



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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9 **Key words**

10 Antarctica, soil organic matter, stabilization, humic acids

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12 **Key points**

13 Investigation of Antarctic soil organic matter stability

14 Humic acids of superficial horizons contain more aromatic carbon

15 Humic acids of isolated layers contain more free radicals

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18 **Abstract**

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20 In this study, the soil organic matter (SOM) was analyzed from different sample areas (surface
21 level and partially isolated supra-permafrost layer) of the tundra-barren landscape of the Fildes
22 Peninsula, King George Island, Western Antarctica. We found that the humic acids (HAs) of the
23 cryoturbated, buried areas had lower amounts of alkylaromatic and protonized aromatic
24 compounds. In contrast, the HAs from the surface layers contain less alkyl carbon components.
25 The free radical content was higher in the surface layers than in the buried layers due to the
26 presence of fresh organic remnants in superficial soil samples. New data on SOM quality from
27 these two representative Cryosols will enable more precise assessment of SOM stabilization rate
28 in sub-Antarctic tundras. Comparison of the ¹³C-NMR spectra of the HAs and the bulk SOM
29 revealed that humification occurs in the Antarctic and results in accumulation of aromatic and
30 carboxylic compounds and reductions in alkylic ones.

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33 **Highlights**

34 Investigation of Antarctic soil organic matter stability

35 Humic acids of superficial horizons contain more aromatic carbon

36 Humic acids of isolated layers contain more free radicals

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39 **1. Introduction**



40 Polar soils play a key role in global carbon circulation and stabilization as they contain
41 maximum stocks of soil organic matter (SOM) within the whole pedosphere (Schuur et al, 2015).
42 Cold climate and continuous and discontinuous permafrost result in the stabilization of essential
43 amounts of organic matter in soils, biosediments, and grounds of the polar biome (Zubrzycki et al,
44 2014).

45 Global climate changes and permafrost degradation have led to the exposure of huge
46 pools of organic matter to microbial degradation (Schuur et al, 2015) and other environmental
47 risks. Polar SOM represents a vulnerable carbon source, susceptible to remobilization under
48 increasing temperatures (Schuur et al, 2015, Ejarque, Abakumov, 2016). In order to better
49 understand the implications of permafrost SOM for greenhouse gas emissions, accurate
50 knowledge of its spatial distribution, both in terms of quantity and quality (e.g. biodegradability,
51 chemical composition, and humification stage) is needed in addition to effective evaluation of
52 SOM's temporal dynamics (Fritz et al, 2014, Vasilevitch et al, 2018).

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

63 The stocks of SOM in the Antarctic are underestimated compared to the Arctic because
64 of the lack of the data for many parts of this continent, due to the high content of stones in the
65 soils and the high variability in the carbon content of the fine earth. Stocks of organic carbon in
66 the Antarctic soil have been reported as 0.5 kg/m² in its polar deserts, about 1.0 kg/m² in its
67 barrens, up to 3 - 5 kg/m² in the sub-Antarctic tundra, and up to 30 kg/m² in the penguin
68 rookeries of the maritime islands (Abakumov, 2010, Abakumov, Mukhametova, 2014,
69 Abakumov et al, 2016).

70 Stability and biodegradability are the key features of SOM that should be taken into
71 account when estimating current and future carbon stocks and organic matter quality and
72 dynamics. Stability is related to humification degree, as more advanced stages in the
73 humification process involve depletion of the labile molecules, as well as an increase in the bulk
74 aromaticity, which confers higher stability to the SOM. A number of proxies have been used to
75 trace humification rate and SOM stability, including aromaticity level (Vasilevitch et al, 2018,
76 Kniker, 2007). Also the ratio of C-Alkyl : C-Aryl and C-Alkyl : O-N-alkyl have been
77 successfully used to assess humification degree (Kinker, 2007). C/H ratio from humic acids
78 (HAs) has been used as an index of molecular complexity, as more degrees of conjugation imply
79 less hydrogenation of the carbon chains (Zaccone et al, 2007) and C/N has been used as a
80 measure of histic material degradation (Lodigin et al, 2014). ¹³C-NMR spectrometry provides
81 information on the diversity in carbon functional structures (carbon species) and has been used to
82 evaluate changes in SOM during decomposition and humification. More specifically, high
83 phenolic (150 ppm), carboxyl-C (175 ppm) and alkyl-C (30 ppm) groups, combined with low O-
84 alkyl carbons, have been associated with advanced humification stages (Zech et al, 1997). So far,
85 studies of SOM quality from polar environments have revealed generally lowly-decomposed
86 organic molecules (Dziadowiec, 1994, Lupachev et al, 2017), which preserve much of the



