



Environmental aspects of molecular composition of humic acids isolated from lake sediments of a permafrost-affected area of the Arctic

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Abstract: Humic substances are ubiquitous in terrestrial and aquatic ecosystems. Humic acids (HAs) actively interact with organic and inorganic components of lake sediments. This interaction depends on the molecular structure and elemental composition of HAs. The presented research focuses on the investigation of the composition and molecular structure of humic acids isolated from lakes located in the Lena Delta in the Russian Arctic. The findings of the research are needed to estimate the potential capacity of humic acids to bind microelements, particularly toxic metals, in stable compounds. Surface sediment samples (0–10 cm) were collected from 8 lakes by Van Veen grab during the summer period of the “Expedition LENA 2019”. We analyzed elemental composition of the HAs samples. The results showed that the studied HAs of lake sediments are characterized by low nitrogen content and prevalence of aliphatic fragments in their molecular structure. Furthermore, it was found that the studied humic acids are less mature, showing mineralization processes dominant over humification, and have relatively low potential to complexation compared with soils of the Lena Delta as well as lake sediments of territories with more boreal climate conditions.

Keywords: Arctic, Siberia, Lena Delta lakes, humic substances, permafrost.

Introduction

The progressive industrialization and urbanization sparked an increasing interest of researchers in Arctic ecosystems, which are entities highly sensitive and vulnerable to anthropogenic impact. Therefore, it is important to estimate the



self-purification capacity of Arctic lakes for further environmental monitoring of the region. For this purpose, it is necessary to conduct comprehensive geochemical research of aquatic ecosystems.

Sediments of small lakes, including Arctic limnosystems, usually contain a significant percentage part of organic matter. Humic substances are ubiquitous in terrestrial and aquatic ecosystems. Furthermore, they constitute a significant accumulation matrix of carbon in the global biogeochemical cycle. According to the prevalent view, humic substances are self-organizing persistent systems that are formed under non-equilibrium environmental conditions (Ostenberg and Shirshova 1997; Kholodov *et al.* 2015). The quality and composition of humic substances differ accordingly with the variability in the parent material (Garcia and Polo 1985), vegetation (Singhal and Sharma 1983) and climate (Dziadowiec *et al.* 1994). Transformation of organic matter in north lake ecosystems proceeds under specific climate conditions – low temperature, considerable humidity, a short period of biological activity, and anoxic aquatic environment. These parameters influence processes of humification and mineralization of organic matter, and consequently – the molecular composition of humic substances. The predominant fractions of humic substances are humic acids (HAs). The acids actively interact with organic and inorganic components of sediment, particularly with contaminants (Szalay 1969; Rashid 1971; Dong *et al.* 2021). However, this interaction depends on the molecular structure and elemental composition of HAs. HAs and metal ions form stable complexes, in particular chelating compounds. This process contributes to the decreasing of toxicity and bioavailability of metals in terrestrial and aquatic ecosystems (Van Dijk 1971; Rashid 1974; Dong *et al.* 2021). Complexation ability is a typical feature of all carboxylic acids, especially in the presence of electron donor groups: NH_2 , $-\text{OH}$, $> \text{C}=\text{O}$, $-\text{COOH}$, $-\text{SH}$, $> \text{NH}$, $=\text{N}$. The considerable potential of HAs to form chelate compounds has been shown for Al, Fe, Cu, Pb, and other polyvalent cations (Atkinson and Wright 1957; Himes and Bcu'ber 1957). Carboxyl and phenol hydroxyl groups are predominantly involved in the binding of metals. Furthermore, it was shown that the presence of quinone and semiquinone groups determines the course of reactions involving the humic acids by a free radical mechanism, in particular the reduction of metal ions (Senesi 1981).

The majority of studies on HAs have focused on the geochemical features of substances extracted from soils (Dziadowiec *et al.* 1994; Pengerud *et al.* 2017; Polyakov *et al.* 2019 a, b; Lodygin and Vasilevich 2020; Polyakov and Abakumov 2020). However, the results obtained for humic substances of lake sediments do not go beyond HAs extracted from lake sediments of permafrost-affected areas (Golebiowska *et al.* 1996; Belzile *et al.* 1997; Klavins and Apsite 1997; He *et al.* 2008). The Lena Delta is a potentially pristine permafrost-affected area of the Arctic. In some cases, it can be used as a reference region for geochemical research of permafrost-affected landscapes. However, dangerous pollutants, especially toxic metals, can be atmospherically transported far from

their sources. Consequently, some metals are accumulated in remote aquatic ecosystems (Bartnicki 1994; Pacyna and Pacyna 2001). The earlier studies (Guzeva and Fedorova 2020), performed in two lakes located on Samoylov Island (the Lena Delta), have demonstrated that organic substances play the significant role in the accumulation of metals (Fe, Mn, Co, Cr, Cu, Ni, Pb, V, and Zn). Therefore, the information about geochemical features (elemental composition and molecular structure) of HAs extracted from lake sediments of this territory is required to estimate the capability of HAs to bind microelements in stable (non-bioavailable) compounds. The goal of this study is to investigate the elemental composition and molecular structure of HAs acquired from the lakes located in the Lena Delta.

The findings of the work are important for further investigations of the global carbon cycle in the Arctic. Among that, the results can be useful for comprehensive geochemical monitoring of lakes located in the other parts of the Arctic region.

