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1 Contribution of peatland permafrost to dissolved 2 organic matter along a thaw gradient in North 3 Siberia

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15 ABSTRACT

16 Permafrost peatlands are important carbon stocks currently experiencing rapid evolution
17 after permafrost thaw. Following thaw, dissolved organic matter (DOM) is a potentially
18 important pathway for the release of permafrost carbon. This study investigates the origin and
19 composition of DOM across sites at different stages of thaw in a discontinuous permafrost area
20 of North Siberia. We determine the optical properties, molecular composition, stable ($\delta^{13}\text{C}$) and
21 radiocarbon (^{14}C) content of DOM. Early stages of thaw are characterized by high DOC
22 concentrations, high aromaticity, contribution of vegetation-derived DOM, and a high
23 contribution of permafrost carbon. In contrast, in later stages, the microbial contribution to
24 DOM increases, and only modern carbon is detected. This work links DOM composition with
25 its radiocarbon content in permafrost peatlands. It shows that DOM originating from previously

26 frozen permafrost peatland is highly aromatic and previously processed. It highlights the
27 variability of post-thaw carbon dynamics in boreal and arctic ecosystems.

28 KEYWORDS: Permafrost peatlands, Thermokarst Bogs, Dissolved Organic Matter,
29 Radiocarbon, Optical properties of DOM, Molecular composition of DOM, Siberia

30 **I. Introduction**

31 In warming boreal and arctic regions, permafrost thaw is expected to affect ecosystems
32 storing half of the global soil organic carbon stock¹. Permafrost thaw, a deepening of the active
33 layer or complete disappearance of frozen layers, exposes this carbon stock to microbial
34 decomposition. The potential release of this large sequestered organic carbon stock into the
35 active carbon cycle as a result of warming could be a significant positive feedback to climate
36 change²⁻⁴. Dissolved organic matter (DOM) is the most dynamic but least characterized carbon
37 pool in boreal and arctic terrestrial ecosystems, and is a potentially important conduit for the
38 release of permafrost carbon following thaw. Estimates of DOM transfer from large Arctic
39 Rivers to the Arctic Ocean range from 25-36TgC yr⁻¹⁵. However, the overall transfer from
40 terrestrial ecosystems to surface water is higher, as a fraction of DOM is mineralized or buried
41 in sediments before reaching the Arctic Ocean⁶. These processes are highly dependent on DOM
42 composition. Therefore, investigating the composition, carbon origin, and potential lability of
43 DOM is crucial to understand the strength of potential feedbacks to climate change as a result
44 of permafrost thaw⁷. In landscapes dominated by permafrost degradation, radiocarbon (¹⁴C)
45 measurements of the carbon released as DOM provide a powerful tool to identify shifts in
46 carbon origin. In particular, they can help identify old permafrost-derived carbon, or carbon
47 which has been more recently fixed from the atmosphere by vegetation, with very different
48 implications for feedback to climate.

49 To date, most studies of radiocarbon content of DOM in the boreal and arctic areas have
50 focused on rivers and streams^{5,8,9}. At the outlet of large Arctic Rivers, the majority of organic
51 carbon exported during the spring flood is young carbon. Older carbon, which may reflect
52 permafrost thaw and/or deeper water flows is exported during low flow periods^{5,10}, and also
53 found upstream in the fluvial network⁶. Despite the important role of headwaters, little research
54 has been done in upstream catchments to characterize DOM composition and origin, or to track
55 permafrost carbon in DOM before its signal disappears as a result of dilution, photodegradation
56 and/or microbial consumption¹¹.

57 Permafrost peatlands are disproportionately important landscapes to study permafrost
58 degradation, as they show the highest carbon density of boreal and arctic soil, and store at least
59 one third of the permafrost soil organic carbon stocks^{1,12}. Furthermore, their degradation as a
60 result of permafrost thaw has increased in recent decades^{13,14}. Following permafrost thaw,
61 ground subsidence and changes in hydrological pathways often lead to the formation of small
62 thermokarst bogs nested in permafrost peatland mounds (palsa), then to larger bogs, and
63 ultimately to inundated fens¹⁵. The composition of DOM evolves with this ecosystem transition,
64 reflecting the increased contribution of new vegetation¹⁶, microbial activity^{17,18}, and the
65 transition from bog to fen¹⁹.

66 Although carbon-rich permafrost peatlands account for 19% of permafrost area^{15,20}, the
67 links between DOM composition, lability and origin have not been established in this context.
68 Permafrost soils have a wide variety of formation histories and geologies²¹, with important
69 implications for organic matter composition and degree of processing prior to thaw, and
70 potential lability after thaw^{20,22}. For example, in studies of ice-rich Yedoma permafrost, ancient
71 organic matter locked in permafrost contained high levels of small molecular weight organic
72 acids, characterized by a low aromaticity, and was highly labile. It was therefore rapidly
73 consumed by microorganisms and released to the atmosphere after thaw^{11,23}. The link between

74 permafrost-derived carbon in DOM and its composition remains underexplored in peatland
75 permafrost context.

76 In a discontinuous permafrost area in Northern Siberia, where permafrost peatland
77 degradation has been recently documented, we investigate the evolution of DOM using a
78 combination of analytical techniques from the bulk (isotopic and optical) to molecular scale, in
79 combination with radiocarbon measurements, which are indicative of the age and origin of
80 DOM, across thermokarst bogs and lakes of different sizes and degrees of thaw. The objectives
81 of this study are (1) to characterize DOM composition in a thawing permafrost landscape and
82 (2) to evaluate the influence of permafrost carbon on the composition of DOM.

83 II. Material & Methods

84 1. Study site

85 The study area is located near Igarka (Figure 1a), on the eastern bank of the Yenisei
86 River (67°27'11''N, 86°32'07''E), in a region of discontinuous permafrost. The mean annual
87 air temperature from 1980-2010 is -7.7 ± 1.1 °C and the mean annual precipitation is 632 ± 86
88 mm, including 320 ± 50 mm in the form of snow²⁴. Sampling focused on the Graviyka catchment
89 (Figure 1b). The Graviyka River, with watershed of 320 km², is one of the northernmost
90 tributaries of the Yenisei River. It is mainly covered by forest, dominated by larch (*Larix*
91 *siberica*), birch (*Betula pendula*), and Siberian pine (*Pinus siberica*), and palsa landscapes
92 (frozen peat mounds). The palsa landscapes are dominated by moss, lichens and small birch.
93 Degraded areas affected by permafrost thaw are characterized by depression (thermokarsts),
94 where thermokarst bogs dominated by *Sphagnum* spp. and *Eriophorum* spp develop. The land
95 cover is an indicator of the permafrost status and the depth of the active layer (seasonally thawed
96 soil layer). Forested areas tend to have a deep active layer thickness associated with Pleistocene
97 permafrost, while palsa dominated landscapes are indicative of the presence of Holocene
98 permafrost, with a shallower active layer depth. At our study site, peatland accumulation began

99 during the mid-Holocene ^{25,26}, likely between 4 to 5 kyr BP. North of Igarka, permafrost
100 aggradation and palsa formation occurred between 3.5 and 2.5 kyr during a period of a period
101 of relatively cooler temperatures ²⁷. At our site, radiocarbon data acquired close to the active
102 layer depth are consistent with these findings, and suggest that permafrost aggradation may
103 have begun around 2.8 ka (Figure SI.1). Permafrost degradation, characterized by the increase
104 of the active layer and in the region surrounding Igarka has been observed for the last 30 years
105 ²⁴.