87 chemical character of their precursor material due to slow progress of humification (Davidson
88 and Jansens, 2006). This is very important because polar soils are characterized by the specific
89 composition of the humification precursors.

90 The structure and molecular composition of the Antarctic SOM has been investigated
91 using ^{13}C -NMR methods (Beyer et al, 1997, Abakumov, 2017) and it was shown that in typical
92 organo-mineral soils the aliphatic carbon prevails over the aromatic one, owing to the non-
93 ligniferous nature of its precursor material (Calace et al, 1995). Also, analyses of cryptogam
94 extracts were conducted towards identification of individual organic precursors (Chapman et al,
95 1994). This feature was then shown to be typical for soils from different regions of the Antarctic
96 (Abakumov, 2010), including soil formed on the penguin rookeries (Abakumov, Fattakhova,
97 2015). The northern most soil of Arctic polar biome shows the same trend in organic molecules
98 organization: higher prevalence of aliphatic structures over aromatic ones. The diversity of the
99 individual components in aromatic and aliphatic areas is usually higher in Arctic soil because of
100 the increased diversity of humification precursors (Ejarque, Abakumov, 2016, Abakumov,
101 2010). The over-moistened Antarctic histic soils under algae are characterized by a
102 predominance of proteins containing nitrogen compounds and a slight degradation of
103 carbohydrates in the SOM. A selective preservation of the alkyl moieties in the deeper soil layers
104 has been suggested, and little transformation processes of the SOM are detectable because soil
105 temperatures are not high enough to stimulate further microbial break-down, even in the summer
106 (Beyer et al, 1997). Previous reports on organic matter mainly focused on gelsols or cryosols
107 derived from bryophytes, algae, and vascular plants from stable habitats without pronounced
108 ornithogenic effects (Carvahlo et al, 2010). It has been shown that ornithochoria play an essential
109 role in redistribution of plant remnants in the Antarctic (Parnikoza et al, 2016) as birds transport
110 considerable amounts of variably composed organic material within its inland landscapes. The
111 presence of organic matter of ornithogenic origin plays an important role in the formation of
112 humic substances. However, published data on SOM composition for the Antarctic are rare, and
113 further studies that detail its structural compounds and their distribution are needed. Recently,
114 ^{13}C -NMR was successfully used to detail the soils found in endolithic communities in Eastern
115 Antarctica and revealed that endolithic organic matter is characterized by a low prevalence of
116 alkyl aromatic compounds (Mergelov et al, 2018).

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. To date, this type of investigation has only been
120 performed on cryosols of the Kolyma lowland (Lupachev et al, 2017), where the organic matter
121 of modern and buried soils vary greatly in terms of their molecular composition and quality. The
122 objectives of the study were: (1) to evaluate the alterations in the elemental compositions of the
123 HAs under partial isolation (2) to assess the ratios of aromatic and aliphatic carbon species in the
124 topsoil and isolated areas; (3) to characterize the biochemical activity of the HAs (e.g. free
125 radical concentration).

