

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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17
18 **Abstract**





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 Soil organic matter from different areas in King George Island, Western Antarctica has been
35 studied. It was found the humic acids of cryoturbated buried horizons have lower amounts of
36 alkylaromatic and protonized aromatic compounds. At the same time humic acids of superficial
37 horizons contain more aromatic carbon. Humification in the Antarctic environments results in
38 accumulation of aromatic and carboxylic compounds and reductions in alkylic ones.

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41 **1. Introduction**

42 Polar soils play a key role in global carbon circulation and stabilization as they contain
43 maximum stocks of soil organic matter (SOM) within the whole pedosphere (Schuur et al, 2015).
44 Cold climate and continuous and discontinuous permafrost result in the stabilization of essential
45 amounts of organic matter in soils, biosediments, and grounds of the polar biome (Zubrzycki et al,
46 2014).

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

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

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

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

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

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

119 This study aimed to compare the structural composition of the SOM from both superficial
120 and partially isolated (i.e. buried spots on the border with permafrost) areas and to evaluated the
121 stabilization rate of Antarctic Cryosols. To date, this type of investigation has only been
122 performed on Cryosols of the Kolyma lowland (Lupachev et al, 2017), where the organic matter
123 of modern and buried soils vary greatly in terms of their molecular composition and quality. The
124 objectives of the study were: (1) to evaluate the alterations in the elemental compositions of the
125 HAs under partial isolation (2) to assess the ratios of aromatic and aliphatic carbon species in the
126 topsoil and isolated areas; (3) to characterize the biochemical activity of the HAs (e.g. free
127 radical concentration).

128 2. Materials and Methods

129 2.1. Study sites

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

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

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

164 **2.2. Basic characterization**

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

169 **2.3. Extraction of humic acids (HAs)**

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

183 2.4. *Characterization of humic acids (HAs)*

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

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

201 2.5. *Statistics*

202 Statistical data analysis was performed using the STATISTICA 10.0 software (~~ANOVA,~~
203 ~~Statistica Base 12.6, Dell, Round Rock, TX, USA~~). One-way analysis of variance (ANOVA) was
204 applied to test the statistical significance of the differences between the data, based on estimation
205 of the significance of the average differences between three or more independent groups of data
206 combined by **one feature (factor)**. Fisher's Least Significance Test (LST) was used for post-hoc
207 analysis to provide a detailed evaluation of the average differences between groups. A feature of
208 this post-hoc test is inclusion of intra-group mean squares when assessing any pair of averages.
209 Differences were considered significant at the 95% confidence level. Concentrations of organic
210 and inorganic contaminants were determined with at least three replicates. The calculated
211 average concentrations are provided as mean ± standard deviation (SD).
212

213 3. **Results and Discussion**

214 Total organic carbon (TOC) content was high in both the superficial and buried soil
215 layers (Table 1). This is indicative of the low degree of decomposition and transformation of the
216 precursor material and is comparable to the data on soils from the Yamal tundra (Ejarque,
217 Abakumov, 2016) and the Argentinian islands (Parnikoza et al, 2016). High TOC content is
218 typical for the Antarctic Peninsula compared to soils of the Eastern Antarctic (Beyer et al, 1997,
219 Mergelov et al, 2017). While both were elevated, the TOC was higher in the superficial levels
220 relative to the lower ones. Previous studies described high variability in the TOC content from
221 the soils of King George and Galindez Islands, mainly depending on the diversity of the ecotopes
222 and the sources of organic matter (Abakumov, 2010, Parnikoza et al, 2016). Isolated (buried) soil
223 spots are not connected with fresh sources of organic matter, explaining why the TOC content in
224 these layers is lower. The carbon to nitrogen ratio was narrowest in SP1, which was affected by
225 the scuas' activity (evidenced by remnants of nests). This is in line with previous studies that
226 documented the well-pronounced ornithogenic effects on soil's nitrogen content (Simas et al,

227 2007, Parnikoza et al, 2016). Fine earth of soils investigated characterized by acid reaction,
228 which is expected for soils of this region.

229 In terms of elemental composition, soil HAs are comparable with those previously
230 reported for the Arctic and Antarctic soil. Current exposed organic layers contain HAs with
231 higher carbon and nitrogen and lower oxygen content (Table 2). Conversely, the HAs of isolated
232 soil patches show increased levels of oxidation. In comparison to soils of the tundra in the Komi
233 Republic (Vasilevitch et al, 2018), HAs found in this study were more oxidized, comparable to
234 those of the Kolyma Lowland (Lupachev et al, 2017) and previously published data from the
235 Fildes Peninsula (Abakumov, 2017).

