

Dear reviewer!

Thank you very much for all remarks and suggestions.

The manuscript text was improved according all remarks.

Also additional reference was given regarding the occurrence of Technosols in Antarctica (this could be especially possible in surroundings of Bellinshausen station)

With Kind Regards,

Evgeny Abakumov, corresponding author

1 **STABILITY OF SOIL ORGANIC MATTER IN CRYOSOLS OF MARITIME**
2 **ANTARCTIC: INSIGHTS FROM ¹³C NMR AND ELECTRON SPIN RESONANCE**
3 **SPECTROSCOPY**

4
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10 **Key words**

11 Antarctica, soil organic matter, stabilization, humic acids

12
13 **Key points**

14 Investigation of Antarctic soil organic matter stability

15 Humic acids of superficial horizons contain more aromatic carbon

16 Humic acids of isolated layers contain more free radicals

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18
19 **Abstract**

20
21 Previously, the structure and molecular composition of the Antarctic SOM has been investigated
22 using ¹³C-NMR methods, which showed that in typical organo-mineral soils the aliphatic carbon
23 prevails over the aromatic one, owing to the non-ligniferous nature of its precursor material. In
24 this study, the soil organic matter (SOM) was analyzed from different sample areas (surface level
25 and partially isolated supra-permafrost layer) of the tundra-barren landscape of the Fildes
26 Peninsula, King George Island, Western Antarctica. We found that the humic acids (HAs) of the
27 cryoturbated, buried areas had lower amounts of alkylaromatic and protonized aromatic
28 compounds. In contrast, the HAs from the surface layers contain less alkyl carbon components.
29 The free radical content was higher in the surface layers than in the buried layers due to the
30 presence of fresh organic remnants in superficial soil samples. New data on SOM quality from
31 these two representative Cryosols will enable more precise assessment of SOM stabilization rate
32 in sub-Antarctic tundras. Comparison of the ¹³C-NMR spectra of the HAs and the bulk SOM
33 revealed that humification occurs in the Antarctic and results in accumulation of aromatic and
34 carboxylic compounds and reductions in alkylic ones. **This indicates that humification is one of**
35 **the ways of soil organic matter stabilization.**

36
37
38 **Highlights**

39 **Stabilization of soil organic matter studied**

40 **Humic acids of superficial horizons contain more aromatic carbon**

Comment [AИИ1]: e-mail:
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Comment [AИИ2]: This indicates
that humification is one of the ways of
soil organic matter stabilization.

41 Humification is one of the ways of soil organic carbon stabilization

42 1. Introduction

43
44 Polar soils play a key role in global carbon circulation and stabilization as they contain
45 maximum stocks of soil organic matter (SOM) within the whole pedosphere (Schoor et al, 2015).
46 Cold climate and continuous and discontinuous permafrost result in the stabilization of essential
47 amounts of organic matter in soils, biosediments, and grounds of the polar biome (Zubrzycki et al,
48 2014). Global climate changes and permafrost degradation have led to the exposure of huge pools
49 of organic matter to microbial degradation (Schoor et al, 2015) and other environmental risks.
50 Polar SOM represents a vulnerable carbon source, susceptible to remobilization under increasing
51 temperatures (Schoor et al, 2015, Ejarque, Abakumov, 2016). In order to better understand the
52 implications of permafrost SOM for greenhouse gas emissions, accurate knowledge of its spatial
53 distribution, both in terms of quantity and quality (e.g. biodegradability, chemical composition,
54 and humification stage) is needed in addition to effective evaluation of SOM's temporal
55 dynamics (Fritz et al, 2014, Vasilevitch et al, 2018).

56 Current estimations of soil organic carbon (SOC) stocks are around 1307 Pg throughout
57 the northern circumpolar region (Hugelius et al, 2014). These amounts surpass previous
58 estimates (Tarnocai et al, 2009) and grossly exceed the total carbon contained in the world's
59 vegetation biomass (460 - 650 Pg) or in the atmosphere (589 Pg) (Tarnocai et al, 2009).
60 However, the aforementioned SOM/SOC stock estimations are still poorly constrained (Hugelius
61 et al, 2014). This uncertainty is largely caused by the estimates having been calculated from
62 observations that are highly spatially clustered (Hugelius et al, 2014) while extensive land areas
63 remain uncharacterized due to the logistic difficulties of reaching these sites. Additionally, the
64 calculation of these stocks are based on estimated data on soil bulk density and carbon values
65 derived from dichromate oxidation methods (Abakumov, Popov, 2005, Polyakov et al, 2017).

66 The stocks of SOM in the Antarctic are underestimated compared to the Arctic because
67 of the lack of the data for many parts of this continent, due to the high content of stones in the
68 soils and the high variability in the carbon content of the fine earth. Stocks of organic carbon in
69 the Antarctic soil have been reported as 0.5 kg/m² in its polar deserts, about 1.0 kg/m² in its
70 barrens, up to 3 - 5 kg/m² in the sub-Antarctic tundra, and up to 30 kg/m² in the penguin
71 rookeries of the maritime islands (Abakumov, 2010, Abakumov, Mukhametova, 2014,
72 Abakumov et al, 2016). To date, investigation on structural composition of the SOM from both
73 superficial and partially isolated areas has only been performed on Cryosols of the Kolyma
74 lowland (Lupachev et al, 2017), where the organic matter of modern and buried soils vary
75 greatly in terms of their molecular composition and quality.

76 Stability and biodegradability are the key features of SOM that should be taken into
77 account when estimating current and future carbon stocks and organic matter quality and
78 dynamics. Stability is related to humification degree, as more advanced stages in the
79 humification process involve depletion of the labile molecules, as well as an increase in the bulk
80 aromaticity, which confers higher stability to the SOM. A number of proxies have been used to
81 trace humification rate and SOM stability, including aromaticity level (Vasilevitch et al, 2018,
82 Kniker, 2007). Also the ratio of C-Alkyl : C-Aryl and C-Alkyl : O-N-alkyl have been
83 successfully used to assess humification degree (Kinker, 2007). C/H ratio from humic acids
84 (HAs) has been used as an index of molecular complexity, as more degrees of conjugation imply
85 less hydrogenation of the carbon chains (Zaccone et al, 2007) and C/N has been used as a
86 measure of histic material degradation (Lodygin et al, 2014). ¹³C-NMR spectrometry provides
87 information on the diversity in carbon functional structures (carbon species) and has been used to

Comment [AИИ3]: Stabilization of soil organic matter studied
Humic acids of superficial horizons contain more aromatic carbon
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Comment [AИИ4]: Paragraphs were joined

Comment [AИИ5]: This text has been moved from the end of Introduction part

88 evaluate changes in SOM during decomposition and humification. More specifically, high
89 phenolic (150 ppm), carboxyl-C (175 ppm) and alkyl-C (30 ppm) groups, combined with low O-
90 alkyl carbons, have been associated with advanced humification stages (Zech et al, 1997). So far,
91 studies of SOM quality from polar environments have revealed generally lowly-decomposed
92 organic molecules (Dziadowiec, 1994, Lupachev et al, 2017), which preserve much of the
93 chemical character of their precursor material due to slow progress of humification (Davidson
94 and Jansens, 2006). This is very important because polar soils are characterized by the specific
95 composition of the humification precursors.