126 2. Materials and Methods

127 2.1. Study sites

128 King George Island is the largest in the South Shetland archipelago and only around 5%
129 of its 1400 km² area is free of ice (Fig. 1) (Rakusa-Suszczewski, 2002). The Fildes Peninsula and
130 Ardley Island, together around 33 km², comprise the largest ice-free area on King George Island
131 and the second largest of the South Shetland Islands. It has a gentle landscape consisting of old
132 coastal landforms with numerous rocky ridges and an average height of 30 m above main sea
133 level (AMSL) (Michel et al, 2014). According to Smellie (Smellie et al, 2014), this area mainly



134 consists of lava with small exposures of tuffs, volcanic sandstones, and agglomerates. The
135 climate is cold and humid with a mean annual air temperature of -2.2°C and mean summer air
136 temperatures above 0°C for only up to four months (Wen et al, 1994). The mean annual
137 precipitation is 350 - 500 mm/year. The Fildes Peninsula and Ardley Island are among the first
138 areas in maritime Antarctica to become ice-free after the last glacial maximum (Birkenmajer,
139 1989). The Fildes Peninsula was covered by glaciers from 8000 to 5000 BP (Mausbacher et al,
140 1989, Haus et al, 2014). The patterned ground in this region dates from 720 to 2640 BP. In the
141 South Shetland Islands, permafrost is sporadic or non-existent at altitudes below 20 m AMSL
142 and occurs discontinuously in altitudes from 30 to 150 m AMSL (Bockheim et al, 2013).
143 Mosses, lichens, and algae are common to this area along with two vascular plants (*Deschampsia*
144 *antarctica* and *Colobanthus quitensis*). Penguins, seals, and seabirds inhabit the coastal areas and
145 greatly impact the soil development. Major cryogenic surface-forming processes in this region
146 include frost creep, cryoturbation, frost heaving and sorting, gravity, and gelifluction (Michel et
147 al, 2014). Eight separate sites on the Fildes Peninsula have been collectively designated an
148 Antarctic Specially Protected Area (ASP 125) largely due to their paleontological properties
149 (Management plan, 2009). The average thickness of the soil is about 15 - 25 cm. Soils from King
150 George Island have been divided into six groups (WRB, 2014): Leptosols, Cryosols, Fluvisols,
151 Regosols, Histosols, and Technosols; this corresponds well with previously published data
152 (Navas et al, 2008).

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

162 **2.2. Basic characterization**

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

167 **2.3. Extraction of humic acids (HAs)**

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



181 2.4. *Characterization of humic acids (HAs)*

182 Isolated HAs were characterized for their elemental composition (C, N, H, and S) using the
183 Euro EA3028-HT analyzer. Data were corrected for water and ash content. Oxygen content was
184 calculated by difference. The elemental ratios reported in this paper are based on weight. Solid-
185 state ¹³C-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer
186 (Karlsruhe, Germany) in a 4-mm ZrO₂ rotor. The magic angle spinning speed was 20 kHz in all
187 cases and the nutation frequency for cross polarization was $u1/2p\ 1/4\ 62.5$ kHz. Repetition delay
188 and number of scans were 3 seconds. Groups of structural compounds were identified by their
189 chemical shifts values: alkyl C (−10 to 45 ppm), O/N-alkyl C (45 to 110 ppm), aryl/olefine C
190 (110 to 160 ppm), and carbonyl/carboxyl/amide C (160 to 220 ppm) (Knicker, 2007). The ¹³C-
191 NMR study was also conducted in bulk soil samples towards characterizing changes in the initial
192 soil material during humification.

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

199 2.5. *Statistics*

200 Statistical data analysis was performed using the STATISTICA 10.0 software (ANOVA,
201 Statistica Base 12.6, Dell, Round Rock, TX, USA). One-way analysis of variance (ANOVA) was
202 applied to test the statistical significance of the differences between the data, based on estimation
203 of the significance of the average differences between three or more independent groups of data
204 combined by one feature (factor). Fisher's Least Significance Test (LST) was used for post-hoc
205 analysis to provide a detailed evaluation of the average differences between groups. A feature of
206 this post-hoc test is inclusion of intra-group mean squares when assessing any pair of averages.
207 Differences were considered significant at the 95% confidence level. Concentrations of organic
208 and inorganic contaminants were determined with at least three replicates. The calculated
209 average concentrations are provided as mean ± standard deviation (SD).
210

211 3. Results and Discussion

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



225 et al, 2016). Fine earth of soils investigated characterized by acid reaction, which is expected for
226 soils of this region.

