic matter (C-alkyl/O-alkyl) and integral indicator of hydrophobicity of HAs (AL h, r + AR h, r) (Figure 7).

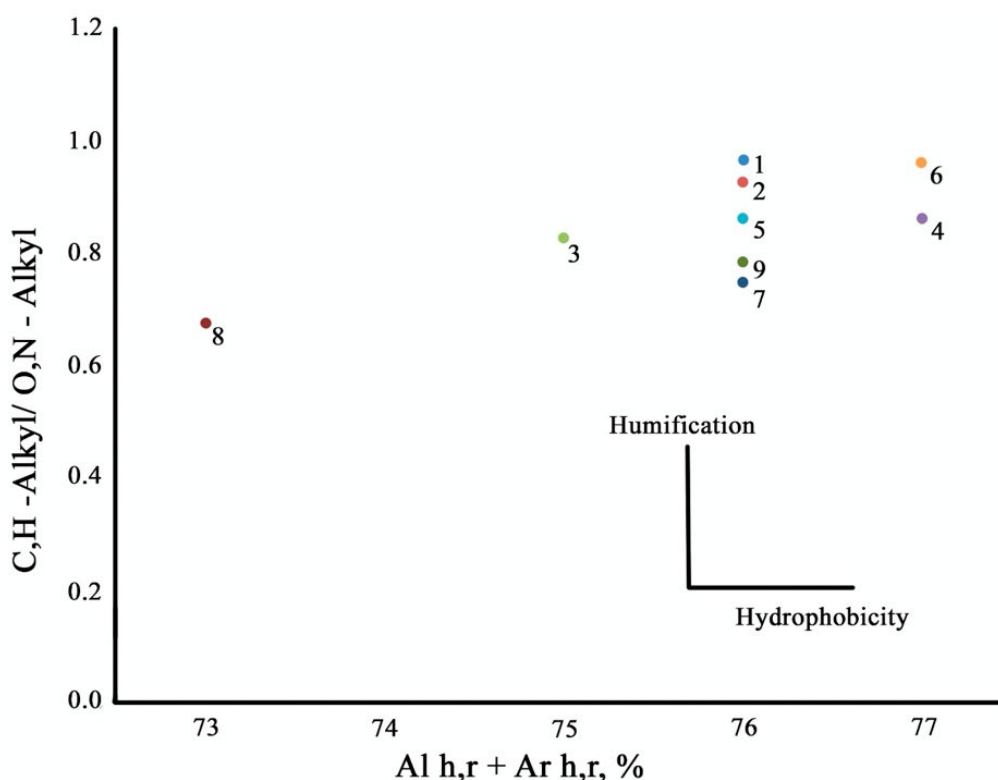


Figure 7. The diagram of integrated indicators of the molecular composition of HAs. Samples correspond to Table 2; AL h,r + AR h,r indicates the total number of unoxidized carbon atoms.

Based on the data obtained, we can conclude that aliphatic compounds ((CH₂)_n/CH/C and CH₃) and aromatic compounds (C–C/C–H, C–O) accumulate in the soils investigated. The ratio of aromatic to aliphatic fragments ranges from 0.69 for the sample on top of the «old» alas up to 0.89 for the frozen organics from the IC. The increased portions of aromatic is associated with the local position of the soils in the relief, the exposure of the slope, wind conditions, altitude, hydromorphism of the territory and plant composition. It should be noted the cryogenic activities in soil under the conditions of the Lena Delta, the parent material of which are alluvial sands, lead to a lesser development of cryogenic processes in soils. Under conditions of good drainage and soil aeration, there is a rapid heat exchange with the atmosphere, which affects the level of soil microbiological activity and thereby increases the rate of humification. Thus, during relatively active microbiological processes, a significant proportion of aromatic fragments accumulate in the delta soils. **Figure 7** shows that the most humified and hydrophobic constituents/structures are those obtained

from the buried organic matter of «young» alas. This is primarily due to the precursors of humification, and thermodynamic evolutionary selection of high-molecular compounds that accumulate at the permafrost table. In general, from the obtained diagram we can conclude that the accumulation oxygen-containing –OCH and –COOH fragments influences the redistribution of organic acids along the profile, which occurs together with the destruction of the mineral part of the soil. An increase in the proportion of aromatic fragments of HAs leads to stabilization of the organic matter in the soils of the Lena River Delta. The condensation of macromolecular compounds, which includes aromatic/unsaturated structures between 110–185 ppm, indicates an increase in the degree of hydrophobicity of soil organic matter and its low availability to soil microbiome (Semenov et al. 2009).

We carried out a statistical analysis of the principal components in the HAs of the studied soils (**Figure 8**).

