Molecular composition of humic substances isolated from selected soils and cryconite of the Grønfjorden area, Spitsbergen

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Abstract: Humic acids, isolated from selected soils of Grønfjorden area (Spitsbergen) were investigated in terms of molecular composition and resistance of decomposition. The degree of soils organic matter stabilization has been assessed with the use of modern instrumental methods (nuclear magnetic resonance spectroscopy (CP/MAS ^{13}C-NMR). Analysis of the humic acids showed that aromatic compounds prevail in the organic matter formed in cryoconites, located on the glaciers surfaces. The predominance of aliphatic fragments is revealed in the soils in tidal zone that form on the coastal terrace. This could be caused by sedimentation of fresh organic matter exhibiting low decomposition stage due to the harsh climate and processes of hydrogenation in the humic acids, destruction of the C-C bonds and formation of chains with a high hydrogen content. These processes result in formation of aliphatic fragments in the humic acids. In general, soils of the studied region characterizes by low stabilized soil organic matter which is indicated by low aromaticity of the HAs.

Key words: Arctic, Svalbard, CP/MAS ^{13}C-NMR, elemental composition, organic matter.

Introduction

Soils of high latitudes accumulate a great amount of organic matter (Schadel *et al*. 2014). About 22% of the Earth's surface in the northern hemisphere is ice-free and in that regions permafrost-affected soils are formed (Jones *et al*. 2010;

Zubrzycki *et al*. 2014). It is classified by the presence of a permafrost layer lying to 1 meter in the soil thickness (IUSS Working Group WRB 2015). In such soils, organic carbon is accumulated due to low biological activity combined with high-redox potential conditions, which impedes the decomposition of organic matter (Schuur *et al*. 2015). The storage of soil organic matter (SOM) in high latitudes was estimated at 1672×10^{12} kg, which comprises about 70% of all SOM in the world (Schimel 1995; Davis 2001; Dutta *et al*. 2006; Polyakov *et al*. 2017). Soil organic matter plays a key role in the formation of soils (Tarnocai 2009). It is considered as important source of nutrients for plants (nitrogen, phosphorus, potassium) and microorganisms. The effect of SOM on pedogenesis is expressed in a change of physic-chemical properties (pH, cation exchange capacity, hydrothermal regime). The degree of SOM stabilization depends on bioclimatic conditions, chemical and molecular structure, structural complexity of the final products of humification, the quality and taxonomy composition of soil microbiome (Dai *et al*. 2002; Kutzbach *et al*. 2004; Boike *et al*. 2013).

The expected global warming can cause deeper and more intensive thawing of permafrost and increase the thickness of soil active layer, which will lead to involvement to the global cycle that part of the carbon that is contained in permafrost (Davidson and Janssens 2006). This may cause significant changes on a planetary scale and affect climate change (Amelung *et al*. 1997; Schuur *et al*. 2008). Another important aspect of organic matter role is the presence of specific formations of combined biogenic-mineral materials on the surface of the glaciers – cryoconites (Gribbon 1979; Langford *et al*. 2010). Cryoconites represent soil like bodies formed not on normal parent material, but on the surface of the ice. This type of accumulations appear in microdepressions, formed due to thawing of ice under accumulation of dark colored organic matter on the surface of ice. During the thawing, the cryoconite substances become located deeper in relation to initial surface and this result in additional accumulation of organic matter in microdepressions, they become wider and deeper. Spatial web of cryoconite became more developed and this result in degradation of the glacier surface. This cryoconite formation result in degradation of upper layers of ice and increases deglaciation rates (Christner *et al*. 2003). The organic carbon of the cryoconite origin could be considered as specific form of natural organic matter stabilization and should be investigated on the molecular level (Xu *et al*. 2010).

In order to better understand the implications of permafrost's SOM for greenhouse gas emissions, accurate knowledge of its spatial distribution, both in terms of quantity and quality (*e.g*. biodegradability, chemical composition, and humification stage) is needed in addition to effective evaluation of SOM temporal dynamics. Therefore, the current researches are focused on determination of elemental composition of HAs, the degree of its decomposition and determination of soil organic matter stabilization degree. One of the methods for studying the

molecular composition of organic matter is nuclear magnetic resonance (NMR), which eneables the study the qualitative and quantitative characteristics of organic matter (Lodygin and Beznosikov 2010; Ejarque and Abakumov 2016; Lodygin *et al*. 2017). An application of this method give a possibility to identify main trends of soil organic matter stabilization. It was shown, that the accumulation of aliphatic compounds is associated with the processes of depositing fresh soil organic remnants, and the group of aromatic compounds indicates the processes of humification and stabilization of organic matter in the soil and accumulation of plant tissues (Celi *et al*. 1997).

