

1 **Soil organic matter molecular composition and state of decomposition in three**
2 **locations of the European Arctic.**

3 Annelene Pengerud¹, Marie-France Dignac^{2*}, Giacomo Certini³, Line Tau Strand¹, Claudia
4 Forte⁴, Daniel P. Rasse⁵

5 ¹ Department of Plant and Environmental Sciences, Norwegian University of Life Sciences
6 (UMB), P.O. Box 5003, N-1432 Ås, NORWAY

7 ² INRA, UMR Ecosys, UMR INRA, AgroParisTech, 78850 Thiverval-Grignon, FRANCE,
8 marie-france.dignac@inra.fr

9 ³ Dipartimento di Scienze delle Produzioni Vegetali, del Suolo e dell'Ambiente Agroforestale
10 (DiPSA), Università degli Studi di Firenze. Piazzale delle Cascine 28, 50144 Firenze, ITALY,
11 giacomo.certini@unifi.it

12 ⁴ ICCOM-CNR, Area della Ricerca, Via G. Moruzzi 1, 56124 Pisa, ITALY,
13 claudia.forte@cnr.it

14 ⁵ Division for Environment and Natural Resources, Norwegian Institute of Bioeconomy
15 Research – NIBIO, Høgskoleveien 7, 1430 Ås, NORWAY daniel.rasse@nibio.no

16 Corresponding author: Marie-France Dignac (marie-france.dignac@inra.fr)

17 **Abstract**

18 Increased mineralization of the organic matter (OM) stored in permafrost is expected
19 to constitute the largest additional global warming potential from terrestrial ecosystems
20 exposed to a warmer climate. Chemical composition of permafrost OM is thought to be a key
21 factor controlling the sensitivity of decomposition to warming. Our objective was to

22 characterise OM from permafrost soils of the European Arctic: two mineral soils –
23 Adventdalen, Svalbard, Norway and Vorkuta, northwest Russia – and a “palsa” (ice-cored peat
24 mound patterning in heterogeneous permafrost landscapes) soil in Neiden, northern Norway,
25 in terms of molecular composition and state of decomposition. At all sites, the OM stored in
26 the permafrost was at an advanced stage of decomposition, although somewhat less so in the
27 palsa peat. By comparing permafrost and active layers, we found no consistent effect of depth
28 or permafrost on soil organic matter (SOM) chemistry across sites. The permafrost-affected
29 palsa peat displayed better preservation of plant material in the deeper layer, as indicated by
30 increasing contribution of lignin carbon to total carbon with depth, associated to decreasing
31 acid (Ac) to aldehyde (Al) ratio of the syringyl (S) and vanillyl (V) units, and increasing S/V and
32 contribution of plant-derived sugars. By contrast, in Adventdalen, the Ac/Al ratio of lignin and
33 the Alkyl C to O-alkyl C ratio in the NMR spectra increased with depth, which suggests less
34 oxidized SOM in the active layer compared to the permafrost layer. In Vorkuta, SOM
35 characteristics in the permafrost profile did not change substantially with depth, probably due
36 to mixing of soil layers by cryoturbation. The composition and state of decomposition of SOM
37 appeared to be site-specific, in particular bound to the prevailing organic or mineral nature of
38 soil when attempting to predict the SOM proneness to degradation. The occurrence of
39 processes such as palsa formation in organic soils and cryoturbation should be considered
40 when up-scaling and predicting the responses of OM to climate change in arctic soils.

41 *Key Words:* Cryogenic processes, lignin, non-cellulosic sugars, ¹³C NMR, palsa, permafrost,
42 climate change.

43

44 **Introduction**

45 Approximately 22 % of ice-free land in Arctic and boreal regions of the Northern
46 Hemisphere has permafrost (Schuur et al. 2008), defined as subsurface material that remains
47 below 0 °C for at least two consecutive years. Permafrost soils store large amounts of C as
48 soil organic matter (SOM) due to low temperatures and, often, anaerobic conditions, which
49 limit decomposition (Shaver et al. 2006; McGuire et al. 2010). Organic carbon (C) stocks in
50 permafrost soils are estimated to amount to 1672 Gt (Tarnocai et al. 2009; Hugelius et al.
51 2014), representing almost 70% of total C stored in soils (2400 Gt), and twice the C present
52 in the atmosphere (800 Gt) (Jobbágy and Jackson 2000). Permafrost from the Southern
53 Hemisphere contributes little to global C stocks because of its limited extent (Schuur et al.
54 2008).

55 Warming for this century is forecasted to be highest in the Arctic (IPCC 2014), which
56 will considerably reduce the area affected by near-surface permafrost (McGuire et al. 2010)
57 and will generally increase the thickness of the “active layer”, which thaws in the summer and
58 refreezes in the winter (Luo et al. 2016). The thickness of the active layer influences plant
59 rooting depth, hydrological processes, and the amount of SOM that is exposed to above-
60 freezing temperatures for parts of the year (Schuur et al. 2008). Due to the large amounts of
61 C in high latitude soils, and the high temperature sensitivity of SOM decomposition measured
62 at low temperatures, permafrost soils are pivotal for the global C cycle (Hofgaard 2003; Hartley
63 et al. 2008). Indeed, increased organic matter (OM) decomposition in permafrost is considered
64 the largest potential release of C from terrestrial ecosystems to the atmosphere (Schuur et al.
65 2008; Tesi et al. 2016). However, high-latitude terrestrial ecosystems are highly diverse (e.g.
66 peatlands and mineral soils, lowlands and uplands), with consequent large variations in C
67 stocks and, plausibly, in their response to climate change (Dutta et al. 2006). Therefore,
68 improved projections of permafrost C stocks for the 21st century and beyond require a better
69 understanding of the amount, composition, and potential biodegradability of OM in a wide
70 range of high-latitude soils (Michaelson et al. 2004; Rodionow et al. 2007).

71 The organic matter composition in permafrost soils might be different from the more
72 studied temperate soils, mainly because low temperature and especially continuous freezing
73 reduces microbial transformations of SOM to a large extent (Schuur et al., 2008). Freezing
74 temperatures are probably not the only mechanism stabilising SOM in permafrost; the
75 significance of secondary mechanisms, such as C exchange between active layer and
76 permafrost by cryoturbation, remains unclear (Schmidt et al. 2011). As a result of freezing
77 conditions, the chemical composition of SOM in the permafrost may differ from that of the
78 overlying active layer (Michaelson et al. 2004; Waldrop et al. 2010; Ping et al. 2015). The
79 chemical composition of SOM in the permafrost is not well documented, although it has been
80 suggested as a driving factor of decomposition relative to the effects of temperature and
81 moisture in Arctic and boreal systems (Nadelhoffer et al. 1991; Hobbie et al. 2000; Updegraff
82 et al. 1995; Paré and Bedard-Haughn 2013). Several authors emphasise the tight linkages
83 between SOM chemical composition and C cycling and stabilisation in soils (e.g. Kögel-
84 Knabner 2000; Shaver et al. 2006). What seems particularly critical is that Arctic permafrost
85 soils have been reported to be rich in soluble compounds and easily degradable
86 carbohydrates, which could decompose rapidly under warmer conditions (Michaelson et al.
87 2004; Mueller et al. 2015). Accurate molecular characterisation of SOM in permafrost soils
88 could be an important tool for predicting the response of ecosystems from extremely cold
89 areas to climate change.

90 Molecular analyses are useful to better understand the nature of stable OM, in
91 particular through combinations of spectroscopic and chemolytic techniques (Kögel-Knabner
92 2000). Among these, Nuclear Magnetic Resonance (NMR) is of relevance, being a non-
93 destructive spectroscopic technique that provides useful information on the gross chemical
94 composition of OM (Kögel-Knabner 2000). However, NMR analyses alone might not be
95 sensitive enough to demonstrate a link between OM composition and OM sensitivity to
96 temperature changes in permafrost soils (Moni et al. 2015). Indeed, wet-chemical analyses of
97 biomarkers can complement global OM features obtained with NMR.

98 Among the major plant-inherited molecular structures in soils, lignins are the
99 predominant ones in the litter layer and display contrasting decomposition rates depending on
100 interaction with the soil environment (Rasse et al. 2006). Lignins have been shown to be
101 rapidly degraded in temperate soils (Dignac et al. 2005), while in extremely cold environments
102 they could presumably have longer permanence in soil. Rodionow et al. (2006) demonstrated
103 a more advanced oxidative decomposition of lignin molecules in permafrost than in
104 permafrost-free soils, possibly due to higher content in the first ones in labile polysaccharides
105 available for their co-metabolic decomposition, or to nitrogen limitation, which is known to
106 enhance lignin decomposition (Berg 2000). But, generally, little is known about the fate of
107 lignins in the permafrost. Analysis of the content and composition of sugar structures is
108 another useful tool for better understanding the decomposition degree of SOM from plant
109 derived to microbially transformed (Grewer et al. 2016). Pentose sugars are derived mainly
110 from plants and are an important source of energy and C for soil microorganisms, which
111 primarily resynthesise hexoses. Therefore, the hexose/pentose (C_6/C_5) ratio is an indicator of
112 plant-microbe contributions to SOM (Amelung and Zech 1996; Amelung et al. 1999;
113 Guggenberger and Zech 1994). According to Oades (1984), C_6/C_5 ratios are <0.5 for plants
114 and >2 for microorganisms. The main fraction of non-cellulosic polysaccharides in soils is
115 microbially derived (Kögel-Knabner 2000).