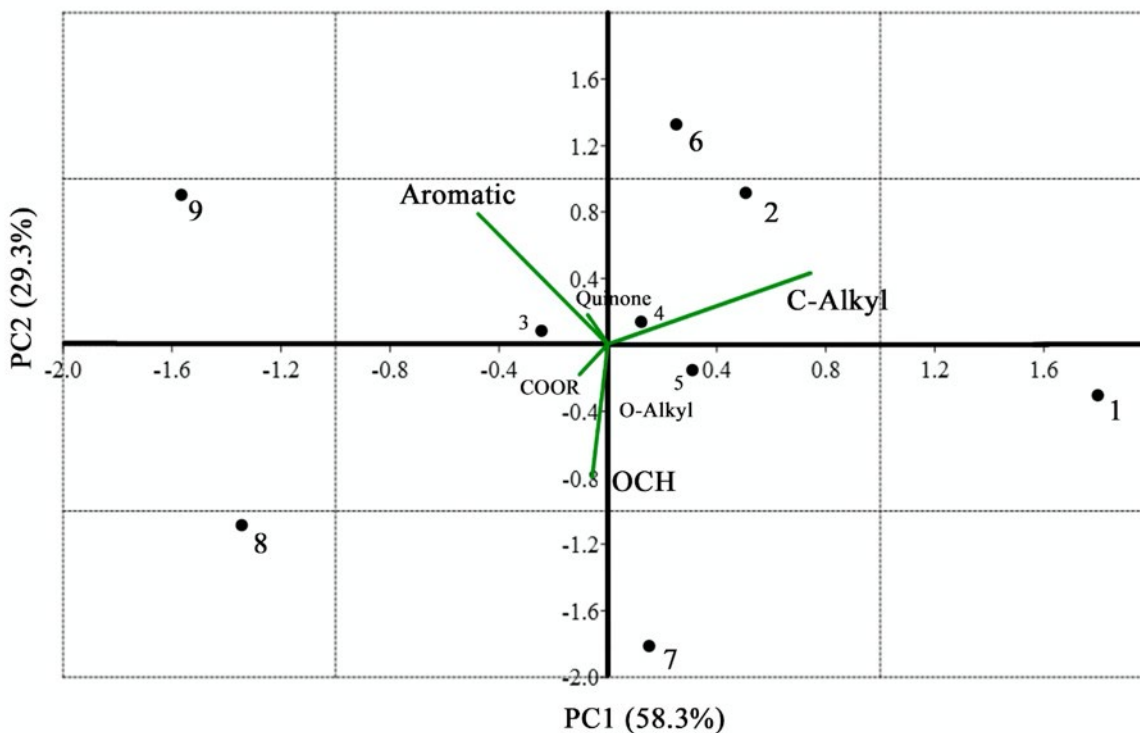


Figure 8. Representation of the samples of humic acids in the plane defined by the first two axes obtained by Principal Component Analysis (88% of the total variance explained).

Based on statistical analysis, we can conclude that there is a high correlation between the studied samples associated with the aliphatic fragments (C-alkyl PC1 (58.3%) and the aromatic fragments PC2 (29.3%). Thus, we can say that the formation processes are primarily responsible for the accumulation of long aliphatic chains present in lipids (fatty acids, paraffins), which are the result of decomposition of moss-lichen plant residues (Karmanov et al. 2015). The aromatic C component, including the aromatic group of chemical compounds, is associated with the transformation of lignin from vascular plants. In general, n-alkyl and carboxylic acids predominate among mosses, which corresponds to the composition of HAs isolated from the studied soils.

Our data are confirmed by previously published materials from scientists working in the Arctic sector and for permafrost-affected soils (Abakumov et al. 2015; Beznosikov and Lodygin 2010; Ejarque and Abakumov 2016). The dominance of aliphatic HAs' fragments is associated with the specific composition of the vegetation cover, soil microbiological composition, and climatic conditions (Lupachev et al. 2017; Polyakov and Abakumov 2020; Szymański 2017). The taiga zones are more similar in terms of HAs composition; here, the aromaticity of the studied HAs of podzols increases to 44% and the European Arctic of Russia to 50% (Lodygin et al. 2014; Pengerud et al. 2017). These regions combine the features of the vegetation cover; the studied tundra and taiga zone is characterized by the predominance of moss-lichen vegetation, which is a source of carbohydrates and various lipids. Thus, the annual change in climatic parameters, cryogenic processes, and the precursors of humification determine the composition of HAs in the study area. The predominance of moss-lichen communities contributes to the formation of long aliphatic chains in the HAs macromolecules. The change of plant communities to vascular plants and the alternation of humid and dry seasons promotes the condensation of aromatic and carboxylic fragments of HAs, which are associated with the resistance of organic material to biodegradation (Abakumov et al. 2015; Beznosikov and Lodygin 2010; Lodygin et al. 2014).

4. Conclusions

The key role in the formation of HAs in the soil is related to the processes of condensation and the polymerization of compounds formed from precursors of plant and microbial origin. Humic acids are structurally dynamic macromolecules, the condensation of which depends on external and internal environmental factors that determine their resistance to biodegradation. During the temporal development of soils, the H/C ratio decreases, which leads to the accumulation of aromatic fragments in the composition of HAs. An increase in the aromaticity of soil HAs lead to a decrease in the rate of soil mineralization and as a result, its destabilization (protection) from microbiological decomposition.

Analysis of the molecular composition of HAs by ¹³C-NMR spectroscopy also shows that aromatic fragments (up to 47%) are accumulated in HAs of the Lena River Delta soils. The ratio AR/AL varies in soils from 0.69 to 0.89, which indicates the leading processes of mineralization in the soil. The predominance of moss-lichen communities consisting of lignin-lacking plants leads to the accumulation of aliphatic fragments of HAs, which are dominant in the Lena River Delta. In comparison with the HAs that were formed under the current processes of humification we can conclude that the organic residues from the IC are the most humified among the studied samples, which may be the result of long-term climatic changes and condensation of HAs macromolecules in the IC. Plant communities with a predominance of lignified vascular plants are characterized by a higher content of aromatic and carboxylic fragments in the composition of HAs, which indicates the maturity of organic matter in the Lena Delta region.

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