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

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Key points

Investigation of Antarctic soil organic matter stability

Humic acids of superficial horizons contain more aromatic carbon

Humic acids of isolated layers contain more free radicals

Abstract

In this study, the soil organic matter (SOM) was analyzed 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 alkylaromatic 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 more precise assessment of SOM stabilization rate in sub-Antarctic tundras. Comparison of the ^{13}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.

Highlights

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

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 continuous and discontinuous permafrost 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. Polar SOM represents a vulnerable carbon source, susceptible to remobilization under increasing temperatures (Schuur et al, 2015, Ejarque, 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's temporal dynamics (Fritz et al, 2014, 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/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, Popov, 2005, Polyakov et al, 2017).

The stocks of SOM in the Antarctic are underestimated compared to the Arctic because of the lack of the 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 kg/m^2 in its polar deserts, about 1.0 kg/m^2 in its barrens, up to 3 - 5 kg/m^2 in the sub-Antarctic tundra, and up to 30 kg/m^2 in the penguin rockeries of the maritime islands (Abakumov, 2010, Abakumov, Mukhametova, 2014, Abakumov et al, 2016).

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, 2007). Also the ratio of C-Alkyl : C-Aryl and C-Alkyl : O-N-alkyl have been successfully used to assess humification degree (Kinker, 2007). 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}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 lowly-decomposed organic molecules (Dziadowiec, 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}C-NMR methods (Beyer et al, 1997, Abakumov, 2017) 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, Fattakhova, 2015). The northern most soil of Arctic polar biome shows the same trend in organic molecules 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, Abakumov, 2016, Abakumov, 2010). The over-moistened Antarctic Histic soils under algae are characterized by a predominance of proteins containing nitrogen compounds and a slight degradation of carbohydrates in the SOM. 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 break-down, even in the summer (Beyer et al, 1997). Previous reports on organic matter mainly focused on gelisols or cryosols derived from bryophytes, algae, and vascular plants from stable habitats without pronounced ornithogenic effects (Carvahlo et al., 2010). It has been shown that ornithochoria play 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. The presence of organic matter of ornithogenic origin plays an important role in the formation of humic substances. 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}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 evaluated the stabilization rate of Antarctic Cryosols. To date, this type of investigation 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. 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; (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 archipelago and only around 5% of its 1400 km^2 area is free of ice (Fig. 1) (Rakusa-Suszczewski, 2002). The Fildes Peninsula and Ardley Island, together around 33 km^2, comprise the largest ice-free area on King George Island and the second largest of the South Shetland Islands. It has a gentle landscape consisting of old coastal landforms with numerous rocky ridges and an average height of 30 m above main sea level (AMSL) (Michel et al., 2014). According to Smellie (Smellie et al, 2014), 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°C and mean summer air temperatures above 0°C for only up to four months (Wen et al., 1994). The mean annual precipitation is 350 - 500 mm/year. 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 Fildes Peninsula was covered by glaciers from 8000 to 5000 BP (Mausbacher et al, 1989, Haus et al, 2014). 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 AMSL and occurs discontinuously in altitudes from 30 to 150 m AMSL (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 an Antarctic Specially Protected Area (ASPA 125) largely due to their paleontological properties (Management plan, 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).

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 suprapermafrost accumulation of organic matter. All three soils are classified as Turbic Cryosols (Histic, Stagnic) (WRB, 2014). Soil profiles 1, 2, and 3 (SP1, SP2, SP3) were collected 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. Sampling depth was 0 - 10 cm for the superficial layers and 50 - 55, 15 - 20, 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* correspondingly.

2.2. Basic characterization

Soil samples were air-dried, 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).