Data related to the quantity and quality of organic matter in the soils of polar biomes are necessary to correct climate change models concerning the emission of greenhouse gases. Recently, many papers have been published relating to the determination of the chemical composition of organic matter in the Arctic soils (Chefetz *et al*. 2002; Szymański *et al*. 2016; Lupachev *et al*. 2017). There are also many methods for determining this composition. Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-ViS), cross polarization, magic-angle spinning, nuclear magnetic resonance spectroscopy (CP/MAS ^{13}C-NMR), molecular fluorescence spectroscopy (MF), and electron spin resonance spectroscopy (ESR) are very useful and often applied in SOM studies (Chen *et al*. 2002; Cocozza *et al*. 2003). The area being under the influence of permafrost in the world occupies 35 million km^2 (about 25% of land area). Therefore, investigation of organic material are the most important in terms of predictable global warming and greenhouse gas emissions in high latitudes. The content of molecular fragments of HAs determined by CP/MAS ^{13}C-NMR spectroscopy contributes to the understanding of the fundamental processes of humus formation and the composition of natural high-molecular HAs compounds in soils subjected to the influence of cryogenesis (Dai *et al*. 2001; Lodygin *et al*. 2014; Chukov *et al*. 2015; Ejarque and Abakumov 2016; Lupachev *et al*. 2017).

The advantage nuclear magnetic resonance spectroscopy method is the ability to quantify the content of groups of structural fragments and identify individual structural fragments in humic acid 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 low-degraded nature of organic molecules that retain most of the chemical nature of their precursor material due to the low progress of humification (Dziadowiec *et al*. 1994; Davidson and Janssens 2006; Abakumov *et al*. 2015).

Thus, the main objective of this study was to determine the molecular composition of organic matter in selected soils of the Grønfjorden area (Spitsbergen) using CP/MAS ^{13}C-NMR spectroscopy.

Study area

The study area is located around Grønfjorden area in western Spitsbergen, Svalbard, between 77°91' and 78°10' N, and 14°00' and 14°85' W (Fig. 1). The climatic characteristics of the region are given according to meteorological observations in Barentsburg (Antsiferova *et al*. 2014). The average annual air temperature is –5.8ºC. The average air temperature of the warmest month (July) is 8ºC, and the average air temperature of the coldest month (February) is –18ºC. The average annual precipitation is 563 mm and the amount of precipitation in summer is 87 mm (Antsiferova *et al*. 2014). On the territory of Spitsbergen both
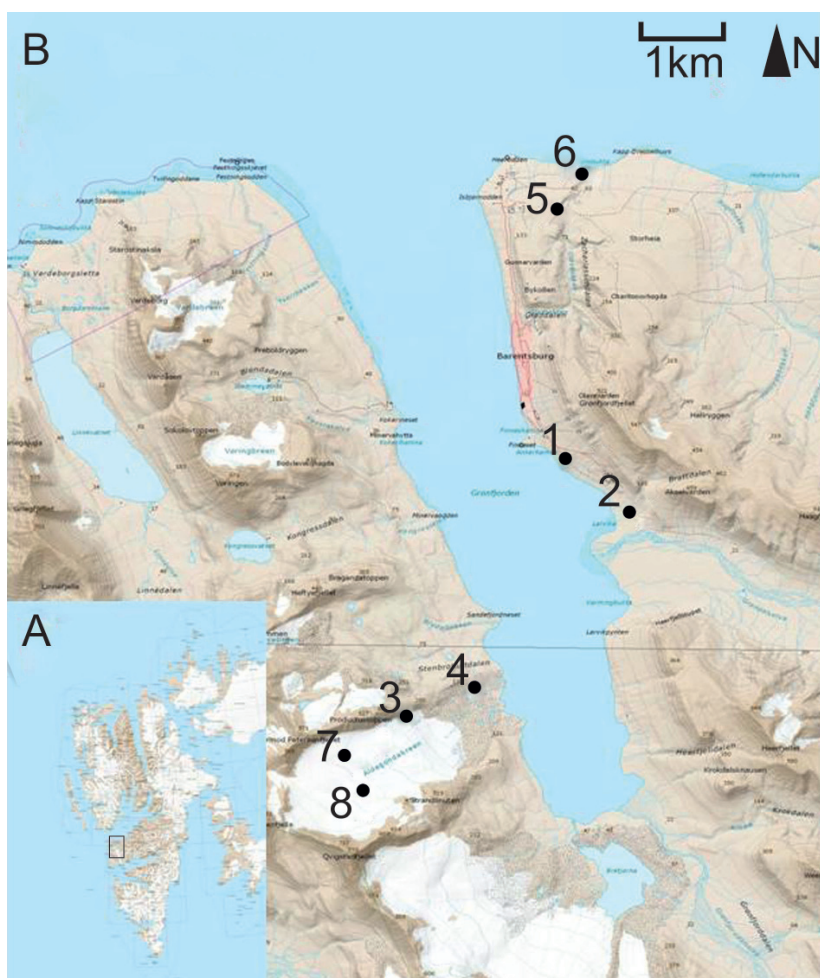