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

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

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

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

289 4. Conclusions

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

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- 453

454 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
1 [CRH]	19.05±0.15	2.20±0.05	8.66	5.67	4.89	2.5 YR 4/4
2 O	20.04±0.17	1.16±0.09	17.13	4.80	4.80	10 YR 4/4
2 [CRH]	12.33±0.24	0.78±0.09	15.80	4.70	4.50	2.5 YR 4/3
3 O	10.16±0.09	0.84±0.07	11.98	4.90	4.21	10 YR 5/3
3 [CRH]	6.66±0.07	0.81±0.09	8.20	4.70	4.35	2.5 YR 5/3

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457

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

Sample №	C	N	H	O	C/N	H/C	O/C
1 O	49.53±0.56	5.55±0.07	6.90±0.11	38.02±0.64	8.92	0.13	0.76
1 [CRH]	47.14±0.45	4.30±0.06	6.79±0.09	41.77±0.21	10.96	0.14	0.88
2 O	45.55±0.32	5.14±0.09	5.80±0.09	43.51±0.35	8.86	0.12	0.95
2 [CRH]	43.77±0.24	4.72±0.11	6.90±0.08	44.61±0.21	9.27	0.15	1.01
3 O	49.99±0.41	4.78±0.08	6.56±0.08	38.67±0.34	10.45	0.13	0.77
3 [CRH]	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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461

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

Sample №	Carbonyl/ carboxyl/ amide	Aromatic	O-N alkyl	Alkyl	Alkyl/O-N Alkyl	Arom/Alkyl
Chemical shift, ppm	220-160	160-110	110-45	45-0		
1 O	11,38	33,59	39,86	14,18	0.35	2.36
1 [CRH]	10,75	30,45	31,86	26,05	0.81	1.16
2 O	19,24	23,34	29,54	27,85	0.94	0.83
2 [CRH]	16,48	21,42	34,23	27,87	0.81	0.77
3 O	16,75	33,40	29,12	20,71	0.71	1.61
3 [CRH]	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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465

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

Sample №	Carbonyl/ carboxyl/ amide	Aromatic	O-N alkyl	Alkyl	Alkyl/O- N Alkyl	Arom/Alkyl
	220-160	160-110	110-45	45-0		
1 O	7.24	11.37	46.20	35.19	0.76	0.32
1 [CRH]	18.23	10.29	40.59	30.89	0.76	0.33
2 O	7.34	20.48	55.12	17.06	0.31	1.20
2 [CRH]	9.34	11.27	49.50	29.90	0.60	0.37
3 O	5.72	13.84	62.22	18.22	0.29	0.75
3 [CRH]	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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469

470 Table 5. Free radical concentration in humic acids of studied soils

Soil horizon	Mass concentration of free radical, 10^{15} spin*g ⁻¹	g-factor
1 O	3.67	2.0314
1 [CRH]	3.04	2.3150
2 O	3.51	2.0314
2 [CRH]	2.13	2.0303
3 O	6.10	2.0310
3 [CRH]	5.86	2.0314

