1   Dear reviewer,

2

3   Thank you very much for taking time to review our manuscript and your vital advices on

4   improving the text. We have corrected our manuscript according to your remarks

Remark	Response
l. 46 continuous and discontinuous permafrost result in the stabilization of essential… Is it really continuous/discontinuous…) or active layer dynamics that drives these processes?	We have changed the term in mentioned sentence
l. 129 be careful, what is the meaning of an average altitude in the area? Fildes consists of two main plateaus separated by a lower relief. I don't understand why you indicate the mean altitude of the ice-free area. It is not representative of the region	We have deleted the information on the mean altitude
	The term has been re-written in a right form
	The wrong information has been corrected
. 135 Last Glacial Maximum	The line mentioned in remark has been checked and corrected
l. 136 this is not true. The onset of deglaciation started as in many other areas in the SSI by 8000-9000 ka and spread during the mid Holocene. Check Oliva et al (2016) in Geomorphology, from Byers, and references about other areas in the SSI therein. Oliva, M.; Antoniades, D.; Giralt, S.; Granados, I.; Pla-Rabes, S; Toro, M.; Sanjurjo, J.; Liu, E.J. & Vieira, G. (2016). The Holocene deglaciation of the Byers Peninsula (Livingston Island, Antarctica) based on the dating of lake sedimentary records. Geomorphology, 261: 89-102.	Results and Discussion chapter has been extended with comparison of soils studied in our work and soils previously investigated in the region of Maritime Antarctica

1 |

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

Evgeny Abakumov[1], Ivan Alekseev[1,2]

[1] *Department of Applied Ecology, Saint-Petersburg State University, 199178, 16-line 2, Vasilyevskiy Island, Russia*

[2] *Otto Schmidt Laboratory for Polar and Marine, Arctic and Antarctic Research Institute, 199397, Beringa str. 38, Russia*

e-mail: e.abakumov@spbu.ru, e_abakumov@mail.ru, st014661@student.spbu.ru

Key words

Antarctica, soil organic matter, stabilization, humic acids

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

Previously, the structure and molecular composition of the Antarctic SOM has been investigated using ^{13}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 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. This indicates that humification is one of the ways of soil organic matter stabilization.

Highlights

47   Stabilization of soil organic matter studied

48   Humic acids of superficial horizons contain more aromatic carbon

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

50
51   **1. Introduction**

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

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

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

84   Stability and biodegradability are the key features of SOM that should be taken into
85   account when estimating current and future carbon stocks and organic matter quality and
86   dynamics. Stability is related to humification degree, as more advanced stages in the
87   humification process involve depletion of the labile molecules, as well as an increase in the bulk
88   aromaticity, which confers higher stability to the SOM. A number of proxies have been used to
89   trace humification rate and SOM stability, including aromaticity level (Vasilevitch et al, 2018,
90   Kniker, 2007). Also the ratio of C-Alkyl : C-Aryl and C-Alkyl : O-N-alkyl have been
91   successfully used to assess humification degree (Kinker, 2007). C/H ratio from humic acids
92   (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). 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). It has been shown that ornitochoria 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. 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 endolitic communities in Eastern Antarctica and revealed that endolitic 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. 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 (Michel et al, 2014). According to 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 onset of deglaciation in Fildes peninsula started as in the SSI by 8000-9000 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 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, Abakumov, 2017).

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 antartica* correspondingly.

2.2. Sampling and laboratory analysis

Soil samples were air-dried (24 hours, 20ºC), 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).

Humic acids (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 $1,516 \times$ 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 $1,516 \times$ 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).

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 ZrO2 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), aryl/olefine 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).

2.3. *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 ± standard deviation (SD).

