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# Stability and biodegradability of humic substances from Arctic soils of Western Siberia: insights from <sup>13</sup>C-NMR spectroscopy and elemental analysis

# E. Ejarque<sup>1,2,3</sup> and E. Abakumov<sup>3</sup>

<sup>1</sup>WasserCluster Lunz – Biologische Station GmbH, Lunz am See, Austria
 <sup>2</sup>Department of Limnology and Oceanography, University of Vienna, Vienna, Austria
 <sup>3</sup>Department of Applied Ecology, Saint Petersburg State University, Saint Petersburg, Russia
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 Correspondence to: E. Ejarque (elisabet.ejarque@wcl.ac.at)
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# Abstract

Arctic soils contain large amounts of organic matter which, globally, exceed the amount of carbon stored in vegetation biomass and in the atmosphere. Recent studies emphasize the potential sensitivity for this soil organic matter (SOM) to be mineralised when

- <sup>5</sup> faced with increasing ambient temperatures. In order to better refine the predictions about the response of SOM to climate warming, there is a need to increase the spatial coverage of empirical data on SOM quantity and quality in the Arctic area. This study provides, for the first time, a characterisation of SOM from the Gydan Peninsula in the Yamal Region, Western Siberia, Russia. On the one hand, soil humic acids
- and their humification state were characterised by measuring the elemental composition and diversity of functional groups using solid-state <sup>13</sup>C-NMR spectroscopy. Also, the total mineralisable carbon was measured. Our results show that there is a uniformity of SOM characteristics throughout the studied region, as well as within soil profiles. Such in-depth homogeneity, together with a predominance of aliphatic carbon
- structures, suggests the accumulation in soil of raw and slightly decomposed organic matter. Moreover, results on total mineralisable carbon suggest a high lability of these compounds. The mineralisation rate was found to be independent of SOM quality, and to be mainly explained solely by the total carbon content. Overall, our results provide further evidence on the fundamental role that the soils of Western Siberia may have
- on regulating the global carbon balance when faced with increasing ambient temperatures.

### 1 Introduction

Polar soils play a key role in the global carbon balance, as they provide maximum stocks of soil organic matter (SOM) within the whole pedosphere (McGuire et al., 2009). Large amounts of organic matter have accumulated during the guaternary pe-

25 2009). Large amounts of organic matter have accumulated during the quaternary period (Schirrmeister et al., 2011; Zubrzycki et al., 2013) due to continuous low temper-



atures and over moisture, which have kept decomposition rates low (Davidson and Janssens, 2006). However, current trends of climate warming and permafrost thawing in the arctic region (Romanovsky et al., 2010) may favour an acceleration of the degradation of SOM, and hence, to an increase in the release of greenhouse gases
like carbon dioxide and methane (Christensen et al., 1999; Gruber et al., 2004; Zimov et al., 2006). Other consequences of climate change on SOM may include an increase of the thickness of the soil active layer – which may affect SOM transformation (Zubrzycki et al., 2014) –, as well as changes in land cover (Desyatkin and Desyatkin, 2006), length of the growing season, and soil evolution (Ivanov et al., 2015) – which may affect the availability and quality of SOM precursor materials.

In order to better predict how Arctic soils may respond to increasing climatic temperatures, recent research has focused in the total quantification of standing stocks of organic matter in soils from polar regions (Hugelius et al., 2012, 2014; Tarnocai et al., 2009). Such quantifications emphasize the large magnitude of stored carbon in arctic soils – estimated around 1024 Pg (Tarnocai et al., 2009) –, which largely exceeds the total carbon globally contained in vegetation biomass (450–650 Pg) or in the atmosphere (589 Pg), according to the latest estimations (IPCC, 2013).

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Parallel to quantification efforts, the characterisation of SOM lability and composition is fundamental in order to better understand (i) the humification degree that it has un-

- <sup>20</sup> dergone during its time residence in soils, and (ii) its further potential biodegradability if faced with increasing temperatures. SOM characteristics like the elemental composition and the carbon chemical structure (via solid-state <sup>13</sup>C-NMR spectorscopy) of humic acids have been commonly used to infer humification status in soils (Kogel-Knabner, 1997; Zech et al., 1997), and more specifically in Arctic soils (Abakumov and
- Fattakhova, 2015; Abakumov et al., 2014; Calace et al., 1995, 2005; Chukov et al., 2015; Dai et al., 2001; Ward and Cory, 2015). Further, the determination of mineralis-able carbon has been used to provide direct evidence of the sensitivity of SOM to be degraded and released to the atmosphere as CO<sub>2</sub> if faced to increasing temperatures.