96 The structure and molecular composition of the Antarctic SOM has been investigated
97 using ^{13}C -NMR methods (Beyer et al, 1997, Abakumov, 2017) and it was shown that in typical
98 organo-mineral soils the aliphatic carbon prevails over the aromatic one, owing to the non-
99 ligniferous nature of its precursor material (Calace et al, 1995). Also, analyses of cryptogam
100 extracts were conducted towards identification of individual organic precursors (Chapman et al,
101 1994). This feature was then shown to be typical for soils from different regions of the Antarctic
102 (Abakumov, 2010), including soil formed on the penguin rookeries (Abakumov, Fattakhova,
103 2015). The northern most soil of Arctic polar biome shows the same trend in organic molecules
104 organization: higher prevalence of aliphatic structures over aromatic ones. The diversity of the
105 individual components in aromatic and aliphatic areas is usually higher in Arctic soil because of
106 the increased diversity of humification precursors (Ejarque, Abakumov, 2016, Abakumov,
107 2010). A selective preservation of the alkyl moieties in the deeper soil layers has been suggested,
108 and little transformation processes of the SOM are detectable because soil temperatures are not
109 high enough to stimulate further microbial break-down, even in the summer (Beyer et al, 1997).
110 It has been shown that ornithochoria play an essential role in redistribution of plant remnants in
111 the Antarctic (Parnikoza et al, 2016) as birds transport considerable amounts of variably
112 composed organic material within its inland landscapes. However, published data on SOM
113 composition for the Antarctic are rare, and further studies that detail its structural compounds
114 and their distribution are needed. Recently, ^{13}C -NMR was successfully used to detail the soils
115 found in endolithic communities in Eastern Antarctica and revealed that endolithic organic matter
116 is characterized by a low prevalence of alkyl aromatic compounds (Mergelov et al, 2018).

Comment [A1116]: The paragraph has been shortened

117 This study aimed to compare the structural composition of the SOM from both superficial
118 and partially isolated (i.e. buried spots on the border with permafrost) areas and to evaluate the
119 stabilization rate of Antarctic Cryosols. The objectives of the study were: (1) to evaluate the
120 alterations in the elemental compositions of the HAs under partial isolation (2) to assess the
121 ratios of aromatic and aliphatic carbon species in the topsoil and isolated areas; (3) to
122 characterize the biochemical activity of the HAs (e.g. free radical concentration).

123 2. Materials and Methods

124 2.1. Study sites

125 King George Island is the largest in the South Shetland archipelago and only around 5%
126 of its 1400 km² area is free of ice (Fig. 1) (Rakusa-Suszczewski, 2002). The Fildes Peninsula and
127 Ardley Island, together around 33 km², comprise the largest ice-free area on King George Island
128 and the second largest of the South Shetland Islands. It has a gentle landscape consisting of old
129 coastal landforms with numerous rocky ridges and an average height of 30 m above main sea
130 level (AMSL) (Michel et al, 2014). According to Smellie (Smellie et al, 2014), this area mainly
131 consists of lava with small exposures of tuffs, volcanic sandstones, and agglomerates. The
132 climate is cold and humid with a mean annual air temperature of -2.2°C and mean summer air
133 temperatures above 0°C for only up to four months (Wen et al, 1994). The mean annual

134 precipitation is 350 - 500 mm/year. The Fildes Peninsula and Ardley Island are among the first
135 areas in maritime Antarctica to become ice-free after the last glacial maximum (Birkenmajer,
136 1989). The Fildes Peninsula was covered by glaciers from 8000 to 5000 BP (Mausbacher et al,
137 1989, Haus et al, 2014). The patterned ground in this region dates from 720 to 2640 BP. In the
138 South Shetland Islands, permafrost is sporadic or non-existent at altitudes below 20 m AMSL
139 and occurs discontinuously in altitudes from 30 to 150 m AMSL (Bockheim et al, 2013).
140 Mosses, lichens, and algae are common to this area along with two vascular plants (*Deschampsia*
141 *antarctica* and *Colobanthus quitensis*). Penguins, seals, and seabirds inhabit the coastal areas and
142 greatly impact the soil development. Major cryogenic surface-forming processes in this region
143 include frost creep, cryoturbation, frost heaving and sorting, gravity, and gelifluction (Michel et
144 al, 2014). Eight separate sites on the Fildes Peninsula have been collectively designated an
145 Antarctic Specially Protected Area (ASPA 125) largely due to their paleontological properties
146 (Management plan, 2009). The average thickness of the soil is about 15 - 25 cm. Soils from King
147 George Island have been divided into six groups (WRB, 2014): Leptosols, Cryosols, Fluvisols,
148 Regosols, Histosols, and Technosols; this corresponds well with previously published data
149 (Navas et al, 2008, Abakumov, 2017).

Comment [AИИ7]: This reference has been added to prove the inclusion of Technosols

150 Three soils were selected for humic substance isolation and further investigation in this
151 study. All soils have top humus layers with a high carbon content and distinguishable layers of
152 suprapermafrost accumulation of organic matter. All three soils are classified as Turbic Cryosols
153 (Histic, Stagnic) (WRB, 2014). Soil profiles 1, 2, and 3 (SP1, SP2, SP3) were collected from
154 locations described by the following coordinates: 62,14,391 S, 58,58,549 W; 62,13,140 S,
155 58,46,067 W; and 62,10,578 S, 58, 51,446 W respectively. Sampling depth was 0 - 10 cm for the
156 superficial layers and 50 - 55, 15 - 20, 20 - 25 for SP1, SP2, and SP3 respectively. Images of the
157 soil profiles are presented in Fig. 2. SP1 is from under the mixed lichen-bryophyta cover, SP2
158 and SP3 are formed under species of *Bryophyta* and *Deschampsia antarctica* correspondingly.