116 The biodegradability of SOM in permafrost soils is related to its composition (Rodionow
117 et al. 2006), which thus might be a main driver for the response of such SOM to climate
118 change. However, there is scarcity of data on the composition of SOM in permafrost. The main
119 hypothesis of the present study was that SOM in permafrost layers has a different chemical
120 composition to that of non-permanently frozen layers, i.e. overlaying active layers and co-
121 located non-permafrost soils. To test this hypothesis we chose three contrasted permafrost
122 regions of the European Arctic. Our specific objectives were: i) investigating SOM in terms of
123 chemical composition and state of decomposition in these soil formations, ii) evaluating
124 systematic differences in permafrost layers vs. active layers and non-permafrost soils from

125 each location, thereby testing our main hypothesis and ii) evaluating site-specific effects on
126 SOM composition and relating these to local soil formation conditions.

127 **Materials and methods**

128 **Sampling sites**

129 For this study, we selected 3 permafrost sites of the European Arctic, which represent
130 contrasted geographical regions and are governed by distinct soil formation processes. The
131 first site is Adventdalen, in the Svalbard archipelago of, Norway (78.2°N, 15.2°E). Profiles
132 were sampled from two dry mineral soils with permafrost, both not cryoturbated but
133 incorporating SOM at different rates (hereafter soils A1 and A2). The second site was Vorkuta
134 in the most eastern part of the European Arctic (67.5°N, 64.1°E) in north-west Russia, where
135 a cryoturbated mineral permafrost soil (V1) and one from a permafrost-free mineral soil (V2)
136 were sampled. The third site was Øvre Neiden, Finnmark, northeast Norway (69.4°N, 29.2°E),
137 representing the palsa peat discontinuous permafrost regions typical of Northern
138 Fennoscandia. From this third site, profiles were sampled from two peat soils, one on a palsa
139 mound with permafrost (N1) and one in an adjacent internal lawn created by localised
140 permafrost degradation (N2). These three sites provided us with the necessary contrast in
141 geography and cryosol type to test our hypothesis that permafrost layers contain SOM that is
142 less decomposed and present specific molecular structures as compared to non-permanently
143 frozen soil layers.

144 Adventdalen was de-glaciated approximately 10.000 years ago (Mangerud et al.
145 1992). There is continuous permafrost in the area, with an active layer normally at around 95
146 -100 cm (Christiansen 2005). The sampled soils are close to the Adventdalen river, and their
147 parent material is braided fluvial sediment (Christiansen 2005) with some loess cover (Bryant
148 1982). An important feature of the Adventdalen area is the presence of Tertiary coal-bearing
149 sandstone formations, which are easily weathered (Major and Nagy 1972). Sediments and

150 soils in Adventdalen may thus contain some geogenic coal. The climate is dry arctic, with an
151 average annual precipitation of 190 mm and mean annual air temperature of -6 °C (1961-
152 1990) in Longyearbyen Airport (Aune 1993; Førland 1993). Two soil trenches were opened
153 1.5 km apart. One soil (A1) was sampled in the driest area with sparse vegetation cover mostly
154 of *Salix polaris* Walenb. The other trench was opened in a patterned ground, a network of
155 large, low-centred hexagonal polygons with parent material of fine-grained loess. The
156 polygons have a clear vegetation cover gradient: tall grasses in the troughs, sparse vegetation
157 on the ramparts and extensive mosses in the centre. The centres of the polygons are
158 substantially wetter than the surrounding area. The studied soil profile (A2) was at the centre
159 of a polygon.

160 The two Vorkuta soil profiles were located near the Ayach-Yakha CALM site
161 (Mazhitova et al. 2004), 13 km northeast of the town of Vorkuta in Komi, Russia. The area is
162 an undulating plain of silt loam material of glacial-marine origin. The area was de-glaciated
163 60-80 thousand years ago (Svendsen et al. 2004) and presently (1948-2002) the mean annual
164 air temperature is -5.9 °C and the mean annual precipitation is 550 mm (Mazhitova et al.
165 2004). The two profiles were approximately 300 m apart, divided by a creek. The V1 soil profile
166 was on a gentle (3°) southwest-facing slope with maximum thawing depth of 65-75 cm,
167 whereas the V2 soil profile was on the opposite side (northeast-oriented) of the creek,
168 permafrost-free in the upper 2 meters. Around V1, there were numerous frost boils and patchy
169 vegetation consisting of dwarf shrubs, *Salix* spp. and *Betula nana* (up to 50 cm), and feather
170 moss (*Hypnaceae*) tundra (Mazhitova et al. 2004). Around V2, the vegetation was continuous
171 tall shrubs (100-120 cm) with *Salix* as dominant component, and a feather moss (*Hypnaceae*)
172 dominated ground cover.

173 Table 1. Overview of profile samples and soil classification and basic soil properties (data from Moni et al. 2015). A for Adventdalen; V for
174 Vorkuta; N for Neiden.

Profile	Classification ^a	Layer	Sampling depth (cm)	Coordinates	Altitude/ m.a.s.l.	pH	Total C mgC g ⁻¹ soil	Total N mgN g ⁻¹ soil	C/N	Other
A1	Typic Haplorthel	Active	20-50	N78 12.091	15	4.6	13.9	0.5	30	Active fluvial plain
		Permafrost	105-173	E15 50.063		4.5	17.6	0.6	29	
A2	Aquic Haplorthel	Active	20-40	N78 11.153	17	5.2	24.7	1.2	21	Lower sedimentation rates
		Permafrost	70-106	E15 55.490		4.8	21.4	0.8	28	
V1	Ruptic-Histic Aquiturbel	Active	20-37	N67°35'23.4",	134	5.8	22.3	1.2	17	Cryoturbation
		Permafrost	55-105	E064°10'00.4"		6.4	13.7	0.9	16	
V2	Typic Dystrocryept	Upper	20-40	N67°35'20.9",	136	4.7	18.9	1.2	16	No cryoturbation
		Deeper (unfrozen)	40-80	E064°09'39.8"		6.1	1.7	0.1	27	
N1	Typic Hemistel	Active	0-57	N69 41.088	82	3.5	589.5	16.7	35	Palsa mound
		Permafrost	57-151	E29 1.954		4.2	543.7	18.8	29	
N2	Typic Cryohemist	Upper	30-50	N69 41.115	79	4.2	574.6	19.5	29	Internal lawn, partly inundated
		Deeper (unfrozen)	100-115	E29 11.769		4.3	439.0	15.6	28	

175 ^a According to the Soil Taxonomy (Soil Survey Staff 2006).

176 The third study site, Neiden, in northern Norway, is located at the transition between
177 the north-boreal and low-Arctic vegetation zones (Moen 1999) and represents a palsa
178 peatland, typically found in areas with discontinuous or sporadic permafrost (Fronzek et al.
179 2006). The importance of permafrost landforms in peatlands for regional C fluxes to the
180 atmosphere has been emphasized by Turetsky et al. (2002). Palsas form in polar and subpolar
181 climates and are characterised as dynamic peat mounds with ice-core (Seppala 1986). The
182 mean annual air temperature in Neiden is -0.7 °C and the mean annual precipitation is 455
183 mm (1961-1990, Øvre Neiden; Aune 1993; Førland 1993). The two soil profiles were located
184 50 m apart, in a peatland formed on a silt rich marine deposit, which by frost action may have
185 intruded to the frozen core of some of the palsas. Profile N1 was on a palsa mound with
186 permafrost and N2 in an internal lawn created by localised permafrost degradation, both
187 excavated in the peat without reaching the mineral sediment. Palsa mounds showed large
188 patches of barren peat, lichens (*Cladonia*) and low prostrate shrubs (e.g. *Betula nana*, *Ledum*
189 *palustre*, *Vaccinium uliginosum* L., *Empetrum hermaphroditum* Hagerup), while internal lawns
190 were covered by *Sphagnum* mosses, cotton grass (*Eriophorum*) and sedges (*Carex* sp.).

191 Further information on the study sites and soil profiles are in Moni et al. (2015).

192 **Soil sampling and sample preparation**

193 Soil sampling was conducted during July-September 2008. Bulk samples (1-3 kg) were
194 collected from the active/upper and permafrost/deeper layers of each soil profile and their
195 basic characteristics determined by Moni et al. (2015). A summary of the latter is reported
196 here in Table 1. Aiming at comparing the composition of SOM at depth in the active layer,
197 which had already undergone some decomposition, with the SOM currently preserved in
198 permafrost, we did not take into account the surface soil (O/A horizon) and the transition
199 between the active layer and the permafrost. The main difference in conditions between the
200 sampled layers might thus be the influence of permafrost or annual freeze-thaw cycles.
201 Profiles were dug in the non-frozen soil and described according to standard procedures and

202 classified according to Soil Survey Staff (2006). Samples from active layers and unfrozen
203 deeper layers were collected from all four profile walls using a trowel or knife, while cylindrical
204 cores, 3.5 (Vorkuta) and 5 (Adventdalen and Neiden) cm in diameter, were drilled into the
205 profile floor to obtain samples from the ice-cemented permafrost. The sampling resulted in
206 one bulk soil sample from each layer of each soil profile (see Table 1 for layer depth). All soil
207 samples were kept frozen at -18 °C after sampling. Prior to chemical analyses, samples were
208 thawed on a filter paper at 10 °C and drained to field capacity (72 h). Subsamples taken out
209 for chemical analyses were air dried and sieved to <2 mm. A sample splitter ensured
210 homogeneity among subsamples used for the different chemical analyses.