However, despite the recent increase in the research efforts in this direction, quantitative estimates of soil carbon stocks and mineralisation potential are still subject to large uncertainties, as extense polar land areas still remain uncharacterised (Horwath Burnham and Sletten, 2010; Hugelius et al., 2014). Moreover, there is a paucity of regional studies thoroughly assessing the quality of SOM across the Arctic and the Antarctic. Therefore, in order to better constrain soil carbon stocks and their potential sensitivity and contribution to climate warming, there is a need for more detailed landscape-scale assessments of SOM in understudied areas.

This study presents, for the first time, a detailed characterization of the bulk organic matter and humic acids from soils of the Yamal region, located in northern Siberia, Russia. This region, as is more than 60% of the Russian land surface, is underlayed by permafrost (Kotlyakov and Khromova, 2002) and is almost entirely covered by tundra grasslands. Within the Arctic, the Yamal region has been especially sensitive to climate warming, as it experienced an increase in the average air temperature of 1– 2°C over the past 30 years (Forbes et al., 2009). As mentioned, such increase in the

<sup>15</sup> 2 C over the past 30 years (Forbes et al., 2009). As mentioned, such increase in the ambient temperatures may enhance SOM humification rates and carbon emissions to the atmosphere, potentially unbalancing the current carbon balance (McGuire et al., 2009).

The Yamal Region presents a diversity of soil types due to regionally-varying conditions of the cryopedogenesis process, including depth of the active layer, texture and structure of parent materials and bedrocks, and historic climatic conditions. As is most common for the whole Siberia, the Yamal pensinsula is covered by Cryosols (according to the World Reference Base for Soil Resources (WRB) system, FAO, 2014), or Cryozems (according to the Russian Soil Taxonomy, Shishov et al., 2004), which are part

of the Gelisol unit. More specifically, the main soil types can be classified as Histosols, Histic Cryosols and Histic Gleysols. They are all permafrost-affected soils containing morphological features of cryoturbation, but each exhibit slight differences in their organic matter content. Histosols contains the maximum stocks of organic matter. Typical Gleysols contain lower percentages of organic matter, but in some cases it is more de-



composed. In Cryosols there is often a cryogenic exchange of organic matter between different horizons which enhances additional long-term accumulation of carbon (Kaiser et al., 2007).

- The general aim of this work is to characterize the humification process in soils of the Yamal region, as well as the mineralization potential of SOM. This is addressed by quantifying and characterizing SOM from different sites across the Yamal Region, in order to eventually unveil landscape-geographical trends of humification. The main methodologies used are <sup>13</sup>C-NMR spectroscopy, elemental composition and total mineralisable carbon analysis.
- <sup>10</sup> More specifically, the objectives are:
  - To quantify total soil organic carbon content, together with the total mineralisable fraction.
  - To characterize the elemental composition of humic acids and observe trends in their ratios.
- To provide detailed structural characteristics of humic acids using <sup>13</sup>C-NMR spectroscopy.
  - To infer the humification degree of soil humic acids based on <sup>13</sup>C-NMR spectroscopy and elemental composition.

# 2 Methods

### 20 2.1 Study sites

The sites where were distributed across the Gydan Peninsula and the Belyi Island, lying within the Yamal-Nenets autonomous region of the Russian Federation (northwestern Siberian coast). The Gydan Peninsula extends into the Kara Sea, between the embayments of Ob and Yenisey rivers; whereas Belyi Island is located at the top northern part



of the Yamal Peninsula (Fig. 1). The Gydan Peninsula is a predominantly flat territory entirely covered by permafrost and tundra/forest-tundra vegetation. Soils have developed on Pleistocene sands underlain by marine clays and alluvial sediments during the late Quaternary (Walker et al., 2009), largely influenced by cryogenesis. The average annual air temperature is -10°C, where the minimal monthly average is registered in January (-25°C) and the maximal in August (+8°C). On average, the air temperature stays at positive values during 70 days per year. The average annual precipitation in the region is 325 mm yr<sup>-1</sup> and the average evaporation is between 50 and 100 mm yr<sup>-1</sup> (Buchkina et al., 1998). Within the Arctic, the Yamal region is especially sensitive to climate warming, as it has experienced an increase of 1–2°C of the average air temperatures over the past 30 years (Forbes et al., 2009), and it is still predicted to increase at a rate of 0.01°C yr<sup>-1</sup> during the next decades (Khrustalev et al., 2003).

In 2012, for the first time the Government of the Yamal-Nenets region in conjunction with the Arctic and Antarctic Research Institute of RosHydromet, performed a comprehensive expedition for the examination of the Yamal Peninsula (KAEMB Arctic Yamal 2012). The second expedition was organized in September–October 2013 (KAEMB Arctic Yamal 2013) and in this occasion stops and field camps were performed in the Gydan Peninsula. In this study we present the results of the soils sampled during

the second expedition.

