Humic Acids Isolated from Selected Soils from the Russian Arctic and Antarctic: Characterization by Two-Dimensional $^1$H-$^{13}$C HETCOR and $^{13}$C CP/Mas NMR Spectroscopy

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Abstract: Here we describe the molecular composition and resistance to decomposition of humic acids isolated from selected soils of the Russian Arctic and Antarctic. The degree of soil organic matter stabilization was assessed using modern instrumental methods: nuclear magnetic resonance spectroscopy (cross peak magic-angle spinning (CP/MAS) $^{13}$C-NMR and $^1$H-$^{13}$C heteronuclear-correlation (HETCOR)). Analysis of the humic acids showed that aromatic compounds prevail in the organic matter formed in cryoconites, located on the surfaces of the glaciers. The predominance of aliphatic fragments is revealed in the soils of the Yamal peninsula and Antarctica. This could be caused by sedimentation of fresh organic matter exhibiting low decomposition stage due to the severe climate and processes of hydrogenation in the humic acids, destruction of the C-C bonds, and formation of chains with high hydrogen content. These processes result in formation of aliphatic fragments in the humic acids.

Keywords: cryoconite; cryosol; ornitogenic soil; permafrost-affected soils; molecular composition

1. Introduction

Polar soils play a key role in the global carbon balance as they contain maximum stocks of soil organic matter (SOM) within the whole pedosphere [1]. The accumulation of humus in the profile of arctic soils is associated with permafrost retinization processes, cryogenic mass exchange processes, in situ organic matter formation from root remnants, as well as with an inheritance from parent rocks [2]. The area occupied by permafrost-affected soils amounts to more than 8.6 million km$^2$, which is about 27% of all land areas north of 50° N [3]. The storage of SOM in high latitudes was estimated at 1672 $\times$ 10$^{12}$ kg, which comprises about 70% of all SOM in the world [3–5].

Low average temperatures and a short vegetation season in the arctic zone cause the accumulation of organic matter throughout the Quaternary period [6]. The biomass formed during the short vegetation season initially accumulates in the upper active soil layer. Thus, there is an annual accumulation of organic matter to which the alluvial sedimentation of organic residues contributes [4]. Cryoturbation and cryogenic mass exchange also lead to the incorporation 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 [5,7].

According 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 [8,9]. As a result of slope processes, organogenic horizons often turn out to be sealed under the material that arrived as a result
of solifluction [9,10]. Unlike cryoturbated material, buried organogenic horizons are characterized by high porosity; plant remnants, including roots, are relatively much less destroyed [11].

Only 0.35% (45,000 km$^2$) of Antarctica is ice-free [12]. The extreme variation in Antarctica’s climate has important effects on soil properties and distribution. In continental Antarctica, plant life is restricted to mosses, lichens, and algae, with vascular plants limited to the Antarctic island north of 67° S, particularly in the South Orkney and South Shetland Islands [13]. Birds play an important role in modifying the soils of coastal Antarctica. Seabirds and nesting birds constitute the dominant factor influencing the soil organic carbon (SOC) and nutrient levels in Antarctic soils. Specific soil-forming processes in the South Orkney Islands (SOI) and South Shetland Islands (SSI) include cryoturbation, phosphatization, brunification, podsolization, sulfurization, and andosolization [14,15]. At higher landscape positions, eutrophic, alkaline soils prevail that are normally devoid of vegetation and with low SOC [16]. Birds are the main source of soil organic carbon in the soils of Antarctica; specific ornithogenic soils are formed in the rookery sites [12]. The organic carbon content in the upper organo-mineral horizons (up to 20 cm) can reach 38%. Significant accumulation of organic matter was found earlier in ornithogenic soil types, and the minimum organic carbon content was identified in Leptosol on basalts and andesites under communities of mosses and lichens [17]. The organic matter of Antarctic soils is poorly humified; fulvic acids and detrital forms of undecomposed humus prevail [18]. The organic matter of Antarctic Leptosol contains a significant proportion of water-soluble fragments. In general, these features are associated with the low microbiological activity typical of Antarctic soils [19].