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

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

260 The C-alkyl : O-N-alkyl ratio used to indicate the degree of organic matter transformation
261 was quite variable in all samples investigated. This can be caused by diversity in the origin and
262 composition of the humification precursors. In case of comparisons with humic and fulvic acids
263 of tundra soils (Vasilevitch et al, 2018), HAs of soils investigates are intermediated between
264 HAs and fulvic acids of tundra Histosols with partially decomposed organic matter. These data
265 are in line with a previous report (Hopkins et al, 2006) that showed soils of the Antarctic Dry
266 Valleys have low alkyl-C : O-alkyl-C ratio using solid-state ¹³C-NMR spectroscopy) and,



267 therefore can serve as a labile, high-quality resource for micro-organisms. Beyer et al (1997)
268 showed that both the CPMAS ^{13}C -NMR and the Py-FIMS spectra of the Terri-Gelic Histosol
269 were dominated by signals from carbohydrates and alkylic compounds, which is corroborated by
270 our findings. They also suggest that the ^{13}C -NMR data reflected decomposition of carbohydrates
271 and enrichment of alkyl-C in deeper soil layers. In regards to the bulk SOM, this was true for
272 SP2 and SP3 but not for SP1 that formed under the vascular plant *Deshampsia Antarctica*.

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

287 4. Conclusions

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

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305

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450



451 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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454

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

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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458

459 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
	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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461



462

463 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
	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.

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465



466

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

Soil horizon	Mass concentration of free radical, 10^{15} spin*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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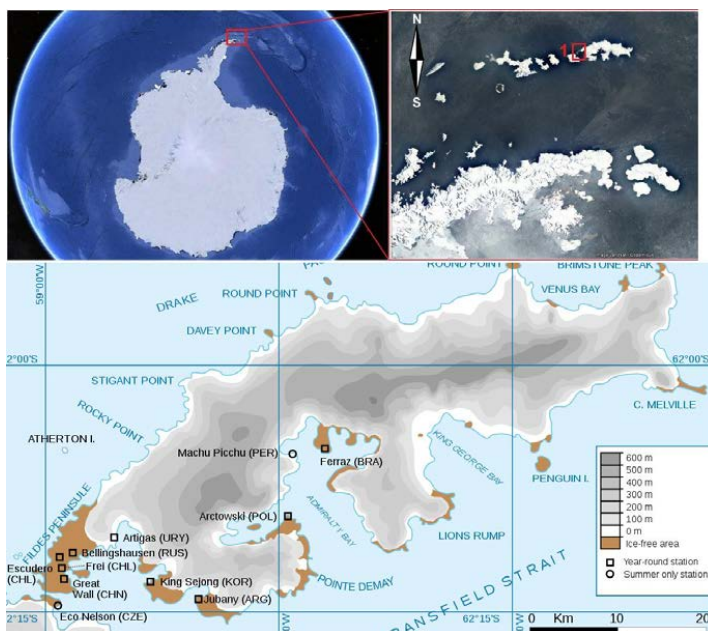
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475 Fig. 1.