211 **Wet-chemical analysis**

212 Lignin monomers were analysed by the cupric oxide (CuO) oxidation method (Hedges
213 and Ertel 1982) as modified by Kögel and Bochter (1985). Triplicate samples (50 to 1000 mg
214 of soil depending on C content) were oxidised with 250 mg CuO and 2 M NaOH at 172 °C
215 under N₂ for 2 h. After oxidation, a standard containing ethylvanillin was added to estimate the
216 recovery of lignin-derived phenols after the preparation procedure. The CuO oxidation
217 products were purified and extracted using a C18 reverse phase column (International Sorbent
218 Technology), and subsequently derivatised with BSTFA (bis-(trimethylsilyl)-trifluoroamide).
219 Phenylacetic acid was added as an internal standard for quantification prior to derivatisation.
220 The lignin monomers were separated with a HP GC 6890 gas chromatograph equipped with
221 a SGE BPX-5 column (60 m length, 0.25 mm internal diameter, 0.32 µm coating) and detected
222 with a flame ionisation detector. Samples were injected in split mode (1:10). The initial GC
223 oven temperature was set at 100 °C for 2 min, with a following increase from 100 to 172 °C at
224 8 °C min⁻¹, from 172 to 184 °C at 4 °C min⁻¹, and from 184 to 310 °C at 10 °C min⁻¹. Finally,
225 there was a 5 min isothermal at 310 °C. The injector was kept at 280 °C and the detector at
226 300 °C. Helium (He) was used as carrier gas with a flow rate of 1.0 ml min⁻¹.

227 The CuO oxidation yields a series of lignin-derived phenolic oxidation products that
228 retain the characteristic substitution pattern of different lignin types during the oxidation

229 procedure (Kögel 1986). The oxidation products are identified as vanillyl (V), syringyl (S) and
230 cinnamyl (C) units, deriving from coniferyl, syringyl and *p*-coumaryl units, respectively, with
231 aldehydic, ketonic, and acidic side-chains. The sum of the concentrations of the structural
232 units of the V-, S- and C-type (VSC) is used as an indicator of intact lignin structural units, i.e.
233 the quantitative lignin contribution to the sample (Thevenot et al. 2010). The ratios of acidic to
234 aldehydic forms of the vanillyl and the syringyl units $(Ac/Al)_{V,S}$ are used as indicators of the
235 degree of lignin oxidation during biodegradation (Kögel1986).

236 The content of non-cellulosic sugars was determined by acid hydrolysis and reduction-
237 acetylation as described by Rumpel and Dignac (2006), modified by addition of
238 ethylenediaminetetraacetic acid (EDTA) as proposed by Eder et al. (2010) to avoid
239 interference by iron (Fe) and possible underestimation of sugars. Triplicate samples (50 to
240 1000 mg of soil depending on C content) were hydrolysed with 4 M trifluoroacetic acid (TFA)
241 for 4 h at 105 °C prior to transformation of sugars into acetate alditols. Myoinositol was added
242 as an internal standard for quantification prior to derivatisation. Non-cellulosic sugar
243 monomers were separated and detected with a HP GC 6890 gas chromatograph, equipped
244 with a BPX70 fused silica capillary column (60 m length, 0.32 mm internal diameter, 0.25 µm
245 film thickness) and a flame ionisation detector. Samples were injected in split mode (1:10).
246 The GC oven temperature was programmed at an increase from 200 to 250 °C at 4 °C min⁻¹,
247 and thereafter a 15 min isothermal at 250 °C. The injector was kept at 250 °C and the detector
248 at 260 °C. Helium (He) was used as carrier gas with a flow rate of 1.0 ml min⁻¹.

249 **Spectroscopic characterisation**

250 NMR experiments were carried out on a Bruker AMX 300-WB spectrometer working
251 at 300.13 MHz for proton and at 75.47 MHz for carbon-13. ¹³C cross-polarization (CP) NMR
252 spectra with magic angle spinning (MAS) were recorded under proton decoupling conditions
253 using a 4 mm CP/MAS probehead for solid-state measurements. The acquisition parameters
254 were: 90° pulse = 3.1 µs, contact time = 3 ms, relaxation delay = 3s, spinning rate = 8 kHz,

255 and number of scans between 8,000 and 32,000. The mineral soil samples were indirectly
256 enriched in C by selectively removing single sand grains (by hand-picking and under a 20x
257 lens) first and then treating the rest with 2% hydrofluoric acid as in Skjemstad et al. (1994).
258 Such a treatment was performed in order to remove paramagnetic materials, which cause
259 broadened resonances and signal loss, and partly other minerals, so increasing the
260 concentration of organic C.

261 Relative abundances of the different C functional groups were determined according
262 to Smernik et al. (2008) by integrating the spectra over the following chemical shift regions:
263 (1) 216-185 ppm (aldehyde/ketone C), (2) 185-165 ppm (carboxyl C), (3) 165-110 ppm (aryl
264 C), (4) 110-45 ppm (O-alkyl C), and (5) 45-0 ppm (alkyl C), and expressing each area as a
265 percentage of the total area integrated between 0 and 322 ppm. These contributions were
266 corrected for the signals of spinning sidebands (ssb) at ± 106 ppm (rotation of 8 kHz) with
267 respect to the corresponding central signal as follows:

268 Alkyl C	I – D
269 O-alkyl C	H – (A + B + C)
270 Aryl C	G + 2x(C + D)
271 Carboxyl C	F + 2xB
272 Ketone/Aldhehyde C	E + 2xA

273 where:

274 A:	291-322 ppm	ssb ketones/aldehydes
275 B:	271-291 ppm	ssb carboxyls
276 C:	257-271 ppm	ssb aryls
277 D:	216-257 ppm	ssb aryls
278 E:	185-216 ppm	aldehydes, ketones
279 F:	165-185 ppm	carboxyls
280 G:	110-165 ppm	aryl
281 H:	45-110 ppm	O-alkyl + ssb carboxyl + ssb aryl C + ssb ketones/aldehydes
282 I:	0-45 ppm	aliphatic + ssb aryl D

283 **Water extractable C**

284 Cold water extractable carbon (C_{WS}) and hot water extractable carbon (C_{HW}) were
285 obtained, in triplicate, from air dried samples (1 g for peat and 6 g for mineral soils) according
286 to the procedure described by Ghani et al. (2003). Carbon in the water extracts was measured
287 on a TOC-V CPN total organic carbon analyzer (Shimadzu, Japan). Cold water extracts
288 contain some microbial biomass C and N (Sparling et al. 1998), and are mainly composed of
289 easily soluble components (e.g. mono- and disaccharides, amino-N species and peptides)
290 that constitute the most bioavailable fraction of SOM in cold frozen soils (Uhlirva et al. 2007),
291 while the SOM extracted with hot water is frequently used as a measure of the labile and
292 potentially bioavailable SOM pool (von Lutzow et al. 2007).

293 **Radiocarbon activity of organic carbon**

294 Mean radiocarbon (^{14}C) ages of the SOM in the active and the permafrost layers of the
295 A2, V1, and N1 profiles were determined by accelerator mass spectrometry (AMS) at the
296 National Laboratory for ^{14}C Dating (Trondheim, Norway). Dry homogenized bulk soil samples
297 (<2mm) were analysed according to the method described in Slota et al. (1987). The
298 radiocarbon age is reported as the conventional radiocarbon age and calibrated calendar age
299 according to Reimer et al. (2004) using the IntCal04 calibration curves. The fraction modern
300 ($F^{14}\text{C}$) carbon was calculated as defined by Stuiver and Polach (1977).

301 **Results**

302 **Molecular composition of SOM**

303 The concentration of lignin-derived phenols estimated as the sum of the concentrations
304 of V, S, C monomers (VSC) ranged between 1.9 and 6.1 mg C g⁻¹ SOC in the mineral soils of
305 Adventdalen and Vorkuta and between 5.0 and 9.8 mg C g⁻¹ SOC in the peat soils of Neiden
306 (Table 2). The ratio $(\text{Ac}/\text{Al})_V$ and $(\text{Ac}/\text{Al})_S$ tended to increase with depth in the mineral soils,
307 indicating more advanced side-chain oxidation and more degraded lignins in the
308 permafrost/deeper layers (Table 2).

309 Table 2. Concentrations (in mg C g⁻¹ SOC) of lignins (expressed as the sum of vanillyl, syringyl and cinnamyl units, Σ VSC) and non-cellulosic
 310 sugars in bulk samples from active/upper and permafrost/deeper layers. Mass ratios of hexose-to-pentose sugars (C₆/C₅), acid-to-aldehyde of
 311 the vanillyl and syringyl units ((Ac/Al)_V and (Ac/Al)_S), syringyl-to-vanillyl (S/V) and lignin (VSC-) C to non-cellulosic sugar C (mean ± st.dev. of
 312 analytical triplicates). A for Adventdalen; V for Vorkuta; N for Neiden.

