



Stability and biodegradability of organic matter from Arctic soils of Western Siberia: insights from ^{13}C -NMR spectroscopy and elemental analysis

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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 emphasise the potential sensitivity for this soil organic matter (SOM) to be mineralised when 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 ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. Also, the total mineralisable carbon was measured. Our results indicate that there is a predominance of aliphatic carbon structures, with a minimal variation of their functional-group composition both regionally and within soil depth. This vertical homogeneity and low level of aromaticity reflects the accumulation in soil of lowly decomposed organic matter due to cold temperatures. Mineralisation rates were 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 sensitivity that the soils of Western Siberia may have to increasing ambient temperatures and highlight the important role that this region can play in the global carbon balance under the effects of climate warming.

1 Introduction

Soils play a key role in the Earth System as they control the hydrological, erosional, biological and geochemical cycles. Moreover, they provide services, goods and resources to humankind (Berendse et al., 2015; Brevik et al., 2015; Decock et al., 2015; Keesstra et al., 2012; Smith et al., 2015). More specifically, soils are now being seen as a key component of the carbon cycle (Bruun et al., 2015; Debasish-Sasha et al., 2014; Muñoz-Rojas et al., 2015; Novara et al., 2015; Parras-Alcantara et al., 2015; Peng et al., 2015; Wasak and Drewnik, 2015; Yu et al., 2014). This is especially the case for Arctic soils, as they contain maximum stocks of soil organic matter (SOM) within the whole pedosphere (Fritz et al., 2015; McGuire et al., 2009; Oliva et al., 2014; Ping et al., 2015; Zubrzycki et al., 2014). Low temperature and high moisture conditions have favoured the accumulation of large amounts of organic matter in permafrost soils over thousands of years (Schirrmeister et al., 2011; Zubrzycki et al., 2013). However, current trends of climate warming and permafrost thawing are exposing this pool of organic matter to microbial degradation (Schuur et al., 2015), as well as to fires and smouldering (Rein, 2013; Tsi bart et al., 2014; Zacccone et al., 2014), for the first time in millennia. These processes, involving SOM mineralisation and combustion, represent an unprecedented source of carbon dioxide and methane to the atmosphere (Christensen et al., 1999; Gruber et al., 2004; Zimov et al., 2006), which might further accelerate climate change effects (Schuur et al., 2008). Because of that, Arctic SOM represents a vulnerable carbon pool, susceptible to be

remobilised under increasing temperatures. This is especially relevant, considering that the Arctic is the region on Earth that experienced the highest temperature increase in recent decades (4 °C increase from 1968 to 1996, NOAA, 2015), and it is also predicted to have the strongest warming in the coming years (between 2 and 9 °C by the year 2100, IPCC, 2007).

In order to better understand the implication of permafrost SOM to greenhouse gas emissions, an accurate knowledge of its spatial distribution, both in terms of quantity and quality (i.e. biodegradability, chemical composition and humification degree) is needed (Fritz et al., 2015). The current state of knowledge estimates soil organic carbon (SOC) stocks of 1307 Pg (uncertainty range between 1140 and 1476 Pg) throughout the northern circumpolar region (Hugelius et al., 2014). These amounts surpass previous estimates (Tarnocai et al., 2009) and largely exceed the total carbon contained in the world vegetation biomass (460–650 Pg) or in the atmosphere (589 Pg, IPCC, 2013). However, these SOC stock estimates are still poorly constrained (Hugelius et al., 2014). One main source of uncertainty is the fact that these estimates have been calculated from observations which are highly spatially clustered (Hugelius et al., 2013), while extensive land areas still remain uncharacterised due to logistic difficulties to reach these sites (Horwath Burnham and Sletten, 2010; Zubrzycki et al., 2013).

Uncertainties become even more important when SOM quality is concerned (Mishra et al., 2013). The chemical composition of SOM determines its decomposability and, therefore, it determines the rate at which carbon may be transferred from soils to the atmosphere under warmer conditions. Biodegradability of SOM has been related to the humification degree, as more advanced stages in the humification process imply a depletion of the labile molecules, as well as an increase in the bulk aromaticity, which provides a higher stability of the SOM. A number of proxies have been used to trace humification. Namely, H / C from humic acids has been used as an index of molecular complexity, as higher degree of conjugation implies a lower hydrogenation of the carbon chains (Andersson et al., 2012) and it has been found to decrease with humification (Zacccone et al., 2007). The optical index E4 / E6, being proportional to the average molecular weight of humic compounds (Chen et al., 1977), has also been used to trace humification (Dziadowiec et al., 1994; Hugelius et al., 2012; Šīre and Klavinš, 2010), during which an increase in the average molecular weight occurs due to condensation and polymerisation processes (McDonald et al., 2004). Similarly, C / N has been used as a measure of decomposition degree in peat soils (Kuhry and Vitt, 1996) and, moreover, has been found to be directly related to SOM lability, as it determines the stoichiometric availability of nitrogen to soil microorganisms (Andersson et al., 2012; Zacccone et al., 2007). Further, ¹³C-nuclear magnetic resonance (NMR) spectroscopy provides information on the diversity in carbon functional structures and has also been used

to track changes in SOM during decomposition and humification (Kogel-Knabner, 1997; Zech et al., 1997) in Arctic soils (Abakumov and Fattakhova, 2015; Calace et al., 1995, 2005; Chukov et al., 2015; Dai et al., 2001; Ward and Cory, 2015). More specifically, high phenolic (150 ppm), carboxyl-C (175 ppm) and alkyl-C (30 ppm) groups, together with low O-alkyl carbons, have been related to advanced stages of humification (Calace et al., 2005; Dai et al., 2001; Zech et al., 1997).

