

Characterisation of humic acids, isolated from selected sub-antarctic soils by ^{13}C -NMR spectroscopy

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Abstract

Soils of Antarctic considered as underestimated in terms of soils organic matter pools, organic remnants humification/mineralization rates and biogenic-abiogenic interactions. Humic acids of selected Sub Antarctic soils were investigated in terms of elemental and structural composition with special reference to evaluation of organic matter stabilisation degree and assessment of carbon species distributions in the molecules with use of solid state ^{13}C -NMR spectroscopy. It was shown, that the prevailing of aliphatic compounds on the aromatic one is more pronounced in Antarctic soils than in Arctic ones. Average portion of the aromatic compounds is about 20% in humic acids, extracted from soils with evident ornitogenic effect from Fildes Peninsula (Norh-West Antarctic peninsula). This indicates that the role of humification precursors composition is the leading in the humification process. The stabilisation rate of the Antarctic HAs can be assessed as low and the potential risk of biodegradation of their molecules are high.

Key words: humic acids, Antarctic, ^{13}C -NMR spectroscopy, soil organic matter

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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 (McGuire et al. 2009). Low temperature and severe conditions provide the accumulation and stabilization of large amounts of organic matter in permafrost soils over thousands of years (Zubrzycki et al. 2013). Nowadays, current trends of climate warming and permafrost thawing are exposing this pool of organic mat-

ter to microbial degradation (Schuur et al. 2015) and other environmental risks. Because possible SOM degradation, polar SOM represents a vulnerable carbon storage, susceptible to be remobilised under increasing temperatures. In order to better understand the implication of permafrost SOM to greenhouse gas emissions, an accurate knowledge of its spatial distribution, both in terms of quantity and quality (*i.e.* biodegradability, chemical composi-

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tion and humification degree) is needed (Fritz et al. 2015). Current state of knowledge estimates soil organic carbon (SOC) stocks of 1307 Pg throughout the northern circumpolar region (Hugelius 2014). These amounts surpass previous estimates (Tarnocai et al. 2009) and largely exceed the total carbon contained in the world vegetation biomass (460-650 Pg) or in the atmosphere (589 Pg, IPCC 2007-[2]). However, these SOC stock estimates are still poorly constrained (Hugelius 2014). The main source of uncertainty is the fact that such estimates have been calculated from observations which are highly spatially clustered (Hugelius 2014), whereas extensive land areas still remain uncharacterised due to logistic difficulties to reach these sites. The second reason is that the calculation of stocks provided on the base of estimated data on soil bulk density and carbon values, derived from dichromate oxidation methods (Abakumov et Popov 2005, Abakumov 2010). At the same time the storages of SOM in Antarctic are more underestimated because of the lack of the data for different parts of this continent, due to high content of the coarse fractions in soils and high variability of carbon content in the fine earth. Stocks of organic carbon in Antarctic soil assessed as 0.5 kg m^{-2} in polar deserts, about 1.0 kg m^{-2} in barrens, up to $3\text{-}5 \text{ kg m}^{-2}$ in sub-Antarctic tundra's and even up to 30 kg m^{-2} for penguin rockeries of the maritime islands (Abakumov 2010, Abakumov et Mukhametova 2014). Uncertainties for SOM storages in polar environments become even more important for SOM quality (Mishra et al. 2013, Abakumov et al. 2014). Nevertheless, the chemical composition of SOM determines its decomposability and, therefore, it determines the rate at which carbon may be transferred from soils to the atmosphere under warming conditions. Biodegradability of SOM has been related to humification degree, as more advanced stages in the humification process imply a depletion of the labile molecules, as well as an in-

crease in the bulk aromaticity, which provides a higher stability of the SOM. A number of proxies have been used to trace humification rate and SOM stability level. C/H from humic acids has been used as an index of molecular complexity, as higher degree of conjugation implies a lower hydrogenation of the carbon chains (Zaccone et al. 2007) and C/N has been used as a measure of Histic materials degradation (Kuhry et Vitt 1996–In Zaccone et al. 2007). ^{13}C -NMR spectrometry provides information on the diversity in carbon functional structures (carbon species) and has also been used to evaluate changes in SOM during decomposition and humification (Abakumov et al. 2015). More specifically, high phenolic (150 ppm), carboxyl-C (175 ppm) and alkyl-C (30 ppm) groups, together with low O-alkyl carbons, have been related to advanced humification stages (Zech 1997). So far, studies of SOM quality from polar environments have revealed a generalised lowly-decomposed character of the organic molecules (Dziedowiec et al. 1994), which preserve much of the chemical character of their precursor material due to low progress of humification (Davidson et Janssens 2006). This is very important, because polar soils characterizes by specific composition of the humification precursors.