3. Results and Discussion

It was previously suggested that temperature and humidity are the most important factors determining the most of soil-forming processes in cold climate and humid environments (Campbell and Claridge, 1982, Matsuoka et al., 1990). However, Maritime Antarctica is differed from the other regions of Earth by the high influence of sea birds and seals on soil-forming processes as they provide additional source of biogenic elements and significantly change the chemistry of soils. Seabird and seal colonies significantly changes biotic activity in marine terraces of Maritime Antarctica (Gonzalez-Guzman et al, 2017). Periglacial features are dominant on Fildes peninsula (King George Island) (Lopez-Martinez et al, 2016). 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, 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, Gonzalez-Guzman et al., 2017, Moura et al., 2012, Parnikoza et al, 2016). TOC was found higher previously 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 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 (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., 2000). Fine earth of soils investigated characterized by acid reaction, which is expected for soils of this region. Values of pH_{H2O} varied from 4.70 to 6.35. These values coincides well with 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. 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, 2017).

Data on the distribution of carbon species in HAs (fig. 3) and in bulk soil (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 alkyl-C : 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 connect 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) 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 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 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.

328

<mark>References</mark>

Abakumov E. Vertical electric resistivity sounding of natural and anthropogenically affected cryosols of Fildes Peninsula, Western Antarctica. Czech Polar Reports, 7 (2), pp. 109-122, 2017

Abakumov, E.V. The sources and composition of humus in some soils of West Antarctica Eurasian Soil Science, 43 (5), pp. 499-508, 2010

Abakumov, E.. Characterisation of humic acids, isolated from selected subantarctic soils by 13C-NMR spectroscopy, Czech Polar Reports, 7 (1). 1-10, 2017

Abakumov, E., Maksimova, E., Tsibart, A. Assessment of postfire soils degradation dynamics: Stability and molecular composition of humic acids with use of spectroscopy methods Land Degradation and Development . Article in Press, 2018

Abakumov, E.V., Lodygin, E.D., Tomashunas V.M. 13-C NMR and ESR characterization of Humic Substances, Isolates from Soils of two Siberian Arctic Islands, International Journal of Ecology. ID 390591, 2015

Abakumov, E , Mukhametova, N. Microbial biomass and basal respiration of selected Sub-Antarctic and Antarctic soils in the areas of some Russian polar stations, Solid Earth, 5. 705-712, 2014

Abakumov, E.V., Parnikoza, I.Y., Vlasov, D.Y., Lupachev, A.V. (2016). Biogenic–abiogenic interaction in Antarctic ornithogenic soils. Lecture Notes in Earth System Sciences, (9783319249858), pp. 237-248.

Abakumov, E. V., Popov, A. I. Determination of the carbon and nitrogen contents and oxidizability of organic matter and the carbon of carbonates content in one soil sample, Eurasian Soil Science, 2:165−172, 2005

Abakumov, E.V., Fattakhova Yu.M. Structural composition of humic acids of ornitogenic soils on the data of 13-C NMR resonance, Russian Ornitology, 1165: 2463-2466, 2014

Beyer, L; Knicker, H; Blume, H-P; Bölter, M; Vogt, B; Schneider. Soil organic matter of suggested spodic horiozns in relic ornitogenic soils of coastal Continental Antarctica (Casey Station, Wilkes Land) in comparison with that of spodic soil horizons in Germany, Soil Science, 7. 518-527, 1997

Birkenmajer K. Geology and climatostratigraphy of Tertiary glacial and interglacial Successions on King George Island, South Shetland Islands (West Antarctica), Ztrbl. Geol. Palaont., 1: 141–151, 1989

Bockheim J., Vieira G., Ramos M., López-Martínez, J., Serrano E., Guglielmin M., Wihelm K., Nieuwendam A., . Climate warming and permafrost dynamics on the Antarctic Peninsula region, Glob. Planet. Change, 100: 215–223, 2013

Calace, N., Campanella, L., Paolis, F., and De Petronio, B. M. Characterization of Humic Acids Isolated from Antarctic Soils: Int. J. Environ. Anal. Chem., 60: 71–78, 1995

Chapman, B., Roser, D., & Seppelt, R. 13C NMR analysis of Antarctic cryptogam extracts. Antarctic Science, 6(3), 295-305, 1994

10

Chukov, S.N., Ejarque, E., Abakumov, E.V. Characterization of humic acids from tundra soils of northern Western Siberia by electron paramagnetic resonance spectroscopy, Eurasian Soil Science, 50 (1): 30-33, 2017