So far, studies of SOM quality from Arctic soils have revealed a generalised lowly-decomposed character of the organic molecules (Dziadowiec et al., 1994), which preserve much of the chemical character of their precursor material due to low progress of humification under cold conditions (Davidson and Janssens, 2006). Also, recent studies provide evidence of a high and long-term mineralisation potential of Arctic SOM under increased temperatures (Elberling et al., 2013; Schädel et al., 2014; Schuur et al., 2015). Based on sites from Alaska and Eastern Siberia, potential carbon losses have been geographically extended for the whole high-latitude permafrost-affected soils, predicting losses between 20 and 90 % of total soil organic carbon under laboratory conditions within 50 years (Schädel et al., 2014). At the same time, this study emphasised the importance of the spatial variability of SOM quality in extrapolating mineralisation rates, which underlines the need to extend the spatial coverage of empirical observations of SOM quality and biodegradability to currently non-explored areas.

One of these regions that remain under-characterised is the Yamal region, located in Western Siberia, Russia. Previous research in this area highlighted that this region is experiencing a more rapid increase in ambient temperatures than other Arctic areas, challenging the socio-ecological systems (Forbes et al., 2009). This study presents, for the first time, a detailed characterisation of the bulk organic matter and humic acids from soils collected in different sites across the Gydan Peninsula. Our aim was to investigate the potential vulnerability of soils from this region in the face of increasing temperatures, and to contextualise it with current estimates of SOM distribution. This was addressed by (a) quantifying SOC content, (b) characterising SOM quality by means of elemental analysis, solid-state ¹³C-NMR spectroscopy and optical measurements, and (c) by analysing the potential biodegradability of SOM.

2 Study region

Samplings were performed in the Gydan Peninsula and 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 terri-



Figure 1. Regional distribution of the study sites in the Gydan peninsula: 1 – Haranasale Cape, 2 – Yavay Cape, 3 – Gyda Yuribey Gulf, 4 – Enisey Gulf, 5 – Belyi Island.

tory entirely covered by permafrost and tundra vegetation. Main vegetation types include grasses, mosses and lichens, while small lignified bushes appear sparsely distributed. This region, as is more than 60% of the Russian land surface, is underlain by permafrost (Kotlyakov and Khromova, 2002). Soils have developed on Pleistocene sands underlain by marine clays and alluvial sediments deposited during the late Quaternary (Walker et al., 2009), largely influenced by cryogenesis. The average annual air temperature is -10°C , with the minimum monthly average being registered in January (-25°C) and the maximum in August ($+8^{\circ}\text{C}$). On average, the air temperature remains positive during 70 days per year. The average annual precipitation in the region is 325 mm yr^{-1} and the average evaporation is between 50 and 100 mm yr^{-1} (Buchkina et al., 1998).

The Gydan Peninsula 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 of Siberia, the Gydan Peninsula is covered by Cryosols – soil taxonomy following the World Reference Base for Soil Resources (WRB) system, (FAO, 2014) here and throughout the text – which are part of the Gelisol unit. More specifically, the main soil types can be classified as Cryic 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 contain the maximum stocks of organic matter, whereas typical Gleysols contain lower percentages of organic matter, al-

though in some cases it is more decomposed. Generally these Cryosols are turbic, due to the cryogenic mixing between different horizons which enhances the accumulation of organic matter in the upper solum.

3 Soil morphology of sampling sites

Sampling sites were specifically located at the Yavay Peninsula, Gyda Yuribey Gulf, Enisey Gulf, Haranasale Cape and Belyi Island (Fig. 1).

Typical Cryosol was sampled in the Yavay Peninsula ($72^{\circ}21.642' \text{ N}$, $75^{\circ}05.144' \text{ E}$; Fig. 2a). It consisted of an upper histic horizon of raw humus, some cryogenic cracks and a fairly homogeneous mineral soil profile. The landscape of the Yavay peninsula is shown on Fig. 2b. The depth of the permafrost table was between 70–80 cm. Features of gleyification were evident on the permafrost table and along the mineral soil layer. The soil was sampled at 0–5 cm.

The soils of Gyda Yuribey Gulf ($71^{\circ}18.812' \text{ N}$, $77^{\circ}33.245' \text{ E}$) consisted on Gleyic Cryosols with two gleyic horizons: an upper and a contact one (Fig. 2c). Landscapes here (Fig. 2d) had a predominantly flat orography and soils were more overmoisted than those in the Yavay peninsula. The permafrost table was at 90 cm depth. The soil was sampled at 0–10 cm.

The landscape of the Enisey Gulf ($72^{\circ}22.451' \text{ N}$, $78^{\circ}38.586' \text{ E}$) was predominantly flat, without any relevant relief differentiation (Fig. 2f). Therefore, soils were highly overmoisted and Histic Cryosols were dominant (Fig. 2e). The depth of the permafrost table was 40–45 cm. The climate was 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 Belyi Island ($73^{\circ}18.421' \text{ N}$, $71^{\circ}23.555' \text{ E}$) were classified as Entic Podzol (Fig. 2g). The upper part of the horizon presented weak features of podzolisation, and it was underlain by material affected by cryoturbation in the middle of the profile (20–45 cm). The lower part was a Gleyic horizon (60–170 cm) of intense blue colour, underlain by the permafrost table at 200 cm depth. The soil was sampled at 0–10 cm.