Fig. 1. Location of the study area and studied soils. (**A**) Spitsbergen archipelago, (**B**) Grønfjorden area with sampling sites indicated; sample numbers correspond to Table 1. Source: Norsk Polarinstitutt | Norsk Polarinstitutt, Sysselmannen på Svalbard | Norwegian Polar Institute

types of the wind are present: cold and warm, which are coming from Arctic Ocean and Norwegian Sea, respectively. The thickness of the snow cover is from 0 to 1 meter. Permafrost occurs at the depth of 1.8 to 2.5 m (Iavid *et al*. 2018).

In the study area, in most cases, the Quaternary deposits were represented by acidic rocks with a high SiO_2 content and extremely low CaO and MgO contents. The surface of modern landscapes in the studied area consists of folded Proterozoic and Lower Paleozoic rocks, which in some areas are covered by mostly horizontal Mesozoic and Cenozoic sediments containing layers of coal. The study area includes areas of marine terraces in the coastal zone and Neogene–Holocene denudational-erosional slopes. In the process of soil formation, the content of all important nutrients: Ca, Mg, K, P and Mn in the upper horizons significantly increases in comparison to the parent material due to biogenic accumulation (Kashulina 2003; Strebel *et al*. 2010).

The key role that changes the topography and the soil cover of the western part of the Svalbard archipelago are glaciers. Glaciers are considered as an important land-forming agent, which is responsible for destruction, transportation and deposition of significant amount of sediments, and also strongly affecting the soil parent materials. The main glaciers in the Grønfjorden area, the Grønfjordbreane is formed from by two glaciers, *i.e*. Vestre Grønfjordbreen and Austre Grønfjordbreen, which occupy two neighbouring valleys, flowing towards southern Grønfjorden. The presence of extent surfaces of the ice caps result in formation of cryoconite in the pores and microcaves of the ice (Mavlyudov 2016). This is a specific form of organic matter accumulation. These cryoconites could be considered as specific type of soil formation, like a biological crusts or endolithic soils of various extreme environments (Mergelov *et al*. 2018)

Distribution of plants in Grønfjorden area is heterogeneous. Vegetation type is classified as a pioneer vegetation, moss and graminoid tundra types (Johansen and Tømmervik 2014), where *Salix polaris*, *Cerastium alpinum*, *Luzula confusa*, *Saxifraga cespitosa*, *Trisetum spicate* prevail. Among the landforms, fluvial forms (terraces, deltas, floodplains) and cryogenic forms (pingoes) prevail, while periglacial are represented by moraines and fluvioglacial deposits (Pengerud *et al*. 2017).

Materials and methods

Samples of soils were collected in various elements of the landforms (tidal terraces, terraces of the slopes, valleys and ice cap). Soil samples from surface horizons were collected during the summer 2017. The sample description is given in Table 1. The soils were classified according to WRB classification (IUSS Working Group WRB 2015).

Description of the studied surface soil samples.