Davidson, E. A. and Janssens, I. A. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440: 165–173, 2006

Dziadowiec, H., Gonet, S., and Plichta, W. Properties of humic acids of Arctic tundra soils in Spitsbergen, Polish Polar Res., (15), 71–81., 1994

Ejarque, E., Abakumov, E. Stability and biodegradability of organic matter from Arctic soils of Western Siberia: Insights from 13C-NMR spectroscopy and elemental analysis (2016) Solid Earth, 7 (1), pp. 153-165, 2016

Fritz, M., Deshpande, B. N., Bouchard, F., Högström, E., Malenfant-Lepage, J., Morgenstern, A., Nieuwendam, A., Oliva, M., Paquette, M., Rudy, A. C. A., Siewert, M. B., Sjöberg, Y., and Weege, S. Brief Communication: Future avenues for permafrost science from the perspective of early career researchers, The Cryosphere, 9: 1715–1720, 2014

González-Guzmán, A., Oliva, M., Ruiz-Fernández, J., Pérez-Alberti, A., de Souza, V.S. and Otero, X.L. Biota and geomorphic processes as key environmental factors controlling soil formation at Elephant Point, Antarctica. Geoderma, 300: 32-43, 2017.

Hopkins D.W., Sparrow A.D., Elberling B., Gregorich E.G., Novis P.M., Greenfield L.G., Tilston E.L.,Carbon, nitrogen and temperature controls on microbial activity in soils from an Antarctic dry valley,Soil Biology and Biochemistry, 38: 3130-3140, 2006

Hugelius, G., Strauss, J., Zubrzycki, S., Harden, J. W., Schuur, E. A. G., Ping, C.-L., Schirrmeister, L., Grosse, G., Michaelson, G. J., Koven, C. D., O'Donnell, J. A., Elberling, B., Mishra, U., Camill, P., Yu, Z., Palmtag, J., and Kuhry, P. Estimated stocks of circumpolar permafrost carbon with quantified uncertainty ranges and identified data gaps, Biogeosciences, 11: 6573–6593, 2014

ICCP – Intergovermental panel on Climate Change: Climate Change 2007.,Cambridge, University Press, United Kingdom and New York, NY, USA, 2007

Kniker H. How does fire affecr the nature and stability of soil organic nitrogen and carbon ? Biogeosciences, 2007, 86: 91-118, DOI 10.1007/s10533-007-9104-4, 2006

Lechman J., Kleber M. The contentious nature of soil organic matter. Nature, 528. 60-68, 2015

Lodygin, E.D., Beznosikov, V.A. and Vasilevich, R.S. Molecular composition of humic substances in tundra soils (^{13}C-NMR spectroscopic study). Eurasian Soil Sc. (47) (5), 400–406, 2014

Lupachev, A., Abakumov, E., Gubin, S. The influence of cryogenic mass exchange on the composition and stabilization rate of soil organic matter in cryosols of the kolyma lowland (North Yakutia, Russia), Geosciences (Switzerland), 7 (2), paper № 24, DOI: 10.3390/geosciences7020024, 2017

Management Plan for Antarctic Specially Protected Area No. 125, Measure 6, Annex., Antarctic Treaty Secretariat, 2009

408   McKnight Diane M. , Andrews Edmund D. , Spaulding Sarah A. , Aiken George R. , Aquatic
409   fulvic acids in algal-rich antarctic ponds, Limnology and Oceanography, 39, 1994

410   Mergelov, N., Mueller, C.W., Prater, I., Shorkunov, I., Dolgikh, A., Zazovskaya, E., Shishkov,
411   V., Krupskaya, V., Abrosimov, K., Cherkinsky, A., Goryachkin, S. Alteration of rocks by
412   endolithic organisms is one of the pathways for the beginning of soils on Earth. Scientific
413   Reports, 8 (1), paper № 3367, 2018

414   Michel, R.F.M., Schaefer, C.E.G.R., López-Martínez, J., Simas, F.N.B., Haus, N.W., Serrano,
415   E., Bockheim, J.G.. Soils and landforms from Fildes Peninsula and Ardley Island, Maritime
416   Antarctica. Geomorphology. 225: 76-86. doi:10.1016/j.geomorph.2014.03.041, 2014

417   Moura, P.A., Francelino, M.R., Schaefer, C., Simas, F. and de Mendonça, B. Distribution and
418   characterization of soils and landform relationships in Byers Peninsula, Livingston Island,
419   Maritime Antarctica. Geomorphology 155–156: 45–54, 2012.