Study area

The Lena, which flows into the Arctic Ocean, is one of the biggest rivers in the Russian Arctic. The most part of the territory of the Lena Delta is characterized by the presence of a permafrost table at a depth of about 1 meter. The Lena Delta is covered with various types of tundra vegetation. The main components are lichens, mosses, grasses, and some types of shrubs. More than 30,000 lakes of different origins and sizes have formed there, due to climatic, hydrological, and permafrost (thermokarst) conditions of the region (Bolshiyarov *et al.* 2013). Three main geomorphological terraces have been distinguished within the area of this delta (Grigoriev 1993; Schwamborn *et al.* 2002). Their different geneses, deposit types, and relief-forming processes were at the root of the differences in predominant lake types (Morgenstern *et al.* 2008). The first terrace is characterized by a high density of small water bodies, mainly polygonal ponds, small thermokarst, and oxbow lakes. Samoylov Island located within this terrace was formed about 3–4 ka BP (Schwamborn *et al.* 2002; Guzeva and Fedorova 2020). There are large elongated thermokarst lakes on the second terrace. Thermokarst lakes also prevail within the third terrace. They are often situated in partially drained deep basins, *i.e.*, alasses. The alasses are major components of the ice-rich permafrost landscape of the third terrace. It was formed between 13 and 12 ka BP (Morgenstern *et al.* 2011).

Our investigation focused on the lakes that have different geneses and flood regimes: those located on the first terrace (Samoylov Island) and the third terrace (Kurungnakh Island) (Fig. 1).

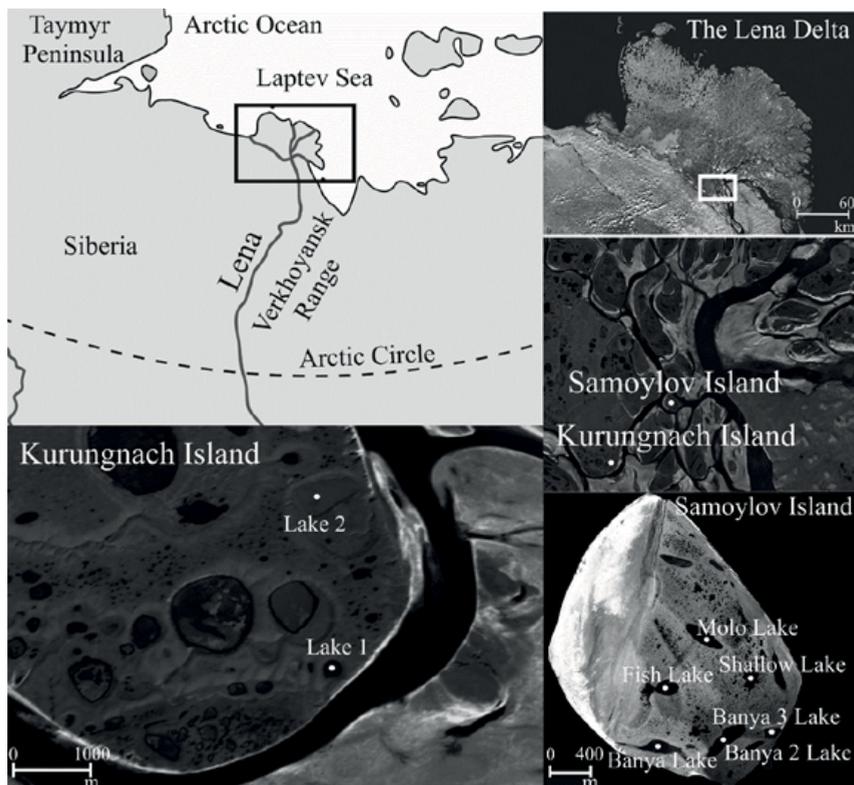


Fig. 1. Location of the studied lakes in the Lena Delta, the Russian Arctic.

Materials and methods

Surface sediment samples (0–10 cm) were collected from eight lakes by Van Veen grab during the summer period of the “Expedition LENA 2019” (Fig. 1). We took five samples from different parts (depths) of each lake to make an integral sample for further laboratory analysis. The hydrological, morphometric (Chetverova *et al.* 2017), and geomorphological characteristics of the studied lakes are presented in Table 1. During the sampling procedure, field description of the lake sediments was made with respect to their colour, smell, granulometric characteristics, and presence of vegetable debris.

Sediment samples were air-dried at 20°C, ground, and passed through 2 mm and 0.2 mm sieves. The total content of dispersed organic matter was analyzed by digestion of absolute dried samples at 550°C for 5 hours. It allows characterizing the degree of enrichment of sediments with decomposing organic material.

Humic acids were extracted from each sample according to a published IHSS protocol (Swift 1996). Elemental analysis (C, H, N % content) was conducted with the element analyzer Euro EA3028-HT (EuroVector, Italy). The combustion

Table 1

Geomorphological, morphometric and hydrological characteristics of the studied lakes of the Lena Delta.

| Lake | Area (island), geomorphological terrace ¹ | Latitude; longitude | Min/max depth of sampling, m | Genesis, hydrological regime ² |
|--------------|--|-----------------------|------------------------------|--|
| Lake 1 | Kurungnakh Isl., 3 rd terrace | 72.17061; 126.120367 | 0.8 / 6.1 | Thermokarst, isolated from river influence |
| Lake 2 | Kurungnakh Isl., 3 rd terrace | 72.30856; 126.245461 | 0.5 / 1.1 | Thermokarst, isolated from river influence |
| Banya Lake | Samoylov Isl., 1 st terrace | 72.368416; 126.485911 | 1 / 5.2 | Oxbow, regularly affected by seasonal river floods |
| Banya 2 Lake | Samoylov Isl., 1 st terrace | 72.370005; 126.504722 | 1 / 16.3 | Oxbow, affected by high seasonal river floods |
| Banya 3 Lake | Samoylov Isl., 1 st terrace | 72.370402; 126.517214 | 1 / 6.3 | Oxbow, regularly affected by seasonal river floods |
| Molo Lake | Samoylov Isl., 1 st terrace | 72.378141; 126.497031 | 2.6 / 6.2 | Thermokarst, isolated from river influence |
| Shallow Lake | Samoylov Isl., 1 st terrace | 72.375062; 126.511043 | 0.5 / 3.1 | Polygonal |
| Fish Lake | Samoylov Isl., 1 st terrace | 72.373635; 126.486923 | 0.5 / 12.7 | Thermokarst, isolated from river influence |

