



# Stability of soil organic matter in Cryosols of the maritime Antarctic: insights from $^{13}\text{C}$ NMR and electron spin resonance spectroscopy

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

**Highlights.** Stabilization of soil organic matter was studied; humic acids of superficial horizons contain more aromatic carbon; humification is one of the ways of soil organic carbon stabilization.

## 1 Introduction

Polar soils play a key role in global carbon circulation and stabilization as they contain maximum stocks of soil organic matter (SOM) within the whole pedosphere (Schuur et al., 2015). Cold climate and active layer dynamics result in the stabilization of essential amounts of organic matter in soils, biosediments, and grounds of the polar biome (Zubrzycki et al., 2014). Global climate changes and permafrost degradation have led to the exposure of huge pools of organic matter to microbial degradation (Schuur et al., 2015) and other environmental risks (IPCC, 2007). Polar SOM represents a vulnerable carbon source, susceptible to remobilization under increasing temperatures (Schuur et al., 2015; Ejarque and Abakumov, 2016). In order to better understand the implications of permafrost SOM for greenhouse gas emissions, accurate knowledge of its spatial distribution, both in terms of quantity and quality (e.g. biodegradability, chemical composition, and humification stage) is needed in addition to effective evaluation of SOM temporal dynamics (Fritz et al., 2015; Vasilevitch et al., 2018).

Current estimations of soil organic carbon (SOC) stocks are around 1307 Pg throughout the northern circumpolar region (Hugelius et al., 2014). These amounts surpass previous estimates (Tarnocai et al., 2009) and grossly exceed the total carbon contained in the world's vegetation biomass (460–650 Pg) or in the atmosphere (589 Pg) (Tarnocai et al., 2009). However, the aforementioned SOM or SOC stock estimations are still poorly constrained (Hugelius et al., 2014). This

uncertainty is largely caused by the estimates having been calculated from observations that are highly spatially clustered (Hugelius et al., 2014) while extensive land areas remain uncharacterized due to the logistic difficulties of reaching these sites. Additionally, the calculation of these stocks are based on estimated data on soil bulk density and carbon values derived from dichromate oxidation methods (Abakumov and Popov, 2005; Polyakov et al., 2017).

The stocks of SOM in the Antarctic are underestimated compared to the Arctic because of the lack of data for many parts of this continent, due to the high content of stones in the soils and the high variability in the carbon content of the fine earth. Stocks of organic carbon in the Antarctic soil have been reported as  $0.5 \text{ kg m}^{-2}$  in its polar deserts, about  $1.0 \text{ kg m}^{-2}$  in its barrens, up to  $3\text{--}5 \text{ kg m}^{-2}$  in the sub-Antarctic tundra, and up to  $30 \text{ kg m}^{-2}$  in the penguin rockeries of the maritime islands (Abakumov, 2010; Abakumov and Mukhametova, 2014; Abakumov et al., 2016). To date, investigation on structural composition of the SOM from both superficial and partially isolated areas has only been performed on Cryosols of the Kolyma Lowland (Lupachev et al., 2017), where the organic matter of modern and buried soils vary greatly in terms of their molecular composition and quality.

Stability and biodegradability are the key features of SOM that should be taken into account when estimating current and future carbon stocks and organic matter quality and dynamics. Stability is related to humification degree, as more advanced stages in the humification process involve depletion of the labile molecules, as well as an increase in the bulk aromaticity, which confers higher stability to the SOM. A number of proxies have been used to trace humification rate and SOM stability, including aromaticity level (Vasilevitch et al., 2018; Kniker, 2006). Also, the ratio of C-alkyl : C-aryl and C-alkyl : O-N-alkyl have been successfully used to assess humification degree (Kinker, 2007). The C / H ratio from humic acids (HAs) has been used as an index of molecular complexity, as more degrees of conjugation imply less hydrogenation of the carbon chains (Zaccone et al., 2007) and C / N has been used as a measure of histic material degradation (Lodygin et al., 2014).  $^{13}\text{C}$ -NMR spectrometry provides information on the diversity in carbon functional structures (carbon species) and has been used to evaluate changes in SOM during decomposition and humification. More specifically, high phenolic (150 ppm), carboxyl-C (175 ppm), and alkyl-C (30 ppm) groups – combined with low O-alkyl carbons – have been associated with advanced humification stages (Zech et al., 1997). So far, studies of SOM quality from polar environments have revealed generally partially decomposed organic molecules (Dziadowiec et al., 1994; Lupachev et al., 2017), which preserve much of the chemical character of their precursor material due to slow progress of humification (Davidson and Jansens, 2006). This is very important because polar soils are characterized by the specific composition of the humification precursors.