Profile	Layer	Concentrations		Ratios				
		Σ VSC	Σ non-cellulosic sugars	Ratio non-cellulosic sugars	Lignins			Ratio lignin-C /non-cellulosic
		mg C . g ⁻¹ SOC		C ₆ /C ₅	(Ac/Al) _V	(Ac/Al) _S	S/V	sugar-C
A1	Active	1.9 ± 0.1	36.2 ± 0.9	2.1 ± 0.1	0.91±0.04	0.51±0.02	0.52±0.04	0.05
	Permafrost	2.8 ± 0.1	36.8 ± 0.8	2.2 ± 0.1	0.94±0.08	0.76±0.09	0.40±0.02	0.07
A2	Active	2.7 ± 0.2	42.4 ± 1.6	1.7 ± 0.1	0.86±0.13	0.57±0.05	0.55±0.03	0.06
	Permafrost	2.7 ± 0.1	44.4 ± 2.1	1.7 ± 0.1	0.95±0.05	0.73±0.07	0.36±0.02	0.06
V1	Active	3.3 ± 0.2	76.3 ± 6.1	1.6 ± 0.1	0.77±0.07	0.53±0.03	0.57±0.05	0.04
	Permafrost	2.7 ± 0.1	62.6 ± 4.1	1.8 ± 0.1	0.82±0.15	0.61±0.03	0.50±0.03	0.04
V2	Upper	2.4 ± 0.2	73.5 ± 6.6	1.8 ± 0.1	0.79±0.02	0.60±0.01	0.45±0.05	0.03
	Deeper (unfrozen)	6.1 ± 0.5	68.4 ± 13.5	1.1 ± 0.2	0.97±0.19	0.57±0.01	0.41±0.04	0.09
N1	Active	6.1 ± 0.5	63.3 ± 1.7	2.2 ± 0.1	0.83±0.17	0.61±0.16	0.72±0.05	0.10
	Permafrost (palsa)	9.8 ± 0.5	65.5 ± 2.5	1.6 ± 0.1	0.39±0.01	0.31±0.02	1.14±0.04	0.15
N2	Upper	6.0 ± 0.3	79.2 ± 3.1	2.0 ± 0.1	1.15±0.17	0.64±0.07	0.67±0.08	0.08
	Deeper (unfrozen)	5.0 ± 0.2	29.2 ± 0.6	1.8 ± 0.1	0.68±0.04	0.54±0.04	0.69±0.03	0.17

For the peat soils, there was a tendency towards less degraded lignins in deeper layers, where both $(Ac/Al)_V$ and $(Ac/Al)_S$ were lower. Concentrations of non-cellulosic sugars ranged between 36.2 and 76.3 mg C g⁻¹ SOC in the mineral soils and between 29.2 and 79.2 mg C g⁻¹ SOC in the peat soils (Table 2). Sugar concentrations generally varied little with depth, for most profiles (except N2) being equal to or slightly lower in permafrost/deeper layers compared to active/upper layers. The highest and the lowest sugar concentrations were found in the upper and deeper layer, respectively, of the unfrozen peat profile (N2). In all soils, sugars were mainly microbially derived (C_6/C_5 being close to 2). In profiles A1, A2, V1 and N2, the C_6/C_5 ratio ranged from 1.7 to 2.2, with little variation with depth (similar ratio in the upper and the deeper soil layer) and between sites. However, for N1 and V2, a slight decrease in C_6/C_5 ratio was observed with depth, indicating larger contribution of plant-derived sugars in depth in these soils.

Radiocarbon age of soil organic matter

The mean radiocarbon age increased considerably with depth in both A2 and N1 profiles, whereas the V1 profile showed substantial vertical homogeneity, most probably due to cryoturbation (Table 3). In terms of calibrated mean age, both the Adventdalen and the Neiden profiles showed marked difference between the two layers. Adventdalen with a relatively young SOM in the upper one (400 years BC) and a much older SOM in the underlying permafrost (3600 years BC). The soil investigated at Neiden contained extremely ancient SOM, the upper layer dating back to more than 3100 years BC and the underlying permafrost dating back more than 7400 years BC, which is symptomatic of very long turnover time of SOM at this site, and consistent with the lack of cryoturbation at this site. The fraction modern carbon $F^{14}C$ was less than 1 for all samples indicating there is little bomb-produced ^{14}C and the predominance of old C.

Table 3. Radiocarbon and calibrated ages of one selected profile from Adventdalen (A), Vorkuta (V) and Neiden (N) profiles.

Profile	Layer	¹⁴ C age (years)	Calibrated age years B.C.
A2	Active	2375±75	435-400
	Permafrost	4770±50	3640-3515
V1	Active	2595±60	820-765
	Permafrost	2955±30	1210-1095
N1	Active	4535±45	7400-7075
	Permafrost (palsa)	8430±95	8180-8030

Solid state ¹³C NMR

The combined physical and chemical treatment prior NMR analysis led to increased C concentrations of 80 to 220% in the mineral soils from Adventdalen and Vorkuta, and high quality NMR spectra were acquired (Fig. 1, Table 4) except for the unfrozen deep layer of V2, where no reliable NMR information was obtained because of a too low signal-to-noise ratio most probably due to insufficient C (less than 0.5%).

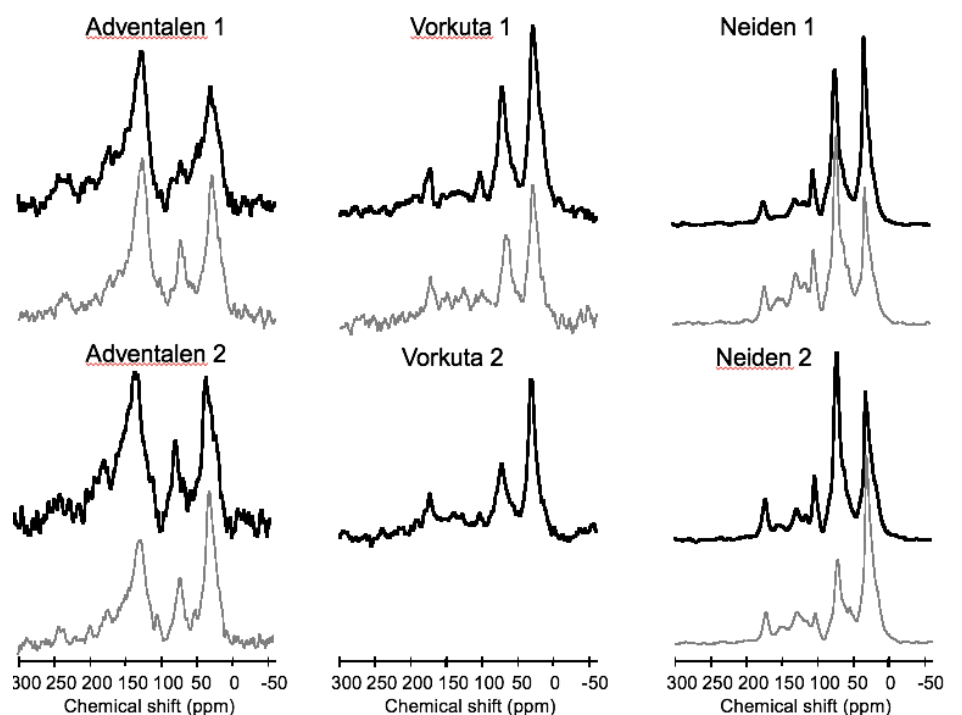


Fig. 1. ^{13}C NMR spectra of SOM in the active/upper layer (black) and the permafrost/deeper layer (grey). The spectrum of the deep layer of V2 is not shown due to a too low signal-to-noise ratio.

The NMR spectra of the soils from Adventdalen are characterised by an intense signal around 130 ppm (Fig. 1), which is within the main aryl C region (110-165 ppm). The intensity and sharpness of this signal may point to the contribution of aromatic C of coal (Rumpel et al. 2000; Suggate and Dickinson 2004), whose presence in the Adventdalen soil parent material was anticipated. In most soil formations, a marked aryl carbon signature can indicate charcoal accumulation from wildfire (Skjemstad et al. 1999; Nocentini et al. 2010), but in the climatic and geologic context of Adventdalen, there is little doubt that the origin is primarily geogenic.

The spectra of the Vorkuta mineral soils were dominated by alkyl C and O-alkyl C, with a slight prevalence of the former; the aryl C region was smaller than that of Adventdalen (Table 4). The active layer of V1 showed an evident signal at 105 ppm, which could be attributed to the anomeric carbon (O-C-O) of the glucose fragment in cellulose and/or the hemi-acetal structures in sugars, along with possible aromatic C2 carbons of guaiacyl lignins.

Table 4. Relative contribution (%) to the total spectral area of different chemical shift regions as determined by solid-state ^{13}C -CPMAS NMR on SOM from Adventdalen (A), Vorkuta (V), and Neiden (N).

Soil profile	Soil layer	Alkyl C	O-alkyl C	Aryl C	Carboxyl C	Ketone, aldehyde C
A1	Active	24±4	17±4	50±3	5±2	4±2
	Permafrost	18±4	10±3	55±2	9±2	8±3
A2	Active	21±3	15±3	51±2	8±3	5±2
	Permafrost	31±3	19±3	42±2	6±2	2±1
V1	Active	42±2	34±2	13±2	7±1	4±1
	Permafrost	35±3	34±3	20±3	8±3	3±1
V2	Upper	38±3	30±3	18±3	9±2	5±2
	Deeper (unfrozen)	<i>too low quality spectrum</i>				
N1	Active	38±2	46±2	12±2	3±1	1±.5
	Permafrost (palsa)	26±2	48±2	20±2	5±1	1±.5
N2	Upper	32±2	48±2	13±2	6±1	1±.5
	Deeper (unfrozen)	46±2	32±2	16±2	5±1	1±.5

The peat soils from Neiden showed much higher contribution of O-alkyl C (even approaching 50% of total signal) than the other soils, except for the deep unfrozen layer of N2, where the intensity of peaks at 75 and 105 ppm and the relative contribution of O-alkyl C were on the order of those of Vorkuta soils. Typical of the Neiden samples was the negligible contribution of ketone/aldehyde C, which accounted for 1% of the total area compared to an average of 5% in the other soils.

A detailed quantitative analysis in terms of lignin and carbohydrate content is not possible due to the complexity of the chemical structure of these components, the strong overlap of the different NMR signals, the generally low signal to noise ratio of the spectra, as well as intrinsic limitations of the method (Preston et al., 1998). Nonetheless, in the well

resolved NMR spectra of the samples from the N1 profile, the distinguishable signals at 147 and 152 ppm, ascribable to carbons bound to methoxy groups in guaiacyl and syringyl lignin moieties and to the hydroxyl group in guaiacyl units, was used to obtain indications on the lignin content. In particular, a higher relative contribution of lignins in the deep sample from N1 with respect to the shallower one was evident (Figure 1). On the other hand, no variation of the relative intensity of lignin signals with depth was observed in the case of the other soil profile from Neiden (N2).