The structure and molecular composition of Antarctic soils organic matter has been investigated previously by ^{13}C -NMR methods and it was shown that in usual organo-mineral soils the aliphatic carbon prevails on the aromatic one, owing to the nature of non-ligniferous material as precursor (Calace et al 1995). Later it was shown that this feature is typical for many soil from different of Antarctic (Abakumov 2010) and even soil, formed on the penguin rockeries show the same trends of prevailing of aliphatic compounds of aromatic ones (Abakumov et Fattakhova 2015). The northern most soil of Arctic polar biome show the same trends in organic molecules organization: prevalence of aliphatic structures on

aromatic ones, but the diversity of individual components in aromatic and aliphatic parts are normally higher in Arctic soil because increases diversity of humification precursors (Ejarque et Abakumov 2016, Abakumov et al. 2016). A wet Antarctic Histic soils from algae is characterized by the predominance of proteins within the nitrogen compounds and a slight degradation of carbohydrates in the SOM. A selective preservation of alkyl moieties in the deeper soil layers is suggested, little transformation processes of SOM is detectable because soil temperatures in summer are low and obviously were not high enough to stimulate a further microbial break-down (Beyer et al. 1995). Previous investigation of organic matter were mainly concentrated to investigation of normal Gelisols or Cryosols with the sources of organic matter derived from bryophytes, algae's or vascular plants of stable habitats without pronounces ornitogenic effect (de Souza Carvalho et al. 2010). It was shown that the ornitochoria play an essential role in plant remnants redistribution in space the Antarctic landscape (Parnikoza et al. 2015, Abakumov et al. 2016), birds use to transport a huge amounts of organic material of different composition inside the inlands

landscapes in Antarctica. Therefore, soils on the King George Island are distributed not only of the marine terraces or ancient uplands with pronounced and long soil formation during the latest Holocene, but also on the new colonized (vegetated) areas, where the plant seedlings and raw organic material were brought by birds, which use these materials for nest building. These soils are presented by traditional Leptosols and Lithosols under the birds nests, composed by the remnants of *Deschampsia antarctica*, or by soils of the seasonal ponds, where cyanobacterial mats occurs due to soil enrichment by nitrogen of the bird origin. These soil materials were selected for isolation and further characterization of humic acids composition and structure by application of ^{13}C -NMR technique. Our aim was to investigate the molecular organisation of the humic acids, isolated from various Leptosols of the King-George Island and to assess the potential vulnerability of soils organic matter in face of possible mineralisation processes. This was addressed by a) quantifying SOM composition, b) characterising SOM quality by means of elemental analysis and solid-state ^{13}C -NMR spectroscopy.

Material and Methods

Sample sites

The soils with evident actual or former effect of the flying birds were sampled during the 61th Antarctic expedition from January 17, 2016 to February 25, 2016.

Because data of ^{13}C -NMR characterization of humic acids of soils formed under fresh guano on the areas of penguin rockeries were obtained and published previously (Abakumov et Fattakhova 2015), this paper considers only the data on soil, formed under transported organic material under effect of skua or kelp gull. 7 Leptosols were sampled from the topsoil horizons

with aim to extract the humic acids powder and to obtain ^{13}C -NMR spectra.

Soils investigated belongs to Sub-Antarctic maritime zone (King George Island, South Shetland Archipelago), Antarctic region. The Bellingshausen station (Russian scientific and logistic center on King George Island, 62° 12' S, 58° 58' W, 40 m a.s.l.) is situated on the Fildes Peninsula of King George Island (Fig. 1). The parent materials here are presented by andesites, basalts, and tuffs, the coastal areas is covered by maritime sands and gravels, while the peri-