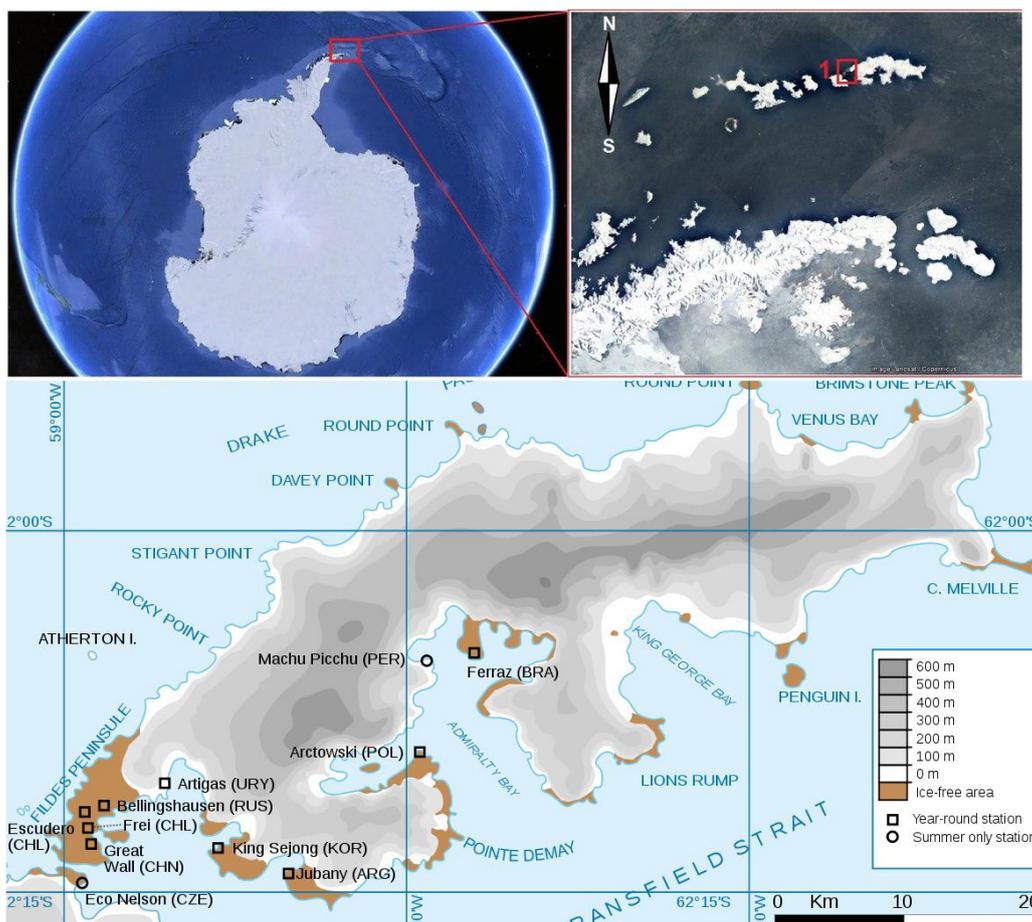
The structure and molecular composition of the Antarctic SOM has been investigated using  $^{13}\text{C}$ -NMR methods (Beyer et al., 1997; Abakumov, 2017b) and it was shown that in typical organo-mineral soils the aliphatic carbon prevails over the aromatic one, owing to the non-ligniferous nature of its precursor material (Calace et al., 1995). Also, analyses of cryptogam extracts were conducted towards identification of individual organic precursors (Chapman et al., 1994). This feature was then shown to be typical for soils from different regions of the Antarctic (Abakumov, 2010), including soil formed on the penguin rockeries (Abakumov and Fatkhova, 2014). The northernmost soil of the Arctic polar biome shows the same trend in organic molecule organization: higher prevalence of aliphatic structures over aromatic ones. The diversity of the individual components in aromatic and aliphatic areas is usually higher in Arctic soil because of the increased diversity of humification precursors (Ejarque and Abakumov, 2016; Abakumov, 2010). A selective preservation of the alkyl moieties in the deeper soil layers has been suggested, and little transformation processes of the SOM are detectable because soil temperatures are not high enough to stimulate further microbial breakdown, even in the summer (Beyer et al., 1997). It has been shown that ornithochory plays an essential role in redistribution of plant remnants in the Antarctic (Parnikoza et al., 2016) as birds transport considerable amounts of variably composed organic material within its inland landscapes. However, published data on SOM composition for the Antarctic are rare, and further studies that detail its structural compounds and their distribution are needed. Recently,  $^{13}\text{C}$  NMR was successfully used to detail the soils found in endolithic communities in Eastern Antarctica and revealed that endolithic organic matter is characterized by a low prevalence of alkyl aromatic compounds (Mergelov et al., 2018).