159 **2.2. Sampling and laboratory analysis**

Comment [AИИ8]: The chapter has been renamed according to reviewers' comment

160 Soil samples were air-dried (24 hours, 20°C), ground, and passed through 2-mm sieve.
161 Routine chemical analyses were performed using classical methods: C and N content were
162 determined using an element analyzer (Euro EA3028-HT Analyser) and pH in water and in salt
163 suspensions using a pH-meter (pH-150 M).

164 Humic acids (Has) were extracted from each sample according to a published protocol
165 (Shnitzer, 1982), <http://humic-substances.org/isolation-of-ihss-samples/>). Briefly, the soil
166 samples were treated with 0.1 M NaOH (soil/solution mass ratio of 1:10) under nitrogen gas.
167 After 24 hours of shaking, the alkaline supernatant was separated from the soil residue by
168 centrifugation at $1,516 \times g$ for 20 minutes and then acidified to pH 1 with 6 M HCl to precipitate
169 the HAs. The supernatant, which contained fulvic acids, was separated from the precipitate by
170 centrifugation at $1,516 \times g$ for 15 minutes. The HAs were then dissolved in 0.1 M NaOH and
171 shaken for four hours under nitrogen gas before the suspended solids were removed by
172 centrifugation. The resulting supernatant was acidified again with 6 M HCl to pH 1 and the HAs
173 were again isolated by centrifugation and demineralized by shaking overnight in 0.1 M HCl/0.3
174 M HF (soil/solution ratio of 1:1). Next, the samples were repeatedly washed with deionized
175 water until pH 3 was reached and then finally freeze-dried. HA extraction yields were calculated
176 as the percentage of carbon recovered from the original soil sample (Vasilevitch et al, 2018,
177 Abakumov et al, 2018).

178 Isolated HAs were characterized for their elemental composition (C, N, H, and S) using the
179 Euro EA3028-HT analyzer. Data were corrected for water and ash content. Oxygen content was

180 calculated by difference. The elemental ratios reported in this paper are based on weight. Solid-
181 state ^{13}C -NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in
182 a 3,2-mm ZrO₂ rotor. The magic angle spinning speed was 20 kHz in all cases and the nutation
183 frequency for cross polarization was $u1/2p\ 1/4\ 62.5$ kHz. Repetition delay and number of scans
184 were 3 seconds. Groups of structural compounds were identified by their chemical shifts values:
185 alkyl C (-10 to 45 ppm), O/N-alkyl C (45 to 110 ppm), aryl/olefine C (110 to 160 ppm), and
186 carbonyl/carboxyl/amide C (160 to 220 ppm) (Kniker, 2007). The ^{13}C -NMR study was also
187 conducted in bulk soil samples towards characterizing changes in the initial soil material during
188 humification.

189 The ESR spectra (only for HAs due to low ash content) were recorded on a JES FA 300
190 spectrometer (JEOL, Japan) in X-diapason with a free-radical modulation amplitude of 0.06 mT
191 and a microwave power in the cavity of 1 mW. Magnesium powder with fixed radical
192 concentration was used as an external standard. The concentration of the paramagnetic centers in
193 powdered samples was determined by comparison to relative signal intensities of the external
194 standard using the program JES-FA swESR v. 3.0.0.1 (JEOL, Japan). (Chukov et al, 2017).

195 **2.3. Statistical analysis**

196 Statistical data analysis was performed using the STATISTICA 10.0 software (TX, USA).
197 One-way analysis of variance (ANOVA) was applied to test the statistical significance of the
198 differences between the data, based on estimation of the significance of the average differences
199 between three or more independent groups of data combined by one factor. Fisher's Least
200 Significance Test (LST) was used for post-hoc analysis to provide a detailed evaluation of the
201 average differences between groups. A feature of this post-hoc test is inclusion of intra-group
202 mean squares when assessing any pair of averages. Differences were considered significant at
203 the 95% confidence level. Concentrations of organic and inorganic contaminants were
204 determined with at least three replicates. The calculated average concentrations are provided as
205 mean \pm standard deviation (SD).
206

207 **3. Results and Discussion**

208 Total organic carbon (TOC) content was high in both the superficial and buried soil
209 layers. This is indicative of the low degree of decomposition and transformation of the precursor
210 material and is comparable to the data on soils from the Yamal tundra (Ejarque, Abakumov,
211 2016) and the Argentinian islands (Parnikoza et al, 2016). High TOC content is typical for the
212 Antarctic Peninsula compared to soils of the Eastern Antarctic (Beyer et al, 1997, Mergelov et al,
213 2017). While both were elevated, the TOC was higher in the superficial levels relative to the
214 lower ones. Previous studies describe high variability in the TOC content from the soils of King
215 George and Galindez Islands, mainly depending on the diversity of the ecotopes and the sources
216 of organic matter (Abakumov, 2010, Parnikoza et al, 2016). Isolated (buried) soil spots are not
217 connected with fresh sources of organic matter, explaining why the TOC content in these layers
218 is lower. The carbon to nitrogen ratio was narrowest in SP1, which was affected by the scuas'
219 activity (evidenced by remnants of nests). This is in line with previous studies that documented
220 the well-pronounced ornithogenic effects on soil's nitrogen content (Simas et al, 2007, Parnikoza
221 et al, 2016). Fine earth of soils investigated characterized by acid reaction, which is expected for
222 soils of this region.

Comment [AИИ9]: The chapter has been renamed according to reviewers' comment

223 In terms of elemental composition, soil HAs are comparable with those previously
224 reported for the Arctic and Antarctic soil. Current exposed organic layers contain HAs with
225 higher carbon and nitrogen and lower oxygen content. Conversely, the HAs of isolated soil
226 patches show increased levels of oxidation. In comparison to soils of the tundra in the Komi
227 Republic (Vasilevitch et al, 2018), HAs found in this study were more oxidized, comparable to
228 those of the Kolyma Lowland (Lupachev et al, 2017) and previously published data from the
229 Fildes Peninsula (Abakumov, 2017).