¹According to Grigoriev (1993) and Schwamborn et al. (2002); ²according to Chetverova et al. (2017).

of the samples was carried out at temperatures of about 1300°C. Data were corrected for water and ash content. Oxygen content was calculated by the difference of whole mass of the sample and gravimetric concentration of C, N, H, and ash. To analyze the molecular structure of humic acids, two modern spectroscopy methods were used. Solid-state CP/MAS ¹³C-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer (Bruker Corporation, USA) in a 3.2-mm ZrO₂ rotor. The magic angle spinning frequency was 20 kHz in all cases and the nutation frequency for cross-polarization was $u/2p \ 1/4 \ 62.5$ kHz. The repetition delay was 3 seconds. The number of scans was 6500–32000. Contact time was 0.2 μ s. The IR spectra of samples were recorded within the range 4000–500 cm^{-1} using a FTIR-spectrometer IRAffinity (Shimadzu Corporation, Japan). All the samples were compressed with KBr in pellets. The spectra were recorded at room temperature.

All analyses were performed in triplicate. The result was accepted as correct if the difference in values did not exceed 20%. Then we used the mean value for each sample.

To calculate ratios C/N, C/H, O/C, mole fractions C, H, N, and O were used. The atomic ratios of C/N, C/H, and O/C are often used to monitor structural changes of humic substances from different sources (Steelink 1985). $H/C_{\text{mod}} = (H/C) + 2(O/C) \times 0.67$ (the number of substituted hydrogen atoms in the HAs) and $W = (2O - H)/C$ (degree of oxidation) indexes were calculated according to Orlov (1985). One of the most widely used approaches for graphical representation of the elemental composition and structure of HAs from soils (that can be used for sediments as well) is the method outlined by Kleinhempel (1970). The technique is based on a graphical representation of the data in the coordinates $H/C_{\text{mod}} - O/C$. This diagram demonstrates the contribution of oxidation and condensation to changes in the elemental composition of HAs (Lodygin *et al.* 2014; Polyakov *et al.* 2019a; Polyakov and Abakumov 2020).

The Fourier transform method with the subsequent adjustment of a baseline was used for processing of ^{13}C -NMR spectra using the program MagicPlot. Quantitative treatment was carried out via numerical integration by the areas corresponding to the positions of functional groups and molecular fragments. To access the qualitative characteristics of HAs macromolecules, the following indexes were used: the ratio of aromatic to aliphatic carbon (AR/AL) (Lorenz *et al.* 2006) and the degree of organic matter decomposition (C,H-alkyl/O, N-alkyl) (Pedersen *et al.* 2011). In addition, the integral parameter of the hydrophobicity of molecules ($AL_{\text{H, R}} + AR_{\text{H, R}}$) was used. This index is the sum of unoxidized carbon atoms in the molecules. The parameter provides information about the amphiphilic properties of HAs (Lodygin *et al.* 2014). CorelDraw Graphics Suite 2018 software was used to graphically illustrate the results.

Results and discussion

Total content of dispersed organic matter in the sediment samples. — First, the total content of dispersed organic matter in the surface layer of lake sediments was analyzed (Table 2). The studied lakes have different geneses, geomorphological locations, and river flood regimes. The thermokarst lakes of Kurungnakh Island are characterized by higher content of organic matter compared with lakes of Samoylov Island. The studied oxbow and thermokarst lakes of Samoylov Island, which are isolated from river waters, have lower organic content (4–6%) than those regularly flooded by the Lena (Banya Lake and Banya 3 Lake). It can be related to influx of allochthonous organic matter from river waters.

The studied lakes of the Lena Delta have argillaceous sediments with a low concentration of dispersed organic matter. However, lake sediments of Samoylov Island contain a lot of poorly decomposed vegetable debris (Table 2). This fact can be explained by the very slow post-depositional degradation of organic carbon. It is supported by results of another research on Arctic lake sediments

Table 2

Total content of dispersed organic matter in the sediment samples.

| Lake | Genesis, hydrological regime | Total content of dispersed organic matter, % | Field description of sediments |
|------------------------------|--|--|--|
| Lake 1 (Kurungnakh Isl.) | Thermokarst, isolated from river influence | 12.5 | Brown sand with aleurite layers; there are no vegetable debris |
| Lake 2 (Kurungnakh Isl.) | Thermokarst, isolated from river influence | 13.5 | Grey sand with aleurite layers; there are no vegetable debris |
| Banya Lake (Samoylov Isl.) | Oxbow, regularly affected by seasonal river floods | 7.8 | Grey aleurite with loam; a lot of vegetable debris |
| Banya 2 Lake (Samoylov Isl.) | Oxbow, affected by high seasonal river floods | 6.0 | Grey aleurite; a lot of vegetable debris |
| Banya 3 Lake (Samoylov Isl.) | Oxbow, regularly affected by seasonal river floods | 15.0 | Grey aleurite with loam; a lot of vegetable debris |
| Molo Lake (Samoylov Isl.) | Thermokarst, isolated from river influence | 6.3 | Grey loam; a lot of vegetable debris |
| Shallow Lake (Samoylov Isl.) | Polygonal, isolated from river influence | 4.5 | Grey loam with aleurite layers; there are vegetable debris |
| Fish Lake (Samoylov Isl.) | Thermokarst, isolated from river influence | 4.0 | Grey loam; a lot of vegetable debris |

(Sobek *et al.* 2010). Additionally, the significant temperature correlation of organic carbon mineralization in lake sediments (Gudasz *et al.* 2010) implies that the generally low water temperatures in Arctic lakes may hamper organic matter mineralization in sediments. Consequently, this process contributes to organic carbon burial. Moreover, humic substances can impregnate undecomposed plant residues and block their further transformation, including mineralization (Aristovskaya 1980).