2.3. Extraction of humic acids (HAs)

HAs were extracted from each sample according to a published protocol (Shnitzer, 1982), http://humic-substances.org/isolation-of-ihss-samples/). Briefly, the soil samples were treated with 0.1 M NaOH (soil/solution mass ratio of 1:10) under nitrogen gas. After 24 hours of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at 1,516 × g for 20 minutes 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 1,516 × g for 15 minutes. The HAs were then dissolved in 0.1 M NaOH and shaken for four hours 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).

2.4. Characterization of humic acids (HAs)

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. The elemental ratios reported in this paper are based on weight. Solid-state ^{13}C-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in a 3,2-mm 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 and number of scans were 3 seconds. Groups of structural compounds were identified by their chemical shifts values: alkyl C (−10 to 45 ppm), O/N-alkyl C (45 to 110 ppm), aromatic C (110 to 160 ppm), and carbonyl/carboxyl/amide C (160 to 220 ppm) (Kniker, 2007). The ^{13}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 centers 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).

2.5. Statistics

Statistical data analysis was performed using the STATISTICA 10.0 software (ANOVA, Statistica Base 12.6, Dell, Round Rock, 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 ± standard deviation (SD).

3. Results and Discussion

Total organic carbon (TOC) content was high in both the superficial and buried soil layers (Table 1). 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, 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 described 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, Parnikoza et al, 2016). 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 scuas’ activity (evidenced by remnants of nests). This is in line with previous studies that documented the well-pronounced ornithogenic effects on soil’s nitrogen content (Simas et al, 2007, Parnikoza et al, 2016). Fine earth of soils investigated characterized by acid reaction, which is expected for soils of this region.

In terms of elemental composition, soil HAs are comparable with those previously reported for the Arctic and Antarctic soil. Current exposed organic layers contain HAs with higher carbon and nitrogen and lower oxygen content (Table 2). 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, 2017).

Data on the distribution of carbon species in HAs (Table 3, fig. 3) and in bulk soil (Table 4, fig. 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 (McKnihct et al, 1994, Beyeret al, 1997). At the same time, the degree of aromaticity of the isolated HAs is three fold higher than in the bulk organic matter. This suggests the presences of the humification process in the soils of Antarctica since humification involves increasing the aromatic compound content in macromolecules. This supports the classical humification hypothesis instead of new arguments, which are critical for this approach (Lehman, Kleber, 2015). Our data shows 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 presented mainly by carboxylic and amid carbon in the interval between 160 - 185 ppm) (Kniker, 2007). HAs extracted form 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 - 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 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).

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 case of comparisons with humic and fulvic acids of tundra soils (Vasilevitch et al, 2018), HAs of soils investigates 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 Antarctic Dry Valleys have low C-alkyl : O-alkyl-C ratio using solid-state ^{13}C-NMR spectroscopy) and, therefore can serve as a labile, high-quality resource for micro-organisms. Beyer et al (1997) showed that both the CPMAS ^{13}C-NMR and the Py-FIMS 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}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 electrone spin resonanse ESR spectrum of HAs is presented in fig. 5 and the ESR parameters are similar to HAs and 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 connected the isolation of buried organic matter in the supra-permafrost 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). At the same time they 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 plains (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 three-fold more aromatic carbon than that in 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.

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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

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.

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.

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.