106 **2. Sample collection**

107 In the thawing palsa areas surrounding Igarka, we sampled sites at different stages of
108 thaw in July 2015 and July 2016, including thermokarst bogs of various sizes, a fen, and
109 thermokarst lakes. Thermokarst bogs form in depressions where palsa thaws and collapses. At
110 the beginning of thaw process, small thermokarst bogs form, perched on palsa mounds. As the
111 thaw process progresses, the size of thermokarst bogs increases. A continuation of the thaw
112 process leads to the formation of fens ^{15,28,29}. In addition to the size of thermokarst features, the
113 different thaw stages are characterized by differences in dominant vegetation, with a shift from
114 plant communities which prefer dry growing conditions to those which prefer wet growing
115 conditions ^{15,16,29}.

116 These selected sites were not intended to represent a time-since-thaw chronosequence.
117 Instead, they were selected to represent a range of thaw-affected landscapes present in the
118 region, from those least affect by thaw (small bogs), to larger thermokarst features which do
119 not retain permafrost (fen and lakes). Our sampling follows the classification defined by
120 Hodgkins et al. (2016) ¹⁶, with adaptations to our site. We sampled “small bogs”, thermokarst
121 bogs perched on palsa, with a size < 40 m² (corresponding to “recently thawed palsa”). We also
122 sampled “large bogs”, which were >100 m² and adjacent to small amounts of remaining palsa
123 (corresponding to “thawing Sphagnum-dominated bogs”). The surface area of the sampled bogs

124 was determined based on field measurements for the smallest bogs, and using Google Earth for
125 the larger bogs. A large (area $\sim 3000 \text{ m}^2$) thermokarst bog developed in a mineral soil context
126 was also sampled as a reference free from permafrost peatland carbon (referred to as MB or
127 “mineral-context bog”). All the sampled bogs are colonized by *Sphagnum*, and the large bogs
128 included *Eriophorum*. We also sampled a fen, in which both *Sphagnum* and *Carex* are found.
129 In all thermokarst bogs, porewater profiles were collected in the active layer and to maximum
130 depth of 2 m using narrow piezometers (0.64 cm diameter) connected to a hand pump.
131 Following in situ pH and conductivity measurements, samples were filtered using pre-
132 combusted GF/F filters and stored in cleaned (acid washed and combusted) amber glass bottles
133 for DOC, $\delta^{13}\text{C}$ -DOC, ^{14}C -DOM, molecular and optical properties of DOM.

134 **3. Sample analyses and calculations**

135 **3.1 DOC concentrations**

136 Non-purgeable organic carbon (NPOC, referred to hereafter as DOC) was analyzed on
137 filtered (GF/F Whatman) samples after acidification to pH 2 (HCl) with a TOC-V CSH analyzer
138 (Shimadzu, Japan), with a quantification limit of 1 mg L^{-1} . Certified materials (ion 915 and ion
139 96.4, Environment and Climate Change Canada, Canada) were included in the analytical loop
140 and recovery was $>95\%$ of the certified value.

141 **3.2 Optical properties of DOM**

142 The UV absorption spectra from 240 to 700 nm of porewater were measured with a
143 spectrophotometer (Secoman UV light XT5), in a 1 cm quartz cell. The baseline was determined
144 with ultra-pure water. The Specific UV Absorbance at 254 nm (SUVA_{254} , $\text{L mg}^{-1} \text{ m}^{-1}$) was
145 calculated as follows: $\text{SUVA} = A_{254}/b * [\text{DOC}]$ ($\text{L mg}^{-1} \text{ m}^{-1}$), where A_{254} is the sample
146 absorbance at 254 nm (non-dimensional), b is the optical path length (m) and DOC is in mg L^{-1} .
147 ¹. SUVA is a proxy for DOM aromaticity³⁰. Fluorescence measurements were performed using

148 a spectrofluorometer (Synergy MX, Biotek). The emission spectrum was recorded for a 370 nm
149 excitation wavelength. The fluorescence Index (FI) was determined for a 370 nm excitation
150 wavelength, as the ratio of the 470 nm emission and 520 nm emission, as defined by McKnight
151 et al. (2001)³¹ and Jaffé et al (2008)³². Potential additional absorbance related to Fe content was
152 checked on a few samples following the procedure described by Poulin et al³³. The additional
153 absorbance $1.4 \pm 1.6\%$ across all samples where Fe was measured, and was therefore neglected.

154 **3.3 Stable isotopes analysis**

155 The $\delta^{13}\text{C}$ -DOC was analyzed at the UC Davis stable isotope facility. The analyses were
156 performed using a O.I. Analytical Model 1030 TOC Analyzer (Xylem Analytics, College
157 Station, TX) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd.,
158 Cheshire, UK) utilizing a GD-100 Gas Trap Interface (Graden Instruments). Reference
159 materials included IAEA-600, USGS-40, USGS-41, Elemental Microanalysis (EM) reference
160 materials, and NIST 8559, 8560, and 8561. The replicates analysis showed an average of 0.25
161 variation, i.e 0.16 ‰.

162 **3.4 Radiocarbon analysis and calculation of permafrost carbon contribution**

163 The radiocarbon content of DOM and soil organic matter (SOM) was measured on selected
164 freeze-dried samples at the LSCE laboratory (GifA and ECHO) on the MICADAS compact
165 AMS system³⁴. From 2 to 4 samples per profile were analyzed. DOM samples were analyzed
166 through the EA-GIS coupling³⁵. For SOM values, bulk samples were analyzed. For DOM, the
167 freeze-dried powder was analyzed. The $\delta^{13}\text{C}$ value of the freeze-dried powder was compared to
168 the direct analysis of $\delta^{13}\text{C}$ -DOM on the liquid sample after acidification, to evaluate the need
169 for removal of inorganic carbon. Typically, 0.5 mg of sample material was prepared in a tin
170 capsule, and acidified with 3 μL of HCl 1M. All samples were duplicated, and reproducibility
171 of duplicates was checked (Chi2 test). Blanks and standard material (C7 and OXA2 oxalic acid)

172 were included in the analysis sequence. All ^{14}C results were corrected for isotopic fractionation
173 according to the conventions of Stuiver et al (1977)³⁶ and reported as $F^{14}\text{C}$ following the
174 recommendation of Reimer et al. (2004)³⁷.