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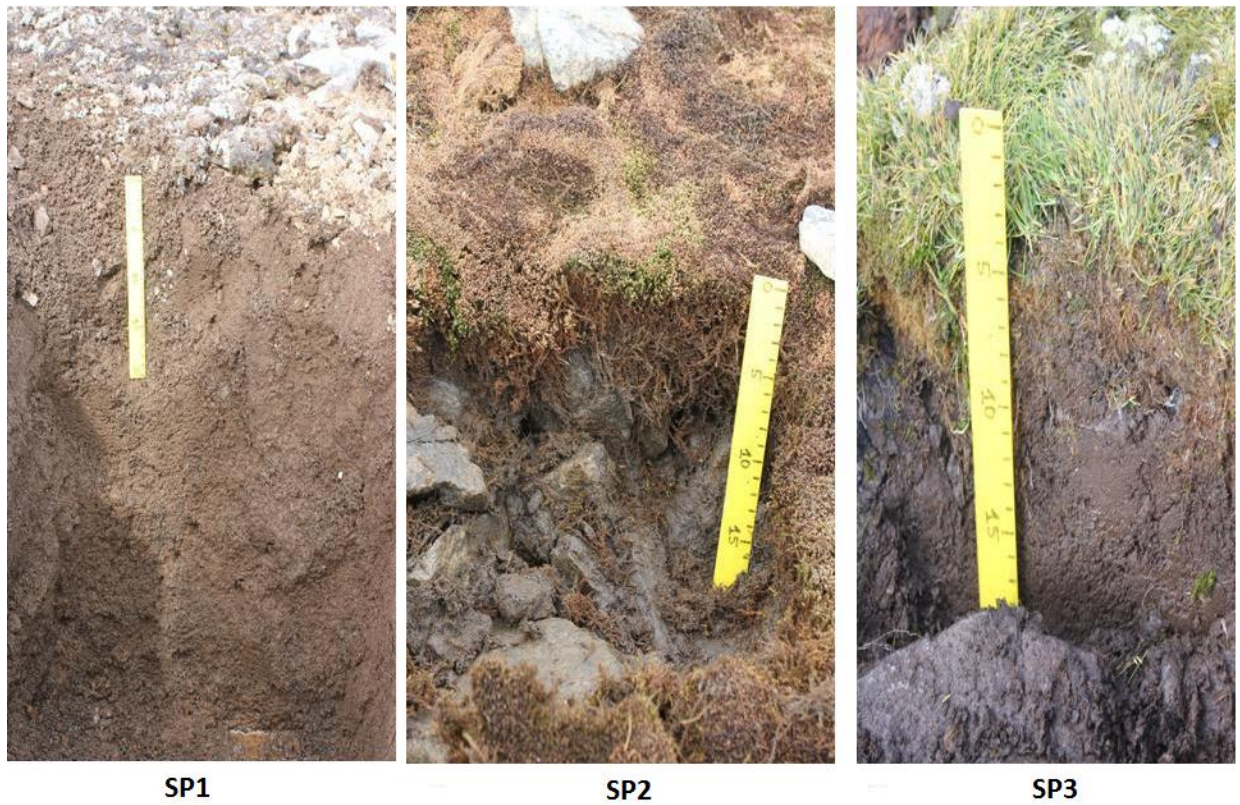
473

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478 Fig. 1.

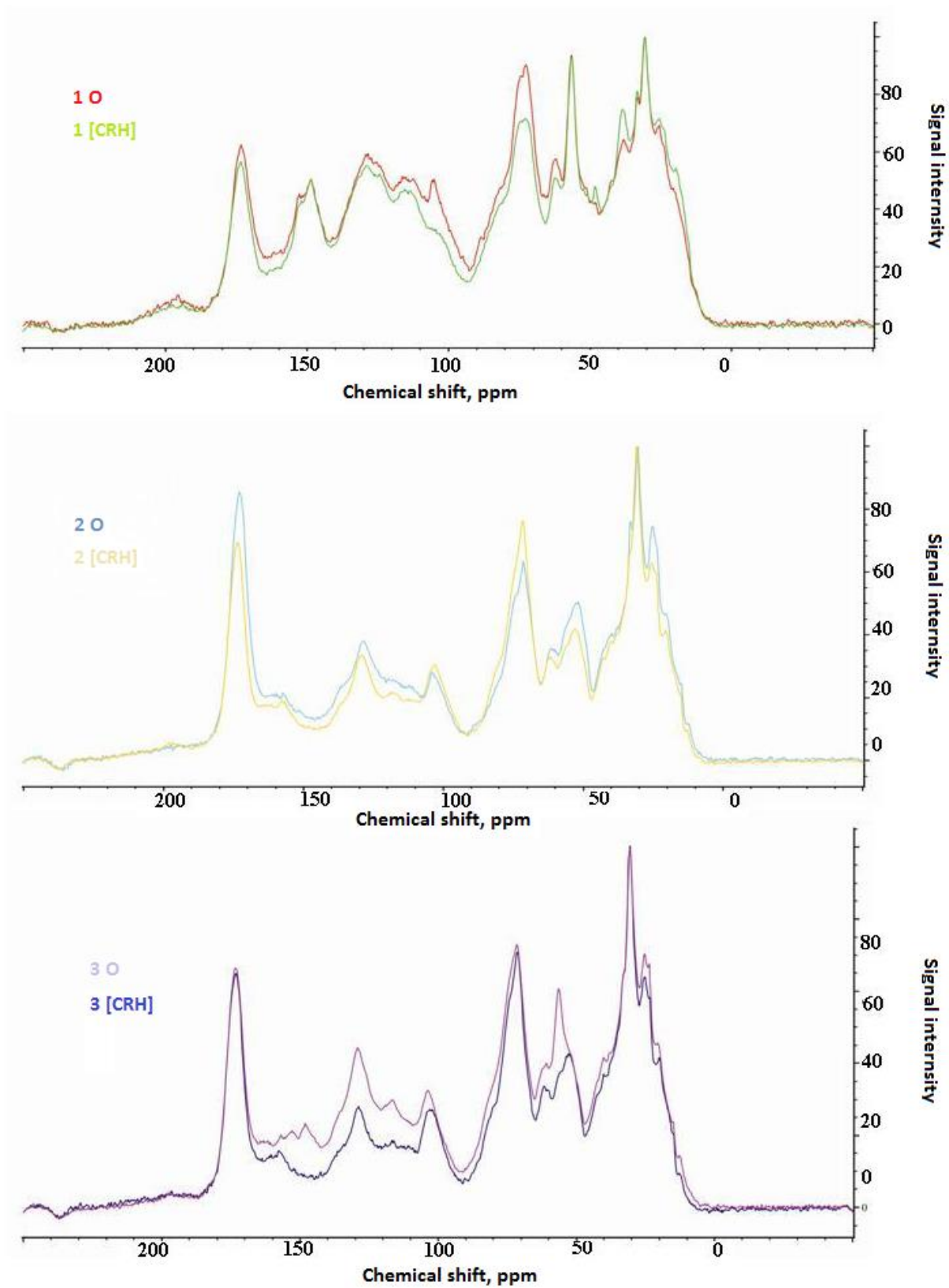
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481 Fig. 2