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# 20 2.2 Soil morphology and general characteristics of the sampling sites

Typical Cryosol was investigated on the Yavay peninsula  $(72^{\circ}21.642' \text{ N}, 75^{\circ}05.144' \text{ E})$  (Fig. 2a). It consists of an upper histic horizon of raw humus, some cryogenic cracks and a fairly homogenous mineral soil profile. The typical landscape of the Yavay peninsula is shown on Fig. 2f. The deepness of the permafrost is about 70–80 cm. On the border of the permafrost and mineral soil the morphological features of gleyification are evident. Here the soil was sampled at 0–5 cm.

The soils of the Mamont cape (Gyda Yuribey Gulf, 71°18.812′ N, 77°33.245′ E) consisted on Gleyic Cryosols with two gleyic horizons: an upper and a contact one (Fig. 2c).



Landscapes here (Fig. 2d) were less differentiated in relation to the elevation and were more overmoisted than the Yavay peninsula. The depth of visible permafrost border was about 90 cm. The soil was sampled at 0-10 cm.

The landscape of the Enisey Gulf (72°22.451′ N, 78°38.586′ E) was predominantly flat, without any relevant relief differentiation (Fig. 2f). Therefore, soils were highly overmoisted and Histic Gleysols were dominant (Fig. 2e). The depth of permafrost in both plots of the Enisey Gulf was about 40–45 cm. The climate of the Enisey Gulf is considered as the most severe in comparison with the other investigated plots. The soil was sampled at two depths: 0–5 and 5–9 cm.

- Soils of the Beliy Island (73°18.421' N, 71°23.555' E) were classified as Entic Podozol (Fig. 2g). The upper part of the horizon presented weak features of podzolisation, and it was underlayed by material affected by cryoturbation in the middle profile. The lower part was a Gleyic horizon (60–170 cm) of intensive blue color, underlayed by permafrost at 200 cm depth. The soil was sampled at 0–7 cm.
- In Haranasale cape (71°25.402′ N, 73°03.758′ E) relief forms were very different and presented hills and lowlands with relative elevation changes of about 100 m. Soils here consisted mainly of Histic Gleysols (Fig. 2h). The upper border of the permafrost layer was about 60–70 cm. Here two soil profiles were sampled: one at 0–5 and 5–11 cm depth (hereafter referred to as Haranasal-1) and another at 0–5, 5–10 and 20–30 cm
   depth (hereafter referred to as Haranasale-2).
  - 2.3 Analytical methods

# 2.3.1 Bulk SOM characterisation

All chemical soil parameters were studied on a fine earth of soil after being passed through a 1 mm sieve. Total soil organic carbon content was determined by dichromate oxidation-titration method (Walkely, 1947). Total mineralisable carbon was determined according to Anderson (1982) aliquots (5 g) of fresh soil, adjusted to a moisture content of 60 % of the water-holding capacity were incubated at 25 °C in sealed plastic bottles



with  $1 \text{ mol L}^{-1}$  NaOH (Anderson, 1982) in duplicate. The amount of CO<sub>2</sub> trapped in the alkali solution was measured by titration after 7 days. Soil pH was determined according to standard procedure using soil/water or salt ratio of 1:2.5.

The optical index E4/E6 was measured on SOM humic substances solution as the absorbance measured at 465 nm divided by that at 690 nm (Chen et al., 1977). SOM humic substances solution was obtained by diluting soil with a 0.1 M NaOH solution at a soil/solution mass ratio of 1 : 10 followed by gravity filtration. Further, E4/E6 data were used to estimate SOM lability using Kumada's classification system (Kumada, 1987). For that, E4/E6 values were transformed into  $\Delta \log K$  using the empirical relationship  $\Delta \log K = 0.135 \times E4/E6$  (Ikeya and Watanabe, 2003).

### 2.3.2 Extraction of humic acids

Humic acids were extracted from each soil sample according to the following procedure (Schnitzer, 1982). Briefly, humic acids (HAs) were extracted with 0.1 M NaOH (soil/solution mass ratio 1 : 10) under nitrogen gas. After 24 h of shaking, the alkaline <sup>15</sup> supernatant was separated from the soil residue by centrifugation at  $1516 \times g$  for 20 min and acidified to pH 1 with 6 M HCl to induce the precipitation of HAs. The supernatant, which contained fulvic acids (FA), was separated from the precipitate (containing HAs) by centrifugation at  $1516 \times g$  for 15 min. The HAs were then redissolved in 0.1 M NaOH and shaken for 4 h under N<sub>2</sub> before the suspended solids were removed by centrifuga-<sup>20</sup> tion. The HA solution was acidified again with 6 M HCl to pH 1, and the HAs were sep-

tion. The HA solution was acidified again with 6 M HCl to pH 1, and the HAs were separated by centrifugation. The HAs were demineralized by shaking overnight in 0.1 M HCl/0.3 M HF (solid/solution ratio 1 : 1) and then repeatedly washed with deionized water until pH3 was reached; they were then freeze-dried.