420   Navas, A., López-Martínez, J., Casas, J., Machín, J., Durán, J.J., Serrano, E., Cuchi, J.A., Mink,
421   S.. Soil characteristics on varying lithological substrates in the South Shetland Islands, maritime
422   Antarctica. Geoderma 144 :123–139. doi:10.116/j.geoderma.2007.10.01, 2008

423   Navas, A., Oliva, M., Ruiz-Fernández, J., Gaspar, L., Quijano, L. and Lizaga, I. Radionuclides
424   and soil properties as indicators of glacier retreat in a recently deglaciated permafrost
425   environment of the Maritime Antarctica. Science of the Total Environment, 609: 192-204, 2017.

426   Oliva, M.; Antoniades, D.; Giralt, S.; Granados, I.; Pla-Rabes, S; Toro, M.; Sanjurjo, J.; Liu, E.J.
427   & Vieira, G. The Holocene deglaciation of the Byers Peninsula (Livingston Island, Antarctica)
428   based on the dating of lake sedimentary records. Geomorphology, 261: 89-102, 2016.

429   Otero, X.L., Fernández, S., de Pablo Hernandez, M.A., Nizoli, E.C., Quesada, A. Plant
430   communities as a key factor in biogeochemical processes involving micronutrients (Fe, Mn, Co,
431   and Cu) in Antarctic soils (Byers Peninsula, maritime Antarctica). Geoderma 195, 145–154,
432   2013.

433   Parnikoza, I., Abakumov, E., Korsun, S., Klymenko, I., Netsyk, M., Kudinova, A., Kozeretska, I.
434   Soils of the argentine islands, antarctica: Diversity and characteristics Polarforschung, 86 (2), pp.
435   83-96. 2016

436   Rakusa-Suszczewski S. King George Island — South Shetland Islands, Maritime Antarctic. In:
437   Beyer L., Bölter M. (Eds.), Geoecology of Antarctic Ice Free Coastal Landscapes. Springer
438   Verlag, Berlín, 23–40, 2002.

439   Polyakov V., Orlova K., Abakumov, E. Evaluation of carbon stocks in the soils of Lena River
440   Delta on the basis of application of "dry combustion" and Tyurin's methods of carbon
441   determination. Biological Communications. 62(2): 67–72, 2017.

442   Tarnocai, C., Canadell, J. G., Schuur, E. A. G., Kuhry, P., Mazhitova, G., and Zimov, S. Soil
443   organic carbon pools in the northern circumpolar permafrost region, Global Biogeochem. , 23,
444   1–11, 2009

445
446   Schnitzer, M. Organic matter characterization, in: Methods of soil analysis, Part 2, chemical and
447   microbiological properties, Agronomy monograph no. 9, edited by: Page, B., Miller, R., and
448   Keeney, D., Soil Science Society of America, Madison, 581–594, 1982.

449 Simas, FNB., Schaefer, CEG.R., Melo, V.F., Albuquerque-Filho, MR., Michel, RFM., Pereira,
450 VV., Gomes, MRM., da Costa, L.M. Ornithogenic cryosols from Maritime Antarctica:
451 Phosphatization as a soil forming process, Geoderma. 138: 191-203, 2007

452 Senesi N, D'Orazio V, Ricca G. Humic acids in the first generation of eurosoils, Geoderma,
453 116, 3-4: 325-344, 2003

454 Senesi N. Molecular and quantitative aspects of the chemistry of fulvic acids and its interactions
455 with mineral ions and organic chemicals. Analytica Chimica Acta. 232: 51-75, 1990