230 Data on the distribution of carbon species in HAs (fig. 3) and in bulk soil (fig. 4) samples
231 indicated that aromatic compound content is generally lower than the alkyl components. This is a
232 well-known peculiarity of the soils of the polar biome (McKniht et al, 1994, Beyer et al, 1997).
233 At the same time, the degree of aromaticity of the isolated HAs is three fold higher than in the
234 bulk organic matter. This suggests the presences of the humification process in the soils of
235 Antarctica since humification involves increasing the aromatic compound content in
236 macromolecules. This supports the classical humification hypothesis instead of new arguments,
237 which are critical for this approach (Lehman, Kleber, 2015). Our data shows that SOM is on a
238 continuum and HAs are the main acting constituent of this continuum; thereby confirming that
239 this model is applicable even in Antarctica. The degree of aromaticity was higher in both isolated
240 HAs and bulk soil samples from superficial levels compared to samples from isolated patches.
241 Carbonyl/carboxyl/amide area (160 - 220 ppm) was more prevalent in the HAs of topsoils and
242 less abundant in the organic matter of bulk samples (this region was presented mainly by
243 carboxylic and amid carbon in the interval between 160 - 185 ppm) (Kniker, 2007). HAs
244 extracted from SP1, located under the *Deshampsia antarctica*, exhibited wide peaks around 110 -
245 140 ppm (H-aryl, C-aryl, olefinic-C) and at 140 - 160 ppm (O-aryl and N-aryl-C), while
246 aromatic components of SP2 and SP3 were mainly represented by peaks between 110 - 140 ppm.
247 This difference can be explained by the organic remnants of *Deshampsia antarctica* serving as
248 the precursor for humification. All HA samples showed intensive areas of alkylic carbon (0 - 45
249 ppm), aliphatic C and N, and methoxyl C (45 - 110 ppm), O-alkyl of carbohydrates and alcohols
250 (60 - 95 ppm), and acetal and ketal carbon of carbohydrates (95 - 110 ppm). Carbon composition
251 of the bulk samples was different from isolated HAs as evidenced mainly by the presence of
252 alkyl carbon (0 - 45 ppm) and O- and N-alkyl carbon (45 - 110 ppm). Characteristic features of
253 the bulk organic matter include carboxylic carbon and aryl compound content was low relative to
254 isolated HAs. Only soils with prior ornithogenic interactions showed increases in carboxylic
255 peaks, which corresponds well to data on relic ornithogenic soil (Beyer et al, 1997).

256 The C-alkyl : O-N-alkyl ratio used to indicate the degree of organic matter transformation
257 was quite variable in all samples investigated. This can be caused by diversity in the origin and
258 composition of the humification precursors. In case of comparisons with humic and fulvic acids
259 of tundra soils (Vasilevitch et al, 2018), HAs of soils investigated are intermediated between
260 HAs and fulvic acids of tundra Histosols with partially decomposed organic matter. These data
261 are in line with a previous report (Hopkins et al, 2006) that showed soils of the Antarctic Dry
262 Valleys have low alkyl-C : O-alkyl-C ratio using solid-state ¹³C-NMR spectroscopy) and,
263 therefore can serve as a labile, high-quality resource for micro-organisms. Beyer et al (1997)
264 showed that both the CPMAS ¹³C-NMR and the Py-FIMS spectra of the Terri-Gelic Histosol

265 were dominated by signals from carbohydrates and alkylic compounds, which is corroborated by
266 our findings. They also suggest that the ^{13}C -NMR data reflected decomposition of carbohydrates
267 and enrichment of alkyl-C in deeper soil layers. In regards to the bulk SOM, this was true for
268 SP2 and SP3 but not for SP1 that formed under the vascular plant *Deshampsia Antarctica*.

269 A representative electron spin resonance ESR spectrum of HAs is presented in fig 5 and the
270 ESR parameters are similar to HAs and FAs of temperate soils (Senesi, 1990, Senesi et al, 2003).
271 The spectra show a single, wide line with a g-factor ranging from 1,98890 to 1,99999,
272 attributable to the presence of stable semiquinone free radicals in the HA-containing
273 macromolecules (Table 5). The free radical content was higher in the superficial levels than in
274 the isolated ones. This corresponds well with previous reports (Chukov et al, 2017, Abakumov et
275 al, 2015) that connect the isolation of buried organic matter in the supra-permafrost with
276 declining free radical content. This reveals the increased biochemical activity of HAs in topsoil.
277 Compared to data from Lupachev (2017), the differences between exposed and isolated areas are
278 less pronounced but, in general, the HAs of the Antarctic soils contain more unstable free
279 radicals on average than the tundra soils of the Kolyma Lowland (Lupachev et al, 2017) and are
280 comparable to the soils from the Yamal tundra (Chukov et al, 2017). Taken together, the free
281 radical content found in our study was lower than in anthropogenically affected boreal and forest
282 steppe soils of the East-European plains (Abakumov et al, 2018).

283 4. Conclusions

284 High TOC content was fixed for the three studies representatives of Turbic Cryosols on
285 King George Island, Northwest of the Antarctic Peninsula, Western Antarctic. High amounts of
286 TOC are characteristic for both superficial and partially isolated soil materials. HAs contained
287 three fold more aromatic carbon than bulk SOM, which indicates that humification appears and
288 is active in soils of the Antarctic. Moreover, the amounts of aromatic carbon and carboxyl groups
289 were higher in the HAs of the superficial layer, which is likely caused by the greater diversity of
290 their organic precursors and more active humification than in sub-aerial conditions. The HAs of
291 the superficial sample layers contained lower concentrations of free radicals, an indicator of
292 active transformation in the topsoil. In general, the organic matter from partially isolated areas is
293 less stable in terms of carbon species and free radical content. This likely results from the
294 relative lack of fresh organic precursors and the different aeration and hydration conditions of
295 stagnification bordering the permafrost table.