### 2.3.3 Characterisation of humic acids

HAs were characterized for their elemental composition (C, N, H, and S) using a Euro EA3028-HT analyzer. Data were corrected for water and ash content. Oxygen content was calculated by difference.

- <sup>13</sup>C-NMR spectra of humic acids were measured with a Bruker Avance 500 NMR spectrometer (Karlsruhe, Germany, 2003) in a 4 mm ZrO2 rotor. The magic angle spinning speed was 20 kHz in all cases, and the nutation frequency of <sup>13</sup>C fields for crosspolarization was u1/2p 1/4 62.5 kHz. Repetition delay and number of scans were 3 s. Groups of structural compounds were identified by the chemical shifts values: 190–
- 170 ppm carboxyl group and amidic carbonyl, 170–150 ppm aromatic C of fenols and fenol esters, 150–135 ppm – alkylaromatic, 135–108 ppm – protonize aromatic carbon, bridgehead C, 108–100 ppm – cellulose anomeric carbon and hemiacetal carbon, 100–70 ppm – resonance region of C–H bonds, secondary alcohols, and other carbon atoms bound to oxygen, 70–50 ppm – methyl group resonance region of aliphatic and
- <sup>15</sup> aromatic ethyl ethers, amino acid carbons, and methyl esters of carboxylic groups, 50– 32 ppm – resonance region of quarternal carbon and CH carbons, 32–27 ppm – resonance region of CH<sub>2</sub> alkyl structures in transconformation, 27–10 ppm – resonance region of alkyl methyls and CH<sub>2</sub> units. Degree of aromaticity was calculated as a sum of signals intensity in regions of 100–170 + 183–190 ppm, while the sum of aliphatic <sup>20</sup> compounds were calculated in intervals 0–100 + 164–183 ppm.

2.4 Statistical analyses

All statistical analyses were performed within the R environment (R Development Core Team, 2015). Simple relationships between variables were explored using univariate linear model correlations based on Pearson's R. For the total mineralisable carbon, a multivariate model analysis was performed to detect what SOM quantitative and qual-

itative variables were significantly explaining SOM mineralisation. This was achieved using a best subset selection procedure, that is, a least squares regression model was



fit for every possible combination of explanatory variables. The best model was considered to be that with a lowest Mallow's Cp (James et al., 2013). Computations were performed using the leaps package for R (Lumley, 2009).

- In order to better understand the regional distribution of carbon structures a multivariate approach was used. A non-metric multidimensional scaling (NMDS) analysis using Bray–Curtis dissimilarities was performed on the structural carbon compounds defined from <sup>13</sup>C-NMR spectra. The quality of the ordination was improved by submitting the data to Wisconsin double standardisation. Interpretation of the NMDS ordination was enhanced by overlaying information on the elemental composition of humic acids and
- <sup>10</sup> characteristics of bulk SOM. This was achieved by performing a vector fitting analysis. Variables were centered by subtracting their mean and scaled by dividing by their standard deviation. Fittings were considered significant at p < 0.01. Computations for the multivariate analysis were performed using the vegan package for R (Oksanen et al., 2012).

### 15 3 Results and discussion

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# 3.1 Bulk soil organic matter characteristics

Across the studied region, soils contained an average of  $14.3 \pm 10.8$  % of total carbon (Table 1). Among the surface layers (0–5 cm), the highest amounts of carbon were found in Enisey Gulf (36.4 %), followed by Gyda Yurivey Gulf (27.4 %, 0–5 cm). More moderate amounts of carbon were found in Yavay Cape (13.7 %) and Haranasale-2 Cape (12.3 and 7.5 %). These amounts are similar to total carbon contents previously reported in tundra Gelic gleysols (Dziadowiec et al., 1994). By contrast, Belyi Island was the location with the lowest carbon content in surface soil (5.7 %).

In Enisey Gulf, the high amounts of carbon in the surface decreased substantially at

<sup>25</sup> subsurface layers (from 36.4 % at 0–5 cm to 18.0 % at 5–9 cm), whereas in Haranasale Cape carbon content either remained stable (7.5 % at 0–5 cm to 6.8 % at 5–11 cm,



site1) or even increased (12.3 % at 0–5 cm to 15.2 % at 5–10 cm, site 2). Such increase of carbon content in depth may indicate cryoturbation, i.e. vertical soil mixing due to freezing and thawing cycles, a common process in Cryosols (Bockheim and Tarnocai, 1998). Further deep in the same soil profile (at 20–30 cm), carbon content was almost inexistent (0.4 %).