456 Schuur, E.A.G., McGuire, A.D., Grosse, G., Harden, J.W., Hayes, D.J., Hugelius, G., Koven,
457 C.D. and Kuhry, P. Climate change and the permafrost carbon feedback. Nature, 520, 171–179,
458 2015

459 Smellie J.L., Pankhurst R.J., Thomson M.R.A., Davies R.E.S. The Geology of the South
460 Shetland Islands: VI. Stratigraphy, Geochemistry and Evolution, British Antarctic Survey
461 Scientific Reports 50: 87, 85, 1984

462 Vasilevich, R., Lodygin, E., Beznosikov, V., Abakumov, E. Molecular composition of raw peat
463 and humic substances from permafrost peat soils of European Northeast Russia as climate
464 change markers. Science of the Total Environment, 615, 1229-1238, 2018

465 Wen,J., Xie,Z., Han J., Lluberas A.. Climate, mass balance and glacial changes on small dome of
466 Collins Ice Cap, King George Island, Antarctica, Antarct. Res., 5, 52–61, 1994

467 WRB. World Reference Base for Soil Resources. International Soil Classification System for
468 Naming Soils and Creating Legends for Soil Maps; World Soil Resources Reports No. 106;
469 FAO: Rome, Italy, 2014.

470 Zaccone, C., Miano, T. M., and Shotyk, W. Qualitative comparison between raw peat and related
471 humic acids in an ombrotrophic bog profile: Org. Geochem., 38: 151–160, 2007

472 Zech, W., Senesi, N., Guggenberger, G., Kaiser, K., Lehmann, J., Miano, T. M., Miltner, A., and
473 Schroth, G. Factors controlling humification and mineralization of soil organic matter in the
474 tropics: Geoderma, 79, 117–161, 1997.

475 Zubrzycki, S., Kutzbach, L. and Pfeiffer, E.-M. Permafrost affected soils and their carbon pools
476 with a focus on the Russian Arctic. Solid Earth, 5, 595–609. 2014