The circumpolar environments are characterized by a low degree of humification of organic matter, which is associated with a short vegetation season, as well as low levels of plant remnant in the soil. In the soils of the coastal zones of Antarctica, the formation of huge carbon stores has been noted, comparable to those in soils of similar regions of the Arctic [20,21].

Various methods have been used to investigate the humic acids (HAs) of soil organic matter. There are also many methods for determining HAs composition. Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), cross-polarization, magic-angle spinning, molecular fluorescence spectroscopy (MF), and electron spin resonance spectroscopy (ESR) are all useful and often applied in SOM studies [22,23]. Here, we use two modern instrumental methods: $^1$H-$^{13}$C HETCOR (heteronuclear-correlation) and $^{13}$C CP/MAS (cross peak magic-angle spinning) NMR spectroscopy. One-dimensional (1D) solid-state $^{13}$C NMR techniques have provided some structural information on HAs, including quantitative determination of various types of chemical groups [19,24–28]. However, this does not provide the opportunity to characterize detailed differences between the atoms included in such groups and in many cases does not allow for the signals to be clearly distinguished as a result of their considerable overlap due to broad lines and the diversity of structures of functional groups [29–32]. By the application of two-dimensional (2D) NMR techniques, such problems of peak overlap can be reduced, and the chemical structure corresponding to a given peak can be identified more specifically. As dipolar interactions act through space, the correlation of unprotonated carbons with unbound protons is possible, which provides additional structural information [30]. Two-dimensional correlation of $^{13}$C chemical shifts with $^1$H chemical shifts, termed 2D heteronuclear-correlation $^1$H-$^{13}$C HETCOR NMR, can provide more structural information than $^{13}$C or $^1$H NMR spectroscopy. The HETCOR method has been used to determine organic compounds in solutions of organic substances and has also been adapted for solids using 1H homonuclear dipolar decoupling and can now be used to determine humic acids in soils [29–33].

The HETCOR experiment correlates chemical shifts of $^1$H with chemical shifts of X-nuclei (for example, $^{13}$C, $^{15}$N). The experiment provides excellent resolution in an indirect $^1$H measurement. Homonuclear decoupling during the $^1$H evolution is achieved using the FSLG (Frequency Switched Lee Goldburg) sequence, which works even at relatively high MAS frequencies. Decoupling from protons during evolution is not necessary, since the high MAS speed already provides this [34,35].
Mixing is carried out during the contact magnetization transfer pulse. Since the transfer of magnetization from protons to X (for example, $^{13}$C) occurs quickly, the contact time should be short in order to avoid transfer over long distances, which leads to a nonspecific cross-peak pattern. There is a modification of the base sequence that uses magnetization transfer at the LG bias frequency for protons. In this case, the magnetization to the X nucleus passes only from closely located protons [34,35].

The bioclimatic conditions determine the soil formation in the polar regions, and their specific composition of HAs; however, their high diversity, low degree of knowledge of the regions, and the use of classical methods for studying organic matter do not allow us to state the molecular composition of HAs in polar soils with a high degree of confidence. The formation and transformation of HAs is a complex process in which a group of factors is involved, such as climate, composition and activity of the microbiological community, quality of plant residues, pH, and hydrophobicity of environment [26–28,36]. At present, there are a number of works devoted to the study of taiga and tundra soils using $^{13}$C (CP/MAS) NMR spectroscopy; however, there are few studies on Antarctic and Arctic soils. Studies on the organic compounds of HAs for the soils of the polar area by the $^1$H-$^{13}$C (HETCOR) NMR spectroscopy have not been carried out to current time. The advantage of this method is that, when analyzing the spectra of HAs, we can observe cross-peaks of H-C bonds, while for the $^{13}$C (CP/MAS) NMR spectroscopy we can only observe chemically bound carbon. The HETCOR method allows the study of single HAs fragments. Thus, the combination of the two methods $^1$H-$^{13}$C (HETCOR) and $^{13}$C (CP/MAS) NMR spectroscopy can reliably determine the molecular structure of HAs [30].