The optical index E4/E6 decreases with the level of carbon conjugation, and hence, has been commonly used to assess the molecular complexity of bulk organic matter (Chen et al., 1977; Peacock et al., 2014; Summers et al., 1987) and to infer the degree of humification of soil HAs (Hugelius et al., 2012; Ikeya and Watanabe, 2003;

- <sup>10</sup> Kumada, 1987). The lowest value was found in the mineral layer of Haranasale-2 (Table 1). This is in accordance with the general finding that SOM in mineral horizons has a higher degree of humification than that in organic horizons (Hugelius et al., 2012). However, all samples exhibited E4/E6 values ranging between 0.15 and 0.86. Corresponding  $\Delta \log K$  values, derived from E4/E6 using the empirical relationship in Ikeya and Watanabe (2003), indicates that all soils correspond to the A-type, which is the
- highest lability class according to Kumada's (1987) classification system of HAs. Our values are also remarkably lower than those previously reported in arctic tundra soils (Dziadowiec et al., 1994).

# 3.2 Elemental composition of humic acids

- <sup>20</sup> The H/C ratio, commonly interpreted as an indicator of the aromatic degree of humic acids (Rice and McCarthy, 1991), had a very narrow range of variation (between 0.105 and 0.116, averaging 0.109  $\pm$  0.004, SD = 0.004), indicating that all samples had practically the same level of molecular complexity. The highest values of these ratios were found in Enisey Gulf, Belyi Island and at the deep mineral layer of Haranasale-2 Cape
- (20–30 cm), indicating a slightly higher predominance of aliphatic structures in the humic acids of these soils. By contrast, the lowest H/C ratios were found in Gyda Yurivey and Yavay Cape (0.105 in both sites), hence, humics substances present a slightly more aromatic nature in these sites.



The H/C ratio was found to be negatively correlated with the C/N ratio (Fig. 3), even though it explained less than 50% of its variance ( $r^2 = 0.439$ , p < 0.05, df = 8, F = 8.035). This indicates that in sites with higher aromaticity, the nitrogen content was lower. This would be indicative of humic acids that are in a slightly more advanced stage in the humification process, during which bacteria would have utilised the nitrogen contained in the organic molecules.

Along soil profiles, the C/N content was found to be slightly lower at deeper layers in Haranasale-1 and Enisey Gulf (Table 2), indicating that humic acids have a slightly increased degree of decomposition in the subsurface layers (Kuhry and Vitt, 1996). However, in Haranasale-2 there was an increase from the surface layer (0–5 cm) to

- 10 However, in Haranasale-2 there was an increase from the subace layer (0-scrift to the subsurface one (5–10 cm) from 10.46 to 11.41. This higher availability of N in the subsurface layer is consistent with the increase in total soil carbon content, and may be related to a lower degree of decomposition due to mobility of organic material from surface layer due to cryoturbation.
- The O/C ratio, indicator of the oxygenation degree of humic acids, is related with the presence of carbohydrates and carboxylic functional groups (Zaccone et al., 2007). In the three measured soil profiles an increase of the O/C ratio can be observed in depth, even though with progress of the humification it is expected to decrease. Due to the low variability in the O/C values (SD = 0.095), such differences between the soil layers could be due to analytical variability rather than to any trends in the humification
- process.

# 3.3 <sup>13</sup>C-NMR characterisation of humic acids

The <sup>13</sup>C-NMR spectra reveal the structural diversity of carbon atoms within soil organic matter (Table 3). Figures 4 and 5 show that there were only small differences in the <sup>13</sup>C-NMR spectral shapes, both accross the different surface layers, and within soil horizons. This emphasizes the little variability in the chemical structures of carbon species accross the studied Yamal region, probably due to similar climatic conditions and vegetation cover among the sites. It has been argued that climatic conditions,



mainly temperature and moisture, are the main drivers of soil humic acids composition, and that chemical properties like C/N ratio and soil pH play only a secondary role (Zech et al., 1997).

In all sites, <sup>13</sup>C-NMR data showed that there was a predominance of aliphatic car-<sup>5</sup> bons (68.85  $\pm$  3.60 %) over aromatic ones (31.15  $\pm$  3.60 %, Table 4). This may reflect the predominance of non-ligneous vegetation as the main precursor of soil humic acids, similarly to what has been previously reported for arctic and antarctic soils (Abakumov et al., 2014; Calace et al., 1995).