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

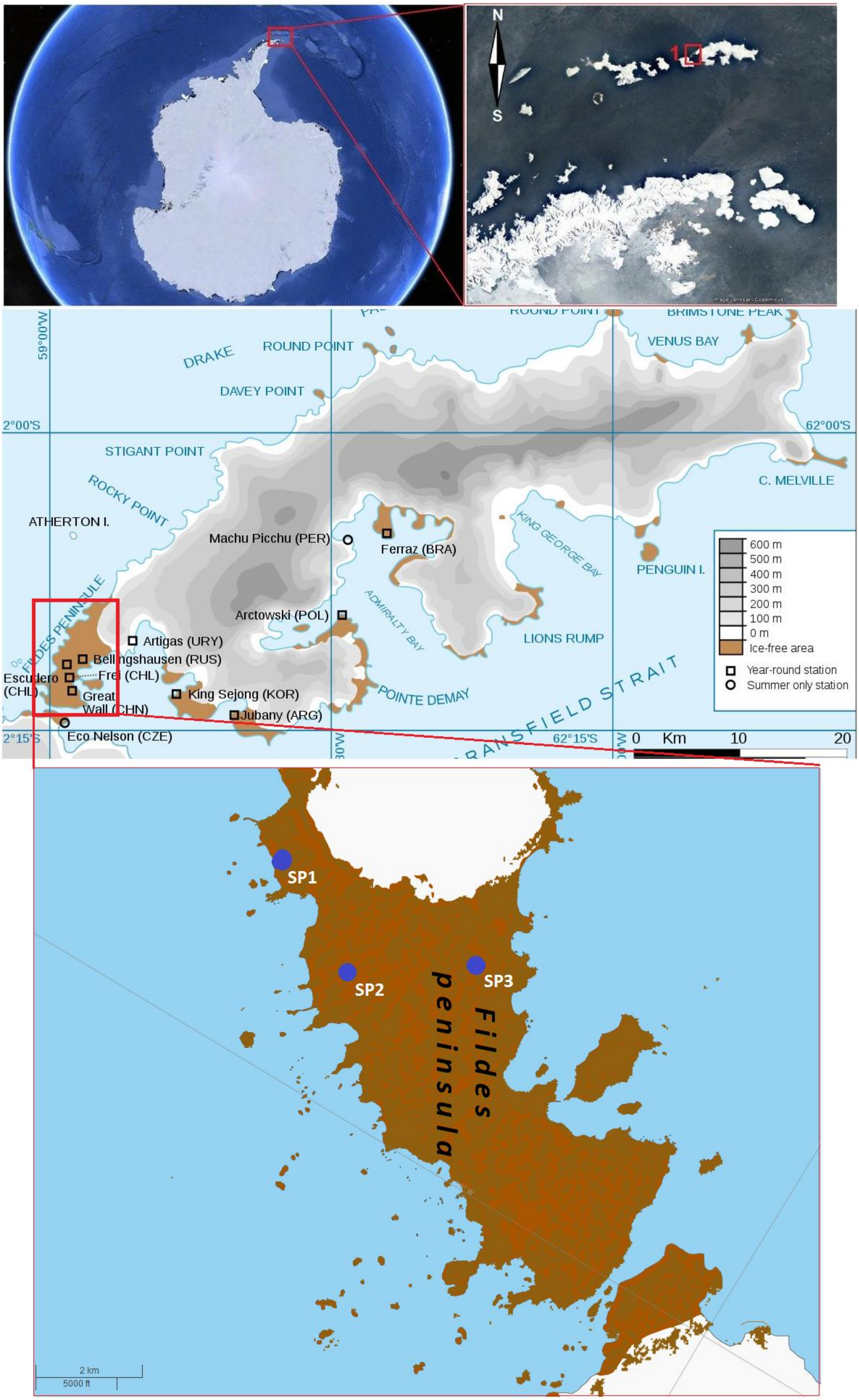
N
S
1
ROUND POINT
BRIMSTONE PEAK
DRAKE
ROUND POINT
VENUS BAY
DAVEY POINT
59°00'W
2°00'S
62°00'S
STIGANT POINT
ROCKY POINT
C. MELVILLE
ATHERTON I.
Machu Picchu (PER)
Ferraz (BRA)
KING GEORGE BAY
PENGUIN I.
FILDES PENINSULE
Arctowski (POL)
ADMIRALTY BAY
LIONS RUMP
Artigas (URY)
Bellingshausen (RUS)
Escudero (CHL)
Frei (CHL)
Great Wall (CHN)
King Sejong (KOR)
Jubany (ARG)
POINTE DEMAY
BRANSFIELD STRAIT
Eco Nelson (CZE)
2°15'S
62°15'S
600 m
500 m
400 m
300 m
200 m
100 m
0 m
Ice-free area
□ Year-round station
○ Summer only station
0 Km 10 20
SP1
SP2
SP3
Fildes peninsula
2 km
5000 ft

Fig. 1.