175 In order to assess the contribution of permafrost carbon to individual DOM samples, a two
176 component mixing model (permafrost and atmospheric pools) was applied to the bulk $F^{14}\text{C}$
177 content. The permafrost pool was determined based on 3 samples from deep frozen palsa (3 to
178 4 meters, SI), with an average radiocarbon content of $F^{14}\text{C} = 0.608 \pm 0.022$ (4000 \pm 290 BP). For
179 the atmospheric pool, 36 independent calculations were performed to represent different
180 possible atmospheric end members, as the radiocarbon content in the atmosphere has changed
181 slightly. Plant material derived from recent photosynthesis will therefore likely represent a mix
182 of these values, including vegetation grown over a range of recent years. Our calculations used
183 atmospheric end members which ranged from the average atmospheric signature from 1980 to
184 2015 ($F^{14}\text{C}=1.12$; represents a mix of vegetation inputs over the time period) to a pure 2015
185 signal ($F^{14}\text{C}= 1.02$; input from the most recent 2015 vegetation only) ³⁸ to account for the
186 possibility of a mix of recent inputs. The proportion of permafrost carbon calculated as follows:

$$187 \quad \alpha_{perm} = \frac{(F^{14}\text{C}_{mes} - F^{14}\text{C}_{Atmo})}{(F^{14}\text{C}_{Perm} - F^{14}\text{C}_{Atmo})}$$

188 **3.5 Molecular analysis and molecular indicators calculations**

189 In order to specifically track permafrost influence on DOM composition, a subset of
190 samples was selected based on their ^{14}C content for molecular analysis. The thermochemolysis
191 using tetramethylammonium hydroxide coupled to gas chromatography and mass spectrometry
192 (THM-GC-MS) was performed according to Jeanneau et al., (2014)³⁹. Briefly, approximately
193 1 mg of freeze-dried solid residue was introduced into an 80 μL stainless steel reactor with an
194 excess of tetramethylammonium hydroxide (6 mg). THM reaction was performed on-line using
195 a vertical micro-furnace pyrolyzer PZ-2020D (Frontier Laboratories, Japan) operating at

196 400°C. The products of this reaction were injected into a gas chromatograph (GC) GC-2010
197 (Shimadzu, Japan) equipped with a SLB 5MS capillary column in the split mode (60 m × 0.25
198 mm ID, 0.25 μm film thickness). Compounds were detected using a QP2010+ mass
199 spectrometer (MS) (Shimadzu, Japan) operating in the full scan mode. The list of analyzed
200 compounds and m/z ratios used for their integration are given in the supplementary materials
201 (Table SI.1). Compounds were identified on the basis of their full-scan mass spectra by
202 comparison with the NIST library and with published data⁴⁰.

203 The peak area of the selected m/z (mass/charge) for each compound was integrated and
204 corrected by a mass spectra factor calculated as the reciprocal of the proportion of the fragment
205 used for the integration and the entire fragmentogram provided by the NIST library. The
206 proportion of each compound class was calculated by dividing the sum of the areas of the
207 compounds in this class by the sum of the peak areas of all analyzed compounds expressed as
208 a percentage. The analytical uncertainty for this analytical method, expressed as a relative
209 standard deviation, ranged from 10 to 20% depending on the samples and the target compounds.

210 Target compounds were classified into four categories: small organic acids (SA), α,ω-
211 diacids containing from 4 (fumaric and succinic acids) to 6 (methylglutaric acid) carbon atoms,
212 phenolic compounds (PHE) including lignin and tannin markers, carbohydrates (CAR)
213 (deoxysaccharinic acids produced by the THM of free monosaccharides and terminal
214 monosaccharides from polysaccharides)⁴¹ and fatty acids (FA), from 8 to 30 carbon atoms. The
215 distribution of target compounds in these categories was used to investigate DOM origin (plant
216 vs microbial origin). The distribution of LMWFA (low molecular weight fatty acids, <C18)
217 was used as an indication of microbial activity. With the exception of n-C16 and n-C18 that can
218 derive from plant-derived input, LMWFA with more than 13 carbon atoms are known as
219 phospholipid fatty acids and serve as specific microbial biomarkers⁴². The proportion of plant-
220 derived compounds (%VEG) was calculated using the deoxyC6/C5 ratio⁴³ and the proportion

221 of plant-derived fatty acids calculated as the proportion of HMW FA among FA excluding n-
222 C16 and n-C18³⁹. Ratios of cinnamyl to vanillyl units (C/V) and of aldehyde to acid moieties
223 for vanillyl ((Al/Ac)_V) and syringyl ((Al/Ac)_S) depend on their botanical origin or, if the
224 botanical origin can be assumed to be constant, on their biodegradation state. As the botanical
225 origins of our samples were homogeneous, their ratios were used as biodegradation indices
226 based on the preferential biodegradation of (i) cinnamyl moieties and (ii) aldehydes among
227 vanillyl and syringyl units^{44,45}.

228 4. Statistical analysis

229 Statistical analysis was performed using R⁴⁶ and the Rstudio software (Version
230 1.2.1335), using ggplot⁴⁷, dplyr⁴⁸, dunn.test⁴⁹ packages. Significant differences ($\alpha < 0.05$)
231 between groups were performed using Kruskal Wallis and Dunn's post hoc multiple test.

232 III. Results & Discussion

233 1. Evolution of DOM composition along a permafrost thaw gradient

234 We observe clear changes in both DOC concentration and DOM composition following
235 permafrost peatland degradation (Table 1 & 2, Figure 2). These are associated with a specific
236 DOM composition as indicated by consistent isotopic, optical and molecular analyses.
237 Significant relationships were observed between bulk optical properties and molecular analysis.
238 The SUVA index was positively correlated to % PHE ($r^2 = 0.48$; $p < 0.05$) and phenol ratios
239 ((Al/Ac)_V given as an example, $r^2 = 0.47$; $p < 0.05$) while FI was positively correlated to the
240 percentage of low molecular weight fatty acids (LMWFA) ($r^2 = 0.5$; $p < 0.05$) and negatively
241 with the calculated percentage of vegetation origin ($r^2 = 0.42$; $p < 0.05$).