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

## 2 Materials and methods

### 2.1 Study sites

King George Island is the largest in the South Shetland Islands archipelago and only around 5 % of its  $1400 \text{ km}^2$  area is free of ice (Fig. 1; Rakusa-Suszczewski, 2002). The Fildes Peninsula and Ardley Island, together around  $33 \text{ km}^2$ , comprise the largest ice-free area on King George Island and the

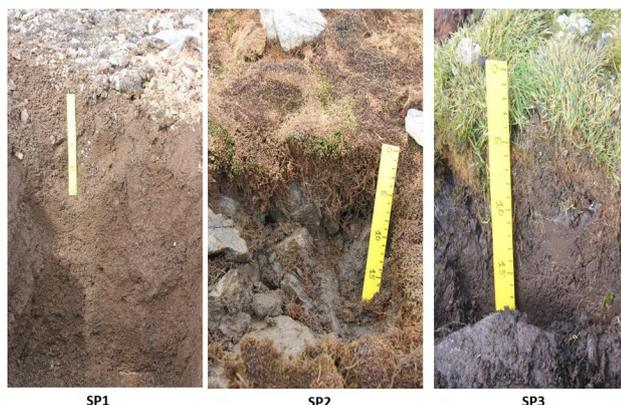


**Figure 1.** Location of the Fildes Peninsula.

second largest of the South Shetland Islands. It has a gentle landscape consisting of old coastal landforms with numerous rocky ridges (Michel et al., 2014). According to Smellie et al. (1984), this area mainly consists of lava with small exposures of tuffs, volcanic sandstones, and agglomerates. The climate is cold and humid with a mean annual air temperature of  $-2.2^{\circ}\text{C}$  and mean summer air temperatures above  $0^{\circ}\text{C}$  for only up to 4 months (Wen et al., 1994). The mean annual precipitation is  $350\text{--}500\text{ mm year}^{-1}$ . The Fildes Peninsula and Ardley Island are among the first areas in maritime Antarctica to become ice free after the Last Glacial Maximum (Birkenmajer, 1989). The onset of deglaciation in the Fildes Peninsula started, as in the South Shetland Islands, by  $8000\text{--}9000\text{ ka}$  and spread during the mid-Holocene (Oliva et al., 2016). The patterned ground in this region dates from 720 to 2640 BP. In the South Shetland Islands, permafrost is sporadic or non-existent at altitudes below 20 m a.m.s.l. and occurs discontinuously in altitudes from 30 to 150 m a.m.s.l. (Bockheim et al., 2013). Mosses, lichens, and algae are common to this area along with two vascular plants (*Deschampsia antarctica* and *Colobanthus quitensis*). Penguins, seals,

and seabirds inhabit the coastal areas and greatly impact the soil development. Major cryogenic surface-forming processes in this region include frost creep, cryoturbation, frost heaving and sorting, gravity, and gelifluction (Michel et al., 2014). Eight separate sites on the Fildes Peninsula have been collectively designated as an Antarctic specially protected area (ASP 125) largely due to their paleontological properties (Management Plan for Antarctic Specially Protected Area No. 125, 2009). The average thickness of the soil is about 15–25 cm. Soils from King George Island have been divided into six groups (WRB, 2014): Leptosols, Cryosols, Fluvisols, Regosols, Histosols, and Technosols; this corresponds well with previously published data (Navas et al., 2008; Abakumov, 2017a).