Despite this eminent homogeneity among sites, some patterns of C structural di-<sup>10</sup> versity could be observed. As shown by the standard deviation of all measured <sup>13</sup>C-NMR spectra (Figs. 4 and 5), the highest variability in the signal intensity was found in the resonance areas between 50–70 ppm and 32–27 ppm, both of which contain eminently aliphatic molecules. This indicates that aromatic compounds are more stable both regionally and along soil profiles, whereas aliphatic molecules are more variable.

<sup>15</sup> This may be due to the fact that this fraction is considered to be more labile and biogeochemically reactive. Among the aromatic species, the highest signal was found at 170 ppm, related to carboxyl-C.

The comparison of the surface soil samples provides an idea of the regional diversity of SOM carbon structures. <sup>13</sup>C-NMR spectra (Fig. 4) show that in Enisey Gulf and Belyi
Island the carbons in aromatic structres are less predominant than in the rest of sites. By contrast, their signal at 70 ppm was markedly higher, indicating an increase of CH units bound to oxygen. On the other hand, the Haranasale-1 site presents a distinctive signature, consisting in a high methoxyl C peak at 55 ppm. Finally, in the region between 0 to 50 ppm, indicating alkyl carbon structures, are higher in Enisey Gulf, Belyi Island and Haranasale-2 sites.

In Enisey Gulf and in the two Haranasale sites, some patterns could be observed along soil profiles. In the three sites it could be observed that the signal intensity for aromatic carbons (135–150 ppm) presented minor changes (Fig. 5). This has been found to be typical of initial stages of the humification processes (Zech et al., 1997),



and hence, may indicate a low humification degree due to the low temperatures. However, some variation could be observed in the aliphatic regions. Interestingly, every site presented different patterns. In Haranasale-1 site, the subsurface soil layer exhibited a higher signal intensity at the O-alkyl C peak at 70 ppm, whereas such signal remained

- <sup>5</sup> constant at Haranasale-2, and increased in Enisey Gulf. On the other hand, the signal at the methoxyl C peak (55 ppm) remained eminently constant in Haranasale-1 and Enisey Gulf, whereas in Haranasale 2 there was a clear decrease in depth. Finally, in the region of 0–50 ppm, the signal at the surface and subsurface layers remained stable in the three sites. However, in Haranasale-2 site, where a third depth was sampled
- <sup>10</sup> (20–30 cm), it can be seen that in this mineral layer there was an increase of the signal intensity, indicating a higher prevalence of simple carbon bonds.

# 3.4 Total mineralisable carbon

The total carbon content of soils was found to be positively correlated with the total mineralisable carbon, explaining nearly 58% of its variability ( $r^2 = 0.576$ , p value = 0.01,

- <sup>15</sup> df = 8, F = 10.86). Accordingly, the highest mineralization rates were found in Yavay Cape (2.34 mg C g soil<sup>-1</sup> day<sup>-1</sup>) and in Enisey Gulf (2.32 and 2.19 mg C g soil<sup>-1</sup> day<sup>-1</sup> at 0–5 and 5–9 cm, respectively; Table 1). Among the surface soil samples, the minimal biodegradability was found in Belyi Island (1.57 mg C g soil<sup>-1</sup> day<sup>-1</sup>). In the three sites were different depths were measured, located at Enisey Gulf and Haranasale Cape,
- the mineralization rates decreased with depth, and were minimal in the mineral deep horizon (20–30 cm) of the Hystic Gleysol in Harnasale (0.58 mg C g soil<sup>-1</sup> day<sup>-1</sup>). In order to better understand the relationship between SOM biodegradability and its chemical quality, a multivariate linear regression analysis was performed, introducing the variables related to bulk SOM properties (total carbon content, pH, E4/E6 ratio),
- as well as those related specifically with the humic acids (elemental composition and the carbon structures revealed by <sup>13</sup>C-NMR spectra). Using the best subset selection procedure, it was found that these qualitative variables did not significantly improve the



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predictability provided by the univariate linear regression with total carbon content (the inclusion of new variables to the model increased the  $C_p$ ).

These results emphasize that the biodegradability of SOM is not controlled by the characteristics of humic acids, most probably due to a high labile character in all sites.

<sup>5</sup> This is in accordance with findings that SOM biodegradability in Cryosols is mainly limited by environmental conditions (freezing and overmoisture) rather than by chemical conditions (Weintraub and Schimel, 2003).