242 During the initial stages of thaw, in small thermokarst bogs, we measure high DOC
243 concentrations ($44.1 \pm 10.1 \text{ mg L}^{-1}$), (Table 1, Figure 2). In these small thermokarst bogs, DOM
244 originates from vegetation and is highly aromatic. This is revealed by significantly lower

245 fluorescence index values (1.35 ± 0.06)⁵⁰, higher value of the % VEG index, and higher SUVA
246 index values ($5.4 \pm 0.6 \text{ L mg}^{-1} \text{ m}^{-1}$). This corresponds to almost 40% aromatic moieties³⁰,
247 consistent with a higher proportion of phenols (PHE). The high $\delta^{13}\text{C}$ -DOC values ($-$
248 $27.7 \pm 0.3 \text{ ‰}$) we observe in small thermokarst bogs are also typical of terrestrial SOM, which
249 has been through oxidation processes. This is further confirmed by lower values of $(\text{Al}/\text{Ac})_{\text{v}}$,
250 $(\text{Al}/\text{Ac})_{\text{s}}$ and C/V ^{51,52}. The significant correlations of $(\text{Al}/\text{Ac})_{\text{s}}$ with C/V ($r^2 = 0.82$; $p = 0.001$)
251 and $(\text{Al}/\text{Ac})_{\text{v}}$ ($r^2 = 0.83$; $p = 0.01$) underline the consistency between these three ratios, which
252 supports their use as biodegradation indices (Figure SI 2).

253 Along the thaw gradient, in larger thermokarst bogs as well as sites that have
254 transitioned to fens and lakes, the composition and origin of DOM evolves. DOC concentrations
255 decrease to $16.7 \pm 1.2 \text{ mg L}^{-1}$ in large bogs to $11.0 \pm 2.4 \text{ mg L}^{-1}$ in fens. Slightly higher values
256 are measured in thermokarst lakes ($14.0 \pm 4.0 \text{ mg L}^{-1}$) and in the bog developed in mineral soil
257 context ($12.9 \pm 2.3 \text{ mg L}^{-1}$). Dissolved organic matter composition evolves, with an increased
258 proportion of microbially-derived compounds in large bogs, fens, and thermokarst lakes. This
259 is evidenced by the increase in the fluorescence index values. The aromaticity of DOM
260 decreases from 60 to 25%, as indicated by the SUVA index. The $\delta^{13}\text{C}$ -DOC values also decrease
261 to -30 ‰ , reaching relatively depleted values, closer to recently produced vegetation, and
262 indicative of lower rates of processing.

263 Shifts of DOM composition after permafrost thaw have been reported at other boreal
264 and arctic sites. They have been related to photodegradation, microbial activity, or change of
265 vegetation. Laurion and Mladenov (2013)⁵³ showed that in the case of thawing ponds in the
266 Canadian high Arctic, UV mostly transformed aromatic and terrestrially derived DOM into
267 more labile molecules. More precisely, an FT-ICR-MS study of the phototransformation of
268 DOM originating from the active layer and permafrost in Alaska⁵⁴, showed that a small
269 proportion of molecules, holding carboxylic groups, participated in photo-oxidation. However,

270 in the context of thermokarst bogs, photo-oxidation is likely to be highly limited since a
271 vegetation mat covers the surface, and this process is only likely to occur in open water. In
272 Central Siberia¹⁷, a decrease in the DOC concentration in thermokarst lakes was linked with a
273 decrease in the size of organic molecules. Pokrovsky et al. (2011)¹⁷ attributed this trend to the
274 progressive consumption of DOM by heterotrophic bacteria and release of exometabolites by
275 phytoplankton. Hodgkins et al (2016)¹⁶ also reported a shift in the elemental and optical
276 properties of DOM along a permafrost thaw gradient from thermokarst bog to fen in Sweden.
277 The primary changes observed between the early stages of palsa thaw and the fen was the
278 decrease of tannin-like and high O/C compounds and the increase of microbially derived DOM.
279 These differences were mainly attributed to the presence or absence of sphagnum. In our study,
280 a similar shift from terrestrial to microbially-derived DOM is observed from thermokarst bogs
281 to fen, although sphagnum was present at all sites. We demonstrate in this study that the origin
282 of DOM, traced using ¹⁴C-DOM, also contributes to the shift in DOM composition.

283 **2. Peatland permafrost influence on DOM composition: Link to potential lability**

284 We observe that the contribution of permafrost carbon to DOM decreases along the thaw
285 gradient, and controls DOM composition. This is revealed by the evolution of the radiocarbon
286 content of DOM (Figure 3a&b). The lowest values of F¹⁴C of DOM are measured in small
287 thermokarst bogs (F¹⁴C = 0.799 ± 0.008 (1800 ± 85 BP)), which correspond to a contribution
288 of 40 to 60 % permafrost carbon. In large thermokarst bogs, the F¹⁴C value covers a wide range
289 of values, depending on sample depth (from F¹⁴C = 0.842 ± 0.005 (1385 ± 45 BP) to
290 F¹⁴C = 1.043 ± 0.005, modern carbon), with a higher contribution of permafrost carbon in deep
291 layers. In thermokarst lakes, surface samples are characterized by modern DOM (permafrost
292 contribution does not exceed 10 %), while old DOM (F¹⁴C = 0.854 ± 0.008, 1275 ± 70 BP) is
293 measured in sediment porewater at a depth of 1 m. In the thermokarst bog developed in the
294 mineral context, modern DOM is analyzed to depths of 2 m, and slightly lower values are

295 measured ($F^{14}C = 0.958 \pm 0.008$, 350 ± 65 BP). No calculation is performed for the bog
296 developed on mineral soils, since the permafrost signature for the mineral context was not
297 measured.

298 We observe that the amount of permafrost peatland carbon remaining in the sampled
299 DOM directly influences DOM composition (Figure 4). A significant negative correlation is
300 observed between ^{14}C -DOM and FI, as well as the percentage of vegetation. A positive
301 correlation is highlighted between ^{14}C -DOM and SUVA index and PHE ratios $((Al/Ac)_V)$ given
302 as an example). This reveals that a higher proportion of permafrost carbon in DOM is associated
303 with a larger proportion of plant-derived DOM, higher aromaticity and a higher degradation
304 state of phenols. As the proportion of permafrost carbon decreases, the microbial contribution
305 to DOM increases.