Water extractable C

We quantified both cold and hot-water extractable C, generally considered as easily biodegradable pools (e.g. Dutta et al, 2006). The proportions of water extractable C (C_{WS}) to total SOC were generally higher in active/upper layers of mineral (0.8-2.0% of SOC) than peat soils (0.5-0.6% of SOC; Fig. 2). A substantial increase in C_{WS} with depth was observed in the mineral soils, with the largest increase for the V2 profile. On the contrary, there was no change in C_{WS} with depth in the peat soils. Hot-water extractable C (C_{HW}) ranged between 1.9 and 3.6% of total SOC in the active/upper layers of the mineral soils, and between 3.3 and 4.1% in the peat soils. C_{HW} largely increased with depth in both Adventdalen profiles, while it decreased in the other profiles.

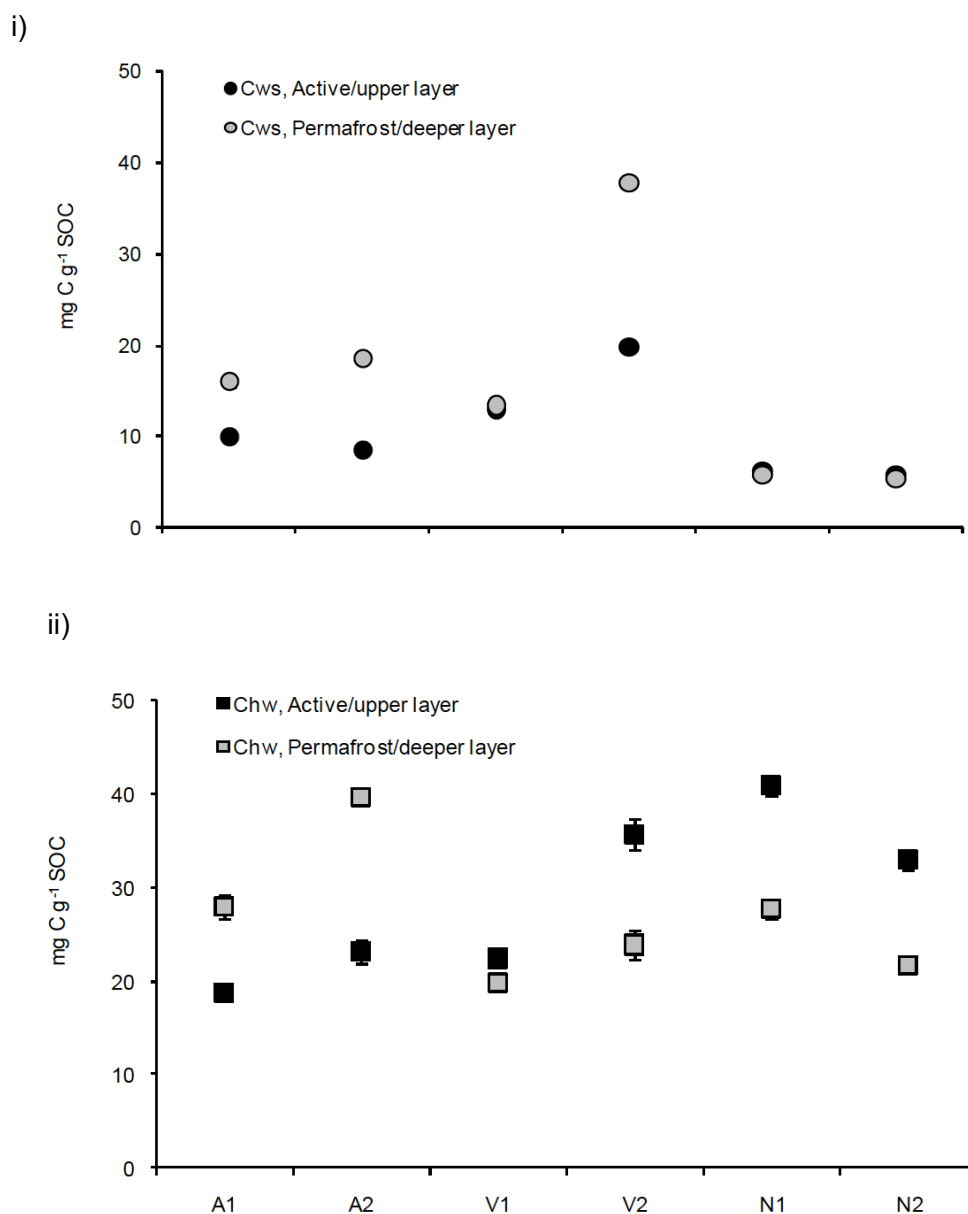


Fig. 2. Concentrations ($\text{mg C g}^{-1} \text{SOC}$; mean \pm st.dev. of analytical triplicates) of *i*) water extractable C (C_{ws}) and *ii*) hot-water extractable C (C_{hw}) in bulk samples from active/upper and permafrost/deeper layers of the studied soil profiles (A for Adventdalen; V for Vorkuta; N for Neiden).

Discussion

Content in easily decomposable compounds: sugars and DOC

Studies have suggested that the SOM contained in permafrost is especially susceptible to biodegradation due to a potentially large proportion of decomposable compounds (Michaelson et al. 2004; Mueller et al. 2015). Our analysis of non-cellulosic sugars does not confirm this hypothesis, as concentrations were not quite high in our permafrost formations, i.e. from 36 to 79 mg C g⁻¹ SOC. By contrast, in temperate soils of Southern Germany, the concentration of non-cellulosic sugars ranged from 139-199 mg C g⁻¹ SOC for forest and agricultural soils (Guggenberger et al. 1994) and from 55 to 220 mg C g⁻¹ SOC in Podzols of the same region (Rumpel et al. 2000). In a recent meta-analysis, Gunina and Kuzyakov (2015) report that non-cellulosic sugars make about 5% of SOC, which is close to our own values. The absence of a substantial pool of readily mineralisable compounds is in agreement with the comparatively low mineralization rates reported for the same samples by Moni et al. (2015).

At the permafrost-affected sites of Adventdalen, Moni et al. (2015) observed a relatively large increase in C mineralisation rates with depth in A2 and a more modest increase in the drier A1. Such higher SOM mineralisation rates in permafrost compared to the above-lying active layer were attributed to an initial mineralisation flush in permafrost, representing less than 1% of total SOC in the sample, suggesting a small contribution of the fast cycling OM pool from the upper layer. In permafrost-affected organic and mineral soils, Schädel et al. (2014) found that this fast cycling SOC represented something less than 5% of total SOC. In both Adventdalen profiles, the flush might be related to the higher concentrations of C_{WS} and C_{HW} in depth (Figure 2). A higher contribution of C_{WS} to SOC in the permafrost than in the active layer was also found by Michaelson and Ping (2003) in soils of Alaska. Wang et al. (2014) showed that freezing-thawing periods favour soil carbon loss by increasing leachates. Actually, Dutta et al. (2006) showed dissolved organic C to be the main C source for heterotrophic respiration during 3-4 month incubation of deep mineral permafrost samples

from north-eastern Siberia. Higher microbial activity in permafrost compared to active layers is not likely. Nonetheless, in boreal forests of Alaska, Waldrop et al. (2010) found that, despite lower microbial abundance and activity in the permafrost compared to the active layer, the higher contribution of labile C to SOC made soil respiration rates (normalised to SOC) higher in the permafrost. Contrary to our findings, in three Siberian permafrost soils, Rodionow et al. (2006) did not observe any consistent trend of the mineralisation rate with depth.

State of decomposition of OM: effect of permafrost

The SOM from all three contrasted ecosystems, ranging from the relatively dry mineral permafrost soils at Adventdalen, the moist cryoturbated mineral soil at Vorkuta, to the permafrost-affected peat soil at Neiden, appeared to have undergone substantial decomposition. This feature of SOM, common among sites, was indicated by the (Ac/Al) ratios of lignins, in the range 0.4-1.1 generally observed for decomposed lignins in clay fractions (Thevenot et al. 2010) and the ratios of alkyl- to O-alkyl-C NMR region generally higher than 1 (except for N1 soil layers and N2 upper layer). The degradation of SOM is generally associated with a decrease of O-alkyl C and an increase of alkyl-C, resulting in an increase of the alkyl/O-alkyl ratio (Kögel-Knabner et al. 1997; Baldock et al. 1997; Grewer et al. 2016).

The decomposition of SOM in permafrost has been suggested to slow down because of low temperatures and anaerobic conditions arising when the active layer is very wet (Kaiser et al. 2007; Rodionow et al. 2007). In general, there was no consistent observation among sites supporting that permafrost layer contain SOM that is less degraded and therefore more susceptible to biodegradation than the overlying active layer. Our results are in line with those of Uhlírova et al. (2007), who found similar SOM biodegradability in permafrost and mineral active layer horizons.

In the dry mineral permafrost soils at the Adventdalen site, there was some indication that SOM is slightly more degraded in the permafrost layer than in the active one. Indeed, the (Ac/Al) ratios of lignins and the alkyl/O-alkyl NMR ratio were higher in the latter (Tables 2 and 4), indicating more oxidized SOM in the permafrost compared to the active layer.

The ratio of lignin C to non-cellulosic sugar C showed that the SOM in the Vorkuta mineral and unfrozen soil (V2) and in both Neiden peat profiles was more decomposed in the deeper layer than in the overlying layer (Table 2). The same could not be said for V1 and the Adventdalen profiles, however. The ratio of lignin C to polysaccharide C increases with increasing decomposition of SOM, but this ratio does not necessarily reflect the actual degradation state of OM if labile sugars are stabilised with subsequent reduced bioavailability. Actually, Amelung et al. (1997) observed decreasing lignin/polysaccharide ratios with depth in mineral soils due to stabilisation of sugars that can be more strongly bound to mineral surfaces than lignins, while Dignac et al. (2005) showed no long-term storage of lignins in soil. Sugars could thus accumulate in older SOM with increasing soil depth, also more than lignins, which are considered chemically more stable (Amelung et al. 1999). Overall, the SOM composition and decomposition state in the studied Arctic soils seem more influenced by site-specific processes, such as cryoturbation, than by general depth and permafrost occurrence.