For further study of the fundamental processes of humus formation and the accumulation of specific organic compounds in the polar regions, modern instrumental methods are required. The methods of analysis of molecular composition that we have proposed will help to understand the fundamental processes of soil formation and create new ideas about the complex composition and structure of natural high molecular compounds of HAs in permafrost-affected soils [26–28].

$^1$H-$^{13}$C (HETCOR) and $^{13}$C (CP/MAS) NMR spectroscopy are powerful tools for studying molecular-level structure and dynamics in HAs. Thus, this study aimed to determine the molecular composition of organic matter in selected soils of the Russian Arctic and Antarctic using $^{13}$C-$^1$H(HETCOR) and $^{13}$C NMR spectroscopy.

2. Materials and Methods

2.1. Study Area

The study area is located around the Grønfjorden area in western Spitsbergen, Svalbard, continental part (Yamal peninsula) of the Arctic and maritime part of Antarctica, King-Gorge isl. The study area is presented in Figure 1. The climatic characteristics of the study regions are given in Table 1.

The Grønfjorden study area is characterized by the presence of glaciers. Glaciers are considered an important land-forming agent, which is responsible for destruction, transportation, and deposition of a significant amount of sediments, and strongly affecting the soil parent materials [37,38]. The presence of extant surfaces of the ice caps results in formation of cryoconite in the pores and microcaves of the ice [39]. This is a specific form of organic matter accumulation. These cryoconites could be considered as specific types of soil formation, similar to biological crusts or endolithic soils of various extreme environments [40]. Yamal is a peninsula in northwestern Siberia, on the territory of the Yamalo-Nenets Autonomous Okrug of Russia. The peninsula is 700 km long and up to 240 km wide. It is washed by the Kara Sea and the Gulf of Ob. The southern part of the peninsula mainly has a parallel-ridge relief, quite rare in the middle and northern latitudes of the Yamal. Excess moisture leads to the formation of numerous lakes and swamps [41,42]. Regarding the soils of King George Island, South Shetland Archipelago, on the territory of Antarctica, the parent materials here are presented by andesites, basalts, and tufts; the coastal areas are covered by maritime sands and gravels; and the periglacial plots are occupied by moraines and some fluvioglacial materials [12,43].
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2.2. Soils and Sampling Strategy and Procedure

The soils were classified according to WRB classification [44]. The soil samples were taken, considering the spatial picture of the vegetation cover and the position in the landscape. Samples of soil were selected in various elements of the landforms. Sample descriptions are given in Table 2.

2.3. Soil Basic Parameters

Soil samples were air-dried (24 h, 20 °C), grounded, and passed through 2 mm sieve. Soil samples were selected for each horizon to analyze physical and chemical properties. Analyses were conducted in the certified laboratory of St. Petersburg State University at the Department of Applied Ecology, Russia. Soils were analyzed according to the following methods: determination of actual acidity (pH$\text{H}_2\text{O}$) by a stationary pH meter in aqueous solution extract with ratio of a 1:2.5. The carbon and nitrogen content was conducted by CHN analyzer (Euro EA3028-HT, Italy). 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. The chemical characteristic of soils are presented in Table 3.

| Area                  | Sample No | Soil         | Description of the Studied Surface Soil Horizons. Soil Description of Upper Horizon | Color Index |
|-----------------------|-----------|--------------|----------------------------------------------------------------------------------|-------------|
| Yamal peninsula        | 1         | Histic Cryosol| The Yamal peninsula has many terraces formed from marine abrasion and accumulation. The terraces have complex structures built of cryogenic-polygonal forms, thermokarst (lakes and depressions), and long-term hydrolaccoliths. Oxidized, loam, rusty spots around root channels, well-aerated. The parent materials are presented by cover loams. Vegetation cover are presented by mosses and lichens community. | 10YR 4/1    |
| Grønfjorden area, Spitsbergen | 2 | Cryoconite | Ground moraine of the Aldegonda glacier in the place of the cryoconite pool; grayish-black; wet; loamy; with inclusions of a pebble. Without vegetation cover. Organic microparticles, which supposedly were derived from aerosols, were sampled on the glacier slope from the locations of cryoconite soil like bodies. | 10YR 5/2    |
| King-George isl., Antarctica | 3 | Leptosol   | The parent materials here are presented by andesites, basalts, and tufts; wet; loamy; ornitic. Vegetation cover are presented by Deschampsia Antarctica. | 7.5 YR 4/2  |