306 The fact that only modern DOM is detected in fens and thermokarst lakes could mean
307 that permafrost-derived DOM has been transferred to the fluvial network, has been diluted by
308 modern sources of DOM in the ecosystem or has been processed on site. At our study site, no
309 surface water connection is observed between the small and large thermokarst bogs and the
310 fluvial network, so it is unlikely that it is transferred to surface waters. Our results suggest that
311 the lability of permafrost peatland derived DOM is limited. Biodegradability of DOM is not
312 strictly determined by its chemical composition, but also depends on environmental factors,
313 such as nutrients, oxygen content or temperature^{7,55}. DOM composition and the anoxic
314 conditions may have suppressed the mineralization rate of permafrost DOM, potentially
315 explaining its high proportion in deep layers of thermokarst bogs. However, several studies
316 have linked higher degradability of DOM to lower aromaticity^{6,7,11,56}, and lower degradation
317 states of phenols^{6,57}, inferring limited lability of peatland permafrost DOM at our site. However,
318 since no direct measurement were made, the fate of DOM originating from permafrost remains
319 uncertain. In Canada, only modern carbon was measured in CO_2 emitted from both young and

320 mature thermokarst bogs⁵⁸, showing that mineralization of permafrost carbon in the case of
321 thermokarst bogs was limited. In the fen and thermokarst lakes, we detect only modern,
322 microbially dominated DOM. However, we cannot differentiate between dilution of the
323 permafrost signal by this modern source of DOM and on-site processing of DOM. These two
324 processes would both result in the same observation of more modern carbon (increasing
325 radiocarbon content) with decreasing DOC concentrations (Figure SI.3). Further work to
326 address this ambiguity and confirm the low lability we infer from our analysis in permafrost
327 peatlands should include the additional investigation of biodegradable DOC⁵⁹, as well as
328 measurements of the ¹⁴C content of GHGs emitted from permafrost peatlands⁶⁰.

329 **3. DOM composition and ¹⁴C content: Variability across geological context and** 330 **spatial scales in the Arctic**

331 Our work links the DOM composition with its ¹⁴C content in the context of permafrost
332 peatlands. Establishing this link between the ¹⁴C-DOM (and therefore the permafrost carbon
333 contribution to DOM) and its composition is key to assessing the potential feedback of
334 permafrost thaw to climate change. In the Arctic, fewer studies have coupled radiocarbon
335 content of DOM to its molecular or elemental composition^{5,11,61}, compared to the optical
336 properties of DOM^{5,9,11,18,61,62}. Establishing a relationship between these cheap and widely
337 measured parameters and ¹⁴C content would allow more widespread assessment of the release
338 of old permafrost carbon following thaw. In addition, our study highlights significant
339 relationships between SUVA and the molecular composition of DOM, especially phenol
340 content and their degradation state, increasing the information given by such an optical index.
341 Such relationships have been established in Alaska, for the hydrophobic fraction of DOM, with
342 older DOM being associated with lower SUVA⁹.

343 In contrast to studies of permafrost in other geological context⁶², in our study we observe
344 higher SUVA values (higher aromaticity) in samples with a larger proportion of permafrost

345 DOM (Figure 5). In existing Arctic studies, none of which were conducted on permafrost
346 peatlands, a larger permafrost influence (lower radiocarbon content) correlates with lower
347 SUVA values, indicating a lower aromaticity and higher lability⁶ (Figure 5 and Table 3). In the
348 case of the Yenisei catchment in Siberia, shifts of DOM bulk age are related to hydrology, with
349 young DOM being exported during spring snowmelt. This spring DOM originates from the
350 flushing of fresh litter and shallow organic soil layers, and therefore has a more aromatic
351 composition¹⁰. In the context of Yedoma, permafrost has been shown to have sequestered high
352 content of aliphatic and small organic acids. For example in an Alaskan core, 24% of permafrost
353 dissolved organic carbon was found in the form of highly labile acetate⁶³, consumed within
354 days. This explains the low SUVA associated with the older samples, and the high lability⁶. In
355 the case of high Canadian Arctic ponds¹⁸, DOM from thawing ponds is a mixture of old DOM
356 and autochthonous DOM, resulting in a low apparent SUVA of old DOM.

357 The apparent contradiction between the trends in these studies and our own observations
358 (Figure 5) can likely be explained by the geological context, permafrost history and scale of our
359 study. In addition, the peatland type²⁰ and the history of permafrost formation²² could influence
360 organic matter composition and lability in permafrost peatlands. At our study site, peatland
361 formation during the Holocene was followed by permafrost aggradation²⁷. Therefore, the
362 formation of permafrost likely froze highly aromatic organic matter, which is typical of
363 peatlands. This organic matter might have already undergone microbial processing over long
364 periods, perhaps further increasing the aromaticity of DOM⁶⁴. This would explain the observed
365 characteristics of old bulk DOM in our study, and a potentially lower lability of peatland
366 permafrost DOM²². This is in agreement with a recent study in central Siberia showing that
367 DOM from previously frozen peat was highly refractory⁶⁵. This highlights the unique nature of
368 permafrost peatlands (19% of permafrost area, 70% in Eurasia, and more than one third of the
369 organic carbon stocks¹²) with regards to post thaw organic carbon dynamics, in comparison to

370 mineral soils in the Arctic. This study indicates that a runaway feedback of old labile carbon
371 released as a result of permafrost thaw should not be expected in all cases. In peatland
372 permafrost, our results suggest that thawing carbon is highly aromatic, and might have
373 undergone previous microbial processing prior to permafrost aggradation. Permafrost peatlands
374 are therefore relatively unlikely to release labile DOM as a result of permafrost thaw.

375

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387 SUPPORTING INFORMATION.

388 Figure SI.1. Age of bulk OC in palsa mounts. Figure SI.2. Relationships between phenol ratios.
389 Figure SI.3 Plot of ^{14}C content versus DOC concentrations. Table SI.1. List of analyzed
390 compounds and m/z ratios used for their integration. This information is available free of charge
391 via the Internet at <http://pubs.acs.org>

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635 Bogs (Permafrost Zone) Are Highly Resistant to Bio- and Photodegradation.
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640 **Table 1.** General water quality (pH, conductivity), DOC concentrations, optical properties (FI and SUVA); and $\delta^{13}\text{C}$ - signature of DOM in
 641 porewater of thermokarst bogs and surface water of thermokarst lakes. sd: Standard deviation.