477

478

479

480

481

482   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

483

484

485

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

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

487

488

489

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

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

491

492

493

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

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

495

496

497

498   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

499

500

501

502

503

504

505

506   Fig. 1.

507

508   1   2   3
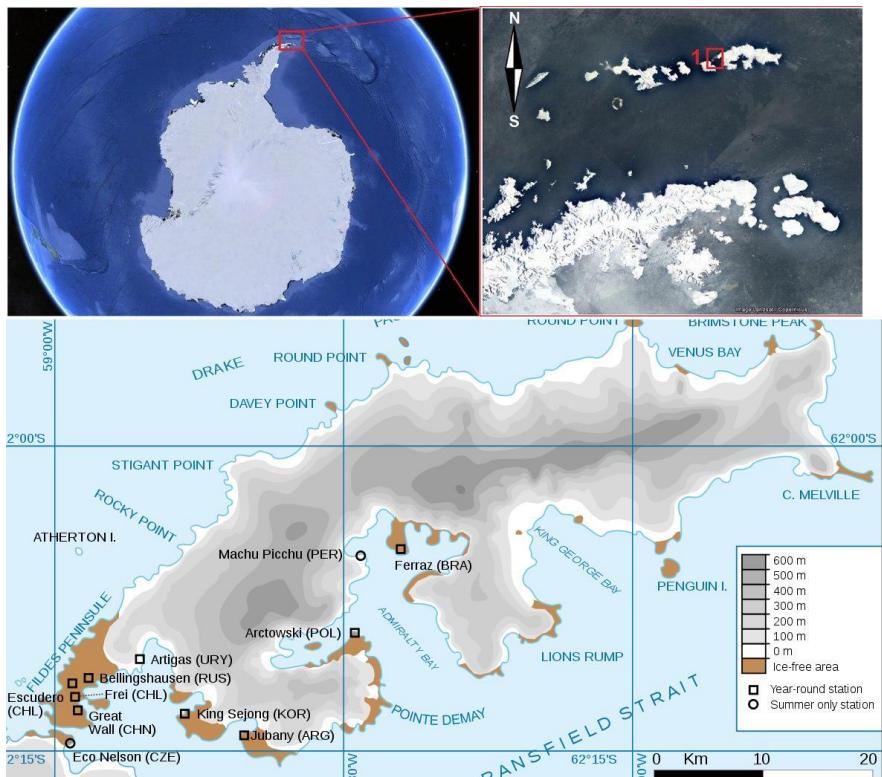
509   Fig. 2

510
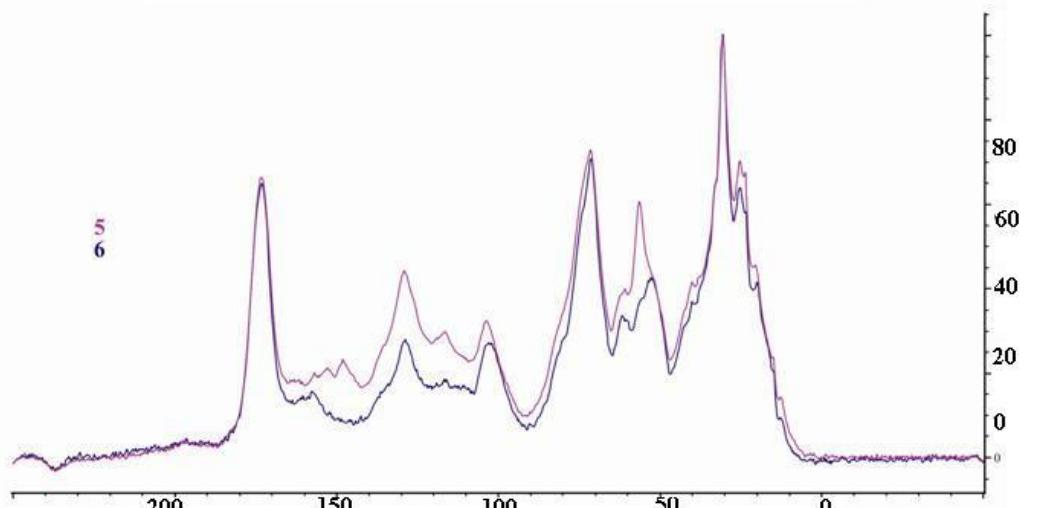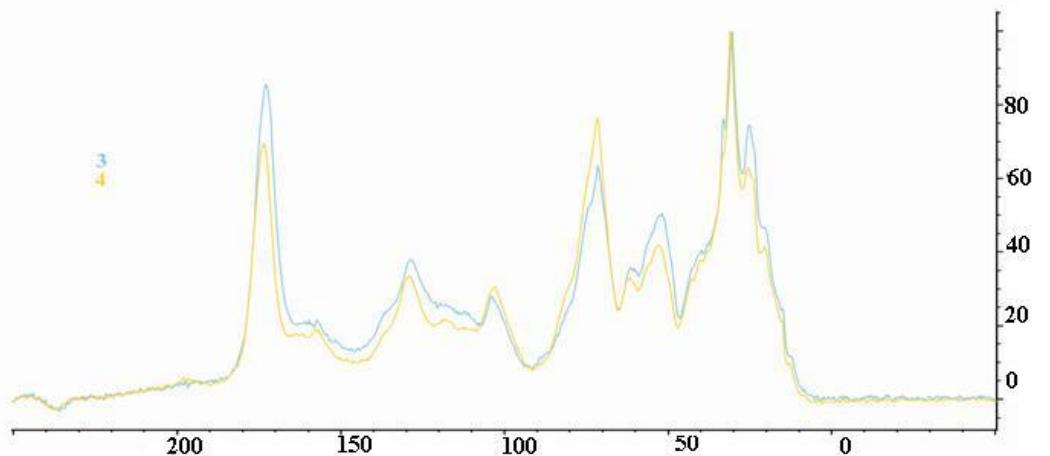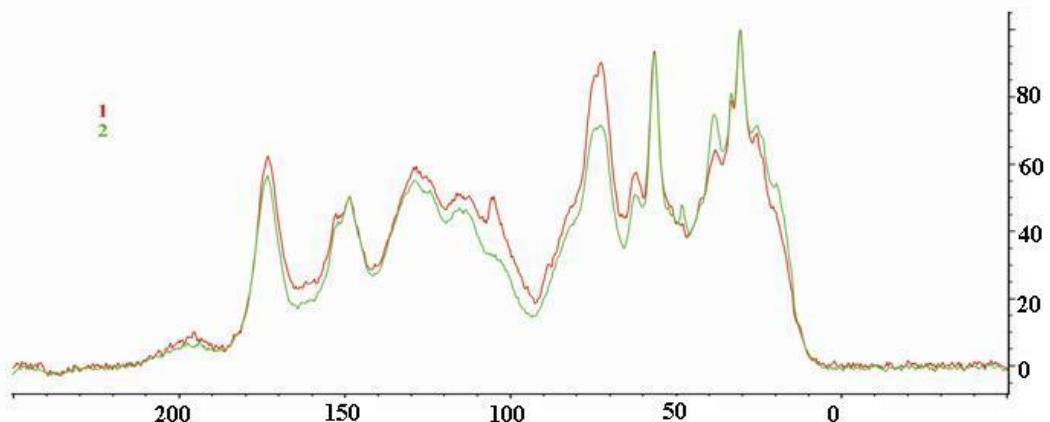
511