SP1 SP2 SP3

Fig. 2

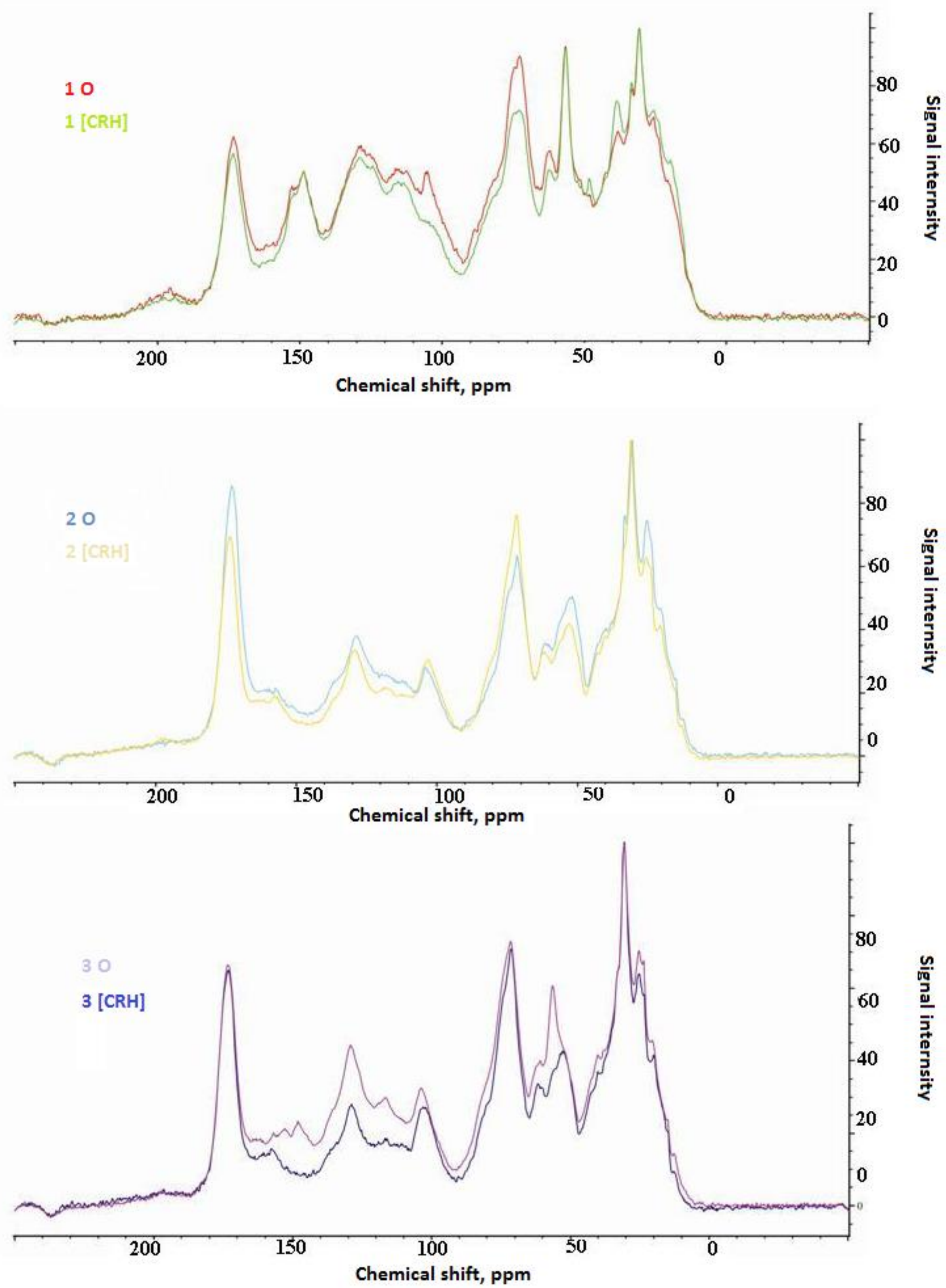
1 O
1 [CRH]
Signal internsity
80
60
40
20
0
200
150
100
50
0
Chemical shift, ppm
2 O
2 [CRH]
Signal internsity
80
60
40
20
0
200
150
100
50
0
Chemical shift, ppm
3 O
3 [CRH]
Signal internsity
80
60
40
20
0
200
150
100
50
0
Chemical shift, ppm