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	n	pH	Cond. ($\mu\text{S cm}^{-1}$)	DOC (mg L^{-1})	FI	SUVA ($\text{L mgC}^{-1} \text{m}^{-1}$)	$\delta^{13}\text{C}$ -DOC (‰)
Small bogs	10	4.5 \pm 0.2	69 \pm 40	44.1 \pm 10.1	1.35 \pm 0.06	5.36 \pm 0.60	-27.7 \pm 0.3
Large bogs	12	5.0 \pm 1.0	82 \pm 38	16.7 \pm 1.2	1.51 \pm 0.06	4.81 \pm 0.34	-29.0 \pm 0.8
Fens	8	5.7 \pm 1.2	47 \pm 48	11.0 \pm 2.4	1.55 \pm 0.06	4.83 \pm 0.63	-28.5 \pm 1.1
Therm. Lakes	12	4.6 \pm 0.9	40 \pm 36	14.0 \pm 4.2	1.5 \pm 0.05	4.88 \pm 0.48	-28.8 \pm 1.0
Mineral Bog	9	5.4 \pm 0.6	44 \pm 24	12.9 \pm 2.3	1.64 \pm 0.05	4.28 \pm 0.80	-29.4 \pm 0.3

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645 **Table 2.** DOM molecular analysis in porewater of thermokarst bogs and lakes (mean±sd). SA: small acids, CAR: carbohydrates, FA: fatty acids,
 646 PHE: phenolic compounds, LMWFA: low molecular weight fatty acids, pcVEG: percentage of vegetation, C/V: ratio of cinnamyl to vanillyl acids,
 647 S/V: ratio of syringyl to vanillyl acids, (Al/Ac)_v: ratio of aldehyde to acid moieties for vanillyl, (Al/Ac)_s: aldehyde to acid moieties for syringyl.

	CAR	FA	LMWFA	pcVEG	C/V	S/V	(Al/Ac) _v	(Al/Ac) _s
SB	31.2±0.4	3.9±0.8	47.6±5.5	86.3±8.2	78.0±5.0	0.10±0.0	0.38±0.1	0.10±0.0
LB	20.0±4.9	6.1±3.0	39.5±6.0	65.8±21.3	70.6±6.7	0.50±0.2	0.43±0.1	0.21±0.1
MB	23.6±4.6	3.3±0.4	45.1±3.2	83.5±11.0	69.5±6.6	0.32±0.1	0.45±0.0	0.13±0.0
Lake	23.7±5.7	8.0±0.4	56.0±4.2	96.5±0.1	81.5±0.7	0.13±0.0	0.29±0.1	0.08±0.0

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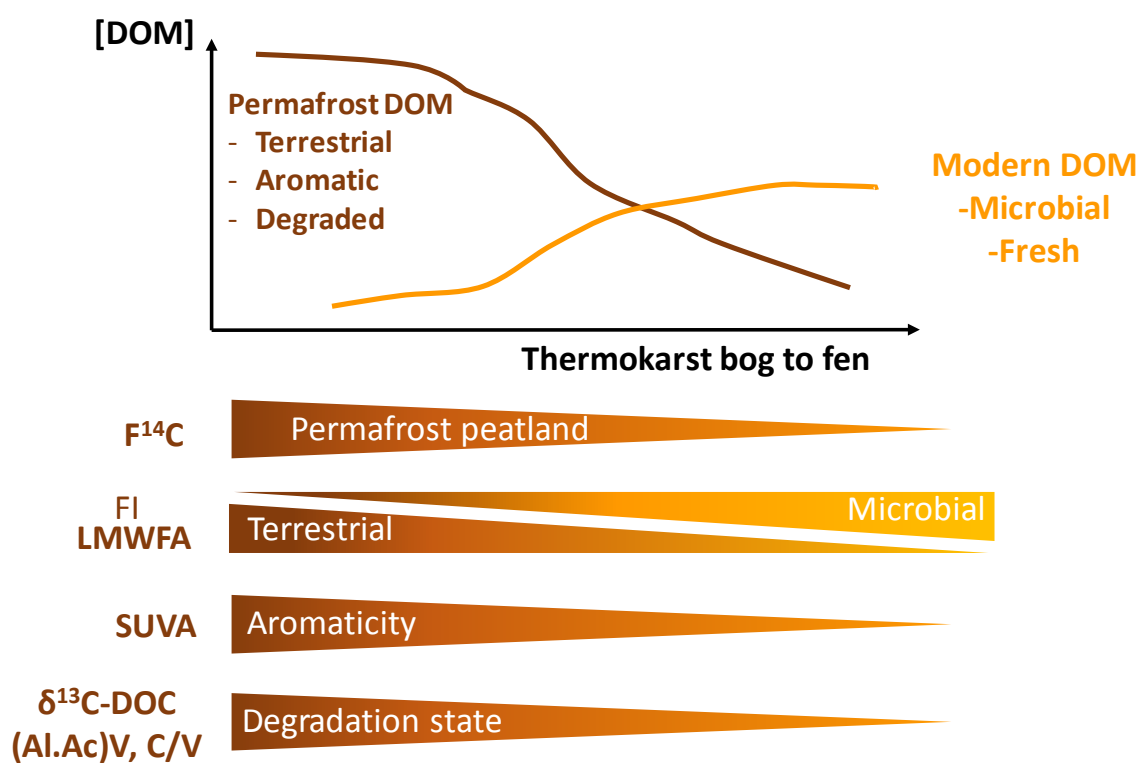
651 **Table 3.** Relationships between radiocarbon content of DOM and SUVA index for this study
 652 and reported results from the literature.

Study	Scale	Geological Context	SUVA = $aF^{14}C+b$
This study	Thermokarst bogs pore water profile	Holocene peatlands	$y = -4.78 x + 9.53$ $r^2 = 0.55, n=21, p<0.001$
Mann et al., 2015	Thaw water, streams	Yedoma	$y = 2.23 x + 1.29$ $r^2 = 0.78, n= 23, p<0.0001$
Barnes et al., 2018	Yenisei River	Yenissei watershed	$y = 5.90 x - 3.14$ $r^2 = 0.25, n=45, p<0.001$
Wang et al., 2018	Pond waters	High Canadian Arctic	$y = 8.17 x - 3.36$ $r^2 = 0.38, n=15, p<0.05$

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664 **Graphical abstract.**

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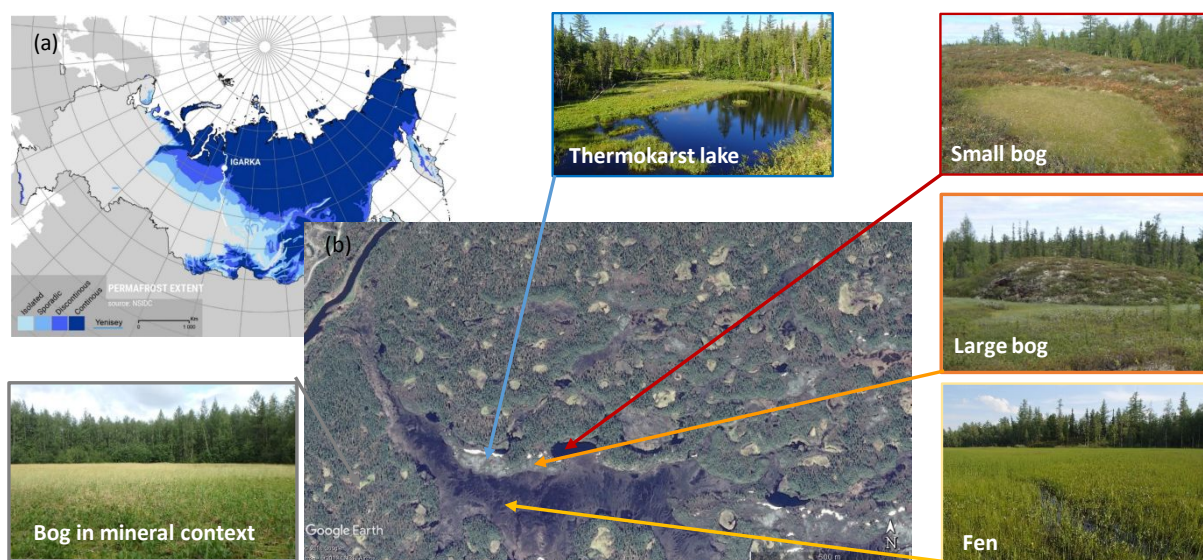
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674 **Figure 1.** (a) Location of Igarka and permafrost status in the Republic of Russia. (b) Sampling