Table 3. The basic chemical characteristic of study soil with ±SD.

| Soil Group     | C, g kg⁻¹ | N, g kg⁻¹ | C/N | pH_H₂O |
|----------------|-----------|-----------|-----|--------|
| Histic Cryosol | 0.74 ± 0.03 | 0.11 ± 0.005 | 6.72 | 5.7    |
| Cryoconite     | 2.80 ± 0.14 | 0.18 ± 0.009 | 15.55 | 5.2    |
| Leptosol       | 1.01 ± 0.05 | 0.08 ± 0.004 | 12.625 | 4.9    |

2.4. \(^{1}H-^{13}C\) (HETCOR) and \(^{13}C\) (CP/MAS) NMR Spectroscopy Methods

HAs were extracted from each sample according to a published IHSS protocol [45]. The soil or cryoconite samples were treated with 0.1 M NaOH (soil/solution mass ratio of 1:10) under nitrogen gas. After 24 h of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at 1.516 × g for 20 min 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 min. The HAs were then dissolved in 0.1 M NaOH and shaken for 4 h 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, then freeze-dried. Solid-state CP/MAS \(^{13}C\)-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in a 3.2-mm ZrO2 rotor. The magic angle spinning speed was 20 kHz in all cases, and the nutation frequency for cross-polarization was u1/2p 1/4 62.5 kHz. Repetition delay was 3 seconds. The number of scans was 6500–32,000. The contact time used was 0.1–0.75 ms. Short contact time can provide more intense cross-peaks in short distance (Alkil zone). By increasing contact time, we can obtain intense cross-peaks in long distance (Aromatic zone and Carboxyl groups). Since the dipolar interaction in solids acts through space, correlation of unprotonated carbons with nearby (nonbonded) protons is possible, identifying the environment of those unprotonated groups; for instance, it can be determined whether COO groups are attached to aliphatic or aromatic cores [30,32]. HAs extraction yields were calculated as the percentage of carbon recovered from the original soil sample [46]. Elemental compositions of studied soils are presented in Table 4.
Table 4. Elemental compositions of the studied humic acids with ± SD.

| Soil Group       | C, %       | H, %       | N, %       | O, %       | H/C  | O/C  | C/N  |
|------------------|------------|------------|------------|------------|------|------|------|
| Histic Cryosol   | 36.1 ± 1.81| 4.6 ± 0.23 | 5.5 ± 0.27 | 53.8       | 0.13 | 1.49 | 6.56 |
| Cryoconite       | 44.1 ± 2.21| 6.1 ± 0.31 | 4.9 ± 0.24 | 44.9       | 0.14 | 1.02 | 9.00 |
| Leptosol         | 35.5 ± 1.77| 4.4 ± 0.22 | 5.7 ± 0.28 | 54.4       | 0.12 | 1.53 | 6.23 |

Solid-state 2D dipolar HETCOR experiments were performed to correlate $^{13}$C and $^1$H chemical shifts. This experiment is analogous to the wideline separation (WISE) experiment previously described by Schmidt-Rohr et al., with the exception that it is performed at a higher MAS speed [29–31]. Two-dimensional C-H correlation spectra were obtained using the standard HETCOR technique [34] with frequency switched Lee-Goldburg (FSLG) homonuclear dipolar decoupling at 13 kHz. All chemical shifts are presented in ppm relative to TMS (tetramethylsilane). The deconvolution of the spectra obtained was performed using the DMFIT software program [35].

Various molecular fragments were identified by CP/MAS $^{13}$C-NMR spectroscopy (Table 5), including carboxyl (-COOR); carbonyl (–C=O); CH$_3$-, CH$_2$-, CH-aliphatic; -C-OR alcohols, esters, and carbohydrates; phenolic (Ar-OH); quinone (Ar=O); and aromatic (Ar-). This indicates the great complexity of the structure of HAs and the polyfunctional properties that cause their active participation in soil processes [26].