Fig. 3

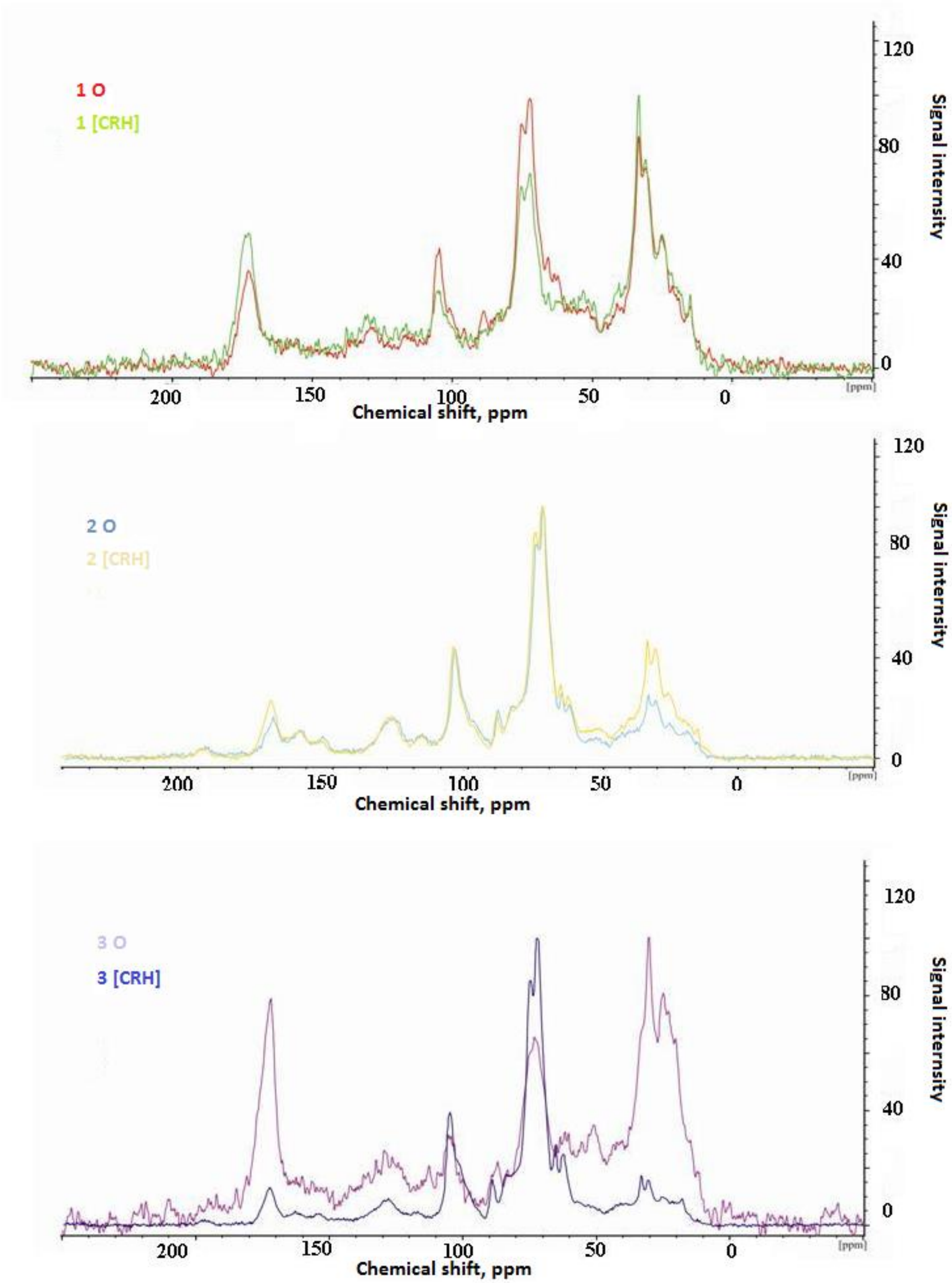
1 O
1 [CRH]
120
80
40
0
Signal internsity
200
150
100
50
0
[ppm]
Chemical shift, ppm
2 O
2 [CRH]
120
80
40
0
Signal internsity
200
150
100
50
0
[ppm]
Chemical shift, ppm
3 O
3 [CRH]
120
80
40
0
Signal internsity
200
150
100
50
0
[ppm]
Chemical shift, ppm