512

513   Fig. 3

514
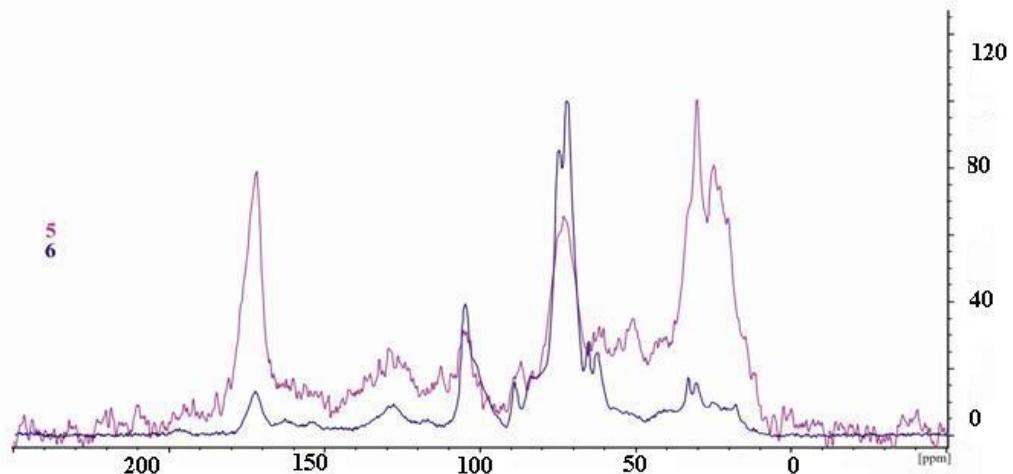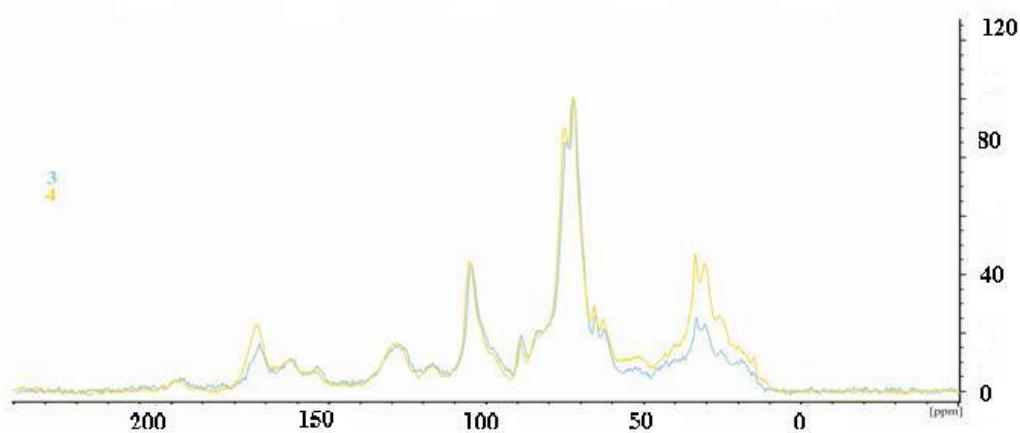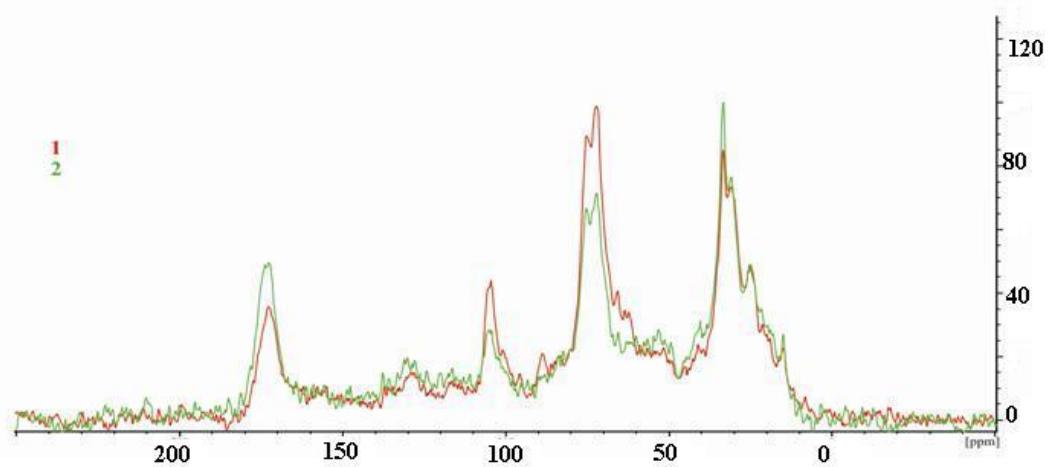
515
516
517   Fig. 4
518