Table 5. 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                                                |

3. Discussion of Results

The relative content of carbon atoms of the main structural fragments of HA was estimated by integrating the absorption lines in the corresponding ranges of chemical shifts. The chemical shifts are shown in Table 6.

Table 6. 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 2; AR—aromatic fraction; AL—aliphatic fraction; C,H-alkyl/O,N-alkyl—C, H-alkyl was summarized in 0–47 ppm, O, N-alkyl—in the range 47–60 and 60–105 ppm.

| Sample | Chemical Shifts, ppm | AR   | AL   | AR/AL | C,H-alkyl/O,N-alkyl |
|--------|-----------------------|------|------|-------|---------------------|
|        | 0–46                  | 46–60| 60–110| 110–160| 160–185| 185–200| 46–60| 60–110| 110–160| 160–185| 185–200|
| 1      | 35                    | 8    | 25    | 18    | 11     | 3      | 29    | 71    | 0.41   | 1.06   |        |
| 2      | 37                    | 8    | 20    | 26    | 8      | 1      | 34    | 66    | 0.52   | 1.32   |        |
| 3      | 44                    | 8    | 18    | 21    | 8      | 1      | 29    | 71    | 0.41   | 1.69   |        |

3.1. $^{13}$C–$^1$H (HETCOR) and $^{13}$C (CP/MAS) NMR Spectroscopy of HAs Isolated from Soils of Yamal Peninsula

According to the $^{13}$C (CP/MAS) NMR spectroscopy, a significant amount of aliphatic fragments accumulate in HAs of soils from the Yamal peninsula (Figure 2A). Our data are in line with previous studies in the Arctic region [28,47–49]. The accumulation of C,H-substituted aliphatic fragments leads to the conservation and accumulation of organic substances in the soils of Yamal peninsula. The accumulation of oxygen-containing (-O-CH) fragments of HAs is also characteristic of Arctic
soils, which is associated with better solubility in water, migration of organic acids along the profile, and their accumulation at the permafrost table [28,49,50].

Table 6. 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 2; AR—aromatic fraction; AL—aliphatic fraction; C, H-alkyl/O,N-alkyl—C, H-alkyl was summarized in 0–47 ppm, O, N-alkyl—in the range 47–60 and 60–105 ppm.

| Sample | Chemical Shifts. ppm | AR AL AR/AL C,H-Alkyl/O,N-Alkyl |
|--------|----------------------|----------------------------------|
| 1      | 35 8 25 18 11 3      | 29 71 0.41 1.06                |
| 2      | 37 8 20 26 8 1       | 34 66 0.52 1.32                |
| 3      | 44 8 18 21 8 1       | 29 71 0.41 1.69                |

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Figure 2. $^{1}$H-$^{13}$C (HETCOR) and $^{13}$C (CP/MAS) NMR spectra of HAs isolated from the soil of the Yamal peninsula. (A) $^{13}$C (CP/MAS) NMR; (B) $^{1}$H-$^{13}$C (HETCOR) NMR with contact time 0.1 ms; and (C) $^{1}$H-$^{13}$C (HETCOR) NMR with a contact time 0.75 ms.

The low content of aromatic fragments in the HAs indicates a low level of humification of organic matter, which is associated with the condensation of low-molecular precursors of humification and a low level of stabilization of organic matter [49]. The accumulation of aliphatic fragments is due to the composition of organic residues entering the soil, moss-lichen tundra vegetation predominates in the Yamal, which is more enriched in aliphatic compounds [27]. A high degree of hydrophobicity of the region is associated with the low microbiological activity of soils, which reduces the rate of transformation of organic residues in the soil and contributes to the accumulation of paraffin fragments [46]. The ratio of C,H-alkyl to O,N-alkyl, which characterizes the degree of decomposition of organic matter, is minimal for Yamal soils, which indicates a low degree of humification of organic matter relative to the other studied soils.