Fig. 4

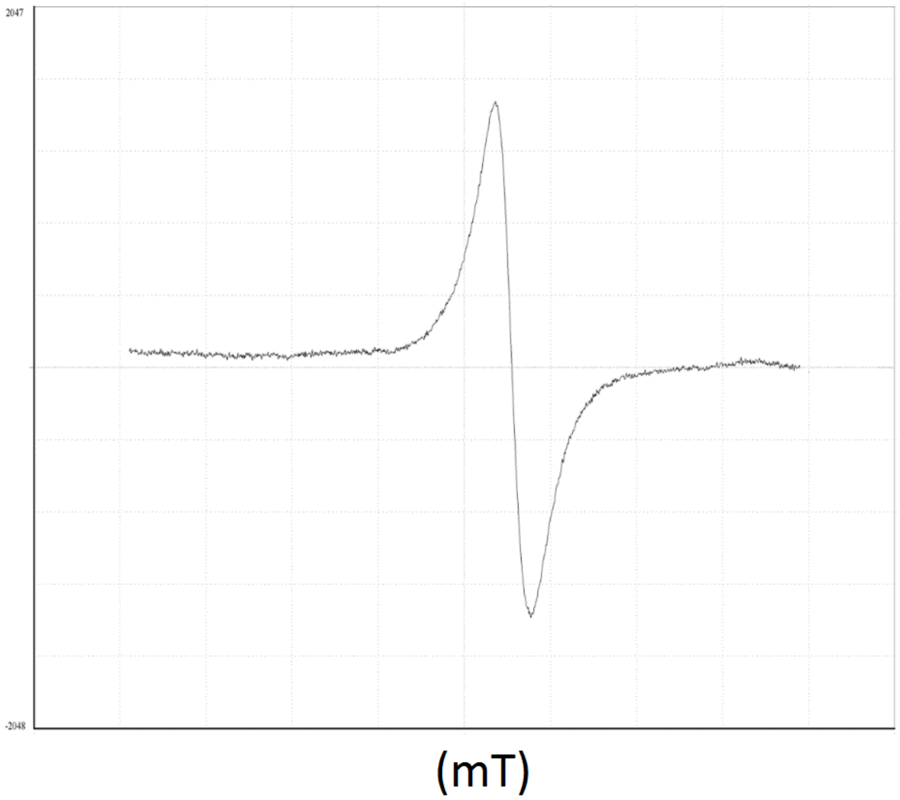

Fig. 5.

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

Fig.2. Soil morphology

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

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

Figure 5. Typical ESR spectrum of humic substances investigated

Table. 1. Basic characteristics of soils

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