In Haranasale Cape ($71^{\circ}25.402' \text{ N}$, $73^{\circ}03.758' \text{ E}$) relief forms were highly variable and presented hills and lowlands with relative elevation changes of about 100 m. Soils here consisted mainly of Histic Gleysols (Fig. 2h). The permafrost table was at 60–70 cm depth. Here two different sites were sampled: one located on a hill slope, at 0–5 and 5–11 cm depth (hereafter referred to as Haranasale-1); and another one located on a depression at 0–5, 5–10 and 20–30 cm depth (hereafter referred to as Haranasale-2).

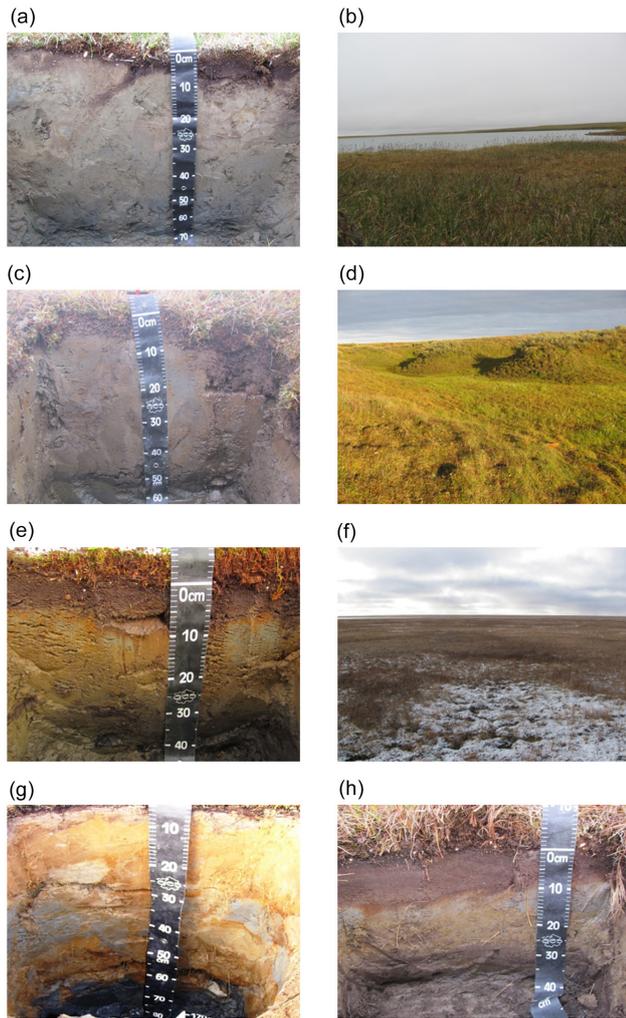


Figure 2. Examples of soils and landscapes analysed in this study. Yavay Cape (a, b), Gyda Yuribey (c, d), Enisey Gulf, (e, f), Belyi Island (g), Haranasale (h).

4 Methods

4.1 Bulk SOM characterisation

All chemical soil parameters were analysed on a fine earth of soil after being passed through a 2 mm sieve. Total SOC content was determined by dichromate oxidation–titration method (Walkely, 1947). Percent content of carbon was multiplied by bulk soil density and by the soil layer thickness to determine SOC stocks in gC m^{-2} . Bulk soil density was determined by weighing the micromonoliths of air dried soils. Total mineralisable carbon was determined according to Anderson (1982): Aliquots (5 g) of fresh soil were adjusted to a moisture content of 60% of the water-holding capacity and were incubated at 25 °C in sealed plastic bottles with 1 M NaOH (Anderson, 1982) in duplicate. The amount of CO_2 trapped in the alkaline solution was measured by titration ev-

ery 7 days during 4 (Belyi Island and Haranasale-2) and 9 (Yavay Cape, Enisey Gulf, Gyda Yurivey and Haranasale-1) weeks. Soil pH was determined according to standard procedure using soil : salt (CaCl_2 0.1 N) ratio of 1 : 2.5.

SOM humic substances solution was obtained by diluting soil with 0.1 M NaOH at a soil : solution mass ratio of 1 : 10 followed by gravity filtration. The optical index E4 / E6 was measured on SOM humic substances solution as the absorbance measured at 465 nm divided by that at 665 nm (Chen et al., 1977).

4.2 Extraction of humic acids

Humic acids were extracted from each SOM humic substance solution according to the following procedure (Schnitzer, 1982). The humic acids were extracted with 0.1 M NaOH (soil : solution mass ratio 1 : 10) under nitrogen gas. After 24 h of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at $1516 \times g$ for 20 min and acidified to $\text{pH} = 1$ with 6 M HCl to induce the precipitation of the humic acids. The supernatant, which contained fulvic acids, was separated from the precipitate by centrifugation at $1516 \times g$ for 15 min. The humic acids were then redissolved in 0.1 M NaOH and shaken for 4 h under N_2 before the suspended solids were removed by centrifugation. The solution was acidified again with 6 M HCl to $\text{pH} = 1$, and the humic acids were separated by centrifugation and demineralised by shaking overnight in 0.1 M HCl / 0.3 M HF (solid/solution ratio 1 : 1). Next, they were repeatedly washed with deionised water until $\text{pH} = 3$ was reached; and then they were finally freeze-dried. Extraction yields of humic acids were calculated as the percentage of carbon recovered from the original soil sample used for extraction.