To obtain additional information regarding the spatial bonds between different functional groups, two-dimensional correlation spectra (2D HETCOR) with different contact times (0.1–0.75 ms) were obtained. The obtained spectra allow the correlation of protons and attached carbons (H-C bound). If either there is a direct C-H bond or the contact time is considerable, it is possible to observe the cross-peaks of the carbons. Depending on the contact time, in these spectra, cross-peaks were observed. In the short contact time spectrum (Figure 2B), we can observe a high degree of correlation of the aliphatic zone of HAs (-CH; -CH$_2$; -O-CH; -O-CH$_3$) and low intensity of the aromatic zone of HAs (AR-H, C).

For a contact time of 0.75 ms (Figure 2C), we can observe intense cross-peaks in aliphatic and aromatic zones. In the alkyl-C$_H$ zone, we observed cross peaks corresponding to fragments -CH-H,C and $\alpha$-CH. Cross-peaks corresponding to -CH-O,N fragments are observed in the range from 50 to 80 ppm. For a contact time of 0.75 ms, there is a cross-peak corresponding to anomers and COO-H,C fragments that were not visible in the short contact time spectrum (0.1 ms), indicating that the group is not attached directly to the aromatic core [30].
Thus, we observe a similar composition of HAs with $^{13}$C (CP/MAS) NMR spectroscopy. According to the data obtained by the 2D HETCOR method, we see intense cross peaks corresponding to the Alkyl zone of HAs and less intense corresponding to the aromatic zone. The data obtained indicate a relatively high concentration of -O-CH group that may lead to high solubility of HAs in complex with trace metals in water during their migration, along with the profile and conservation of organic matter in the soils of Yamal.

3.2. $^1$H-$^{13}$C (HETCOR) and $^{13}$C (CP/MAS) NMR Spectroscopy of HAs Isolated from Cryoconite of Grønfjorden Area, Spitsbergen

HAs were isolated from cryoconite in the Aldegonda glacier region; aliphatic fragments predominate in them, accounting for up to 66% of the total (Table 3), but the content of aromatic fragments reaches 34%, which is more typical of the taiga zone [51,52]. In comparison with other studied regions, the organic matter of cryoconites is more humified [24,51,52]. The specificity of the accumulation of organic matter in cryoconites is associated with wind accumulation and water redistribution of organic matter in glacier regions. The relatively high aromaticity of HAs could be interpreted as a result of the 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. Moreover, that effect might be related to coal dust, for example, from the adjacent coal mines of Barentsburg. The aromaticity of HAs indicates the stabilization of organic matter in Svalbard cryoconites. According to the C, H-Alkyl to O, N-Alkyl ratio in Svalbard cryoconite, there is a relatively high degree of decomposition of organic remnants relative to the organic horizons of Arctic cryogenic soils, which is reflected in the relatively high degree of humification of the organic matter of Svalbard cryoconites.

Spectra were obtained for HAs of cryoconites using the $^1$H-$^{13}$C (HETCOR) NMR spectroscopy with different contact times (0.1–0.75 ms). Depending on the contact time, in these spectra, cross-peaks were observed. In the short contact time spectrum (Figure 3B), we can observe a high level of correlation of the Alkyl zone and, to a lesser extent, the aromatic zone. In the aliphatic zone, long chains predominantly accumulate with methylene (up to 20 ppm), peptides (-C(O)NH- groups up to 45 ppm), the highest degree of correlation, amines (CN(H)-CH-) with 45–55 ppm, a large group of oxygen-containing fragments, esters and ethers (-O-CH$_3$) and (-O-CH) from 55 to 80 ppm, anomers (-OH-CH-X), from 103 to 105 ppm, as well as a large aromatic zone ($^{13}$C$_{AR}$H) 110 to 135 ppm, H-substituted aromatic fragments.