State of decomposition of SOM: Effects of cryogenic processes

In the moist cryoturbated mineral soils of Vorkuta, the V1 profile displayed little difference in SOM composition, decomposition state and potential mineralisation rate between the active/permafrost layer, which is probably related to cryoturbation causing mixing of the active layer with the permafrost. Soil genesis in the Arctic is strongly affected by cryogenic processes that may lead to the incorporation of surface OM into deeper soil layers (Ugolini et al. 2006; Tarnocai 2009) in ways that are very different from what is observed in soils of temperate regions. Cryoturbation may contribute to the stabilisation of SOM by incorporation into deeper soil layers (Rodionow et al. 2006), where it experiences mineral interactions, lower temperatures and oxygen availability, often more reducing conditions and possible encasement in permafrost (Michaelson et al. 2004). Other processes suggested for the allocation of SOM at depth (e.g. leaching, root exudation, bioturbation) might take place as well (Rumpel and Kögel-Knabner 2011). In the permafrost-free V2 profile, larger contributions

of lignin C (by approx. 50%) and plant-derived sugars with depth were observed, indicating a preferential preservation over degradation of these compounds.

Spatial heterogeneity in permafrost landscapes influencing SOM composition

The soil profiles studied here were sampled in different European Arctic regions and their SOM displayed contrasting chemical compositions. The lignin contents we measured (Table 2) are comparable to those found by Rodionow et al. (2006) in mineral permafrost soils of Northern Siberia. Lignin contents were higher and their S/V ratios were higher at the peat site in Neiden than in Adventdalen and Vorkuta (mineral soils) (Table 2), probably due to different vegetation inputs in the peatland (different plants, see materials section). The SOC normalized lignin and sugar contents in the Adventdalen profiles were low as compared to the profiles from the two other sites, possibly due to a dilution effect by the high content of coal C. Samples from the Vorkuta permafrost affected mineral soils were characterized by relatively low lignin to sugar ratios (Table 2) and a predominance of the alkyl-C region of NMR spectra (Figure 1). Although the variability in SOM composition was higher between sites, substantial differences were also observed within sites.

In the dry mineral permafrost soils at Adventdalen, although the two profiles were quite similar in molecular composition of SOM, there was a slightly smaller contribution of lignin C to SOC in the active layer of the drier A1, which could reflect the less established vegetation (active pluvial plain) and lower C input at this site. The higher input of plant-derived material (more established vegetation) at A2 was confirmed by the lower C6/C5 ratio for this profile, as this ratio decreases with increasing contribution of plant-derived sugars (Amelung et al. 1999). The SOM composition in the Adventdalen profiles, both in the active layer and the permafrost, was clearly affected by condensed aromatic structures, as those present in geogenic coals (Rumpel et al. 2000; Suggate and Dickinson 2004). In spite of the coal fraction, the ¹⁴C calibrated age of the SOM extracted from the active layer of Adventdalen was about 400 years BC (Table 3), suggesting that the non-coal SOM is quite recent.

The Neiden palsa peat soils displayed the least degraded SOM, since the lower contributions of aldehyde/ketone and carboxyl functional groups observed by NMR compared to the other soils and the lower alkyl-C to O-alkyl C ratios suggest the presence of less oxidised OM (Baldock and Preston 1995). Actually, Uhlirva et al. (2007) observed substantial differences in SOM biodegradability between mineral and organic horizons within the active layer.

In the peats of Neiden, the N1 permafrost affected profile showed an increased contribution of lignin C to SOC with depth, which could mean better resistance to degradation of lignin and/or ligno-cellulosic material in the permafrost. Decreasing $(Ac/Al)_{V,S}$ ratios and increasing S/V with depth (Table 2) are consistent with such preservation (Kögel 1986; Thevenot et al. 2010). Also, there was a larger contribution of plant-derived sugars with depth (as indicated by a lower C_6/C_5 , according to Amelung et al. 1999), probably due to a preservation of ligno-cellulosic material and other plant material. In the permafrost affected N1 profile, the contribution of non-cellulosic sugar-C to SOC could not account for the large O-alkyl proportion observed by NMR, indicating a substantial contribution of cellulosic sugars. By contrast, in the permafrost-free peat profile N2, the contributions to SOC of both lignin C and non-cellulosic sugar C decreased with depth. The OM in the unfrozen deeper layer of N2 thus appeared more decomposed than the permafrost layer at N1, which could be an effect of palsa formation, less limiting thermal conditions and/or the dry nature of these palsa mounds (Pengerud et al. 2013). The relatively high $(Ac/Al)_V$ and sugar concentrations in the active layer suggests the occurrence of oxic conditions and/or co-metabolic lignin decomposition. In fact, Amelung et al. (1999) found an increasing degree of lignin side chain oxidation (denoted by higher $(Ac/Al)_V$) with decreasing mean annual temperature, and on this basis advanced that, in colder climates, labile sugars are available to foster co-metabolic lignin oxidation. Nitrogen limitation is another factor known to favour lignin decomposition (Rodionow et al. 2006).

Conclusions

Two mineral permafrost soils (Adventdalen, Svalbard, Norway and Vorkuta, northwest Russia) and a palsa peat soil (Neiden, northern Norway) were investigated in order to understand the composition and potential biodegradability of OM in contrasted high-latitude soils. The nature and degradation state of SOM at these three contrasted Arctic sites seemed to be site-specific while the influence of permafrost was unclear. Our study did not suggest any evidence for less degraded SOM in permafrost layer, which therefore does not appear more susceptible to biodegradation than in the overlying active layer. Even, the chemical composition of SOM at all three sites suggested an advanced stage of decomposition for the OM stored in the permafrost layer. Overall, site-specific processes appeared to influence the SOM composition and decomposition state in the studied Arctic soils more than permafrost occurrence. At the dry mineral permafrost soils of the Adventdalen site, our results suggest that the unexpectedly higher decomposition rate of the permafrost layer compared to the active layer could be due to a higher availability of soluble labile C compounds in the permafrost, possibly added to this layer through leakage of soluble compounds from the active layer. In Vorkuta, SOM composition and decomposition state showed little difference with depth, which is probably due to the mixing of the active layer with the permafrost by cryoturbation, which may contribute to the stabilisation of SOM by incorporation into deeper soil layers. OM appeared better preserved in the peat soil of Neiden than in the permafrost mineral soils. Our results suggest the importance of considering whether permafrost is within organic or mineral soil when attempting to predict vulnerability of SOM to degradation. SOM in peat soil permafrost might have a large potential for further SOM mineralisation with warming and permafrost thaw. Given the large C stocks in permafrost of northern peatlands, and their expected increased degradation induced by the ongoing climate change, our findings further support the need to take into careful account the spatial distribution of permafrost landforms in peatlands in regional estimates of C fluxes to the atmosphere.

Acknowledgements

This study was conducted as a part of the research project “Organic matter in permafrost: molecular composition and associated response to increasing temperature (PERMASOM)” (Norwegian Research Council (NFR) project no. 184754/S30). Additional funding was also provided by the European Science Foundation (ESF) activity entitled “Natural molecular structures as drivers and tracers of terrestrial C fluxes” (MOLTER Network). Valerie Pouteau (Ecosys, France) is highly acknowledged for technical assistance with molecular analyses. We would also like to thank those who facilitated the soil sampling at the three different sites: Hanne H. Christiansen, Paul Eric Aspholm, Tore Sveistrup, Galina Mazhitova and Alexander Pastukhov. We wish to thank two anonymous reviewers for their useful comments, which helped improving the manuscript.

References

- Amelung W, Zech W (1996) Organic species in ped surface and core fractions along a climosequence in the prairie, North America. *Geoderma* 74:193–206. doi:10.1016/S0016-7061(96)00063-8
- Amelung W, Flach KW, Zech W (1997) Climatic effects on soil organic matter composition in the great plains. *Soil Science Society of America Journal* 61:115–123. doi:10.2136/sssaj1997.03615995006100010018x
- Amelung W, Flach KW, Zech W (1999) Neutral and acidic sugars in particle-size fractions as influenced by climate. *Soil Sci Soc Am J* 63:865–873. doi:10.2136/sssaj1999.634865x
- Aune B (1993) Temperature normals for the period 1961-1990. Oslo, Norway: DNMI - The Norwegian Meteorological Institute.
- Bahri H, Dignac M-F, Rumpel C, Rasse DP, Chenu C, Mariotti A (2006) Lignin turnover kinetics in an agricultural soil is monomer specific. *Soil Biol Biochem* 38:1977–1988. doi:10.1016/j.soilbio.2006.01.003