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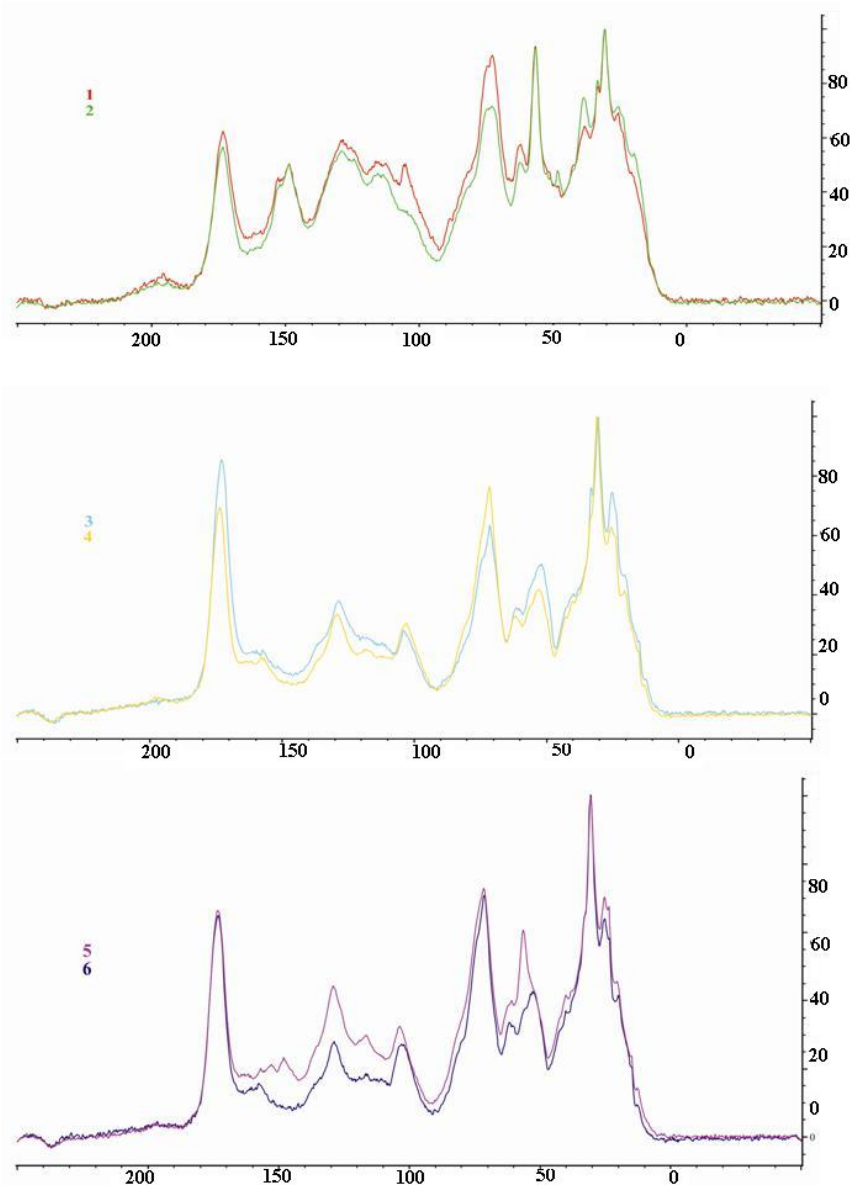
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478 Fig. 2