675 area, with location of sampling points. Pictures are representative of sampling locations.

676 Data from IPA (International Permafrost Association) and Google Earth.

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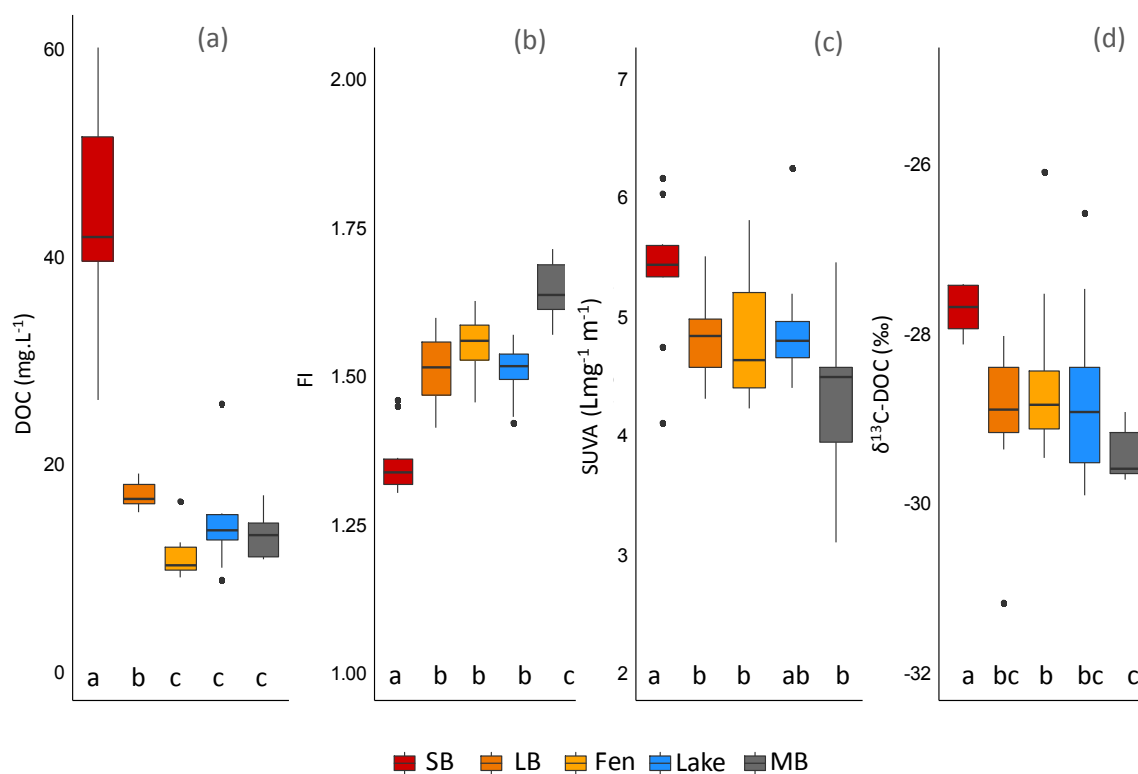
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688 **Figure 2.** (a) DOC concentration, (b) Fluorescence Index (FI), (c) Specific UV Absorbance
 689 (SUVA) and (d) $\delta^{13}\text{C}$ of DOM of the different sample types. The black line is the
 690 median. The lower and upper levels of the box represent the 25 and 75 % quartile,
 691 respectively. The lower whisker is smallest observation greater than or equal to lower
 692 hinge - 1.5 * IQR (inter-quartile range), the upper whisker, the upper whisker is the
 693 largest observation less than or equal to upper hinge + 1.5 * IQR. SB= small bogs, LB
 694 = large bogs, lake = thermokarst lake, MB = thermokarst bog developed in mineral
 695 context. Letters represent significantly different groups (Kruskall Wallis and Dunn's
 696 post hoc multiple test ($p > 0.05$)).

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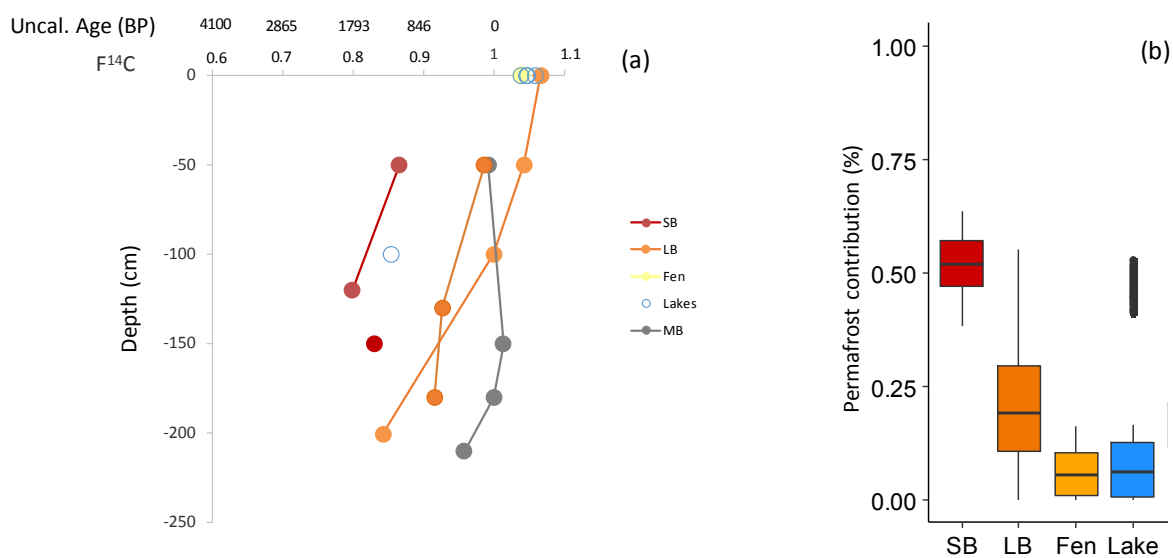
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704 **Figure 3.** (a) Profiles of radiocarbon content of selected samples of DOM in thermokarst bogs profiles,

705 porewater surface, sediment porewater of lake and surface water of lakes. (b) Proportion of

706 permafrost to DOM. The distribution corresponds to calculation with atmospheric signature

707 ranging from 1980 to 2015 (sampling date). SB= small bogs, LB = large bogs, Lake =

708 thermokarst lake, MB = thermokarst bog developed in mineral context.