Elemental analysis of the HAs samples. — The elemental composition of HAs is an important indicator determining the progress of humification, oxidation, and condensation degree of this type of humic substances (Beznosikov and Lodygin 2010; Abakumov *et al.* 2015). The obtained data on HAs elemental composition, atomic ratios, and degree of oxidation (W) are presented in Table 3.

The carbon content varied over a wide range, from 28 to 48%, in the studied sediment samples. The nitrogen content did not exceed 2% in most samples, but a single sample (from Molo Lake) contained 3% of N. The C/N ratio varied from 16 to 43. A low level of enrichment of carbon by nitrogen was also observed in soil HAs of Kurungnakh Island in the Lena Delta (Polyakov and Abakumov

Table 3

Elemental composition of the studied HAs isolated from the lake sediments. Gravimetric concentration is given for C, H, O, and N content. Mass measurement error is 0.3% for C, 0.2% for N and H; C/N, H/C, O/C, H/C_{mod}, and W were calculated from mole fraction of C, H, O, and N content; H/C_{mod} and W indexes were calculated according to (Orlov 1985).

| Lake | N, % | C, % | H, % | O, % | C/N | H/C | O/C | H/C _{mod} ¹ | W ² |
|--------------------------------|------|------|------|------|------|-----|-----|---------------------------------|----------------|
| Kurungnach Isl., Lake 1 | 2.1 | 33.9 | 3.9 | 56.1 | 18.8 | 1.4 | 1.2 | 3.0 | 1.1 |
| Kurungnach Isl., Lake 2 | 1.3 | 48.2 | 5.6 | 39.9 | 43.9 | 1.4 | 0.6 | 2.2 | - 0.1 |
| Samoylov Isl., Banya Lake | 1.6 | 28.5 | 3.7 | 61.2 | 21.0 | 1.5 | 1.6 | 3.7 | 1.7 |
| Samoylov Isl., Banya 2 Lake | 2.0 | 41.7 | 4.7 | 46.6 | 24.2 | 1.3 | 0.8 | 2.5 | 0.3 |
| Samoylov Isl., Banya 3 Lake | 1.0 | 30.9 | 3.4 | 59.8 | 37.7 | 1.3 | 1.5 | 3.2 | 1.6 |
| Samoylov Isl., Molo Lake | 3.1 | 43.0 | 4.8 | 45.0 | 16.1 | 1.3 | 0.8 | 2.4 | 0.3 |
| Samoylov Isl., Shallow Lake | 2.0 | 41.7 | 4.7 | 47.6 | 24.2 | 1.3 | 0.9 | 2.5 | 0.4 |
| Samoylov Isl., Fish Lake | 1.6 | 31.1 | 3.7 | 58.5 | 22.8 | 1.4 | 1.4 | 3.3 | 1.4 |

¹H/C mod – the number of substituted hydrogen atoms in the HAs, $(H/C)_{mod} = (H/C) + 2(O/C) \times 0.67$;

²W – oxidation coefficient, $W = (2O - H)/C$.

2020) and other regions of the Arctic (Polyakov *et al.* 2019a). It could be associated with the specific conditions of nitrogen accumulation in the Arctic systems, where the processes of nitrogen fixation and ammonification are low due to the low microbiological activity. However, HAs of water objects are generally characterized by relatively low nitrogen content (Müller-Wegerener 1988). For example, high values of C/N ratio for HAs molecules were observed in sediments of lakes located in more southern regions (boreal climate conditions) (Belzile *et al.* 1997; Klavins and Apsite 1997). This aspect of the elemental composition of HAs extracted from permafrost-affected lake sediments should be further investigated.

The oxygen content in studied samples varied from 40 to 61%. The highest values corresponded to the HAs isolated from Banya and Banya 3 Lakes (Samoylov Island). The H/C ratio varied from 1.3 to 1.5 (Table 3). The H/C is the most reliable integral parameter, which reflects indirectly a degree of condensation (stability) of HAs molecules. The lower this indicator, the higher the process of condensation of monomers in high-molecular substances. However, for HAs this ratio should be corrected (H/C_{mod}) taking into account the oxygen content (Orlov 1985). The patterns of HAs formation are shown in the H/C_{mod} – O/C diagram (Fig. 2).

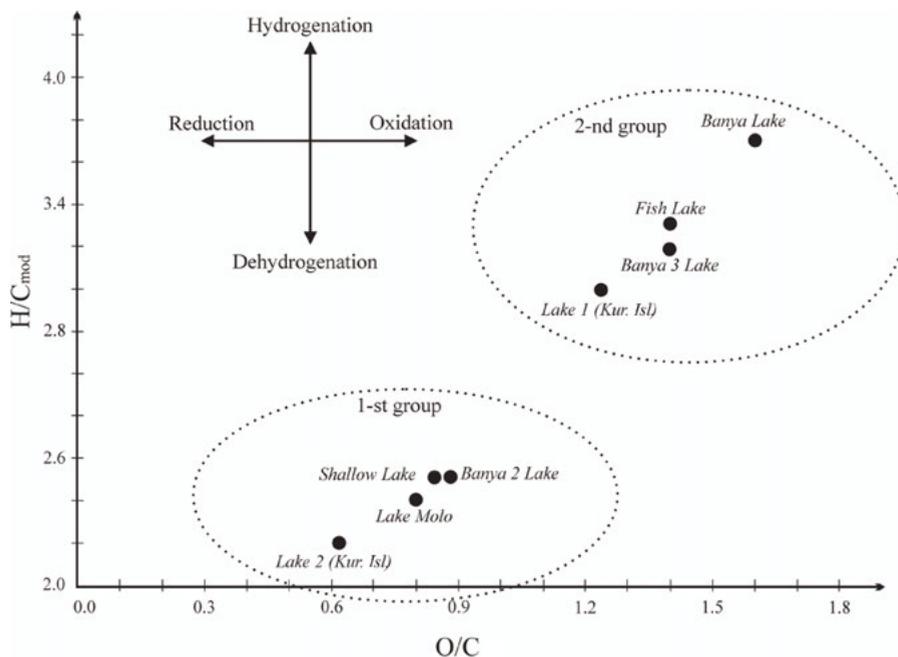


Fig. 2. Elemental composition of the studied HAs isolated from lake sediments. H/C_{mod} stands for the number of substituted hydrogen atoms; O/C is the atomic ratio of O and C.