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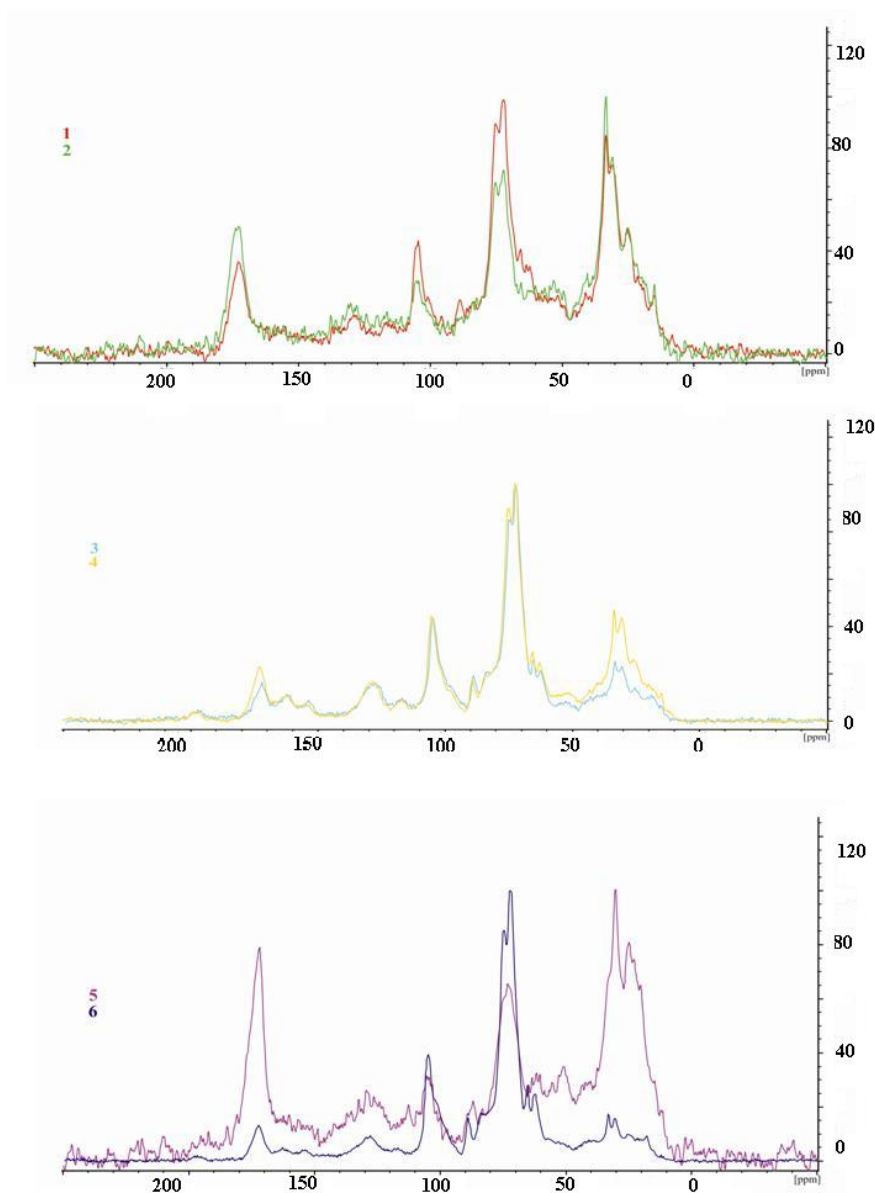


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482 Fig. 3

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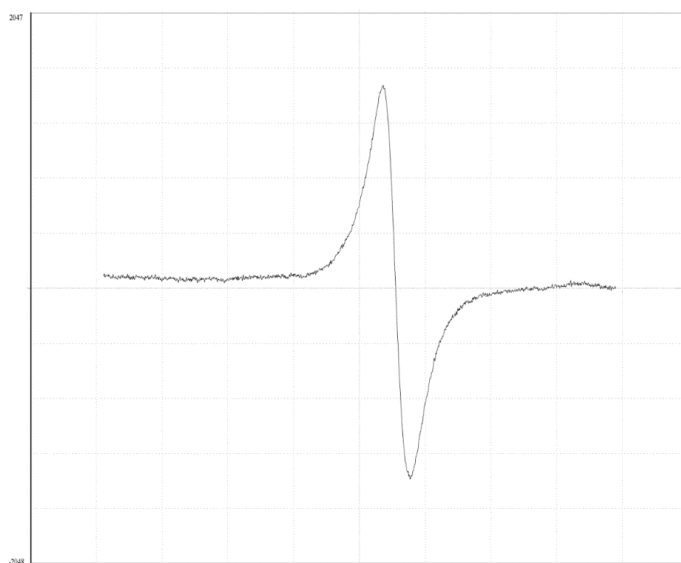


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486 Fig. 4

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489 Fig. 5.

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492 Fig. 1. Location of the Fildes peninsula

493 Fig.2. Soil morphology

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

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

496 Figure 5. Typical ESR spectrum of humic substances investigated

497 Table. 1. Basic characteristics of soils

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

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

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

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

502