- Baldock JA, Preston CM (1995) Chemistry of carbon decomposition processes in forests as revealed by solid-state carbon-13 nuclear magnetic resonance. In: Carbon forms and functions in forest soils. SSSA, Madison, Wisconsin, USA, pp. 89–117.
- Baldock JA, Oades JM, Nelson PN, Skene TM, Golchin A, Clarke P (1997) Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. *Aust J Soil Res* 35:1061–1083. doi:10.1071/S97004
- Berg B (2000) Litter decomposition and organic matter turnover in northern forest soils. *Forest Ecology and Management* 133:13–22. doi:10.1016/S0378-1127(99)00294-7
- Bryant ID (1982) Loess deposits in lower Adventdalen, Spitsbergen. *Polar Res* 1982:93–103. doi:10.1111/j.1751-8369.1982.tb00479.x
- Christiansen HH (2005) Thermal regime of ice-wedge cracking in Adventdalen, Svalbard. *Permafrost and Periglacial Processes* 16:87–98. doi:10.1002/ppp.523
- Dignac M-F, Bahri H, Rumpel C, Rasse DP, Bardoux G, Balesdent J, Girardin C, Chenu C, Mariotti A (2005) Carbon-13 natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France). *Geoderma* 128:3–17. doi:10.1016/j.geoderma.2004.12.022
- Dutta K, Schuur EAG, Neff JC, Zimov SA (2006) Potential carbon release from permafrost soils of Northeastern Siberia. *Glob Chang Biol* 12:2336–2351. doi:10.1111/j.1365-2486.2006.01259.x
- Eder E, Spielvogel S, Kolbl A, Albert G, Kögel-Knabner I (2010) Analysis of hydrolysable neutral sugars in mineral soils: Improvement of alditol acetylation for gas chromatographic separation and measurement. *Org Geochem* 41:580–585. doi:10.1016/j.orggeochem.2010.02.009
- Førland EJ (1993) Precipitation normals for the period 1961-1990. Oslo, Norway: DNMI - The Norwegian Meteorological Institute.
- Fronzek S, Luoto M, Carter TR (2006) Potential effect of climate change on the distribution of palsa mires in subarctic Fennoscandia. *Clim Res* 32:1–12. doi:10.3354/cr032001
- Ghani A, Dexter M, Perrott KW (2003) Hot-water extractable carbon in soils: a sensitive

- measurement for determining impacts of fertilisation, grazing and cultivation. *Soil Biol Biochem* 35:1231–1243. doi:10.1016/S0038-0717(03)00186-X
- Grewer DM, Lafrenière MJ, Lamoureux SF, Simpson MJ (2016) Redistribution of soil organic matter by permafrost disturbance in the Canadian High Arctic. *Biogeochem* 128: 397–415. doi:10.1007/s10533-016-0215-7
- Guggenberger G, Zech W (1994) Composition and dynamics of dissolved carbohydrates and lignin-degradation products in 2 coniferous forests, NE Bavaria, Germany. *Soil Biol Biochem* 26:19–27. doi:10.1016/0038-0717(94)90191-0
- Guggenberger G, Christensen BT, Zech W (1994) Land-use effects on the composition of organic matter in particle-size separates of soil: I. Lignin and carbohydrate signature. *Eur J Soil Sci* 45(4):449–458. doi:10.1111/j.1365-2389.1994.tb00530.x
- Gunina A, Kuzyakov Y (2015) Sugars in soil and sweets for microorganisms: Review of origin, content, composition and fate. *Soil Biol Biochem* 90:87–100. doi:10.1016/j.soilbio.2015.07.021
- Hartley IP, Hopkins DW, Garnett MH, Sommerkorn M, Wookey PA (2008) Soil microbial respiration in arctic soil does not acclimate to temperature. *Ecol Lett* 11:1092–1100. doi:10.1111/j.1461-0248.2008.01223.x
- Hedges JI, Ertel JR (1982) Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Anal Chem* 54:174–178. doi:10.1021/ac00239a007
- Hobbie SE, Schimel JP, Trumbore SE, Randerson JR (2000) Controls over carbon storage and turnover in high-latitude soils. *Glob Chang Biol* 6:196–210. doi:10.1046/j.1365-2486.2000.06021.x
- Hofgaard A (2003) Effects of climate change on the distribution and development of peatlands: background and suggestions for a national monitoring project, NINA Project Report 21. Trondheim, Norway: Norwegian Institute for Nature Research (NINA). 31 p.
- Hugelius G, Strauss J, Zubrzycki S, Harden JW, Schuur EAG, Ping CL, Schirmermeister L, Grosse G, Michaelson GJ, Koven CD, O'Donnell JA, Elberling B, Mishra U, Camill P, Yu Z, Palmtag J, Kuhry P (2014) Estimated stocks of circumpolar permafrost carbon with

- quantified uncertainty ranges and identified data gaps. *Biogeosciences* 11:6573–6593. doi:10.5194/bg-11-6573-2014
- IPCC (2014) Climate change 2014: synthesis report. Contribution of working groups I, II and III to the fifth assessment report of the intergovernmental panel on climate change [Core Writing Team, RK Pachauri and LA Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.
- Jobbágy EG, Jackson RB (2000) The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecol Appl* 10:423–436. doi:10.1890/1051-0761(2000)010[0423:TVDOSO]2.0.CO;2
- Kaiser C, Meyer H, Biasi C, Rusalimova O, Barsukov P, Richter A (2007) Conservation of soil organic matter through cryoturbation in arctic soils in Siberia. *J Geophys Res* 112:G02017. doi:10.1029/2006JG000258
- Kögel-Knabner I (1997) ^{13}C and ^{15}N NMR spectroscopy as a tool in soil organic matter studies. *Geoderma* 80:243–270. doi:10.1016/S0016-7061(97)00055-4
- Kögel-Knabner I (2000) Analytical approaches for characterizing soil organic matter. *Org Geochem* 31:609–625. doi:10.1016/S0146-6380(00)00042-5
- Kögel I, Bochter R (1985) Characterization of lignin in forest humus layers by high-performance liquid-chromatography of cupric oxide oxidation-products. *Soil Biol Biochem* 17:637–640. doi:10.1016/0038-0717(85)90040-9
- Kögel I (1986) Estimation and decomposition pattern of the lignin component in forest humus layers. *Soil Biol Biochem* 18:589–594. doi:10.1016/0038-0717(86)90080-5
- Luo D, Wu Q, Jin H, Marchenko SS, Lü L, Gao S (2016) Recent changes in the active layer thickness across the northern hemisphere. *Environmental Earth Sciences* 75:Article number 555. doi:10.1007/s12665-015-5229-2
- Major H, Nagy J (1972) Geology of the Adventdalen map area. *Norsk Polarinstitut Skrifter* 138, 58 pp.
- Mangerud J, Bolstad M, Elgersma A, Helliksen D, Landvik JY, Lonne I, Lycke AK, Salvigsen O, Sandahl T, Svendsen JI (1992) The last glacial maximum on Spitsbergen, Svalbard. *Quat Res* 38:1–31. doi:10.1016/0033-5894(92)90027-G

- Mazhitova G, Malkova G, Chestnykh O, Zamolodchikov D (2004) Active-layer spatial and temporal variability at European Russian circumpolar-active-layer-monitoring (CALM) sites. *Permafrost and Periglacial Processes* 15:123–139. doi:10.1002/ppp.484
- McGuire AD, Macdonald RW, Schuur EAG, Harden JW, Kuhry P, Hayes DJ, Christensen TR, Heimann M (2010) The carbon budget of the northern cryosphere region. *Current Opinion in Environmental Sustainability* 2:231–236. doi:10.1016/j.cosust.2010.05.003
- Michaelson GJ, Ping CL (2003) Soil organic carbon and CO₂ respiration at subzero temperature in soils of Arctic Alaska. *J Geophys Res: Atmospheres* 108:2156–2202. doi:10.1029/2001JD000920
- Michaelson GJ, Dai XY, Ping CL (2004) Organic matter and bioactivity in cryosols of arctic Alaska, In: Kimble JM (Ed.) *Cryosols. Permafrost-Affected Soils*, Springer-Verlag, New-York, pp. 463–477.
- Moen A (1999) *Atlas of Norway: vegetation*. Norwegian Mapping Authorities, Hønefoss, Norway. 200 pp. ISBN 82-7945-000-9.
- Moni C, Lerch TZ, Knoth de Zarruk K, Strand LT, Forte C, Certini G, Rasse DP (2015) Temperature response of soil organic matter mineralisation in arctic soil profiles. *Soil Biol Biochem* 88:236–246. doi:10.1016/j.soilbio.2015.05.024
- Mueller CW, Rethemeyer J, Kao-Kniffin J, Löppmann S, Hinkel KM, G Bockheim J (2015) Large amounts of labile organic carbon in permafrost soils of northern Alaska. *Glob Chang Biol* 21:2804–2817. doi:10.1111/gcb.12876
- Nadelhoffer KJ, Giblin AE, Shaver GR, Laundre JA (1991) Effects of temperature and substrate quality on element mineralization in six arctic soils. *Ecology* 72:242–253. doi:10.2307/1938918
- Nocentini C, Certini G, Knicker H, Francioso O, Rumpel C (2010) Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. *Org Geochem* 41:682–689. doi:10.1016/j.orggeochem.2010.03.010
- Oades JM (1984) Soil organic-matter and structural stability: Mechanisms and implications for management. *Plant Soil* 76:319–337. doi:10.1007/BF02205590