4.3 Characterisation of humic acids

Humic acids were characterised for their elemental composition (C, N and H) using a Euro EA3028-HT analyser. Data were corrected for water and ash content. Oxygen content was calculated by difference taking into account the ash content. The elemental ratios reported in this paper are based on weight.

Solid-state ^{13}C -NMR spectra of humic acids were measured with a Bruker Avance 500 NMR spectrometer (Karlruhe, Germany, 2003) in a 4 mm ZrO₂ rotor. The magic angle spinning speed was 20 kHz in all cases, and the nutation frequency ^{13}C fields for cross-polarisation 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 ($f_a^{\text{CO}_2}$); 170–150 ppm – aromatic C of fenols and fenol esters (f_a^{P}); 150–135 ppm – alkylaromatic (f_a^{S}); 135–108 ppm – protonise aromatic carbon, bridge-head C (f_a^{H}); 108–100 ppm – cellulose anomeric carbon and

Table 1. Properties of bulk soil organic matter. *Humic acids.

Site	Soil depth (cm)	Total C (%)	E465/E650	pH (CaCl ₂)	HA* extraction yield (%)	Mineralisable C (mgC gsoil ⁻¹ day ⁻¹)
Yavay Cape	0–5	13.7	2.495	5.47	0.68	2.341
Gyda Yuribey	0–10	27.4	1.207	3.94	0.46	2.103
Enisey Gulf	0–5	36.4	2.654	3.64	1.85	2.318
Enisey Gulf	5–9	18	1.409	4.54	2.30	2.189
Haranasale-1	0–5	7.5	2.684	3.79	0.16	0.910
Haranasale-1	5–11	6.8	1.164	3.56	0.42	0.875
Beliy Island	0–10	5.7	2.244	5.07	0.46	1.572
Haranasale-2	0–5	12.3	2.816	6.26	1.85	1.945
Haranasale-2	5–10	15.2	1.952	4.75	0.99	1.553
Haranasale-2	20–30	0.4	6.679	3.01	0.13	0.583

hemiacetal carbon ($f_{al}^{O_1}$); 100–70 ppm – resonance region of C–H bonds, secondary alcohols, and other carbon atoms bound to oxygen ($f_{al}^{O_2}$), 70–50 ppm – methyl group resonance region of aliphatic and aromatic ethyl ethers, amino acid carbons, and methyl esters of carboxylic groups (f_{al}^{OM}); 50–32 ppm – resonance region of quaternary carbon and CH carbons (f_{al}^Q); 32–27 ppm – resonance region of CH₂ alkyl structures in transconformation (f_{al}^{trans}); 27–10 ppm – resonance region of alkyl methyls and CH₂ units (f_{al}^{Met}). The total aromatic content was determined by integrating the signal intensity in the intervals 100–170 and 183–190 ppm, while the total aliphatic content was determined at the intervals 0–110 and 164–183. Both fractions were expressed as percentages to the total spectral integration.

4.4 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*. Prior to analysis, data were tested for normality using the Shapiro test (base R). Normality was observed in all cases and no data transformations were necessary. The only exception was an extreme outlier for E4/E6 which was removed from analysis. Those models which presented a significant correlation were tested for homoscedasticity using the Breusch–Pagan test (lmtest package for R, Zeileis and Hothorn, 2002). No models presented significant heteroscedasticity, therefore, no adjustment of the coefficients and their associated errors was necessary. Regressions were considered significant at $p > 0.05$.

For the total mineralisable carbon, a multivariate linear model analysis was performed to detect what SOM quantitative and qualitative 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 carbon functional groups defined by the ¹³C-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 characteristics of bulk SOM. This was achieved by performing a vector fitting analysis. Variables were centred 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).

5 Results

5.1 Bulk soil organic matter characteristics

Across the studied region, soils contained an average of 14.3 ± 10.8 % of total carbon (Table 1). Among the surface layers, the highest amounts of carbon were found in Enisey Gulf (36.4 %), followed by Gyda Yurivey Gulf (27.4 %). More moderate amounts were found in Yavay Cape (13.7 %) and Haranasale-2 Cape (12.3 and 7.5 %). By contrast, Beliy 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 the subsurface layer (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, site 1) or even increased (12.3 % at 0–5 cm to 15.2 % at 5–10 cm, site 2). Deeper in the same soil profile (at 20–30 cm), carbon content was minimal (0.4 %).

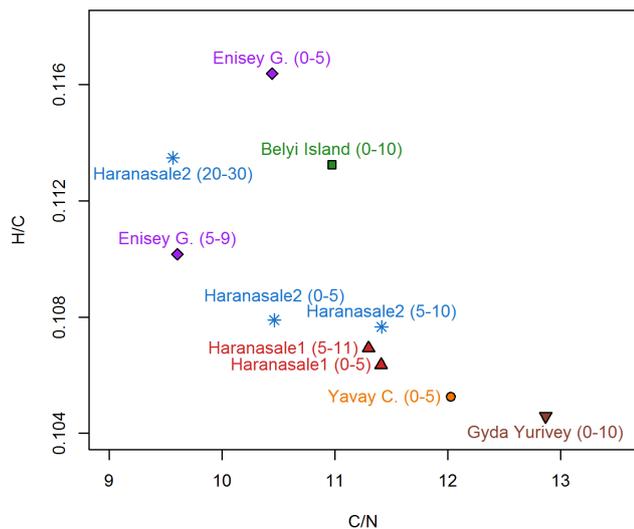


Figure 3. H / C vs. C / N scatter plot. Numbers in parentheses indicate the sampled soil depth in centimetres.