For a contact time of 0.75 ms (Figure 3C), we can observe intense cross-peaks in the aliphatic and aromatic zones. With increasing contact time on the spectra, single structural fragments become more noticeable; at 0.1 ms, we can generally observe aliphatic and aromatic zones. Thus, a significant amount of H-substituted aliphatic fragments (-C-CH$_3$; -C-CH$_2$) accumulates in the HAs of cryoconites. With an increase in time, we observe a cross-peak in the region of methoxy fragments (CH$_3$-O) from 4.2 to 5.8 ppm for 1Hδ. Only H-substituted aromatic fragments are present in the aromatic zone of HAs ($^{13}$C$_{AR}$H), and O, N substituted aromatic fragments are absent. At a contact time of 0.75 ms, a cross-peak appears in the –COO-H, C region, from 165 to 176 ppm $^{13}$Cδ. As in the Yamal spectra, the group –COO-H,C was not visible in the short contact time spectrum (0.1 ms), indicating that the group is not directly attached to the aromatic core.

According to the obtained data, $^1$H-$^{13}$C (HETCOR) completely correlates with $^{13}$C (CP/MAS) NMR peaks; there is an intense correlation of cross-peaks in the regions of aliphatic zones and lower in aromatic ones, which indicates with relatively high rates of humification of organic matter in severe Arctic climate.
According to the C,H-Alkyl to O, N-Alkyl ratio, the degree of decomposition of organic remnants decreases, which leads to low migration rates of HAs along the soil profile and a low degree of solubility of HAs in water, which might be associated with a low degree of hydromorphism of the studied area. The accumulation of H-substituted aliphatic fragments is associated with the conservation and storage of organic matter in the soil and a low degree of humification. This leads directly connected with restriction in such humification precursors as lignin-derived compounds.

Soil formation here is directly related to avifauna. The main source of organic carbon and nitrogen is guano [14,18,53]. A significant amount of aliphatic HAs fragments accumulates in these soils, accounting for up to 71%, while the content of aromatic fragments reaches 29%; the same ratio was found for the soils of Yamal. From the data obtained, it can be concluded that the composition of the HAs of the Arctic and Antarctic soils are highly homogeneous. At the same time, the composition of the aliphatic group differs from Arctic soils; the proportion of oxygen-containing groups in the Antarctic soil decreases, which leads to low migration rates of HAs along the soil profile and a low degree of solubility of HAs in water, which might be associated with a low degree of hydromorphism of the studied area. The accumulation of H-substituted aliphatic fragments is associated with the composition of precursors of humification and the condensation of low molecular in HAs. This leads to the conservation and storage of organic matter in the soil and a low degree of humification. This is directly connected with restriction in such humification precursors as lignin-derived compounds. According to the C,H-Alkyl to O, N-Alkyl ratio, the degree of decomposition of organic remnants is the highest among the soils studied. We suppose that this is a result of the fact that birds use mainly remnants of Deschampsia antarctica for nest building, which contain an increased portion of phenyl-propanoid organic precursors [6].

HAs spectra of soils were isolated from the soils of King-George Island located in the maritime part of Antarctica. Soil formation here is directly related to avifauna. The main source of organic carbon and nitrogen is guano [14,18,53]. A significant amount of aliphatic HAs fragments accumulates in these soils, accounting for up to 71%, while the content of aromatic fragments reaches 29%; the same ratio was found for the soils of Yamal. From the data obtained, it can be concluded that the composition of the HAs of the Arctic and Antarctic soils are highly homogeneous. At the same time, the composition of the aliphatic group differs from Arctic soils; the proportion of oxygen-containing groups in the Antarctic soil decreases, which leads to low migration rates of HAs along the soil profile and a low degree of solubility of HAs in water, which might be associated with a low degree of hydromorphism of the studied area. The accumulation of H-substituted aliphatic fragments is associated with the composition of precursors of humification and the condensation of low molecular in HAs. This leads to the conservation and storage of organic matter in the soil and a low degree of humification. This is directly connected with restriction in such humification precursors as lignin-derived compounds. According to the C,H-Alkyl to O, N-Alkyl ratio, the degree of decomposition of organic remnants is the highest among the soils studied. We suppose that this is a result of the fact that birds use mainly remnants of Deschampsia antarctica for nest building, which contain an increased portion of phenyl-propanoid organic precursors [6].