According to above diagram (Fig. 2) and W-index (oxidation degree) values (Table 3), the studied lakes can be divided into two groups: the HAs of the second group are characterized by a more oxidized state (high content of oxygen-containing fragments) than those in the first group of lakes. Furthermore, the sample from Lake 2 (Kurungnach Island) had weak reducing conditions. It can suggest that the sediment organic matter in the studied lakes of the second group is relatively more mature, because the humification process is associated with the increase of the degree of oxidation of its products (Orlov 1985). According to Lupachev *et al.* (2017), and Polyakov and Abakumov (2020), HAs formed in cold climate conditions, especially in permafrost-affected soils, have a relatively high H-content and a reduced O-content compared to boreal and sub-boreal soils. Generally, HAs isolated from the studied permafrost-affected lakes were characterized by the same feature – H/C ratio exceeds O/C ratio in most samples. The opposite results (O/C ratio exceeded H/C) were obtained for HAs extracted from lakes located in boreal climate zone (Belzile *et al.* 1997; Klavins and Apsite 1997).

CP/MAS ^{13}C -NMR analysis of the HAs samples. — HA samples were characterized by broad absorption spectral areas resulting from the overlapping of several lines (Fig. 3). The first intensive signal was detected in the range of unsubstituted aliphatic fragments 0–46 ppm in all studied samples. All ^{13}C -NMR spectra had one relatively sharp peak in the 29–30 ppm region. It can be associated with methylene atoms of carbon in positions α , β , δ , and ϵ from methyl

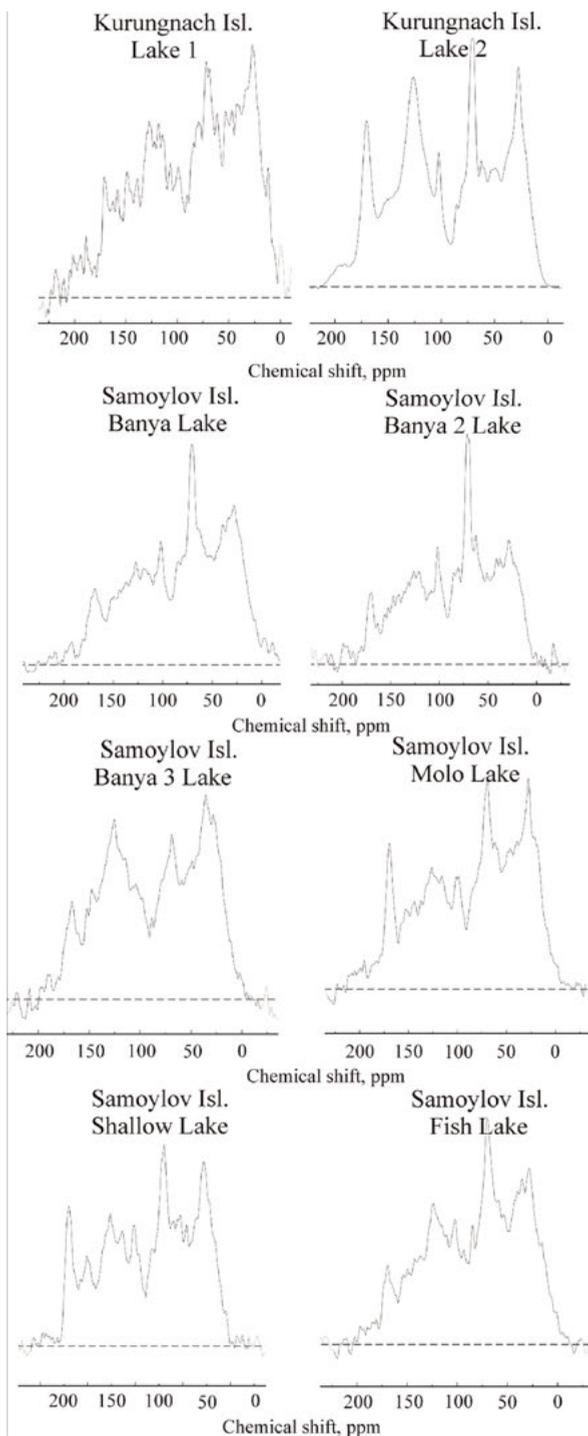


Fig. 3. ^{13}C -NMR spectra of humic acids isolated from lake sediments of the permafrost affected area of the Lena Delta, the Russian Arctic.

end-groups (15 ppm) in alkyl chains (Simpson and Simpson 2009; Lodygin and Vasilevich 2020). According to some authors (Lodygin and Beznosikov 2005; Vasilevich *et al.* 2018), for soil and peat HAs, these methylene carbon atoms can originate from an accumulation of wax resins, lipids, and suberin plant structures. Furthermore, all spectra demonstrated a relatively weak signal in the range of 47–60 ppm. Some researchers relate this signal to methoxyl groups resulting from the presence of lignin fragments (Kovaleva and Kovalev 2015; Tadini *et al.* 2015) or to carbon atoms in the α position in polypeptides ($-\text{C}(\text{O})-\text{C}^*(\text{R})\text{H}-\text{NH}-$) $_n$ (Knicker *et al.* 2008; Lodygin and Vasilevich 2020). Therefore, the studied sediment HAs were characterized by relatively low content of lignin fragments (substances of vascular plant cells) or N-contend polypeptides. All spectra also had an intense signal at the range of 70–71 ppm, which is characteristic of carbons in CH(OH) groups – the ring carbons of carbohydrates (Simpson and Simpson 2009).