- Paré MC, Bedard-Haughn A (2013) Soil organic matter quality influences mineralization and GHG emissions in cryosols: a field-based study of sub- to high Arctic. *Glob Chang Biol* 19:1126–1140. doi:10.1111/gcb.12125
- Pengerud A, Cecillon L, Johnsen LK, Rasse DP, Strand LT (2013) Permafrost distribution drives soil organic matter stability in a subarctic tundra peatland. *Ecosystems* 16:934–947. doi:10.1007/s10021-013-9652-5
- Ping CL, Jastrow JD, Jorgenson MT, Michaelson GJ, Shur YL (2015) Permafrost soils and carbon cycling. *Soil* 1:147–171. doi:10.5194/soil-1-147-2015
- Preston C.M., Schmidt MWI (2006) Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3:397–420. doi:10.5194/bg-3-397-2006
- Preston CM, Trofymow JA, Niu J, Fyfe CA (1998) ^{13}C CPMAS-NMR spectroscopy and chemical analysis of coarse woody debris in coastal forests of Vancouver Island. *For Ecol Manage* 111:51–68. doi:10.1016/S0378-1127(98)00307-7
- Rasse DP, Dignac M-F, Bahri H, Rumpel C, Mariotti A, Chenu C (2006) Lignin turnover in an agricultural field: from plant residues to soil-protected fractions. *Eur J Soil Sci* 57:530–538. doi:10.1111/j.1365-2389.2006.00806.x
- Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Bertrand CJH, Blackwell PG, Buck CE, Burr GS, Cutler KB, Damon PE, Edwards RL, Fairbanks RG, Friedrich M, Guilderson TP, Hogg AG, Hughen KA, Kromer B, McCormac G, Manning S, Ramsey CB, Reimer RW, Remmele S, Southon JR, Stuiver M, Talamo S, Taylor FW, van der Plicht J, Weyhenmeyer CE (2004) IntCal04 terrestrial radiocarbon age calibration, 0-26 cal kyr BP. *Radiocarbon* 46:1029–1058. doi:10.1017/S0033822200032999
- Rodionow A, Flessa H, Kazansky O, Guggenberger G (2006) Organic matter composition and potential trace gas production of permafrost soils in the forest tundra in northern Siberia. *Geoderma* 135:49–62. doi:10.1016/j.geoderma.2005.10.008
- Rodionow A, Flessa H, Grabe M, Kazansky OA, Shibistova O, Guggenberger G (2007) Organic carbon and total nitrogen variability in permafrost-affected soils in a forest tundra

- ecotone. *Eur J Soil Sci* 58:1260–1272. doi:10.1111/j.1365-2389.2007.00919.x
- Rumpel C, Skjemstad JO, Knicker H, Kogel-Knabner I, Huttli RF (2000) Techniques for the differentiation of carbon types present in lignite-rich mine soils. *Org Geochem* 31:543–551. doi:10.1016/S0146-6380(00)00026-7
- Rumpel C, Dignac M-F (2006) Chromatographic analysis of monosaccharides in a forest soil profile: Analysis by gas chromatography after trifluoroacetic acid hydrolysis and reduction-acetylation. *Soil Biol Biochem* 38:1478–1481. doi:10.1016/j.soilbio.2005.09.017
- Rumpel C, Kogel-Knabner I (2011) Deep soil organic matter—a key but poorly understood component of terrestrial C cycle. *Plant Soil* 338:143–158. doi:10.1007/s11104-010-0391-5
- Schädel C, Schuur EAG, Bracho R, Elberling B, Knoblauch C, Lee H, Luo Y, Shaver GR, Turetsky MR (2014) Circumpolar assessment of permafrost C quality and its vulnerability over time using long-term incubation data. *Glob Chang Biol* 20:641–652. doi:10.1111/gcb.12417
- Schmidt MWI, Torn MS, Abiven S, Dittmar T, Guggenberg G, Janssens IA, Kleber M, Kögel-Knabner I, Lehmann J, Manning M, Nannipieri P, Rasse DP, Weiner S, Trumbore SE (2011) Persistence of soil organic matter as an ecosystem property. *Nature* 478:49–56. doi:10.1038/nature10386
- Schuur EAG, Bockheim J, Canadell JG, Euskirchen E, Field CB, Goryachkin SV, Hagemann S, Kuhry P, Lafleur PM, Lee H, Mazhitova G, Nelson FE, Rinke A, Romanovsky VE, Shiklomanov N, Tarnocai C, Venevsky S, Vogel JG, Zimov SA (2008) Vulnerability of permafrost carbon to climate change: Implications for the global carbon cycle. *Bioscience* 58:701–714. doi:10.1641/B580807
- Seppala M (1986) The origin of palsas. *Geografiska Annaler, Series A* 68:141–147.
- Shaver GR, Giblin AE, Nadelhoffer KJ, Thieler KK, Downs MR, Laundre JA, Rastetter EB (2006) Carbon turnover in Alaskan tundra soils: effects of organic matter quality, temperature, moisture and fertilizer. *J Ecol* 94:740–753. doi:10.1111/j.1365-

2745.2006.01139.x

Skjemstad JO, Clarke P, Taylor JA, Oades JM, Newman RH (1994) The removal of magnetic-materials from surface soils - a solid state C-13 CP/MAS NMR-study. *Aust J Soil Res* 32:1215–1229. doi:10.1071/SR9941215

Skjemstad JO, Taylor JA, Smernik RJ (1999) Estimation of charcoal (char) in soils. *Communications in Soil Science and Plant Analysis* 30:2283–2298. doi:10.1080/00103629909370372

Slota PJ et al. (1987). Preparation of small samples for C-14 accelerator targets by catalytic reduction of CO. *Radiocarbon* 29(2): 303-306.

Smernik RJ, Eckmeier E, Schmidt MWI (2008) Comparison of solid-state C-13 NMR spectra of soil organic matter from an experimental burning site acquired at two field strengths. *Aust J Soil Res* 46:122–127. doi:10.1071/SR0712

Soil Survey Staff (2006) *Keys to soil taxonomy*, Tenth edition. United States Department of Agriculture, Natural Resources Conservation Service. U.S. Government Printing Office, Washington, D.C.

Sparling G, Vojvodic-Vukovic M, Schipper LA (1998) Hot-water-soluble C as a simple measure of labile soil organic matter: the relationship with microbial biomass C. *Soil Biol Biochem* 30:1469–1472. doi:10.1016/S0038-0717(98)00040-6

Spielvogel S, Prietzel J, Kögel-Knabner I (2007) Changes of lignin phenols and neutral sugars in different soil types of a high-elevation forest ecosystem 25 years after forest dieback. *Soil Biol Biochem* 39:655–668. doi:10.1016/j.soilbio.2006.09.018

Stuiver M, Polach HA (1977). Reporting of C-14 data – discussion. *Radiocarbon* 19(3): 355-363.

Stuiver M, Reimer PJ (1987) *User's guide to the programs CALIB & DISPLAY 2.1*, Quaternary Isotope Lab, University of Washington.

Suggate RP, Dickinson WW (2004) Carbon NMR of coals: the effects of coal type and rank. *International Journal of Coal Geology* 57:1–22. doi:10.1016/S0166-5162(03)00116-2

Svendsen JI, Alexanderson H, Astakhov VI, Demidov I, Dowdeswell JA, Funder S, Gataullin

- V, Henriksen M, Hjort C, Houmark-Nielsen M, Hubberten HW, Ingolfsson O, Jakobsson M, Kjaer KH, Larsen E, Lokrantz H, Lunkka JP, Lysa A, Mangerud J, Matiouchkov A, Murray A, Moller P, Niessen, F, Nikolskaya O, Polyak L, Saarnisto M, Siegert C, Siegert MJ, Spielhagen RF, Stein R (2004) Late quaternary ice sheet history of northern Eurasia. *Quaternary Science Reviews* 23:1229–1271. doi:10.1016/j.quascirev.2003.12.008
- Tarnocai C (2009) Arctic permafrost soils, In: Margesin, R. (Ed.) *Soil Biology*, vol. 16, *Permafrost Soils*, Springer-Verlag, Berlin Heidelberg, pp. 3–16.
- Tesi T, Muschitiello F, Smittenberg RH, Jakobsson M, Vonk JE, Hill P, Andersson A, Kirchner N, Noormets R, Dudarev O, Semiletov I, Gustafsson Ö (2016) Massive remobilization of permafrost carbon during post-glacial warming. *Nat Commun* 7:13653. doi:10.1038/ncomms13653
- Thevenot M, Dignac M-F, Rumpel C (2010) Fate of lignins in soils: A review. *Soil Biol Biochem* 42:1200–1211. doi:10.1016/j.soilbio.2010.03.017
- Turetsky MR, Wieder RK, Vitt DH (2002) Boreal peatland C fluxes under varying permafrost regimes. *Soil Biol Biochem* 34:907–912. doi:10.1016/S0038-0717(02)00022-6
- Ugolini FC, Corti G, Certini G (2006) Pedogenesis in the sorted patterned ground of Devon plateau, Devon Island, Nunavut, Canada. *Geoderma* 136:87–106. doi:10.1016/j.geoderma.2006.03.030
- Uhlířova E, Santrůcková H, Davidov SP (2007) Quality and potential biodegradability of soil organic matter preserved in permafrost of Siberian tussock tundra. *Soil Biol Biochem* 39:1978–1989. doi:10.1016/j.soilbio.2007.02.018
- Updegraff K, Pastor J, Bridgham SD, Johnston CA (1995) Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. *Ecological Applications* 5:151–163. doi:10.2307/1942060
- von Lutzow M, Kögel-Knabner I, Ekschmittb K, Flessa H, Guggenberger G, Matzner E, Marschner B (2007) SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms. *Soil Biol Biochem* 39:2183–2207. doi:10.1016/j.soilbio.2007.03.007

- Waldrop MP, Wickland KP, White R, Berhe AA, Harden JW, Romanovsky VE (2010) Molecular investigations into a globally important carbon pool: permafrost-protected carbon in Alaskan soils. *Glob Chang Biol* 16:2543–2554. doi:10.1111/j.1365-2486.2009.02141.x
- Wang J, Song C, Hou A, Wang L (2014) CO₂ emissions from soils of different depths of a permafrost peatland, Northeast China: response to simulated freezing–thawing cycles. *J Plant Nut Soil Sci* 177:524–531. doi:10.1002/jpln.201300309
- Webster EA, Chudek JA, Hopkins DW (2000) Carbon transformations during decomposition of different components of plant leaves in soil. *Soil Biol Biochem* 32:301–314. doi:10.1016/S0038-0717(99)00153-4