In terms of carbon stocks, among surface soils there was an average of $12.1 \pm 7.2 \text{ gC m}^{-2}$ (Table 1). From surface to subsurface layers (0–5 to 5–10 cm depth), there was a notorious increase in the Haranasale Cape sites (from 5.3 and 8.6 gC m^{-2} , to 11.5 and 25.8 gC m^{-2} in sites 1 and 2, respectively). However, there was a 50 % decrease in the Enisey Gulf site (from 25.5 to 12.6 gC m^{-2}). The deep mineral soil layer from Haranasale-2 had minimal carbon stocks (0.75 gC m^{-2}).

E4 / E6 averaged 2.383 ± 0.592 in surface soils (Table 1). This average decreased at subsurface layers to 1.508 ± 0.403 , although this difference was not statistically significant (*t* test, $p > 0.05$). The mineral layer of Haranasale-2 showed a unique signal consisting in an outlying high value of 6.679.

5.2 Elemental composition of humic acids

Humic acid extractions produced maximum yields in Enisey Gulf (especially in the subsurface layer, 2.30 %) and in Haranasale-2 surface sample (1.85 %), whereas minimum yields were obtained for the deep mineral layer in Haranasale-2 (0.13 %, Table 1). The elemental compositions of humic acids and their corresponding elemental ratios were characterised by very low variabilities ($\text{CV} < 9.1 \%$, Table 2). H / C was the elemental ratio with the lowest variability ($\text{CV} = 3.5 \%$) and averaged 0.109. The highest values of this ratio were found in Enisey Gulf, Belyi Island and at the deep mineral layer of Haranasale-2 Cape (20–30 cm). By contrast, the lowest H / C ratios were found in Gyda Yurivey and Yavay Cape (0.105 in both sites). The H / C ratio was found to be significantly negatively correlated with the C / N ratio (Fig. 3), explaining more than 40 % of its variance ($r^2 = 0.439$, $p < 0.05$).

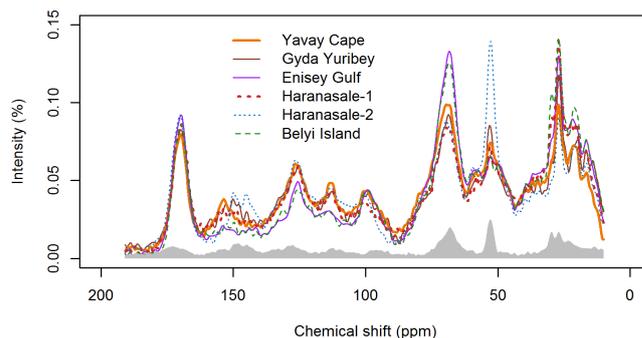


Figure 4. ^{13}C -NMR spectra of surface soil samples. The grey spectrum corresponds to the standard deviation of all ^{13}C -NMR spectra.

The C / N content averaged 11.0 ± 1.0 . In depth, it was found to be slightly lower at deeper layers in Haranasale-1 and Enisey Gulf (Table 2). However, in Haranasale-2 there was an increase from the surface layer (0–5 cm) to the subsurface one (5–10 cm) from 10.46 to 11.41. The O / C ratio averaged 0.81 ± 0.09 and the mineral layer in Haranasale-2 had a remarkably higher value. No clear patterns could be observed between O / C and the other elemental ratios.

5.3 ^{13}C -NMR characterisation of humic acids

^{13}C -NMR spectra revealed that there were only small differences in the structural diversity of carbon atoms both among the surface samples, as well as within soil layers. In all samples there was a statistically significant predominance of aliphatic carbons ($68.85 \pm 3.60 \%$) over aromatic ones ($31.15 \pm 3.60 \%$; *t* test, $p < 0.001$; Table 4). The standard deviation of all measured ^{13}C -NMR spectra (Fig. 4 and 5) showed that the highest variability among samples occurred in the resonance areas between 50–70 ppm (resonance area for methoxyl carbon, including amino acids and peptides) and 27–32 ppm (corresponding to CH_2 alkyl structures like alkanes and fatty acids), both of them corresponding to aliphatic carbon structures.

When only surface samples are considered, ^{13}C -NMR spectra show (Fig. 4) that Enisey Gulf and Belyi Island had a lower signal intensity across the aromatic resonance areas compared with the rest of the sites. By contrast, their signal at 70 ppm was markedly higher, indicating an increase of O-alkyl C structures. Haranasale-1 site presents a distinctive signature, consisting in a high methoxyl C peak at 55 ppm. Finally, Enisey Gulf, Belyi Island and Haranasale-2 sites had slightly higher signal intensities in the region between 0 to 50 ppm, which corresponds to alkyl C structures.

In Enisey Gulf and in the two Haranasale sites, some patterns could be observed in depth (Fig. 5). In the three sites it could be observed that the signal intensity for aromatic carbons (135–150 ppm) presented minor changes. However, some variation could be observed in the aliphatic regions. Interestingly, every site presented different patterns.

Table 2. Elemental composition and elemental ratios of the extracted humic acids. *Coefficient of variation.