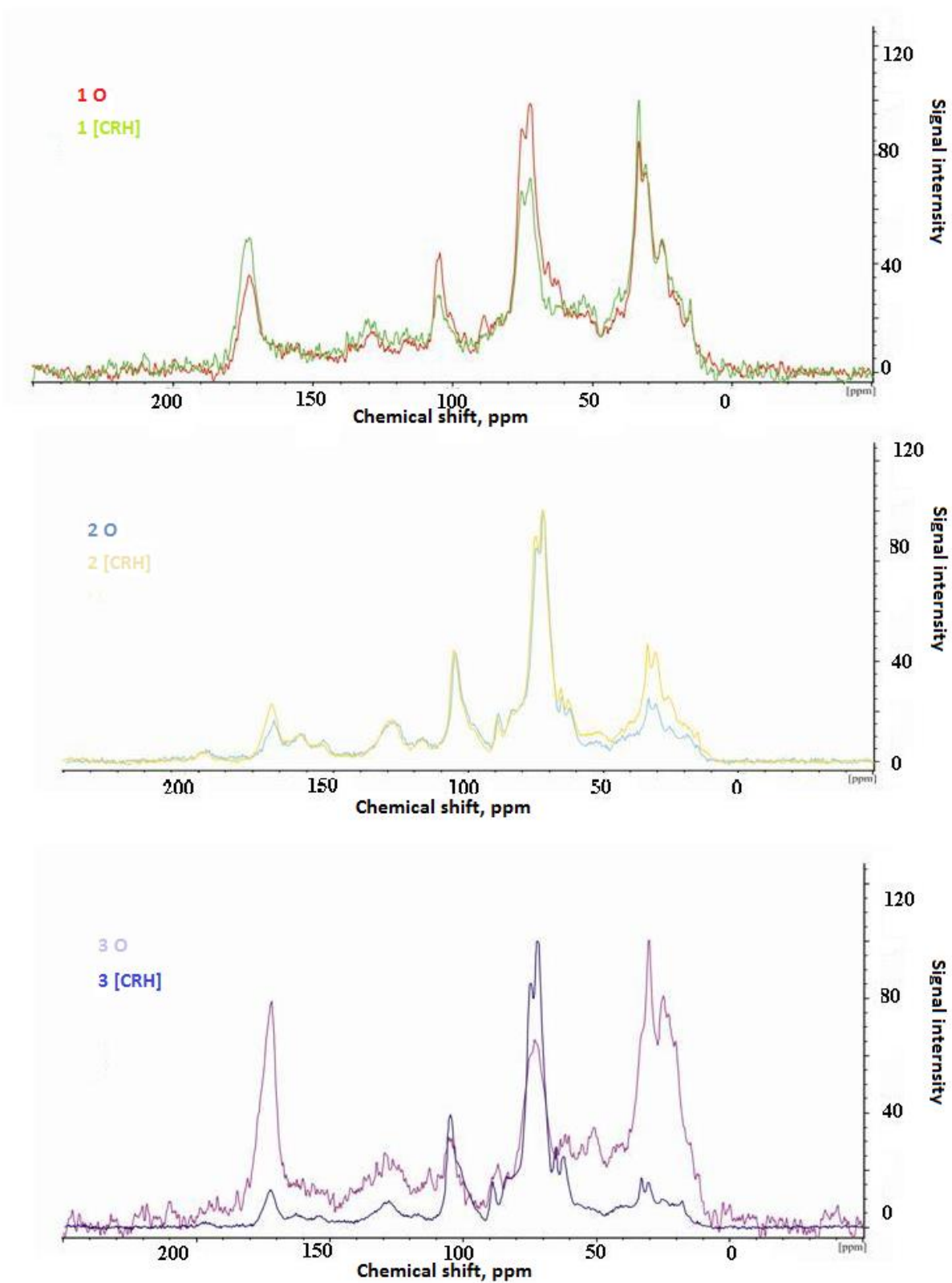
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484 Fig. 3