# 3.5 Multivariate analysis of soil organic matter properties

An NMDS analysis provided further insight about the spatial distribution of the C structural diversity of humic acids in the Yamal region, and its relationship with its elemental composition and bulk SOM properties. An NMDS analysis (fit-based  $R^2 = 0.999$ , Nonmetric fit  $R^2 = 1$ , Fig. 6) performed on the <sup>13</sup>C-NMR groups, showed that a first axis of variation defined a gradient from aromatic (Haranasale-2 and Gyda Yurivey Gulf sites) to aliphatic carbon predominance (Belyi Island, Enisey Gulf and Haranasale-1 sites). An additional vector fitting analysis (variables significant at p < 0.01) onto the NMDS ordination, revealed that the secondary axis created an oxygenation gradient between C% and H% on the positive site ( $r^2 = 7473$ , p < 0.01 and  $r^2 = 0.7717$ , p < 0.01, respectively), and O% and O/C% on the negative site ( $r^2 = 0.8135$ , p < 0.01 and  $r^2 = 0.7783$ , p < 0.01, respectively). According to that, the humic acids of Yavay Cape,

<sup>20</sup> and upper layers of Enisey Gulf and Haranasale-2 are related to low levels of oxygenation, whereas those of Haranasale-1 and deep layer of Haranasale-2 appear with higher levels of oxygenation. Furthermore, the positive secondary axis grouped sites with higher pH ( $r^2 = 0.6074$ , p < 0.05) and total mineralisable carbon ( $r^2 = 0.6655$ , p < 0.05). Interestingly, the N elemental composition and C/N ratio of humic acids where not significantly correlated within the NMDS ordination. Similarly, the optical index E4/E6 and the total carbon content were found not to be related with the distribution of carbon structures defined by <sup>13</sup>C-NMR spectra.



### 4 Conclusions

This study presents, for the first time, a detailed characterization of the humic acids of soils from western Siberia. Moreover, it expands the regional coverage of recent local scale studies of SOM lability in permafrost soils in periglacial environments (Dutta et al., 2006; Weintraub and Schimel, 2003). This may contribute to better depict the regional variability of humic acids characteristics across the arctic region.

- Our results revealed little spatial variability in the characteristics of soil organic matter and humic acids across the Yamal region. This reflects a homogeneity of the climatic conditions, as well as of the precursor materials, due to a homogeneous vegetation cover across the studied region. This is in line with previous studies which have identified temperature, water regime and vegetation as the main drivers of humification (Zech et al., 1997). Also, there was little differentiation along soil profiles. The predominance of aliphatic carbon structures in depth indicates that soils remain at early stages of the humification process. This phenomenon has also been observed in other polar
- <sup>15</sup> areas due to the effects of permafrost, were the low temperatures hinder the microbial processes responsible for the humification and decomposition of the precursor organic materials.

Our results also showed that the bioavailability of soil organic matter is mainly related to the total quantity of organic carbon, but not so much to its quality (i.e. elemental composition and carbon chemical structure). This reveals that most of the stored carbon is highly labile, and therefore the limitation for bacterial utilization is not its quality but its quantity. These results further emphasize the potential sensitivity of these soils towards increasing climatic temperatures, and the rapid mineralization of organic matter that they may undergo.

<sup>25</sup> Overall, we conclude that soils of western Siberia may play a key role in the global warming. Therefore, more regionally intensive studies in these regions are required to better constrain the predictions about the consequences of global warming.



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We would like to dedicate this work to the memory of Petr Reihet and Vladimir Vanuito who died on 14 September 2013 during the expedition "KAEMB Arctic Yamal 2013".

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 Table 1. Properties of bulk soil organic matter.

Site	Soil depth (cm)	Total C (%)	E465/E650	pH (CaCl <sub>2</sub> )	Mineralisable C $(mg C g soil^{-1} day^{-1})$
Yavay	0–5	13.7	0.400	5.47	2.341
Gyda Yuribey	0–10	27.4	0.828	3.94	2.103
Enisey Gulf	0–2	36.4	0.376	3.64	2.318
Enisey Gulf	5–9	18	0.709	4.54	2.189
Haranasale-1	0–5	7.5	0.372	3.79	0.910
Haranasale-1	5–12	6.8	0.859	3.56	0.875
Beliy Island	0–10	5.7	0.409	5.07	1.572
Haranasale-2	0–5	12.3	0.355	6.26	1.945
Haranasale-2	5–10	15.2	0.512	4.75	1.553
Haranasale-2	20–30	0.4	0.149	3.01	0.583

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**Table 2.** Elemental composition and elemental ratios of the studied soils.