Three soils were selected for humic substance isolation and further investigation in this study. All soils have top humus layers with a high carbon content and distinguishable layers of supra-permafrost accumulation of organic matter. All three soils are classified as Turbic Cryosols (Histic, Stagnic; WRB, 2014). Soil profiles 1, 2, and 3 (labelled SP1, SP2, and SP3) were collected



**Figure 2.** Soil morphology.

from locations described by the following coordinates: 62°14'391" S, 58°58'549" W; 62°13'140" S, 58°46'067" W; and 62°10'578" S, 58°51'446" W, respectively. The sampling depth was 0–10 cm for the superficial layers and 50–55, 15–20, and 20–25 for SP1, SP2, and SP3, respectively. Images of the soil profiles are presented in Fig. 2. SP1 is from under the mixed lichen–bryophyta cover, SP2 and SP3 are formed under species of *Bryophyta* and *Deshampsia antarctica*, respectively.

## 2.2 Sampling and laboratory analysis

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

HAs were extracted from each sample according to a published protocol (Schnitzer, 1982; <http://humic-substances.org/isolation-of-ihss-samples/>, last access: 11 May 2018). Briefly, the soil samples were treated with 0.1 M NaOH (soil : solution mass ratio of 1 : 10) under nitrogen gas. After 24 h of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at  $1516 \times g$  for 20 min and then acidified to pH 1 with 6 M HCl to precipitate the HAs. The supernatant, which contained fulvic acids, was separated from the precipitate by centrifugation at  $1516 \times g$  for 15 min. The HAs were then dissolved in 0.1 M NaOH and shaken for 4 h under nitrogen gas before the suspended solids were removed by centrifugation. The resulting supernatant was acidified again with 6 M HCl to pH 1 and the HAs were again isolated by centrifugation and demineralized by shaking overnight in 0.1 M HCl / 0.3 M HF (soil : solution ratio of 1 : 1). Next, the samples were repeatedly washed with deionized water until pH 3 was reached and then finally freeze-dried. HA extraction yields were calculated as the percentage

of carbon recovered from the original soil sample (Vasilevitch et al., 2018; Abakumov et al., 2018).

Isolated HAs were characterized for their elemental composition (C, N, H, and S) using the Euro EA3028-HT analyzer. Data were corrected for water and ash content. Oxygen content was calculated by difference from the whole sample. The elemental ratios reported in this paper are based on weight. Solid-state  $^{13}\text{C}$ -NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in a 3.2 mm  $\text{ZrO}_2$  rotor. The magic angle spinning speed was 20 kHz in all cases and the nutation frequency for cross polarization was  $u1 / 2p 1/4 62.5$  kHz. Repetition delay between the number of scans was 3 s. Groups of structural compounds were identified by their chemical shift values: alkyl C (–10 to 45 ppm), O / N-alkyl C (45 to 110 ppm), aryl / olefine C (110 to 160 ppm), and carbonyl / carboxyl / amide C (160 to 220 ppm) (Knicker, 2007). The  $^{13}\text{C}$ -NMR study was also conducted in bulk soil samples towards characterizing changes in the initial soil material during humification.

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

## 2.3 Statistical analysis

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

## 3 Results and discussion

It was previously suggested that temperature and humidity are the most important factors determining most soil-forming processes in cold climate and humid environments (Campbell and Claridge, 1982; Matsuoka et al., 1990). However,

**Table 1.** Basic characteristics of soils. [CRH] represents buried humic cryogenic horizon.

Sample	TOC, %	N, %	C / N	pH <sub>H<sub>2</sub>O</sub>	pH <sub>CaCl<sub>2</sub></sub>	Colour
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

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

Sample no.	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.