glacial plots are occupied by moraines and some fluvioglacial materials (Peter 2008). The average annual temperature of air is -2.8°C , in Austral summer (January and February) the average monthly temperature rise up to $0.7\text{--}0.8^{\circ}\text{C}$ (Abakumov et Andreev 2011), but it is need to consider that the soil surface temperature is essentially higher when it is free from ice and snow (Markov 1956, 1958). The total annual precipitation reaches 729 mm, the number of days with precipitation is from 22 to 30 days in month. The wind velocity is about 9.3 m s^{-1} (Petter 2008) with maximum about 28 m s^{-1} . Vegetation diversity of the Fildes peninsula is quite high in comparison with landscapes of other Antarctic regions (Abakumov et Andreev 2011), mono species plant communities as well as mixed ones are common for both: coastal part and in plateau of peninsula. This provides a possibility to many authors to identify it as tundra or Antarctic tundra (Convey 2013, Casanova-Katny et Cavieres 2012). Plant communities of King George Island are the most developed and rich in whole the Antarctic. There are plots of former penguin rockerries (*Pygoscelis* sp.), rocks affected by sea petrel (*Larus dominicanus*) and fresh moraines in periglacial part. Fildes peninsula presented mainly by tundra environment, or in some cases, by barrens communities. Soils, sampled for further analyses are following: 1. Leptosol, under the nest of skua, composed of lichens and *Deschampsia antarctica* remnants, well drained positions, coarse textured soil ($62^{\circ}13.361' \text{ S}$, $52^{\circ}47.273' \text{ W}$); 2. Leptosol, under typical bryophyte-lichens tundra, over moisted position, coarse textured soils ($62^{\circ}13.140' \text{ S}$, $58^{\circ}46.067' \text{ W}$); 3. Postor-

nitogenic soil, composed by remnants of *Deschampsia antarctica* and *Prasiola crispa* ($62^{\circ}11.024' \text{ S}$, $58^{\circ}51.340' \text{ W}$); 4. Leptosol under the bryophyte cover, with admixture of *Deschampsia antarctica*, marine terrace, over moisted position ($62^{\circ}14.175' \text{ S}$, $58^{\circ}58.542' \text{ W}$); 5. Leptosol under the skua nest, composed of remnants of lichens and *Deschampsia*, well drained positions, coarse textured soil ($62^{\circ}13.361' \text{ S}$, $52^{\circ}47.273' \text{ W}$); 6. Turf (Histic material) near the ISZ building, total thickness of the turf is 150 cm, sample selected from the depth of 0-10 cm, the bird transportation effect is expressed in accumulation of *Deschampsia remnants* ($62^{\circ}11.287' \text{ S}$, $58^{\circ}58.337' \text{ W}$); 7. Leptosol under the bryophyte cover, marine terrace, over moisted position ($62^{\circ}10.450' \text{ S}$, $58^{\circ}58.525' \text{ W}$).

The routine soil chemical analyses were performed by classical methods: C and N content with use of element analyzer and pH in water and in salt suspension with use of pH-meter pH-150 M. Basic chemical characteristic of soil samples, selected for extraction of humic acids provided in Table 1. Soils, investigated characterises by high amount of total organic carbon in comparison with usual mineral soils (Abakumov 2010). This is caused by additional accumulation of organic materials by birds. Sea birds use to brigs additional organic matter in landscapes, where the concentration of those are not high (Abakumov et al. 2016, Parnikoza et al. 2015). This is also the reason of relatively increased nitrogen content, which expressed in C/N ratio. All the soils investigated are acids with developed potential acidity, connected, with exchange capacity of organic matter.