Site	Soil depth (cm)	N %	C %	H %	O %	C / N	O / C	H / C
Yavay Cape	0–5	4.3	51.4	5.4	38.9	12.0	0.8	0.1
Gyda Yuribey	0–10	3.9	50.2	5.3	40.6	12.9	0.8	0.1
Enisey Gulf	0–5	5.0	52.3	6.1	36.7	10.4	0.7	0.1
Enisey Gulf	5–9	5.3	50.5	5.6	38.7	9.6	0.7	0.1
Haranasale-1	0–5	4.4	50.1	5.3	40.2	11.4	0.8	0.1
Haranasale-1	5–11	4.4	49.7	5.3	40.6	11.3	0.8	0.1
Beliy Island	0–10	4.4	48.7	5.5	41.3	11.0	0.9	0.1
Haranasale-2	0–5	4.9	51.5	5.6	38.0	10.5	0.7	0.1
Haranasale-2	5–10	4.3	49.4	5.3	40.9	11.4	0.8	0.1
Haranasale-2	20–30	4.6	43.7	5.0	46.8	9.6	1.11	0.1
CV (%) *		9.1	4.3	4.9	6.1	9.6	11.2	3.5

Table 3. ^{13}C -NMR section integrals (percent of total carbon) for key carbon structures of soil humic acids.

Site	$\delta(^{13}\text{C})\text{ppm}$ Key structures	10–27	27–32	32–50	50–70	70–100	100–108	108–135	135–150	150–170	170–190
		$f_{\text{al}}^{\text{Met}}$	$f_{\text{al}}^{\text{trans}}$	f_{al}^{Q}	$f_{\text{al}}^{\text{OM}}$	$f_{\text{al}}^{\text{O}_2}$	$f_{\text{al}}^{\text{O}_1}$	f_{a}^{H}	f_{a}^{S}	f_{a}^{P}	$f_{\text{a}}^{\text{CO}_2}$
Yavay Cape	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	0–5 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	5–11 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

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 constant at Haranasale-2, and increased in Enisey Gulf. On the other hand, the signal at the methoxyl C peak (55 ppm) remained constant in Haranasale-1 and Enisey Gulf, whereas it clearly decreased in depth in Haranasale-2. 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 (20–30 cm), it can be seen that in this mineral layer there was a further increase of the signal intensity, indicating a higher prevalence of simple carbon bonds.

5.4 Total mineralisable carbon

The total mineralisable carbon during the first 7 days of incubation was found to be positively correlated with the total carbon in soil, explaining nearly 58% of its variability ($r^2 = 0.576$, $p < 0.01$). Accordingly, the highest rates were found in Yavay Cape ($2.34 \text{ mgC gsoil}^{-1} \text{ d}^{-1}$) and in Enisey Gulf (2.32 and $2.19 \text{ mgC gsoil}^{-1} \text{ d}^{-1}$ at 0–5 and 5–9 cm, respectively; Table 1). Among the surface soil samples, the lowest mineralisation rate was found in Belyi Island ($1.57 \text{ mgC gsoil}^{-1} \text{ d}^{-1}$). In the three sites were differ-

ent depths were measured, located at Enisey Gulf and Haranasale Cape, the mineralisation rates decreased with depth, and were minimal in the mineral deep horizon (20–30 cm) of the Hystic Gleysol in Haranasale ($0.58 \text{ mgC gsoil}^{-1} \text{ d}^{-1}$). During the following weeks of incubation (9 for Yavay Cape, Enisey Gulf and Haranasale-1, and 4 for Belyi Island and Haranasale-2 sites), mineralisation rates remained constant, so that CO_2 degassing increased linearly over time (adj $r^2 > 0.860$, $p < 0.05$) in all sites without reaching a saturation point.

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 ^{13}C -NMR spectra). Using best subset selection, it was found that these qualitative variables did not significantly improve the predictability provided by the univariate linear regression with total carbon content (the inclusion of new variables to the model increased the C_p).

Table 4. Total aromatic and aliphatic carbons, and maximal signal intensity at the three ppm of maximum variability in the ^{13}C -NMR spectra. Data are expressed as percent of total carbon.

Site	Depth (cm)	Aromatic	Aliphatic	27 ppm	55 ppm	70 ppm
Yavay Cape	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	0–5	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	5–11	29.11	70.89	0.13	0.08	0.10
Belyi 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