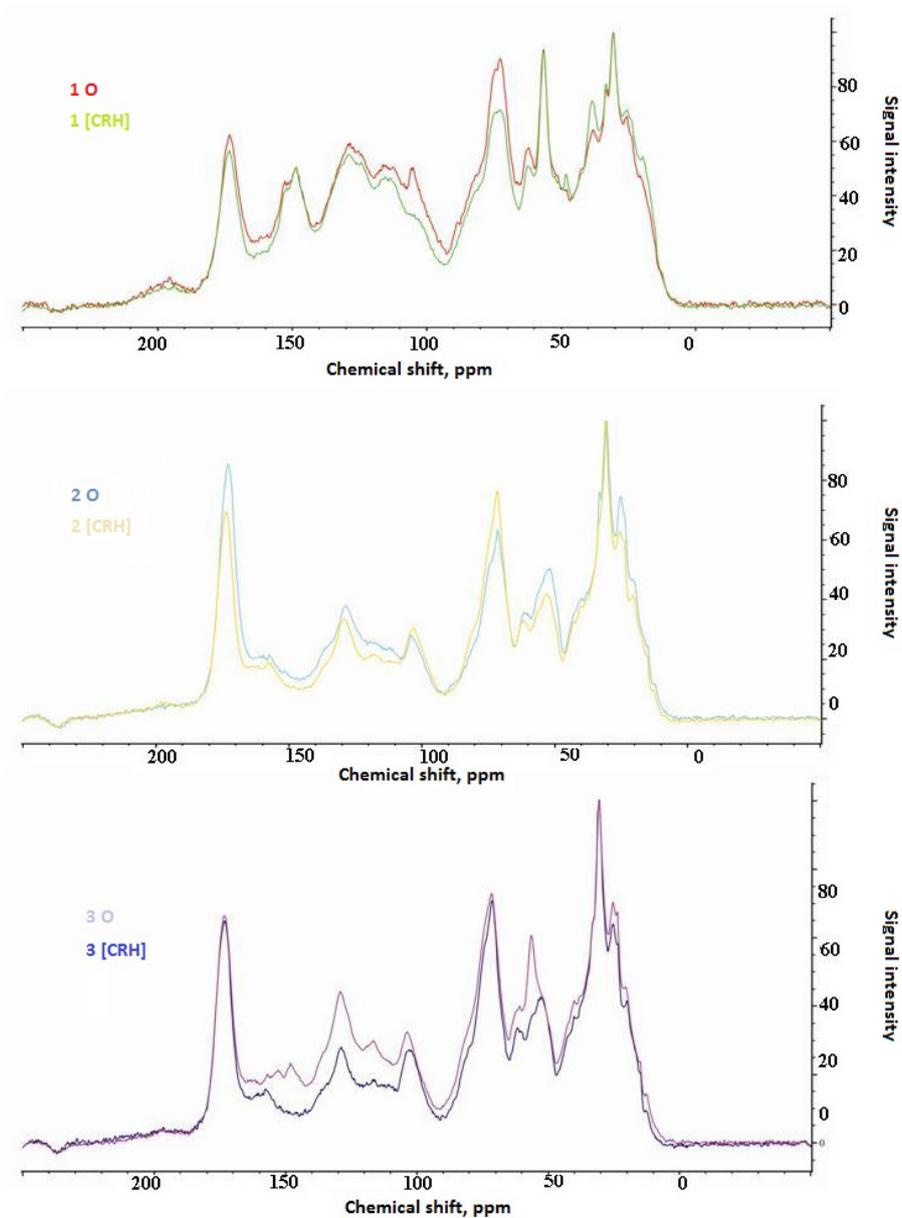
maritime Antarctica is different from the other regions of Earth by the high influence of seabirds and seals on soil-forming processes as they provide additional sources of biogenic elements and significantly change the chemistry of soils. Seabird and seal colonies significantly change biotic activity in marine terraces of maritime Antarctica (González-Guzmán et al., 2017). Periglacial features are dominant on Fildes Peninsula (King George Island; Lopez-Martinez et al., 2012). Total organic carbon (TOC) content was high in both the superficial and buried soil layers. This is indicative of the low degree of decomposition and transformation of the precursor material and is comparable to the data on soils from the Yamal tundra (Ejarque and Abakumov, 2016) and the Argentinian islands (Parnikoza et al., 2016). High TOC content is typical for the Antarctic Peninsula compared to soils of the Eastern Antarctic (Beyer et al., 1997; Mergelov et al., 2017). While both were elevated, the TOC was higher in the superficial levels relative to the lower ones. Previous studies describe high variability in the TOC content from the soils of King George and Galindez islands, mainly depending on the diversity of the ecotopes and the sources of organic matter (Abakumov, 2010; González-Guzmán et al., 2017; Moura et al., 2012; Parnikoza et al., 2016). TOC was previously found higher in ornithogenic soils of rocky platforms compared to non-ornithogenic soils (Moura et al., 2012). Isolated (buried) soil spots are not connected with fresh sources of organic matter, explaining why the TOC content in these layers is lower.