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301

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307 **References**

- 308 Abakumov E. Vertical electric resistivity sounding of natural and anthropogenically affected
309 cryosols of Fildes Peninsula, Western Antarctica. *Czech Polar Reports*, 7 (2), pp. 109-122, 2017
310
- 311 Abakumov, E.V. The sources and composition of humus in some soils of West Antarctica
312 *Eurasian Soil Science*, 43 (5), pp. 499-508, 2010
- 313 Abakumov, E.. Characterisation of humic acids, isolated from selected subantarctic soils by ¹³C-
314 NMR spectroscopy, *Czech Polar Reports*, 7 (1). 1-10, 2017
- 315 Abakumov, E., Maksimova, E., Tsibart, A. Assessment of postfire soils degradation dynamics:
316 Stability and molecular composition of humic acids with use of spectroscopy methods *Land*
317 *Degradation and Development* . Article in Press, 2018
- 318 Abakumov, E.V., Lodygin, E.D., Tomashunas V.M. ¹³-C NMR and ESR characterization of
319 Humic Substances, Isolates from Soils of two Siberian Arctic Islands, *International Journal of*
320 *Ecology*. ID 390591, 2015
- 321 Abakumov, E , Mukhametova, N. Microbial biomass and basal respiration of selected Sub-
322 Antarctic and Antarctic soils in the areas of some Russian polar stations, *Solid Earth*, 5. 705-712,
323 2014
- 324 Abakumov, E.V., Parnikoza, I.Y., Vlasov, D.Y., Lupachev, A.V. (2016). Biogenic–abiogenic
325 interaction in Antarctic ornithogenic soils. *Lecture Notes in Earth System Sciences*,
326 (9783319249858), pp. 237-248.
- 327 Abakumov, E. V., Popov, A. I. Determination of the carbon and nitrogen contents and
328 oxidizability of organic matter and the carbon of carbonates content in one soil sample,
329 *Eurasian Soil Science*, 2:165–172, 2005
- 330 Abakumov, E.V., Fattakhova Yu.M. Structural composition of humic acids of ornitogenic soils
331 on the data of ¹³-C NMR resonance, *Russian Ornithology*, 1165: 2463-2466, 2014
- 332 Beyer, L; Knicker, H; Blume, H-P; Bölter, M; Vogt, B; Schneider. Soil organic matter of
333 suggested spodic horiozns in relic ornitogenic soils of coastal Continental Antarctica (Casey
334 Station, Wilkes Land) in comparison with that of spodic soil horizons in Germany, *Soil Science*,
335 7. 518-527, 1997
- 336 Birkenmajer K. Geology and climatostratigraphy of Tertiary glacial and interglacial Successions
337 on King George Island, South Shetland Islands (West Antarctica), *Ztrbl. Geol. Palaont.*, 1: 141–
338 151, 1989
- 339 Bockheim J., Vieira G., Ramos M., López-Martínez, J., Serrano E., Guglielmin M., Wihelm K.,
340 Nieuwendam A., . Climate warming and permafrost dynamics on the Antarctic Peninsula region,
341 *Glob. Planet. Change*, 100: 215–223, 2013
- 342 Calace, N., Campanella, L., Paolis, F., and De Petronio, B. M. Characterization of Humic Acids
343 Isolated from Antarctic Soils: *Int. J. Environ. Anal. Chem.*, 60: 71–78, 1995
- 344 Chapman, B., Roser, D., & Seppelt, R. ¹³C NMR analysis of Antarctic cryptogam extracts.
345 *Antarctic Science*, 6(3), 295-305, 1994

- 346 Chukov, S.N., Ejarque, E., Abakumov, E.V. Characterization of humic acids from tundra soils of
347 northern Western Siberia by electron paramagnetic resonance spectroscopy, *Eurasian Soil*
348 *Science*, 50 (1): 30-33, 2017
- 349 Davidson, E. A. and Janssens, I. A. Temperature sensitivity of soil carbon decomposition and
350 feedbacks to climate change, *Nature*, 440: 165–173, 2006
- 351 Dziadowiec, H., Gonet, S., and Plichta, W. Properties of humic acids of Arctic tundra soils in
352 Spitsbergen, *Polish Polar Res.*, (15), 71–81., 1994
- 353 Ejarque, E., Abakumov, E. Stability and biodegradability of organic matter from Arctic soils of
354 Western Siberia: Insights from ¹³C-NMR spectroscopy and elemental analysis (2016) *Solid*
355 *Earth*, 7 (1), pp. 153-165, 2016
- 356 Fritz, M., Deshpande, B. N., Bouchard, F., Högström, E., Malenfant-Lepage, J., Morgenstern,
357 A., Nieuwendam, A., Oliva, M., Paquette, M., Rudy, A. C. A., Siewert, M. B., Sjöberg, Y., and
358 Weege, S. Brief Communication: Future avenues for permafrost science from the perspective of
359 early career researchers, *The Cryosphere*, 9: 1715–1720, 2014
- 360 Haus, W., Serrano, E., Bockheim, J.G.. Soils and landforms from Fildes Peninsula and Ardley
361 Island, Maritime Antarctica, *Geomorphology*, 225, 76–86, 2014
- 362 Hopkins D.W., Sparrow A.D., Elberling B., Gregorich E.G., Novis P.M., Greenfield L.G.,
363 Tilston E.L., Carbon, nitrogen and temperature controls on microbial activity in soils from an
364 Antarctic dry valley, *Soil Biology and Biochemistry*, 38: 3130-3140, 2006
- 365 Hugelius, G., Strauss, J., Zubrzycki, S., Harden, J. W., Schuur, E. A. G., Ping, C.-L.,
366 Schirrmeister, L., Grosse, G., Michaelson, G. J., Koven, C. D., O'Donnell, J. A., Elberling, B.,
367 Mishra, U., Camill, P., Yu, Z., Palmtag, J., and Kuhry, P. Estimated stocks of circumpolar
368 permafrost carbon with quantified uncertainty ranges and identified data gaps, *Biogeosciences*,
369 11: 6573–6593, 2014
- 370 ICCP – Intergovernmental panel on Climate Change: *Climate Change 2007.*, Cambridge,
371 University Press, United Kingdom and New York, NY, USA, 2007
- 372 Kniker H. How does fire affect the nature and stability of soil organic nitrogen and carbon ?
373 *Biogeosciences*, 2007, 86: 91-118, DOI 10.1007/s10533-007-9104-4, 2006
- 374 Lechman J., Kleber M. The contentious nature of soil organic matter. *Nature*, 528. 60-68, 2015
- 375 Lodygin, E.D., Beznosikov, V.A. and Vasilevich, R.S. Molecular composition of humic
376 substances in tundra soils (¹³C-NMR spectroscopic study). *Eurasian Soil Sc.* (47) (5), 400–406,
377 2014
- 378
379 Lupachev, A., Abakumov, E., Gubin, S. The influence of cryogenic mass exchange on the
380 composition and stabilization rate of soil organic matter in cryosols of the kolyma lowland
381 (North Yakutia, Russia), *Geosciences (Switzerland)*, 7 (2), paper № 24, DOI:
382 10.3390/geosciences7020024, 2017
- 383 Management Plan for Antarctic Specially Protected Area No. 125, Measure 6, Annex., Antarctic
384 Treaty Secretariat, 2009
- 385 Mausbacher R., Muller J., Munnich M., Schmidt R. Evolution of postglacial sedimentation in
386 Antarctic lakes (King Georges Island), *Z. Geomorphologie*, 33: 219–234, 1989