HAs spectra of soils were obtained by 1H-13C (HETCOR) NMR spectroscopy with different contact times (0.2–0.75 ms). Depending on the contact time, in these spectra, cross-peaks were observed. In the short contact time spectra (Figure 4B), we can observe an intense correlation of cross-peaks in the region of the aliphatic group and less so in the aromatic zone. As part of the aliphatic group, H-substituted aliphatic fragments (CH-H,C and α-CH) were detected in the range from 24 to 40 ppm, as well as oxygen-containing functional groups (CH₃-O; CH₂-O, N; CH-O, N). Cross-peaks for the aromatic zone are observed only in the range from 118 to 130 ppm.
HAs of the polar regions as a whole have a similar structure; aliphatic fragments over aromatic
are important in their composition. However, HAs from cryoconite of Spitsbergen differ from typical
soils of the Arctic and Antarctic; up to 34% of aromatic structural fragments accumulate in its
composition, which is associated with the specifics of the formation of cryoconites on the Svalbard
archipelago. Condensation of low molecular HAs fragments in the soils of Yamal and Antarctica
was noted, which leads to the conservation of organic matter in these soils.

4. Conclusions

Based on the analysis of a $^1$H-$^{13}$C (HETCOR) and $^{13}$C (CP/MAS) NMR spectroscopy of HAs, it can
be concluded that:

- HAs of the polar regions as a whole have a similar structure; aliphatic fragments over aromatic
  fragments prevail in their composition. HAs from cryoconite of Spitsbergen differ from typical
  soils of the Arctic and Antarctic; up to 34% of aromatic structural fragments accumulate in its
  composition, which is associated with the specifics of the formation of cryoconites on the Svalbard
  archipelago. Condensation of low molecular HAs fragments in the soils of Yamal and Antarctica
  was noted, which leads to the conservation of organic matter in these soils.

For a contact time of 0.75 ms (Figure 4C), as well as for the spectra described above, we observe
intense cross-peaks in the aliphatic region and the lowest intensity in the aromatic region. Functional
group COO-H,C also appears, which is not attached directly to the aromatic core.

HAs of soils of Antarctica mainly consist of low molecular chains of H-substituted aliphatic
fragments, which leads to the conservation of organic matter in the studied soils of Antarctica.

The use of modern instrumental methods such as one- and two-dimensional NMR spectroscopy is
a reliable way to study the molecular composition of HAs in soils. Our results about $^{13}$C (CP/MAS) NMR
spectroscopy are in agreement with previous studies [6,11,18,19,24,26–28,46,47,49]; the accumulation of
aliphatic compounds in HAs composition can be related to the activity and composition of microbiota,
hydrophobicity, and the composition of humification precursors [27,28,36,46,47]. Excessive moisture in
the areas of King George isl. and the Yamal Peninsula may be the main factor affecting the composition
of HAs in soils, as they limit the development of aerobic microorganisms in the soil and lead to the
formation of anaerobic communities [28,36,46]. This method allows you to calculate the integrated
signal intensities, as well as to separate the signals when they are imposed or at a high noise level.
However, the use of $^1$H-$^{13}$C (HETCOR) NMR spectroscopy can complement the $^{13}$C (CP/MAS) NMR
spectroscopy method, thereby increasing the accuracy of detection of individual HAs fragments
in soils. At present, the use of $^1$H-$^{13}$C (HETCOR) NMR has been performed mostly for kerogen
and polymers [29,30,32]. However, we were unable to find any works devoted to the study of
two-dimensional NMR spectroscopy of HAs of polar soils, so further studies using this method are
necessary to expand the database on the structure of HAs of polar soils.

Figure 4. $^1$H-$^{13}$C (HETCOR) and $^{13}$C (CP/MAS) NMR spectra of HAs isolated from soils of King-George
isl., Antarctica. (A) $^{13}$C (CP/MAS) NMR; (B) $^1$H-$^{13}$C (HETCOR) NMR with contact time 0.2 ms;
and (C) $^1$H-$^{13}$C (HETCOR) NMR with contact time 0.75 ms.
The use of two methods of NMR spectroscopy allowed for a more detailed study and analysis of the composition of HAs in soils and cryoconites. Analysis of cross-peaks at different time contacts allowed us to correlate H-C bonds and reveal the composition of the HAs.

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