The carbon to nitrogen ratio was narrowest in SP1, which was affected by the skua activity (evidenced by remnants of nests). This is in line with previous studies that documented the well-pronounced ornithogenic effects on soil nitrogen

content (Otero et al., 2013; Parnikoza et al., 2016; Simas et al., 2007). Organic matter is one of the main soil components that contributes to the development of many of the physical, chemical, and biological properties and is of particular importance in Antarctic soils (Beyer et al., 1997). The fine earth of the investigated soils were characterized by acid reaction, which is expected for soils of this region. Values of pH<sub>H<sub>2</sub>O</sub> varied from 4.70 to 6.35. These values coincide well with those previously obtained for maritime Antarctica (Moura et al., 2012; Navas et al., 2017).

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

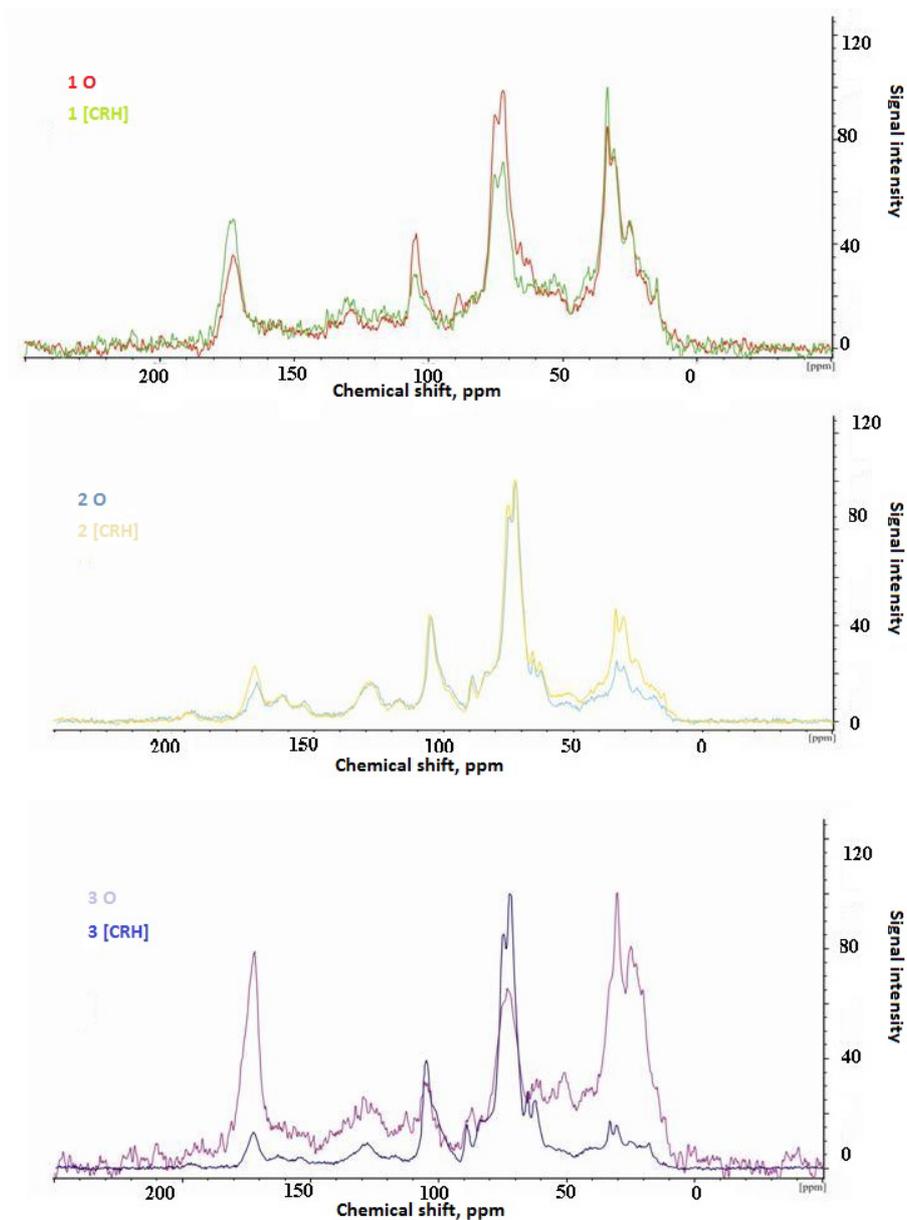
Data on the distribution of carbon species in HAs (Fig. 3, Table 3) and in bulk soil (Fig. 4, Table 4) samples indicated that aromatic compound content is generally lower than the alkyl components. This is a well-known peculiarity of the soils of the polar biome (McKnight et al., 1994; Beyer et al., 1997). At the same time, the degree of aromaticity of the isolated HAs is 3 fold higher than in the bulk organic matter. This suggests the presence of the humification process in the soils of Antarctica since humification involves increasing the aromatic compound content in macromolecules. This supports the classical humification hypothe-