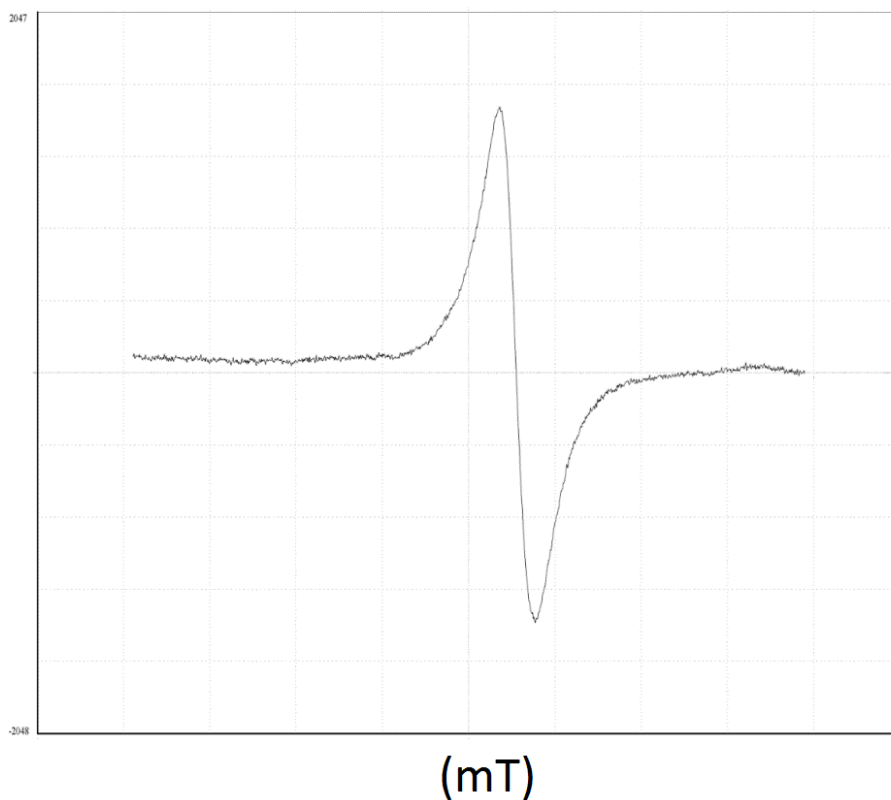
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487 Fig. 4

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490 Fig. 5.

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493 Fig.1. Location of the Fildes peninsula and sampling plots (SP1, SP2, SP3).

494 Fig.2. Soil morphology

495 Figure 3. ¹³C NMR spectras of the HAs, isolated from soils (O, [CRH] labels - according table 1)

496 Figure 4. ¹³C NMR spectras of bulk organic matter of soils (O, [CRH] labels - according table 1)

497 Figure 5. Typical ESR spectrum of humic substances investigated

498 Table. 1. Basic characteristics of soils

499 Table 2. Elemental composition (% , mass percents) and atomic ratios in HAs

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

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

502 Table 5. Free radical concentration in humic acids of studied soils