Sample No.	Soil	Description of the studied surface soil horizons Soil description of upper horizon	Color index
1	Umbric Cryosol	The abrasive ledge of the east coast of the Grønfjorden with moss-cereal vegetation. There was a high amount of quaternary deposit of gravel-pebble material; dark gray structureless horizon; loose; friable; moist; sandy loamy.	7.5YR 8/1
2	Umbric Cryosols Fluvic Cryosol, Umbric, Turcbic, Fluvic	The right terrace of river Grøndalselva, near the coastline (on the depositions of the sea terrace); brownish gray; with inclusions of plant residues; content of rock fragments is 10%; noticeable cryoturbation features.	7.5YR 8/1
3	Cryoconite	Ground moraine of the Aldegonda glacier in the place of the cryoconite pool; grayish black; wet; loamy; with inclusions of a pebble.	10YR 5/2
4	Skeletic Cryosol	Bottom of the moraine ridge; gray; with inclusions of moraine deposits (particles of different granulometric composition), rock fragments constitute 50% of soil material.	7.5YR 2/1
5	Umbric Reductaquic Turbic Cryosol	Marine terrace; gray; loamy; moist; compacted; with inclusions of roots, the structure is fine-platy.	7.5YR 8/1
6	Cambic Cryosol, Turbic	First marine terrace; reddish brown; compacted; moist; loamy, the structure is fine granular, cryoturbation features are well-pronounced, there are inclusions of segregation ice (ice lenses).	7.5YR 4/2
7	Cryoconite	Ground moraine of the Aldegonda glacier in the place of the cryoconite pool; grayish black; wet; loamy; with inclusions of a pebble.	10YR 5/2
8	Cryoconite	Ground moraine of the Aldegonda glacier in the place of the cryoconite pool; grayish black; wet; loamy; with inclusions of a pebble.	10YR 5/2

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 (Euro EA3028-HT Analyser) and 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 using a pH meter (pH-150 M).

Humic acids (HAs) were extracted from each sample according to a published IHSS protocol (Swift 1996). 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 (Vasilevitch *et al*. 2018).

Data were corrected for water and ash content. Oxygen content was calculated by difference of whole samples mass and gravimetric concentration of C, N, H and ash.

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 and number of scans were 3 seconds.

Results

Elemental Composition of HAs. — The obtained data on the HAs elemental composition, atomic ratios and degree of oxidation are presented in Table 2. The carbon content in the ashless HAs were comparable for all materials and variates from 42 to 47%. This give us a possibility to classify the substances investigated as relatively high carbon containing HAs. The oxygen content was also comparable for all investigated substances. High oxygen content indicates increased degree of oxidation, this well corresponds with the oxidation coefficient values (Table 2). The molecular ratios were typical for normal HAs materials.

Characterisation of HAs by ^{13}C-NMR spectroscopy. — Spectra's of the CP/MAS ^{13}C-NMR are given on Fig 3. Various molecular fragments were identified by CP/MAS ^{13}C-NMR spectroscopy (Table 3): carboxyl (–SOOR); carbonyl (–C=O); CH3–, CH2–, CH–aliphatic; –C–OR alcohols, esters and carbohydrates; phenolic (Ar–OH); quinone (Ar=O); aromatic (Ar–), 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).

The presence of carboxyl, hydroxyl, and carbonyl groups in combination with aromatic structures ensures the ability of HAs to enter exchange and donor-

Table 2

Elemental composition of the studied humic acids from surface soil horizons.
Gravimetric concentration are given for C, H, H, N contents. H/C mod
– 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 are calculated after Orlov (1985).

Sample No.	C [%]	H [%]	N [%]	O [%]	C/N	H/C	O/C	H/C mod**	W***
1	45.20	5.78	5.32	43.70	9.9	1.52	0.73	2.49	-0.07
2	47.90	6.02	4.78	41.30	11.7	1.50	0.65	2.36	-0.19
3	43.20	5.88	4.79	46.10	10.5	1.62	0.80	2.69	-0.02
4	44.20	5.34	5.45	44.90	9.4	1.44	0.76	2.45	0.09
5	42.30	5.67	5.25	46.70	9.4	1.59	0.83	2.70	0.06
6	43.20	4.98	5.02	46.80	10.1	1.37	0.81	2.45	0.25
7	44.20	5.93	4.90	44.97	9.02	1.62	0.72	2.69	-0.02
8	43.70	6.23	4.95	45.12	8.82	1.70	0.78	2.74	-0.01