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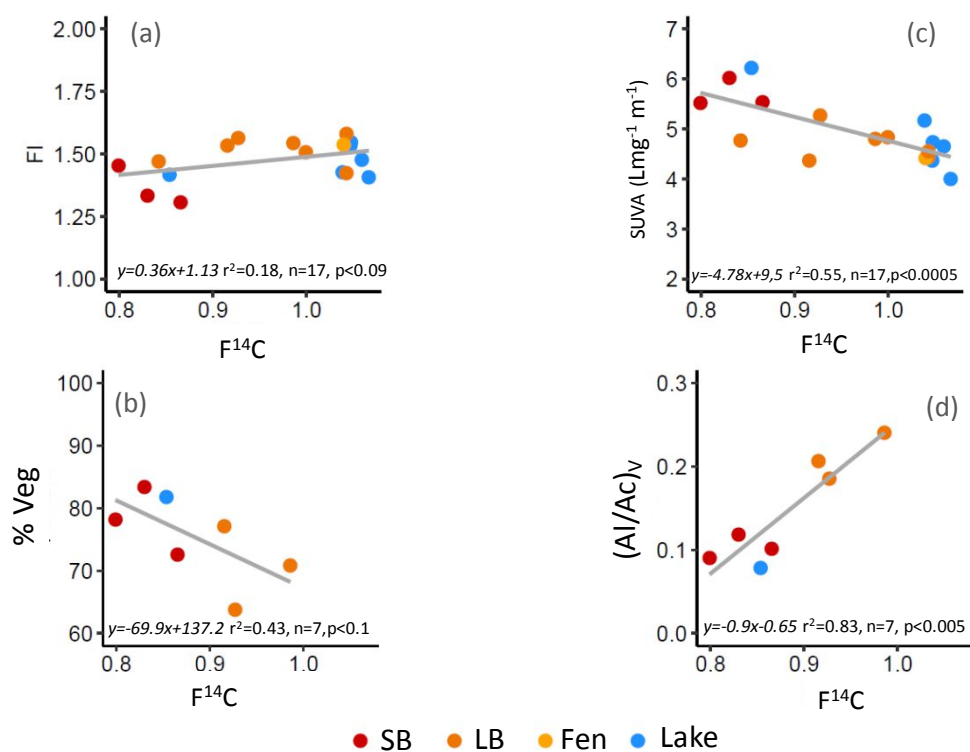
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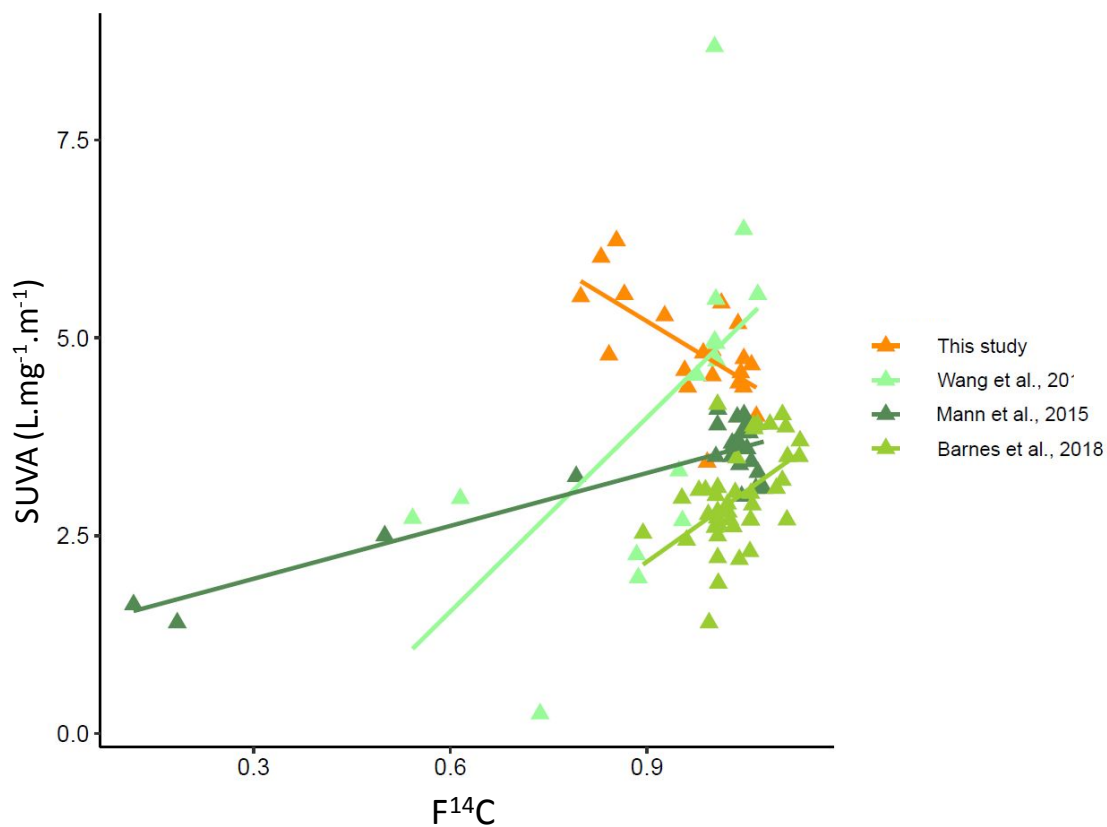
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719 **Figure 4.** Relationship between radiocarbon content of DOM with (a) FI (Fluorescence Index), (b),
 720 SUVA (Specific UV Absorbance), (c) percentage of vegetation origin of DOM, (d)
 721 $(Al/Ac)_v$: ratio of aldehyde to acid moieties for vanillyl. SB= small bogs, LB = large bogs, Lake
 722 = thermokarst lake.

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727 **Figure 5:** Relationship radiocarbon content of DOM and SUVA in different geological contexts
728 and at different scales. (Wang et al., 2018 : High Arctic ponds, Mann et al., 2015 :
729 Streams and thaw water in Yedoma Context, Barnes et al., 2018 : Yenisei watershed).

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