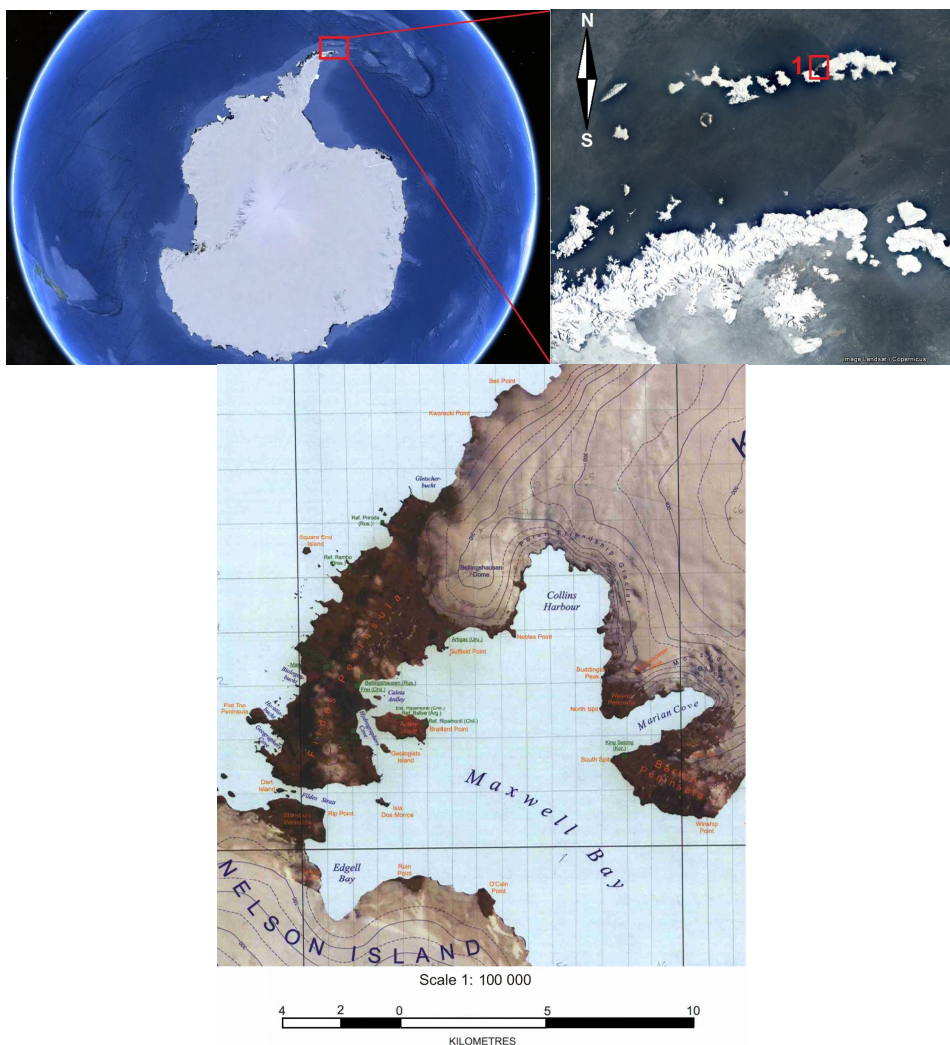


Fig. 1. Location of study sites: Antarctic peninsula, King-George Island, Fildes Peninsula.

Sample	TOC, %	N, %	C/N	pH _{H2O}	pH _{CaCl2}	Color
1	8.05	0.66	12.19	4.47	4.40	10 YR 4/2
2	6.41	0.39	16.43	4.20	4.10	2.5 YR 4/4
3	10.16	0.84	12.09	4.90	4.21	2.5 YR 4/4
4	2.20	0.26	8.46	3.55	3.10	10 YR 5/3
5	38.43	1.40	27.45	4.76	4.70	10 YR 5/3
6	31.33	2.26	13.86	5.48	5.05	10 YR 5/3
7	35.71	1.78	20.06	5.24	4.70	10 YR 4/2

Table 1. Chemical characteristics of the fine earth and color of the topsoil material.

Extraction of humic acids

Humic acids were extracted from each sample according to the following procedure (Schnitzer 1982, [1]): Humic acids were extracted with 0.1 M NaOH (soil/solution mass ratio 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 acidified to pH=1 with 6 M HCl to induce the precipitation of the humic acids. The supernatant, which contained fulvic acids, was separated from the precipitate by centrifugation at 1,516×g for 15 min. The humic acids were then redissolved in 0.1 M

NaOH and shaken for 4h under N₂ before the suspended solids were removed by centrifugation. The solution was acidified again with 6 M HCl to pH=1, and the humic acids were separated by centrifugation and demineralized by shaking overnight in 0.1 M HCl/0.3 M HF (solid/solution ratio 1:1). Next, they were repeatedly washed with deionized water until pH=3 was reached; and then they were finally freeze-dried. Extraction yields of humic acids were calculated as the percentage of carbon recovered from the original soil sample used for extraction.

Characterization of humic acids

Humic acids were characterized for their elemental composition (C, N, H, and S) using a Euro EA3028-HT analyzer. Data were corrected for water and ash content. Oxygen content was calculated by difference taking into account the ash content. The elemental ratios reported in this paper are based on weight. Solid-state ¹³C-NMR spectra of humic acids were measured with a Bruker Avance 500 NMR spectrometer (Karlsruhe, Germany, 2003) in a 4-mm ZrO₂ rotor. The magic angle spinning speed was 20 kHz in all cases, and the nutation frequency ¹³C fields for crosspolarization was u1/2p 1/4 62.5 kHz. Repetition delay and number of scans were 3 s. Groups of structural compounds were identified by the chemical shifts values: 190–170 ppm—carboxyl group and amidic carbonyl ($f_a^{CO_2}$); 170–150 ppm—aromatic C of fenols and fenol esters (f_a^P); 150–135 ppm—alkylaro-