** H/C mod – the number of substituted hydrogen atoms in the HAs
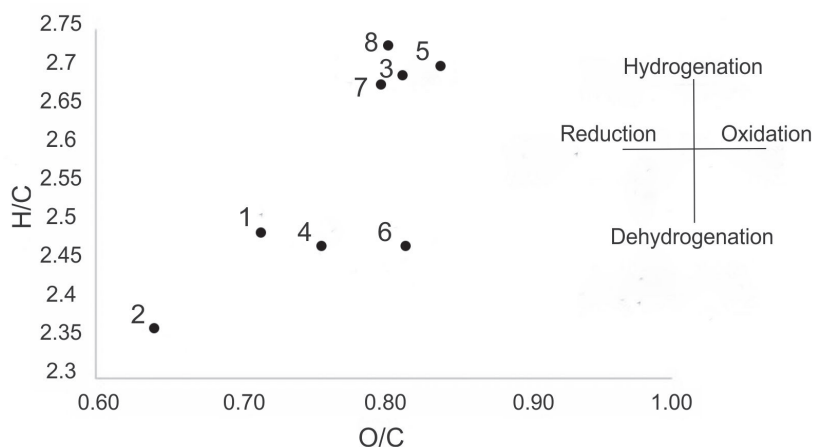(H/C)mod = (H/C) + 2(O/C) x 0.67
*** W – oxidation coefficient; W = (2C – H)/O

Fig. 2. H/C and O/C atomic ratios of the elements in humic acids. H/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.

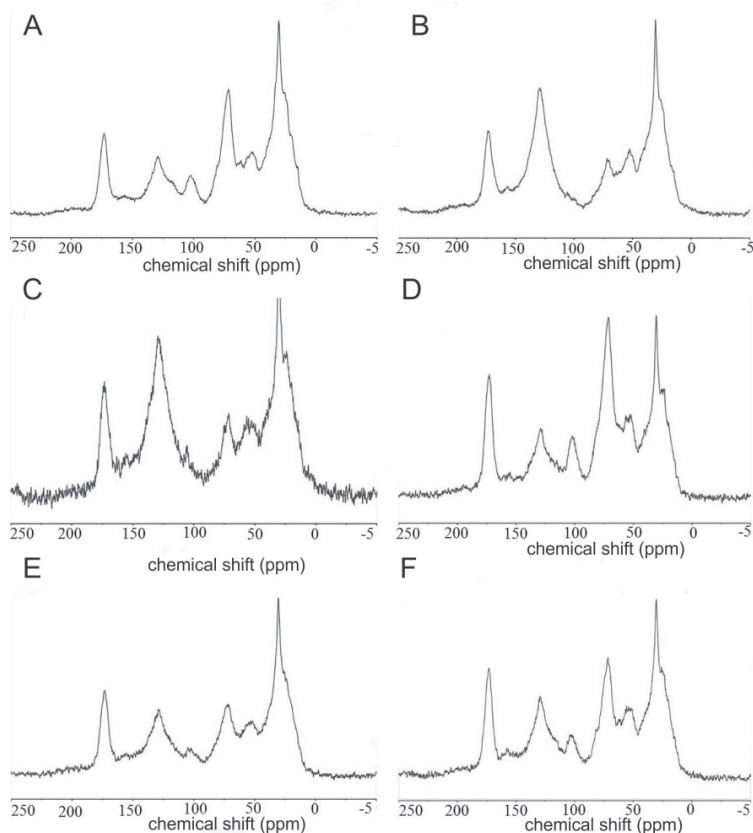Fig. 3. CP/MAS ^{13}C-NMR spectra of soils from the Grønfjorden area (Spitsbergen). (**A**) Umbric Cryosol; (**B**) Umbric Cryosols Fluvic Cryosol, Umbric, Turbic, Fluvic; (**C**) Cryoconite; (**D**) Skeletic Cryosol; (**E**) Umbric Reductaquic Turbic Cryosol; (**F**) Cambic Cryosol, Turbic Cryosols; horizontal axis–chemical shift, ppm, vertical scale-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.

Sample No.	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	110–160	160–185	185–200					
1	38	10	29	18	4	1	22	78	0.28	57	1.00
2	33	9	14	32	11	1	43	57	0.75	65	1.43
3	34	8	16	31	10	1	41	59	0.69	65	1.42
4	27	10	34	16	12	1	28	72	0.39	43	0.61
5	36	10	21	21	11	1	32	68	0.47	56	1.13
6	30	10	26	21	12	1	33	67	0.49	51	0.83
7	26	8	20	36	9	1	45	55	0.81	71	0.92
8	28	8	19	33	11	1	44	56	0.78	61	1.03

acceptor interactions, formation of hydrogen bonds, and actively participation in sorption processes.