Furthermore, a weak signal at about 62 ppm is typical of CH₂O hexose groups in polysaccharide fragments. There were also relatively intensive lines at 101 ppm, which suggest the presence of carbohydrate fragments in the studied HAs (Duarte *et al.* 2008). All spectra had signal in the spectral range of aromatic fragments (110–160 ppm), which was produced by H-substituted or O, N-substituted aromatic carbon atoms. The area 160–185 ppm (with a maximum line at 168–170 ppm) was assigned to atoms of carboxyl fragments (Lodygin and Beznosikov 2010) or it could also refer to the carbonyl-amide group (Keeler *et al.* 2006). The atoms of quinone fragments, the carbonyl groups of ketones and aldehydes provided weak peaks in the ranges of 185–200.

Thus, different molecular fragments were identified in the studied HAs samples using CP/MAS ¹³C-NMR spectroscopy (Table 4): carboxyl ($-\text{COOR}$), carbonyl ($-\text{C}=\text{O}$); CH₃–, CH–aliphatic, $-\text{C}-\text{OR}$ alcohols, esters and carbohydrates, phenolic (Ar–OH), quinone (Ar = O) and aromatic (Ar–) groups. All lines of the carbon species, required for the identification of the analyzed substances as humic acids, were obtained. The observed molecular fragments indicate the significant complexity of the molecular structure of HAs (Lodygin *et al.* 2014;

Table 4

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

| Chemical shift, ppm | The type of molecular fragments |
|---------------------|--|
| 0–47 | C, H-substituted aliphatic fragments (non-polar alkyls) |
| 47–60 | Methoxyl 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 |

Yao *et al.* 2019; Lodygin and Vasilevich 2020) and, therefore, influence their specific role in natural geochemical processes.

The chemical shifts of studied HAs samples are presented in Table 5. We identified three main groups of molecular fragments in the HAs of the studied lakes. These were 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 was calculated from the sum of the shifts of 110–185 ppm. Aliphatic fragments were calculated from the sum of the shifts of 0–110 ppm, 185–200 ppm.

Table 5

Percentage of carbon in the main structural fragments of humic acids isolated from the studied lake sediments (according to CP/MAS ¹³C-NMR data).

| Lake | Chemical shifts, % of total ¹³ C signal | | | | | | | | | | |
|-----------------------------|--|-------|--------|---------|---------|---------|-----------------|-----------------|-------|---|-----------------|
| | 0-47 | 47-60 | 60-110 | 110-160 | 160-185 | 185-200 | AR ¹ | AL ² | AR/AL | AL _{H,R} + AR _{H,R} , % | C, H-AL/O, N-AL |
| Kurungnach Isl., Lake 1 | 29 | 2 | 29 | 27 | 12 | 3 | 38.6 | 61.4 | 0.6 | 55.4 | 0.9 |
| Kurungnach Isl., Lake 2 | 21 | 11 | 24 | 33 | 8 | 3 | 41.3 | 58.8 | 0.7 | 54.4 | 0.6 |
| Samoylov Isl., Banya Lake | 29 | 7 | 22 | 37 | 4 | 0,3 | 41.1 | 58.9 | 0.7 | 66.4 | 1.0 |
| Samoylov Isl., Banya 2 Lake | 20 | 12 | 29 | 34 | 5 | 1 | 38.3 | 61.8 | 0.6 | 53.3 | 0.9 |
| Samoylov Isl., Banya 3 Lake | 30 | 10 | 23 | 29 | 7 | 1 | 36.0 | 64.0 | 0.6 | 58.5 | 0.9 |
| Samoylov Isl., Molo Lake | 28 | 4 | 34 | 25 | 7 | 2 | 31.6 | 68.3 | 0.5 | 52.7 | 0.7 |
| Samoylov Isl., Shallow Lake | 29 | 5 | 34 | 25 | 7 | 1 | 31.7 | 68.2 | 0.5 | 54.0 | 0.8 |
| Samoylov Isl., Fish Lake | 35 | 7 | 28 | 26 | 3 | 2 | 28.4 | 71.6 | 0.4 | 60.5 | 1.0 |

¹AR – aromatic fraction; ²AL – aliphatic fraction; AL_{H,R} + AR_{H,R} % – hydrophobicity degree; C, H-AL / O, N-AL – the degree of decomposition of organic matter.

Aliphatic fragments of HAs (58–71%) significantly prevailed in the studied sediments. It was also observed for HAs of some soil types of the Lena Delta (Polyakov and Abakumov 2020). This fact indicates the dominant mineralization process of organic matter in the soils and lake sediments of this territory. The predominance of aliphatic fragments suggests the low maturity of humic substances. However, this molecular feature is typical of humic substances formed under anoxic conditions. The significant predominance of aliphatic fragments in the structure of aquatic HAs was also observed in other regions with boreal climate conditions (Belzile *et al.* 1997; Klavins and Apsite 1997).

Lakes of the second group (Fig. 4) were characterized by a higher degree of humification and hydrophobicity (maturity) of HAs in sediments than those from the first group. The results obtained are in agreement with the results of elemental analysis. However, according to Polyakov and Abakumov (2020), the total portion of unoxidized HA carbon in the soils of the Lena Delta (Kurungnach Island) ranges from 73 to 76%. Therefore, soil HAs of this territory are more mature and resistant to oxidation compared to the studied HAs of lake sediments.