matic (f_a^S); 135–108 ppm—protonize aromatic carbon, bridgehead C (f_a^H); 108–100 ppm—cellulose anomeric carbon and hemiacetal carbon ($f_{al}^{O_1}$); 100–70 ppm—resonance region of C–H bonds, secondary alcohols, and other carbon atoms bound to oxygen ($f_{al}^{O_2}$), 70–50 ppm—methyl group resonance region of aliphatic and aromatic ethyl ethers, amino acid carbons, and methyl esters of carboxylic groups (f_{al}^{OM}); 50–32 ppm—resonance region of quaternary carbon and CH carbons (f_{al}^Q); 32–27 ppm—resonance region of CH₂ alkyl structures in transconformation (f_{al}^{trans}); 27–10 ppm—resonance region of alkyl methyls and CH₂ units (f_{al}^{Met}). The total aromatic and aliphatic content was determined by integrating the signal intensity in the intervals 100-170 and 183-190 ppm on the one hand, and 0-110 and 164-183 ppm on the other hand, respectively.

Results and Discussion

Data on elemental composition of the HAs (Table 2) show that they are comparable with those, extracted from Antarctic soils previously (Chukov et al. 2016, Abakumov et Fattakhova 2015). The O/C is more increased while compare with previous ones, this can reflect the specificity of humification under organic material, transported by birds. Extremely increased O/C

ration were revealed in sample № 3 which indicates the high degree of oxidation of the molecules. But, in general, the elemental composition of soils investigated were compared with those for previously investigated Arctic (Ejarque et Abakumov 2016) and Antarctic (Bölter 2001, Calace et al. 1995, Chukov et al. 2015) soils.

Sample №	C	N	H	O	C/N	H/C	O/C
1	48.23	5.28	6.60	39.83	9.13	0.13	0.82
2	50.05	4.54	6.77	38.45	11.00	0.13	0.76
3	35.55	4.44	5.69	54.20	8.00	0.15	1.52
4	50.66	5.72	6.83	36.80	8.85	0.13	0.72
5	47.85	4.85	6.34	40.83	9.86	0.13	0.85
6	48.41	4.89	6.38	40.73	9.89	0.13	0.84
7	45.76	4.95	6.18	42.90	9.23	0.13	0.93

Table 2. Elemental composition (%) and atomic ratios in HAs.

^{13}C -NMR spectra's (see Fig. 2) and data on carbon species and aliphatic-aromatic groups distribution (Table 3) indicates that soils, formed under the effect of sea birds contains the humic acids comparable to typical HAs of the high latitudes terrestrial environments. ^{13}C -NMR spectra revealed indicates that there were only small differences in the structural diversity of carbon atoms among the surface samples of selected soils. The characteristic feature of the HAs, extracted from investigated soils is the prevalence of aliphatic carbon species groups on the aromatic ones. This indicates that both, Arctic and Antarctic soils characterizes by a regional homogeneity of HAs composition. There are two reasons of this. The first is short vegetation period combined with severe climatic conditions. The seconds is a restriction in lignin derived compounds content in Arctic and, especially Antarctic environments. This reflected in our founding's for Arctic, where more than 60% of carbon species presented by aliphatic compounds and this is more pronounced in Antarctic soils, where the por-

tion of aliphatic structure increases in some cases up to 80%. We think that this is directly connected with restriction in such humification precursor as lignin-derived compounds. At the same time our data shows that the portion of aromatic compounds is little higher in soils under birds transported materials that under the mono species bryophyta or lichens communities (Chukov et al. 2015). We suppose that this is a result of that fact that birds use for nest building mainly remnants of *Deschampsia antarctica* which contains increased portion of phenyl-propanous organic precursors (Abakumov 2010). In general, the forms of spectra's indicated that HAs of the soils investigated are the substances with more pronounced dominance of the aliphatic fragments than soils of high latitudes of the Siberian Arctic. This well corresponds to previously published data (Abakumov et al. 2015) and support the conclusion that the possible risks of organic matter degradation under the coming climate change are high for still stabilized organic matter of both permafrost affected regions.