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 0–47 ppm, O, N–alkyl at regions 46–60 and 60–110 ppm (Lodygin *et al*. 2014). The presence of all peaks of the carbon species which are required for identification of the studied substances as humic acids has been revealed. The most pronounced peaks were related to the aliphatic carbon groups. But also, the presence of evident peaks of aromatic and carboxylic areas was obvious as well. This indicates that powders investigated could be identified as humic substances, namely, as a humic acids.

Discussion

Elemental Composition of HAs. — In general, the elemental composition of the HAs is comparable with previously reported data for soils of polar environments (Beznosikov and Lodygin 2010; Abakumov *et al*. 2015; Ejarque

and Abakumov 2016; Szymański 2017; Lupachev *et al*. 2017). 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 elemental composition of HAs is the most important indicator determining the progress of humification, oxidation and degree of condensation of HAs (Beznosikov and Lodygin 2010).

According to the obtained data the HAs of soil investigated contain relatively high portions of carbon (up to 47.9%). Elevated H values are observed in samples taken from cryoconites (sediments, predominantly of eolian genesis, which accumulate on the surface of the glacier and include both mineral and biological components). When the glacier retreats, cryoconite material is transported by water currents and precipitates, most often in places protected from the wind (wind shelters). Due to its properties of high content of biogenic elements and fine dispersion, the cryoconite material serves as a unique soil-forming rock with favorable conditions for the settlement of higher plants and for soil formation in comparison with other sediments that are formed in the modern pereglacial zone. According to the data on ratios of H/C and O/C, we can note that the organic matter not deep humified in all the soils studied, which is typical for permafrost-affected soils (Lodygin *et al*. 2014). We can suggest that the HAs of soils located in tidal zone can have increased migration ability and oxygen-containing functional groups predominate in them. The increase in H/C ratio is associated with an increase in the degree of hydromorphism as well as with decrease in microbiota activity and contributes to the deposition of organic substances (Vasilevich *et al*. 2015). Relatively low H/C ratios could be connected to the accumulation in the soil of aromatic fragments of HAs (Fig. 2).

An important characteristic of HAs is their degree of oxidation. The process of oxidation of organic compounds can equally be described either by the addition or the release of hydrogen (Orlov 1985). From the oxidation coefficient (W), we can identify which compounds predominate in HAs. In the studied soils, weakly oxidized and slightly reduced compounds predominate. The humification process as a whole is characterized by an increase in the oxidation state of the products formed (Lodygin *et al*. 2014). All the values of oxidation indexes obtained in this study are close to zero, which is characteristic of HAs of spodosols (Lodygin *et al*. 2014).

The term hydrogenation refers to a chemical reaction involving the addition of a hydrogen molecule to an organic substance (Orlov 1985). An increase in the hydrogen content of the humification products indicates that long aliphatic chains are formed or can be inherited from parent material. The deceased content of the aromatic compounds is typical for humified materials of the soils studied and are characteristic for the Arctic zone (Strebel *et al*. 2010; Pengerud *et al*. 2017). High atomic ratios H/C mod can be interpreted as a combination of aliphatic compounds and aromatic compounds, with the proportion of aromatic compounds being about 30–40%, calculated according to the integrated chemical shifts area.

In soil of fluvic origin dehydrogenation takes place leading to the formation of chains between carbon (C–C) and a decrease in the hydrogen content in HAs (Fig. 2). Such a process leads to an increase in the proportion of aromatic fragments and it is responsible for humification of organic matter in soils.