- 387 McKnight Diane M. , Andrews Edmund D. , Spaulding Sarah A. , Aiken George R. , Aquatic
388 fulvic acids in algal-rich antarctic ponds, *Limnology and Oceanography*, 39, 1994
- 389 Mergelov, N., Mueller, C.W., Prater, I., Shorkunov, I., Dolgikh, A., Zazovskaya, E., Shishkov,
390 V., Krupskaya, V., Abrosimov, K., Cherkinsky, A., Goryachkin, S. Alteration of rocks by
391 endolithic organisms is one of the pathways for the beginning of soils on Earth. *Scientific*
392 *Reports*, 8 (1), paper № 3367, 2018
- 393 Michel, R.F.M., Schaefer, C.E.G.R., López-Martínez, J., Simas, F.N.B., Haus, N.W., Serrano,
394 E., Bockheim, J.G.. Soils and landforms from Fildes Peninsula and Ardley Island, *Maritime*
395 *Antarctica. Geomorphology*. 225: 76-86. doi:10.1016/j.geomorph.2014.03.041, 2014
- 396 Navas, A., López-Martínez, J., Casas, J., Machín, J., Durán, J.J., Serrano, E., Cuchi, J.A., Mink,
397 S.. Soil characteristics on varying lithological substrates in the South Shetland Islands, *maritime*
398 *Antarctica. Geoderma* 144 :123–139. doi:10.116/j.geoderma.2007.10.01, 2008
- 399 Parnikoza, I., Abakumov, E., Korsun, S., Klymenko, I., Netsyk, M., Kudinova, A., Kozeretska, I.
400 Soils of the argentine islands, antarctica: Diversity and characteristics *Polarforschung*, 86 (2), pp.
401 83-96. 2016
- 402 Rakusa-Suszczewski S. King George Island — South Shetland Islands, *Maritime Antarctic*. In:
403 Beyer L., Bölter M. (Eds.), *Geoecology of Antarctic Ice Free Coastal Landscapes*. Springer
404 Verlag, Berlin, 23–40, 2002.
- 405 Polyakov V., Orlova K., Abakumov, E. Evaluation of carbon stocks in the soils of Lena River
406 Delta on the basis of application of “dry combustion” and Tyurin’s methods of carbon
407 determination. *Biological Communications*. 62(2): 67–72, 2017.
- 408 Tarnocai, C., Canadell, J. G., Schuur, E. A. G., Kuhry, P., Mazhitova, G., and Zimov, S. Soil
409 organic carbon pools in the northern circumpolar permafrost region, *Global Biogeochem.* , 23,
410 1–11, 2009
- 411 Schnitzer, M. Organic matter characterization, in: *Methods of soil analysis, Part 2, chemical and*
412 *microbiological properties, Agronomy monograph no. 9*, edited by: Page, B., Miller, R., and
413 Keeney, D., Soil Science Society of America, Madison, 581–594, 1982.
- 415 Simas, FNB., Schaefer, CEG.R., Melo, V.F., Albuquerque-Filho, MR., Michel, RFM., Pereira,
416 VV., Gomes, MRM., da Costa, L.M. Ornithogenic cryosols from *Maritime Antarctica*:
417 Phosphatization as a soil forming process, *Geoderma*. 138: 191-203, 2007
- 418 Senesi N, D’Orazio V, Ricca G. Humic acids in the first generation of eurosoils, *Geoderma*,
419 116, 3-4: 325-344, 2003
- 420 Senesi N. Molecular and quantitative aspects of the chemistry of fulvic acids and its interactions
421 with mineral ions and organic chemicals. *Analytica Chimica Acta*. 232: 51-75, 1990
- 422 Schuur, E.A.G., McGuire, A.D., Grosse, G., Harden, J.W., Hayes, D.J., Hugelius, G., Koven,
423 C.D. and Kuhry, P. Climate change and the permafrost carbon feedback. *Nature*, 520, 171–179,
424 2015
- 425 Smellie J.L., Pankhurst R.J., Thomson M.R.A., Davies R.E.S. *The Geology of the South*
426 *Shetland Islands: VI. Stratigraphy, Geochemistry and Evolution*, *British Antarctic Survey*
427 *Scientific Reports* 50: 87, 85, 1984

- 428 Vasilevich, R., Lodygin, E., Beznosikov, V., Abakumov, E. Molecular composition of raw peat
429 and humic substances from permafrost peat soils of European Northeast Russia as climate
430 change markers. *Science of the Total Environment*, 615, 1229-1238, 2018
- 431 Wen, J., Xie, Z., Han, J., Lluberas, A.. Climate, mass balance and glacial changes on small dome of
432 Collins Ice Cap, King George Island, Antarctica, *Antarct. Res.*, 5, 52–61, 1994
- 433 WRB. World Reference Base for Soil Resources. International Soil Classification System for
434 Naming Soils and Creating Legends for Soil Maps; World Soil Resources Reports No. 106;
435 FAO: Rome, Italy, 2014.
- 436 Zaccone, C., Miano, T. M., and Shotyck, W. Qualitative comparison between raw peat and related
437 humic acids in an ombrotrophic bog profile: *Org. Geochem.*, 38: 151–160, 2007
- 438 Zech, W., Senesi, N., Guggenberger, G., Kaiser, K., Lehmann, J., Miano, T. M., Miltner, A., and
439 Schroth, G. Factors controlling humification and mineralization of soil organic matter in the
440 tropics: *Geoderma*, 79, 117–161, 1997.
- 441 Zubrzycki, S., Kutzbach, L. and Pfeiffer, E.-M. Permafrost affected soils and their carbon pools
442 with a focus on the Russian Arctic. *Solid Earth*, 5, 595–609. 2014
- 443
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- 447