519
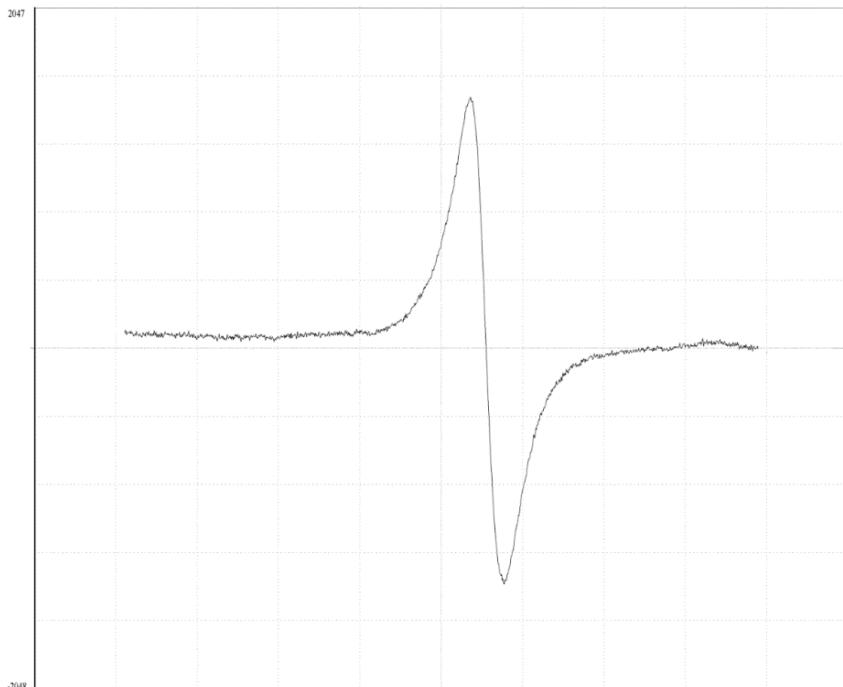
520   Fig. 5.

521

522

523   Fig. 1. Location of the Fildes peninsula

524   Fig.2. Soil morphology

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

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

527   Figure 5. Typical ESR spectrum of humic substances investigated

528   Table. 1. Basic characteristics of soils

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

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

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

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

533