Characterisation of HAs by ^{13}C-NMR spectroscopy. — From the obtained morphological data, we can conclude that the development of soils of the Grønfjorden area area proceeds through a cryogenic type of soil formation with the accumulation of long aliphatic chains (fatty acids, phospholipids). They are dominated by oxygen-containing fragments, which can cause their high migration ability. They promote the mobilization of mineral compounds and their migration along the soil profiles. The evident processes of current humification and stabilization of organic matter are presented only in samples of soil, located on coastal zone (sample 2) and cryoconite (sample 3). The portion of aromatic fragments in these HAs reaches 41–43% (Fig. 4). The same was obtained for samples of cryoconite samples 7 and 8; it was also high at 45 and 44%, respectively. This may be due to the specifics of the accumulation of organic material on cryoconites, the smallest dusty material formed as a result of weathering of moraine deposits and accumulating on the surface of glaciers and snowfields, since the chemical composition of SOM is generally similar to the chemical composition of permafrost-affected soils from other regions. In addition, that effect may be related with coal dust, for example from the adjacent coal mines of Barentsburg (Strebel *et al*. 2010; Lodygin *et al*. 2014; Pengerud *et al*. 2017). The content of aromatic carbon was essentially lower in HAs, isolated form the true soils of the Grønfjorden area. Minimal aromaticity was 22%, which is comparable with HAs of the Antarctic soils (Abakumov 2017; Mergelov *et al*. 2018), the highest was 33%, which is comparable with
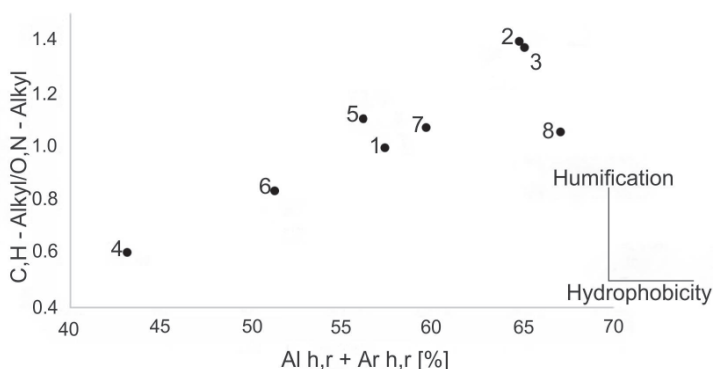

Fig. 4. The diagram of integrated indicators of the molecular composition of humic acids. Sample numbers correspond to Table 1; Al $_{H,R}$ + Ar $_{H,R}$ indicates total number of unoxidized carbon atoms.

soils of Komi Republic (Lodygin *et al*. 2017) and Yamal region (Ejarque and Abakumov 2016).

According to the obtained diagram, we can consider that samples 2 and 3 of the HAs are more humified, and they also have a higher hydrophobicity level, which causes the solubility of HAs in water and their migratory capacity. Therefore, we can state that the organic matter formed in cryoconites is more humified, more mature and resistant to oxidation by microbial communities, because the degree of its oxidation is -0.19 to -0.02. The soils from coastal zone of Grønfjorden area are characterized by a lower degree of humification and hydrophobicity, which indicates the accumulation of aliphatic structural fragments.

Data obtained illustrate that the two types of humification in the area investigated. First is humification, accompanied by accumulation of increased portions of the aromatic carbon in comparison with normal polar cryogenic soils. This type of humification appear in cryoconite type of organic matter and could be interpreted as result of strong alteration of transported organic matter in conditions of strong insolation and absence of intensive organic precursors of humification accumulation in semi-isolated micro-depressions. The second way of humification is accumulation of relatively low humified organic substances in soils of cryogenic type. In this case, humic acids formed show the prevalence of aliphatic carbon groups on aromatic ones, which indicates lesser stabilization rate in normal terrestrial soils than is soil-like bodies, formed on the surfaces of the glacier in cryoconites. It is also should be emphasized, that the HAs hydrophobicity degree indexes (Lodygin *et al*. 2014) were higher in cryoconite than in terrestrial soils (Table 4). This could we caused by absence of the fresh organic humification precursors in case of partially isolated cryoconites.

Conclusions

The elemental and molecular composition of HAs in the surface soil horizons Grønfjorden area, Spitsbergen, Svalbard, has been studied. Analysis of the molecular composition of HAs showed that the molecules of HAs formed on cryoconites and related soil of terrace are enriched with aromatic fragments and they contain in their composition a considerable number of aromatic fragments (41–43%) with a relatively small fraction of carbohydrate periphery, as evidenced by higher values of Ar/Al (0.75 and 0.69). Higher aromaticity of HAs causes their high stability and the degree of hydrophobicity of HAs in these soils is also higher, which indicates the stabilization of HAs. The other soils studied are characterized by the accumulation of long aliphatic chains which result in decreasing of aromaticity of organic matter and simultaneous declining of the soil organic matter stabilization rate. Because of the increased oxidation, HAs molecules have a high degree of solubility in water and a correspondingly high migration ability to HAs molecules formed on cryoconites.

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