448 Table. 1. Basic characteristics of soils

Sample	TOC, %	N, %	C/N	pH _{H2O}	pH _{CaCl2}	Color
1 O	27.63±0.23	5.18±0.42	5.33	6.35	5.30	10 YR 4/7
2 [CRH]	19.05±0.15	2.20±0.05	8.66	5.67	4.89	2.5 YR 4/4
3 O	20.04±0.17	1.16±0.09	17.13	4.80	4.80	10 YR 4/4
5 [CRH]	12.33±0.24	0.78±0.09	15.80	4.70	4.50	2.5 YR 4/3
4 O	10.16±0.09	0.84±0.07	11.98	4.90	4.21	10 YR 5/3
6 [CRH]	6.66±0.07	0.81±0.09	8.20	4.70	4.35	2.5 YR 5/3

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451

452 Table 2. Elemental composition (%) and atomic ratios in HAs. Data presented in atomic values.

Sample №	C	N	H	O	C/N	H/C	O/C
1	49.53±0.56	5.55±0.07	6.90±0.11	38.02±0.64	8.92	0.13	0.76
2	47.14±0.45	4.30±0.06	6.79±0.09	41.77±0.21	10.96	0.14	0.88
3	45.55±0.32	5.14±0.09	5.80±0.09	43.51±0.35	8.86	0.12	0.95
4	43.77±0.24	4.72±0.11	6.90±0.08	44.61±0.21	9.27	0.15	1.01
5	49.99±0.41	4.78±0.08	6.56±0.08	38.67±0.34	10.45	0.13	0.77
6	44.45±0.034	3.99±0.07	6.77±0.10	44.79±0.25	11.14	0.15	1.01
P, One way Anova, superficial/buried	0.14	0.05	0.29	0.05	n.d.	n.d.	n.d.

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455

456 Table 3. Carbon species integration in molecules of the HAs, %

Sample №	Carbonyl/ carboxyl/ amide	Aryl- olefine	O-N alkyl	Calkyl	Calkyl/O-N alkyl	Caryl/Calkyl
Chemical shift, ppm	220-160	160-110	110-45	45-0		
1	11,38	33,59	39,86	14,18	0.35	2.36
2	10,75	30,45	31,86	26,05	0.81	1.16
3	19,24	23,34	29,54	27,85	0.94	0.83
4	16,48	21,42	34,23	27,87	0.81	0.77
5	16,75	33,40	29,12	20,71	0.71	1.61
6	14.39	26.86	40.07	18.68	0.46	1.43
P, One way Anova, superficial/buried	0.02	0.03	0.02	0.73	n.d.	n.d.

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458

Comment [AИИ10]: This cell has been filled with name "Chemical shift, ppm"

459

460 Table 4. Carbon species integration in molecules of the bulk organic matter, %

Sample №	Carbonyl/ carboxyl/ amide	Aryl- olefine	O-N alkyl	Calkyl	Calkyl/O -N alkyl	Caryl/Calkyl
Chemical shift, ppm	220-160	160-110	110-45	45-0		
1 =113=O	7.24	11.37	46.20	35.19	0.76	0.32
2 113-Ch	18.23	10.29	40.59	30.89	0.76	0.33
3 123 O	7.34	20.48	55.12	17.06	0.31	1.20
4 123 Ch	9.34	11.27	49.50	29.90	0.60	0.37
6 149 O	5.72	13.84	62.22	18.22	0.29	0.75
6 149 Ch	22.95	9.89	46.92	20.24	0.43	0.48
P, One way Anova, superficial/buried	0.53	0.01	0.05	0.56	n.d.	n.d.

Comment [AИИ11]: This cell has been filled with name "Chemical shift, ppm"

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464 Table. 5. Mass concentration of free radical in humic acids

Soil horizon	Mass concentration of free radical, 10^{15} spin \cdot g $^{-1}$	g-factor
1	3.67	2.0314
2	3.04	2.3150
3	3.51	2.0314
4	2.13	2.0303
5	6.10	2.0310
6	5.86	2.0314

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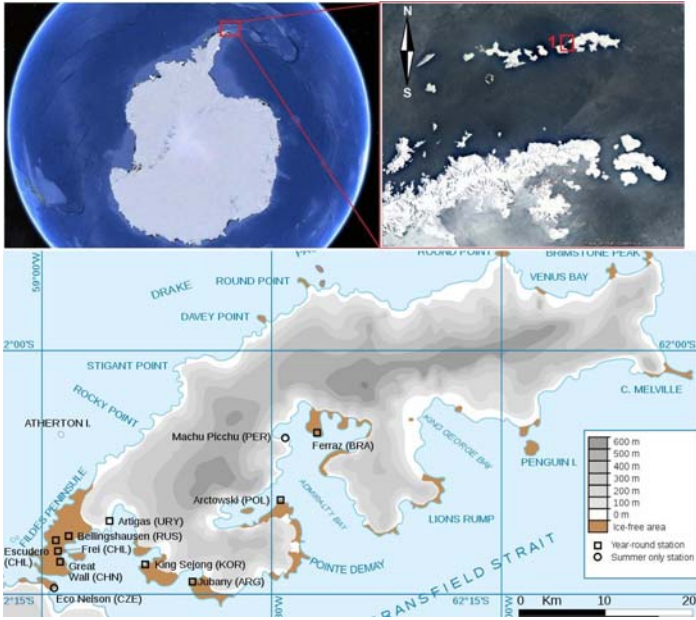
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472 Fig. 1.