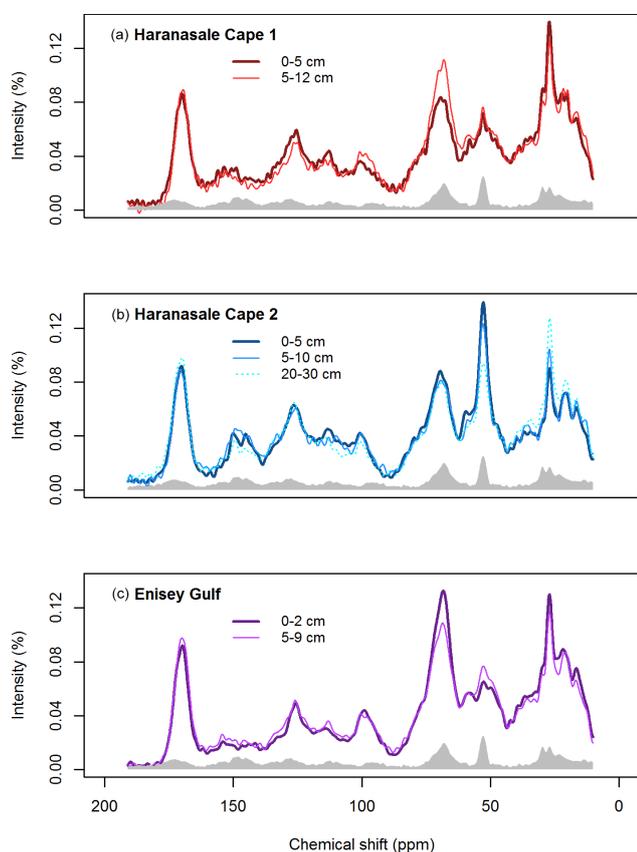


Figure 5. ^{13}C -NMR spectra at different soil depths. The grey spectrum corresponds to the standard deviation of all ^{13}C -NMR spectra.

5.5 Multivariate analysis of soil organic matter properties

The spatial distribution of the carbon structural diversity of humic acids in the Gydan Peninsula was explored using an NMDS analysis. The fitted NMDS ordination (fit-based $r^2 = 0.999$, non-metric fit $r^2 = 1$, Fig. 6), defined a gradient from aromatic (Haranasale-2 and Gyda Yuribey Gulf sites)

to aliphatic carbon predominance (Belyi Island, Enisey Gulf and Haranasale-1 sites) on the primary axis. 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 a predominance of C% and H% on the positive side ($r^2 = 0.747$, $p < 0.01$ and $r^2 = 0.772$, $p < 0.01$, respectively), and O% and O/C% on the negative side ($r^2 = 0.814$, $p < 0.01$ and $r^2 = 0.778$, $p < 0.01$, respectively). According to that, the humic acids of Yavay Cape, and upper layers of Enisey Gulf and Haranasale-2 are related to low levels of oxygenation, whereas those of Haranasale-1 and the deep layer of Haranasale-2 are related to higher levels. 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 were 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 ^{13}C -NMR spectra.

6 Discussion

In this study we performed a detailed characterisation of SOM from the Gydan Peninsula, an Arctic region in Western Siberia whose soils remained, to date, unexplored. Total carbon quantification was complemented with a multiproxy approach to determine SOM composition from multiple perspectives: elemental analysis, functional composition and optical characteristics. These methodologies consistently showed that soils of the Gydan Peninsula contain carbon stocks which are in the range of the latest estimations (Hugelius et al., 2014). Moreover, most of this carbon is contained in aliphatic carbon structures which have little compositional variability, both regionally and in soil depth. Finally, soil incubations highlighted the high mineralisation potential of these carbon compounds.

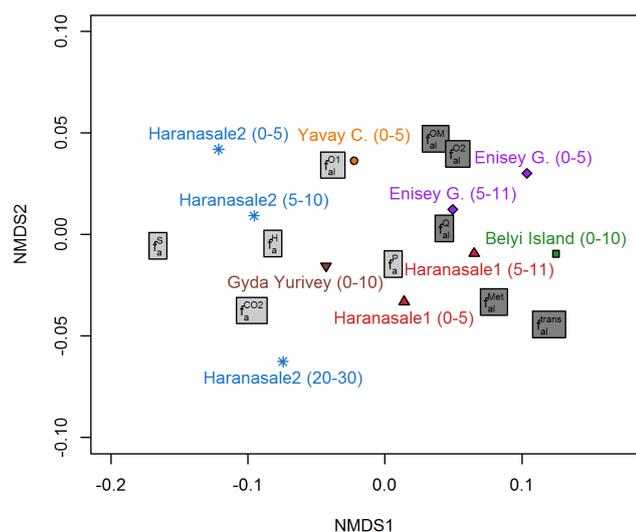


Figure 6. Non-metric multidimensional scaling (NMDS) analysis of humic acids based on their carbon functional groups, derived from ^{13}C -NMR spectral integration. Dark-grey and light-grey groups indicate aliphatic and aromatic carbon structures, respectively. Carbon functional group symbols are specified in Sect. 4.3. Numbers in parentheses indicate the sampled soil depth in centimetres.

6.1 Total soil carbon content

Hugelius et al. (2014) estimated that, in the region of the Gydan Peninsula, there are $15\text{--}30\text{ gC m}^{-2}$ in the 0–30 cm soil layer. In this study, we did not sample to 30 cm depth at most sites. However, if we integrate the carbon stocks in the first 10 cm that we sampled, then we can do some estimative comparison. According to Hugelius et al. (2014) values, in the first 10 cm layer (which is the range sampled in this study), there should be a minimum of $5\text{--}10\text{ gC m}^{-2}$ (if we consider that SOM is evenly vertically distributed) and a maximum of $15\text{--}30\text{ gC m}^{-2}$ (if we consider that all SOM is accumulated at the upper part), considering that SOM content is usually higher at the surface and decreases with depth. According to our data, in the first 10 cm depth there would be stocks within this range (9.53 to 19.18 gC m^{-2}). Therefore, our results are in agreement with current estimations of Arctic SOC stocks based on spatial extrapolations.