**Figure 3.** The  $^{13}\text{C}$ -NMR spectra of the HAs, isolated from soils (labelled 1–6 according to Table 1). [CRH] represents the buried humic cryogenic horizon.

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

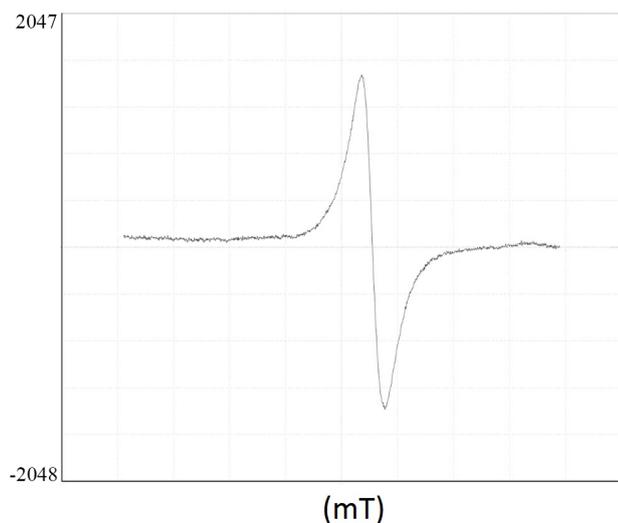
Sample no. 1	Carbonyl / carboxyl / amide	Aryl-olefine	O-N alkyl	Calkyl	Calkyl / O-N alkyl	Caryl / calkyl
Chemical shift, ppm	220–160	160–110	110–45	45–0		
1	11.38	33.59	39.86	14.18	0.35	2.36
2	10.75	30.45	31.86	26.05	0.81	1.16
3	19.24	23.34	29.54	27.85	0.94	0.83
4	16.48	21.42	34.23	27.87	0.81	0.77
5	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.



**Figure 4.**  $^{13}\text{C}$  NMR spectra of bulk organic matter of soils (labelled 1–6 according to Table 1). [CRH] represents the buried humic cryogenic horizon.

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

Sample no.	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.



**Figure 5.** Typical ESR spectrum of humic substances investigated.

sis instead of new arguments, which are critical for this approach (Lehman and Kleber, 2015). Our data show that SOM is on a continuum and HAs are the main acting constituent of this continuum, thereby confirming that this model is applicable even in Antarctica. The degree of aromaticity was higher in both isolated HAs and bulk soil samples from superficial levels compared to samples from isolated patches. Carbonyl / carboxyl / amide area (160–220 ppm) was more prevalent in the HAs of topsoils and less abundant in the organic matter of bulk samples (this region was mainly presented by carboxylic and amide carbon in the interval between 160–185 ppm) (Kniker, 2007). HAs extracted from SP1, located under the *Deshampsia antarctica*, exhibited wide peaks around 110–140 ppm (H-aryl, C-aryl, olefinic-C) and at 140–160 ppm (O-aryl and N-aryl-C), while aromatic components of SP2 and SP3 were mainly represented by peaks between 110 and 140 ppm. This difference can be explained by the organic remnants of *Deshampsia antarctica* serving as the precursor for humification. All HA samples showed intensive areas of alkylic carbon (0–45 ppm), aliphatic C and N and methoxyl C (45–110 ppm), O-alkyl of carbohydrates and alcohols (60–95 ppm), and acetal and ketal carbon of carbohydrates (95–110 ppm). Carbon composition of the bulk samples was different from isolated HAs as evidenced mainly by the presence of alkyl carbon (0–45 ppm) and O- and N-alkyl carbon (45–110 ppm). Characteristic features of the bulk organic matter include carboxylic carbon and that the aryl compound content was low relative to isolated HAs. Only soils with prior ornithogenic interactions showed increases in carboxylic peaks, which corresponds well to data on relic ornithogenic soil (Beyer et al., 1997).