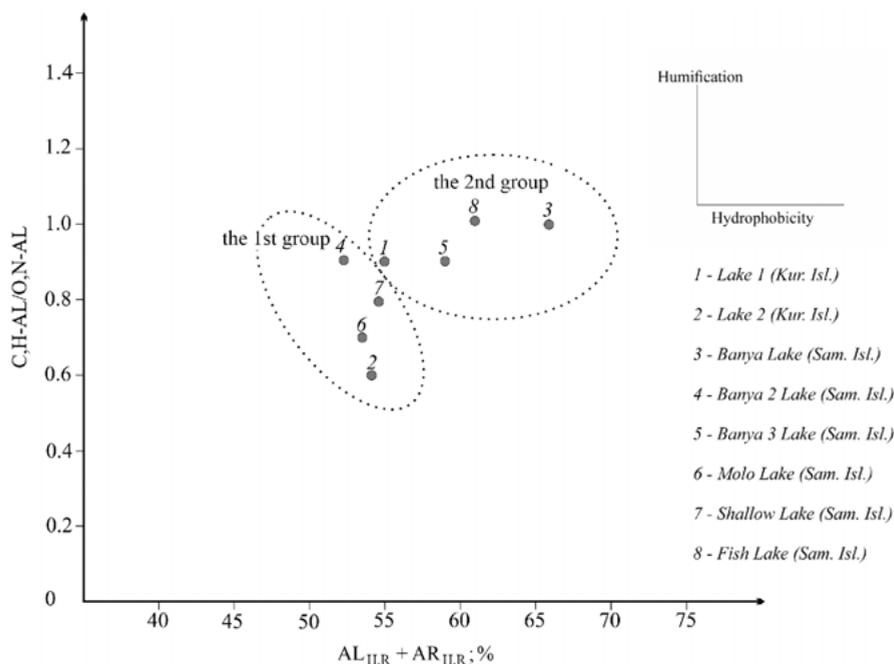


Fig. 4. The diagram of integrated indicators of the molecular composition of the HAs. $AL_{H,R} + AR_{H,R}$ indicates the total number of unoxidized carbon atoms.

The potential complexing ability of humic acids in relation to metals is due to the presence of O/N-containing functional groups that give peaks in the region of 160–200 ppm (carboxyl groups, esters, amides and their derivatives, quinone groups, carbonyl groups of aldehydes and ketones). The portion of these molecular fragments in the studied samples ranges from 4 to 15%. Lakes of Kurungnach Isl. were characterized by relatively higher saturation by these functional groups than lakes of Samoylov Isl. However, the complexing ability of soil HAs (Polyakov and Abakumov 2020) of this territory is potentially higher (the portion of the functional groups ranges from 16 to 18%). According to the results of CP/MAS ^{13}C -NMR spectroscopy of HAs from other regions of the Arctic (Polyakov *et al.* 2019a, b) and northeastern European Russia (Lodygin and Vasilevich 2020), soil humic acids contain relatively larger percentage (8–17%, 5–13%, and 13–20%, respectively) of complex-forming groups. Furthermore, we

compared the results of this study with the research of HAs of lake sediments of more southern territories. HAs extracted from lake sediments of China and Canada, according to the results of CP/MAS ^{13}C -NMR spectroscopy (Belzile *et al.* 1997; He *et al.* 2008), contain significantly larger percentage of C-carboxyl and C-carbonyl fragments: 24–25% and 17–18% respectively.

FTIR-analysis of the HAs samples. — The results of CP/MAS ^{13}C -NMR spectroscopy were additionally verified by FTIR-spectroscopy. The obtained spectra are presented in Fig. 5. Spectral bands typical of HAs (Stevenson 1994; Chen