6.2 Stability of SOM

Results on SOM elemental analysis and ^{13}C -NMR spectroscopy revealed very low levels of compositional variability, both regionally and in depth. The main drivers of soil humic acids' composition have been identified as the quality of the precursor materials (Andersson et al., 2012), followed by the climatic conditions (i.e. temperature and moisture) which shape the biophysical conditions necessary for humification to take place (Zech et al., 1997). Hence, the regional homogeneity in SOM and humic acids' composition observed in

this study reflects, on the one hand, the fact that all sites are covered by similar tundra plant communities. The main vegetation types are grasses, mosses and lichens, rich in aliphatic compounds such as carbohydrates, lipids and proteins. By contrast, the source of lignins – main precursor molecules for the synthesis of humic substances (McDonald et al., 2004) – is restricted to sparse bushes and, therefore, the low presence of lignins would be a main restriction for the formation of humic acids, hence favouring the presence of aliphatic compounds. This is reflected in our findings, which revealed the presence of more than 60 % of aliphatic carbon structures in all sites.

Further, prolonged cold temperatures and high moisture conditions typical of the Arctic climate would limit the progress of humification (Weintraub and Schimel, 2003) and keep organic molecules in soils preserving to a large extent their original chemical properties. This preservation effect from humification explains the vertical homogeneity observed in the chemical composition of humic acids, as revealed by ^{13}C -NMR spectra. This vertical homogeneity was most prominent for the aromatic functional groups, indicated by a low standard deviation in those resonance shift regions corresponding to aromatic carbon, alkylaromatic and carboxyl-carbonyl C groups (108 to 170 ppm). This vertically constant aromatic signal has been described to be typical of initial stages of the humification process (Zech et al., 1997). By contrast, the aliphatic fraction showed some vertical patterns. The main variability was found in the resonance regions of alkyl-C, methoxyl and O-alkyl C groups (at 27, 55 and 70 ppm). However, the patterns in depth were not consistent among sites. This may be due to the presence of cryoturbation, a common process in Cryosols (Bockheim and Tarnocai, 1998), which hinders the vertical distribution of SOM quality to be comparable among sites. However, such variability reflects the lower stability that aliphatic compounds have in comparison to the aromatic ones, being more prone to microbial processing. The functional composition of humic acids in our sites were consistent with those previously reported for Arctic tundra soils from Alaska (Dai et al., 2001; Ward and Cory, 2015) and Eastern Siberia (Abakumov et al., 2014), sharing the common fact that there was a predominance of alkyl-C and O-alkyl C groups over aromatic and carboxyl-carbonyl carbons.

6.3 High sensitivity of SOM to mineralisation

Low aromaticity has been considered to be indicative of a higher availability of SOM to mineralisation. Hence, a number of proxies tracing SOM aromaticity have been used to infer its lability degree. Both the elemental composition and optical properties have been interpreted in terms of lability (Kalbitz et al., 2003). Further, Dai et al. (2001) found carboxyl-carbonyl C groups to be correlated with SOM mineralisation. However, we did not find any correlation between the total mineralisable carbon and any of the measured qual-

itative SOM variables. By contrast, the total mineralisable carbon was found to be related only to the total carbon content in soil. This lack of relationship between SOM mineralisation and SOM quality might be attributed to two reasons: (a) the presence of a high proportion of highly labile SOM compounds, which may be hindering a quality-related limiting effect, and (b) the qualitative variability in our samples would be too low to recreate any relationship between aromaticity and mineralisation. The former reason could be proved using longer-term incubations, as some limiting effects may be observed once the most highly labile pool of SOM is depleted. Evidence in this line arose in some recent papers which provided unique data on long-term permafrost soil incubations (Elberling et al., 2013; Schädel et al., 2014). This unprecedented data revealed a major role of C/N on the landscape-scale variation of SOM mineralisation (Schädel et al., 2014). Even though we did not find a significant relationship between C/N and SOM mineralisation, we did find a significant correlation between C/N and H/C (i.e. level of conjugation of humic acids), providing indirect evidence of the influence of C/N on SOM biodegradability. Overall, our results indicate that the mineralisation rate of SOM from the Gydan Peninsula is not limited by qualitative aspects, at least at early decomposition stages. Moreover, longer incubation times would be needed in order to further identify specific qualitative aspects of SOM that control its biodegradability on longer timescales.

7 Conclusions

This study presents, for the first time, a detailed characterisation of the humic acids of soils from the Gydan Peninsula, Western Siberia. Thereby, it expands the regional coverage of recent local-scale studies of SOM lability in permafrost soils in periglacial environments, what may contribute to better depict the regional variability of humic acids' characteristics across the Arctic region.

Our results reveal that the total carbon content of soils of this region is in agreement with latest regional estimates of Arctic SOC stocks. Moreover, we found that SOM compounds are predominantly aliphatic (more than 60%) and that their elemental and functional composition remains highly constant, both regionally and in depth. This aliphatic compositional homogeneity reflects common vegetation cover (which supplies restricted lignified material), together with common cold climatic conditions across the studied region (which keep humification rates low).

Our results also suggest that the mineralisation rate of this highly aliphatic material depends primarily on the total quantity of organic carbon in soil, while qualitative aspects (elemental and functional composition, and optical properties) were not found to have a significant influence. We argue that this may be due to a high predominance and availability of labile compounds, so that during our short-term incubations

(weekly scale) compositional aspects did not play a limiting role of the mineralisation rate.

Overall, we conclude that soils of the Gydan Peninsula contain SOM whose composition is highly stable at present climatic conditions. However, this stability can be jeopardised in the future by increasing warming temperatures which can induce the mineralisation of high amounts of stored labile organic compounds.

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