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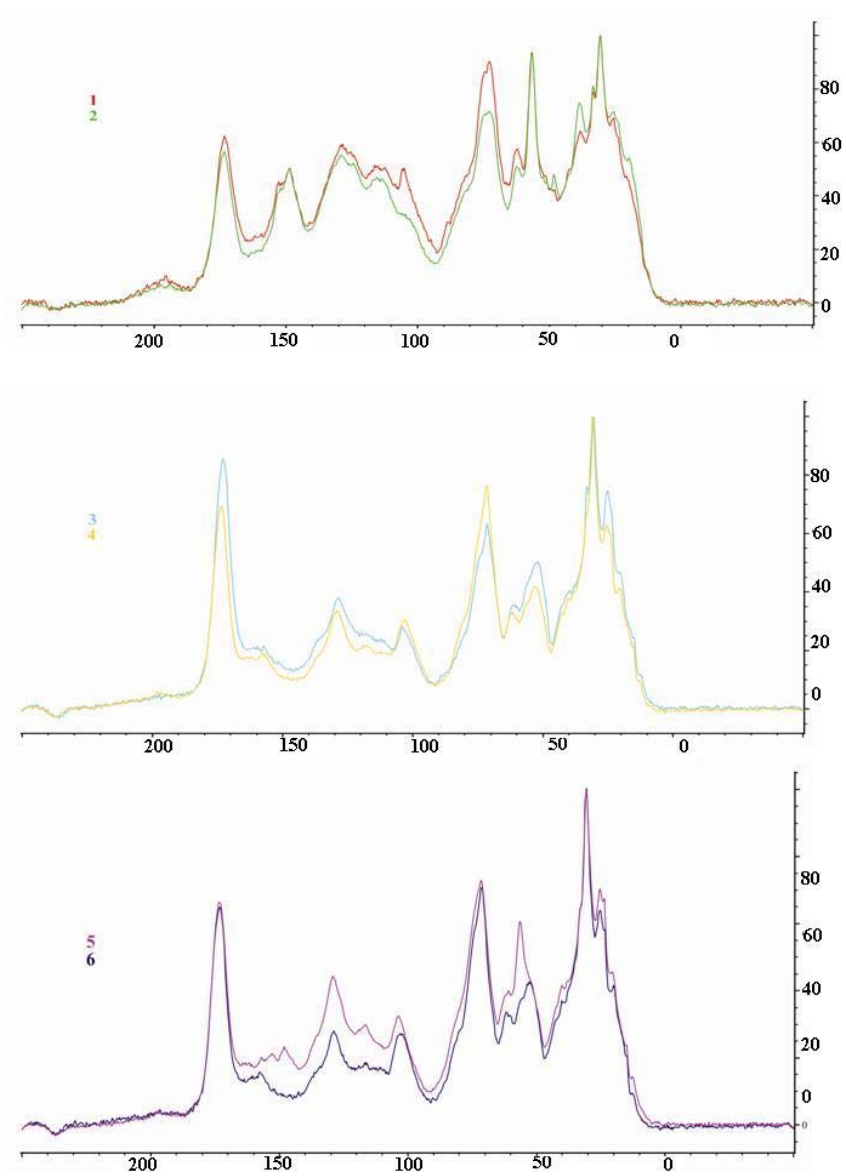
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475 Fig. 2

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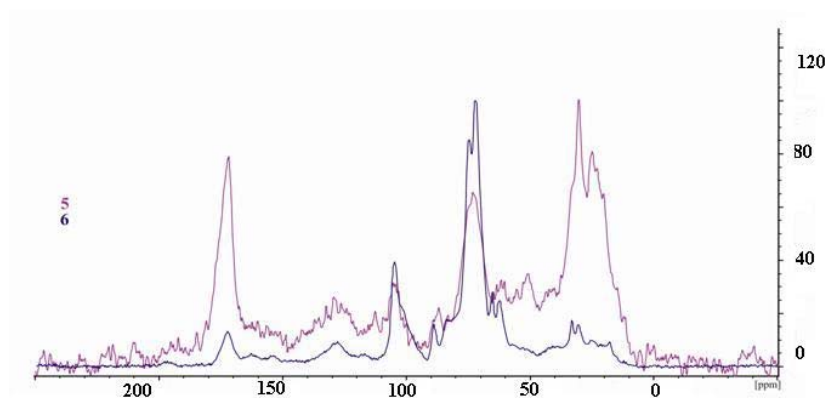
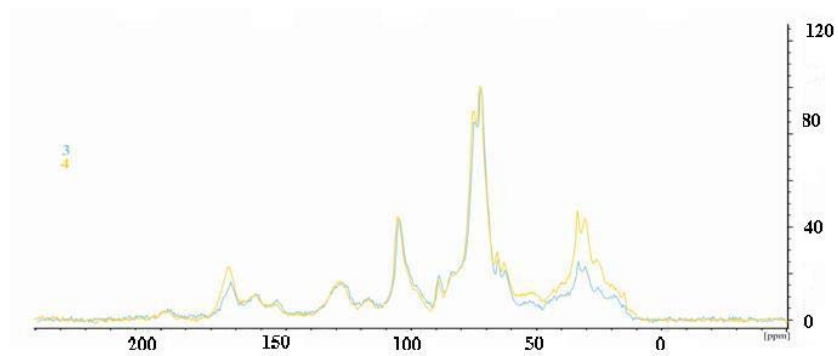
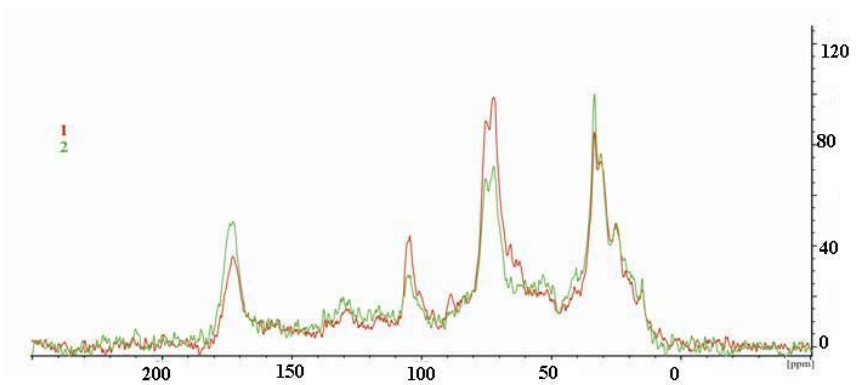


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479 Fig. 3

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486 Fig. 5.

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489 Fig. 1. Location of the Fildes peninsula

490 Fig.2. Soil morphology

491 Figure 3. ¹³C NMR spectras of the HAs, isolated from soils (1-6 – according table 1)

492 Figure 4. ¹³C NMR spectras of bulk organic matter of soils ((1-6 – according table 1)

493 Figure 5. Typical ESR spectrum of humic substances investigated

494 Table. 1. Basic characteristics of soils

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

496 Table 3. Carbon species integration in molecules of the HAs, %

497 Table 4. Carbon species integration in molecules of the bulk organic matter, %

498 Table. 5. Mass concentration of free radical in humic acids

499