Site	Soil depth (cm)	N%	C%	H%	O%	C/N	O/C	H/C
Yavay	0–5	4.27	51.40	5.41	38.91	12.03	0.76	0.11
Gyda Yuribey	0–10	3.90	50.21	5.25	40.64	12.87	0.81	0.10
Enisey Gulf	0–2	5.00	52.25	6.08	36.66	10.44	0.70	0.12
Enisey Gulf	5–9	5.26	50.51	5.56	38.66	9.60	0.77	0.11
Haranasale-1	0–5	4.39	50.08	5.33	40.20	11.41	0.80	0.11
Haranasale-1	5–12	4.40	49.70	5.32	40.58	11.30	0.82	0.11
Beliy Island	0–10	4.44	48.74	5.52	41.30	10.97	0.85	0.11
Haranasale-2	0–5	4.93	51.54	5.56	37.97	10.46	0.74	0.11
Haranasale-2	5–10	4.33	49.41	5.32	40.94	11.41	0.83	0.11
Haranasale-2	20–30	4.57	43.71	4.96	46.75	9.56	1.07	0.11

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**Table 3.** <sup>13</sup>C-NMR section integrals (percent of total carbon) and key structures of soil humic substances.

Site	$\delta$ ( <sup>13</sup> C) ppm Key structures	10–27 f <sub>al</sub> <sup>Met</sup>	27-32 $f_{\rm al}^{\rm trans}$	32–50 f <sup>Q</sup> <sub>al</sub>	50–70 f <sub>al</sub> <sup>OM</sup>	70–100 f <sub>al</sub> <sup>O2</sup>	100–108 f <sub>al</sub> <sup>O1</sup>	108–135 f <sub>a</sub> <sup>H</sup>	135–150 f <sup>S</sup> a	150–170 f <sub>a</sub> <sup>P</sup>	170–190 f <sub>a</sub> <sup>CO</sup> 2
Yavay	0–5 cm	12.55	4.59	11.97	17.92	14.76	3.69	15.80	4.37	8.77	5.59
Gyda Yuribey	0–10 cm	14.99	4.60	11.29	17.14	12.70	3.41	15.52	5.11	9.13	6.11
Enisey Gulf	0–2 cm	16.72	5.68	12.57	20.35	14.12	2.97	11.50	3.27	7.53	5.29
Enisey Gulf	5–9 cm	15.24	5.13	12.52	19.29	14.09	3.13	12.70	3.64	8.78	5.48
Haranasale-1	0–5 cm	16.08	6.09	12.26	15.77	12.45	3.30	15.05	4.52	9.10	5.37
Haranasale-1	5–12 cm	16.43	5.40	12.17	19.00	13.67	3.42	12.99	3.73	8.78	4.42
Beliy Island	0–10 cm	17.76	6.62	12.12	19.91	13.55	2.98	11.46	3.25	7.75	4.60
Haranasale-2	0–5 cm	12.86	3.82	10.93	19.77	12.10	3.90	16.37	6.00	7.59	6.67
Haranasale-2	5–10 cm	13.54	4.05	11.04	18.34	12.06	3.58	15.86	6.68	8.39	6.47
Haranasale-2	20–30 cm	15.17	4.97	11.58	16.46	11.24	3.12	15.78	5.38	8.18	8.12

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**Table 4.** Fraction of aromatic and aliphatic carbons, and maximal signal intensity at the three ppm of maximal variability within the data set.

Site	Depth (cm)	Aromatic	Aliphatic	27 ppm	55 ppm	70 ppm
Yavay	0–5	33.22	66.78	0.10	0.07	0.10
Gyda Yuribey	0–10	33.90	66.10	0.12	0.09	0.08
Enisey Gulf	0–2	25.59	74.41	0.13	0.06	0.12
Enisey Gulf	5–9	28.55	71.45	0.12	0.08	0.10
Haranasale-1	0–5	32.44	67.56	0.14	0.07	0.08
Haranasale-1	5–12	29.11	70.89	0.13	0.08	0.10
Beliy Island	0–10	25.71	74.29	0.14	0.07	0.11
Haranasale-2	0–5	34.48	65.52	0.09	0.14	0.09
Haranasale-2	5–10	35.11	64.89	0.10	0.12	0.08
Haranasale-2	20–30	33.43	66.57	0.13	0.09	0.08

![](_page_26_Figure_0.jpeg)

**Figure 1.** Regional distribution of study sites in the Gydan peninsula. 1 – Haranasale cape, 2 – Yavay cape, 3 – Mamont cape (Gyda Yuribey), 4 – Enisey gulf, 5 – Belyi Island.

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Figure 2. Examples of soils and environments analized in this study. Yavay 1 (a and b), Gyda Yuribey (c and d), Enisey Gulf, (e and f), Beliy Island (g), Haranasale (h).

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Figure 3. H/C vs. C/N diagram.

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**Figure 4.** <sup>13</sup>C-NMR spectra of surface soil samples. For reference, the gray spectra corresponds to the standard deviation of all <sup>13</sup>C-NMR spectra.

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**Figure 6.** Non-metric multidimensional scaling analysis of humic acids based on their carbon structural groups, derived from <sup>13</sup>C-NMR spectral integration. Dark-grey groups indicate aliphatic carbons, whereas light-grey groups correspond to aromatic carbons.

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