**Table 5.** Mass concentration of free radicals in humic acids.

Soil horizon	Mass concentration of free radical, $10^{15} \text{ spin g}^{-1}$	<i>g</i> -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

The C-alkyl : O-N-alkyl ratio used to indicate the degree of organic matter transformation was quite variable in all samples investigated. This can be caused by diversity in the origin and composition of the humification precursors. In the case of comparisons with humic and fulvic acids of tundra soils (Vasilevitch et al., 2018), HAs of soils are intermediated between HAs and fulvic acids of tundra Histosols with partially decomposed organic matter. These data are in line with a previous report (Hopkins et al., 2006) that showed soils of the McMurdo Dry Valleys have a low alkyl-C : O-alkyl-C ratio using solid-state  $^{13}\text{C}$ -NMR spectroscopy, and therefore can serve as a labile high-quality resource for microorganisms. Beyer et al. (1997) showed that both the cross-polarization magic angle spinning  $^{13}\text{C}$  NMR and the Py-FIMS (pyrolysis-field ionization mass spectrometry) spectra of the Terri-Gelic Histosol were dominated by signals from carbohydrates and alkylic compounds, which is corroborated by our findings. They also suggest that the  $^{13}\text{C}$ -NMR data reflected decomposition of carbohydrates and enrichment of alkyl C in deeper soil layers. In regards to the bulk SOM, this was true for SP2 and SP3 but not for SP1 that formed under the vascular plant *Deshampsia antarctica*.

A representative electron spin resonance ESR spectrum of HAs is presented in Fig. 5 and the ESR parameters are similar to HAs and fulvic acids (FAs) of temperate soils (Senesi, 1990; Senesi et al., 2003). The spectra show a single, wide line with a *g*-factor ranging from 1.98890 to 1.99999, attributable to the presence of stable semiquinone free radicals in the HA-containing macromolecules (Table 5). The free-radical content was higher in the superficial levels than in the isolated ones. This corresponds well with previous reports (Chukov et al., 2017; Abakumov et al., 2015) that connect the isolation of buried organic matter in the suprapermafrost with declining free-radical content. This reveals the increased biochemical activity of HAs in topsoil. Compared to data from Lupachev (2017), the differences between exposed and isolated areas are less pronounced but, in general, the HAs of the Antarctic soils contain more unstable free radicals on average than the tundra soils of the Kolyma Lowland (Lupachev et al., 2017) and are comparable to the soils from the Yamal tundra (Chukov et al., 2017). Taken together, the free-radical content found in our study was lower

than in anthropogenically affected boreal and forest steppe soils of the East European Plain (Abakumov et al., 2018).

#### 4 Conclusions

High TOC content was fixed for the three studies representatives of Turbic Cryosols on King George Island, northwest of the Antarctic Peninsula, Western Antarctic. High amounts of TOC are characteristic for both superficial and partially isolated soil materials. HAs contained 3 times more aromatic carbon than bulk SOM, which indicates that humification appears and is active in soils of the Antarctic. Moreover, the amounts of aromatic carbon and carboxyl groups were higher in the HAs of the superficial layer, which is likely caused by the greater diversity of their organic precursors and more active humification than in sub-aerial conditions. The HAs of the superficial sample layers contained lower concentrations of free radicals, an indicator of active transformation in the topsoil. In general, the organic matter from partially isolated areas is less stable in terms of carbon species and free radical content. This likely results from the relative lack of fresh organic precursors and the different aeration and hydration conditions of stagnification bordering the permafrost table.

*Data availability.* Our underlying research data belong to the Research Centre of Saint Petersburg State University, since we performed the analysis there.

*Author contributions.* IA contributed humic substances isolation; EA contributed field soil survey, NMR spectra collection, and interpretation.

*Competing interests.* The authors declare that they have no conflict of interest.

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