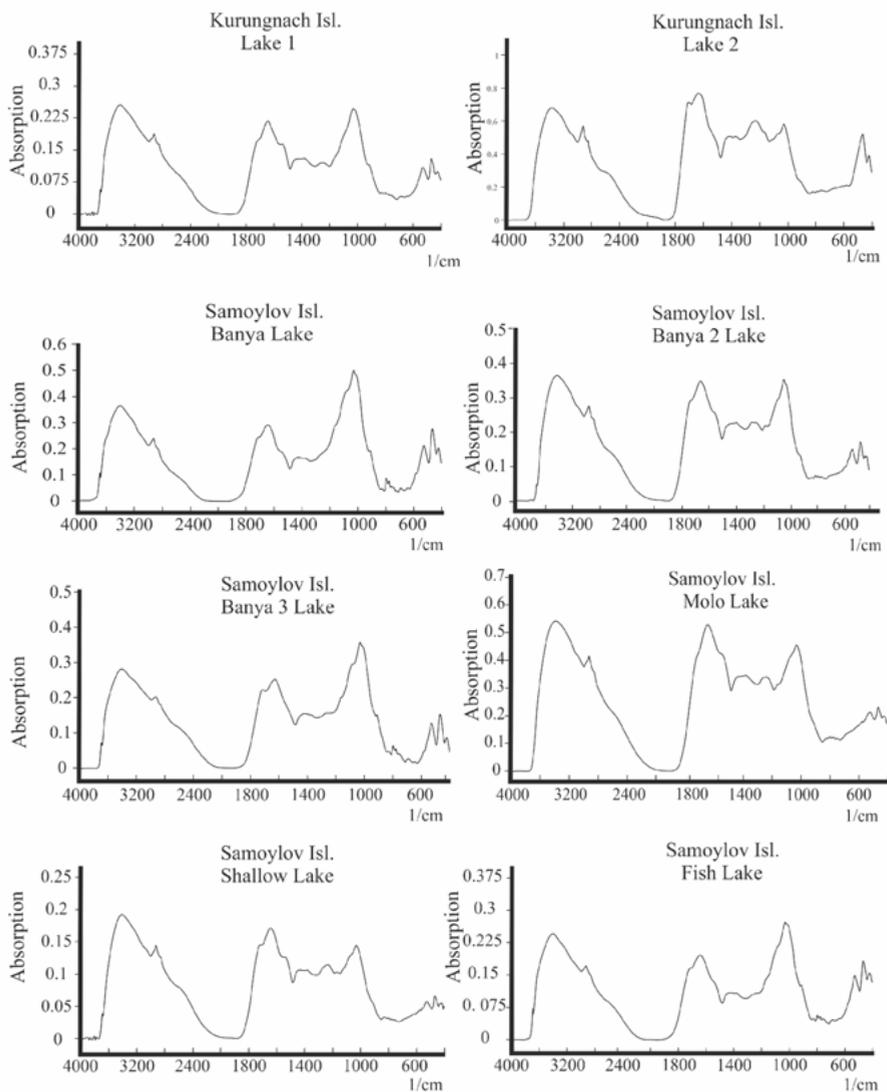


Fig. 5. FTIR- spectra of humic acids isolated from lake sediments of the permafrost affected area of the Lena Delta, the Russian Arctic.

et al. 2002; He *et al.* 2008) were observed for all analyzed samples. The broad band at 3500–3300 cm^{-1} was provided by H-bonded OH. The presence of the same functional groups was confirmed by the existence of weak absorption bands in the range of 1270–1220 and 1170–1040 cm^{-1} . The shoulder in the range of 3100–3000 cm^{-1} was due to vibrations of aromatic groups =C–H in arenes with several substituents in the ring. The band at 2800–3000 cm^{-1} spectral area was associated with aliphatic C–H stretching as well as weak bands at area 1300–1500 cm^{-1} .

A shoulder or a peak at 1711 cm^{-1} was provided by C=O stretching of COOH and ketonic carbonyls. The bands at 1590–1700 cm^{-1} area were produced by aromatic C=C stretching, C=O stretching of amide groups (bands at 1660–1630 cm^{-1}), NH_2 deformation. Weak absorption at 1540–1510 cm^{-1} spectral range was assigned to N–H deformation and C=N. The stretching vibrations of hydroxyl groups (νOH) of alcohols and carbohydrates were responsible for the absorption bands in the short-wavelength part of the spectrum in the 1175–1000 cm^{-1} area (Schepetkin *et al.* 2003; Zaccone *et al.* 2007). In particular, bands at 1075–1013 cm^{-1} ($\nu\text{C-O}$) were assigned to primary alcohols. It was observed in spectra of all analyzed samples. At range 1000–600 cm^{-1} weak absorption bands were possibly due to out-of-plane bending vibrations ($\delta\text{C-H}$) in aromatic rings containing two or more unsubstituted hydrogen atoms (He *et al.* 2008), including the presence of condensed multinuclear arenes (755–760 cm^{-1}) as well as bending vibrations at the range of 625–600 cm^{-1} of terminal alkynes ($\equiv\text{C-H}$) (Orlov and Osipova 1988).

It should be noted that infrared spectroscopy is not sensitive enough to cover minor structural differences between HAs samples. However, we can identify the presence of O-containing molecular fragments that potentially can interact with metals. For all analyzed samples dominant O-containing fragments are H-bonded hydroxyl (at 3500–3300 cm^{-1}) and primary alcohol hydroxyls ($\nu\text{C-O}$ at 1075–1013 cm^{-1}). Carboxyl groups and their functional derivatives ($\nu\text{C=O}$ 1725–1700 cm^{-1} , $\nu\text{C-O}$ 1260–1225 cm^{-1}) were identified in all samples, but their absorption intensity was lower than the intensity of hydroxyl groups. Furthermore, the relative absorption intensity of mentioned hydroxyl groups is higher in the HAs spectra of lakes of the second group than of the first group (Figs 2 and 4). Therefore, it may suggest that humification processes in the studied lakes are associated with increasing of quantity of hydroxyl groups of aliphatic and aromatic molecular fragments, including polysaccharides, esters, and alcohols.

Conclusion

The studied lake sediments are characterized by a relatively low content of dispersed organic matter. At the same time, the presence of undecomposed plant residues in the sediments suggests the slow processes of organic matter decomposition in the studied permafrost-affected lakes. The HAs isolated from lake sediments have a low content of nitrogen. It is a typical composition feature

of HAs of territories with a low level of microbial activity. Furthermore, the percentage of H and O content suggests the relatively low degree of maturity of the studied HAs. This fact was confirmed by the results of ^{13}C -NMR-spectroscopy. The predominance of aliphatic fragments over aromatic fragments in all analyzed samples indicates that the processes of mineralization of organic matter prevail over humification. Moreover, when comparing the results obtained with the works of other authors who studied the soils of the region, it was noticed that the soil HAs on the territory of the Lena Delta were more mature and resistant to oxidation than HAs of the lakes sediments. Additionally, in the HAs of the soil, the percentage of functional (complex-forming) groups is higher than in the analyzed HAs of sediments. Despite the generally low maturity of the studied HAs, the oxygen-containing functional groups, which can form stable complex compounds with metals, were identified in the molecular structure of the acids. The results also show that the humification process of the HAs is associated with the increase of the relative quantity of hydroxyl groups in their molecular structure. It was found that there is the difference in the degree of maturity of sediment HAs among the studied lakes. However, the obtained data have not revealed any specific correlation between the degree of humic acid humification and the location, origin, or hydrological regime of the lakes. This aspect will be studied in further works. In conclusion, the results of the research demonstrate the relatively low potential complexing ability of the HAs of lake sediments in the studied permafrost-affected area of the Arctic, compared with territories with more boreal climate conditions.

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