Sample №	190-170	170-150	150-135	135-108	108-100	100-70	70-50	50-32	32-0	Aromatic	Aliphatic
	$f_a^{CO_2}$	f_a^P	f_a^S	f_a^H	f_{al}^{O1}	f_{al}^{O2}	f_{al}^{OM}	f_{al}^Q	f_{al}^{trans}		
1	11.32	4.70	8.92	3.47	6.16	23.85	11.00	11.53	19.03	17.09	82.91
2	9.28	7.24	0.44	10.78	8.92	19.12	9.34	16.56	18.53	18.46	81.54
3	9.69	12.02	10.15	3.67	10.45	13.50	17.82	12.58	10.12	25.84	74.16
4	11.78	1.66	3.36	13.75	3.85	18.29	12.48	17.24	17.72	18.77	81.23
5	10.98	4.60	10.46	4.25	2.61	27.80	9.00	20.00	10.38	19.31	80.69
6	11.50	4.28	3.75	11.35	7.68	21.29	9.73	19.59	10.63	19.38	80.62
7	11.67	3.37	5.24	11.87	6.71	18.60	9.88	20.57	12.05	20.48	79.52

Table 3. ^{13}C -NMR section integrals (percent of total carbon) for key carbon structures of soil humic acids (ppm).

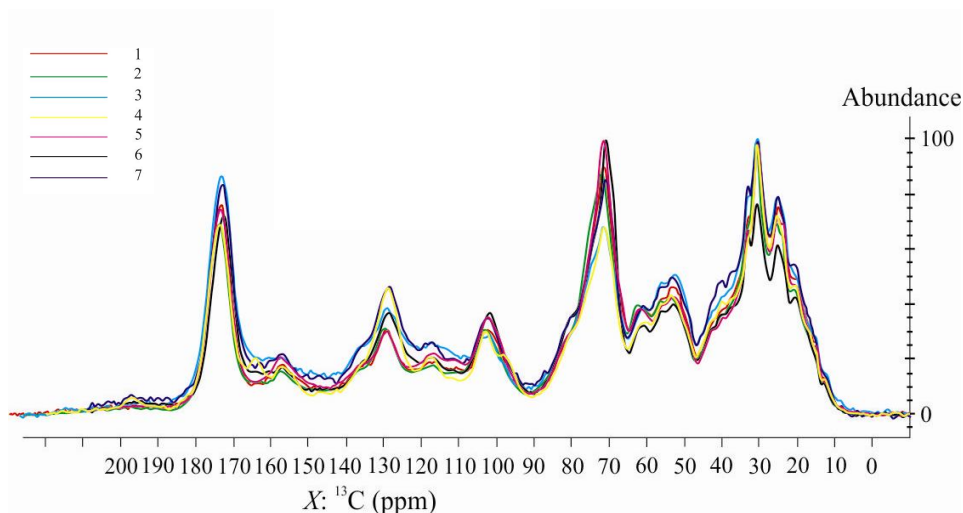


Fig. 2. ^{13}C -NMR spectra in soil humic acids. *Sample:* 1 – Leptosol, under the nest of skua, composed of lichens and *Deschampsia antarctica* remnants, 2 – Leptosol, under typical bryophyte-lichens tundra, 3 – Postornithogenic soil, composed by remnants of *Deschampsia antarctica* and *Prasiola crista*, 4 – Leptosol under the bryophyte cover, with admixture of *Deschampsia antarctica*, 5 – Leptosol under the skua nest, composed of remnants of lichens and *Deschampsia*, 6 – Turf (Histic material) near the ISZ building, total thickness of the turf is 150 cm, sample selected from the depth of 0-10 cm, the bird transportation effect is expressed in accumulation of *Deschampsia* remnants, 7 – Leptosol under the bryophyte cover.

Conclusions

Humic acids of Antarctic soils, formed under bird transported materials were investigated by ^{13}C -NMR spectroscopy with aim to reveal the humification degree and specificity of their molecular structure. Humic substances of 7 soils investigated shows the predominance of the aliphatic compounds on aromatic ones. The degree

of aromaticity is connected with presence of the remnants of *Deschampsia antarctica* in the nest material. The components of these remnants play an important role as precursors of humification. The key characteristic feature of plant remnants which regulated the aromaticity of humic acids is the portion lignin-derived compounds. Data

obtained for soils, formed under cereal plants is different from those for obtained for soils, formed under mono species bryophyte or lichens communities. The HAs in soils, affected by accumulation of *Deschampsia remnants* in nests exhibit increased content of aromatic part. There is no essential variation of carboxylic groups content between soils formed under various humification precursors which indicated that functional activity of all investigated humic substances is equal.

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