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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 ( $^{14}\text{C}$ ) 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 stock<sup>1</sup>. 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 change<sup>2-4</sup>. 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<sup>-15</sup>. 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 Ocean<sup>6</sup>. 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 thaw<sup>7</sup>. In landscapes dominated by permafrost degradation, radiocarbon (<sup>14</sup>C)  
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<sup>5,8,9</sup>. 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<sup>5,10</sup>, and also  
53 found upstream in the fluvial network<sup>6</sup>. 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 consumption<sup>11</sup>.

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<sup>1,12</sup>. Furthermore, their degradation as a  
60 result of permafrost thaw has increased in recent decades<sup>13,14</sup>. 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 fens<sup>15</sup>. The composition of DOM evolves with this ecosystem transition,  
64 reflecting the increased contribution of new vegetation<sup>16</sup>, microbial activity<sup>17,18</sup>, and the  
65 transition from bog to fen<sup>19</sup>.

66 Although carbon-rich permafrost peatlands account for 19% of permafrost area<sup>15,20</sup>, 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 geologies<sup>21</sup>, with important  
69 implications for organic matter composition and degree of processing prior to thaw, and  
70 potential lability after thaw<sup>20,22</sup>. 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<sup>11,23</sup>. 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  $-7.7 \pm 1.1$  °C and the mean annual precipitation is  $632 \pm 86$   
88 mm, including  $320 \pm 50$  mm in the form of snow<sup>24</sup>. Sampling focused on the Graviyka catchment  
89 (Figure 1b). The Graviyka River, with watershed of 320 km<sup>2</sup>, 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 <sup>25,26</sup>, 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 <sup>27</sup>. 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 <sup>24</sup>.

## 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 <sup>15,28,29</sup>. 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 <sup>15,16,29</sup>.

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) <sup>16</sup>, with adaptations to our site. We sampled “small bogs”, thermokarst  
121 bogs perched on palsa, with a size < 40 m<sup>2</sup> (corresponding to “recently thawed palsa”). We also  
122 sampled “large bogs”, which were >100 m<sup>2</sup> 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,  $^{14}\text{C}$ -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  $1 \text{ mg L}^{-1}$ . 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 ( $\text{SUVA}_{254}$ ,  $\text{L mg}^{-1} \text{ m}^{-1}$ ) 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  $\text{mg L}^{-1}$ .  
147 <sup>1</sup>. SUVA is a proxy for DOM aromaticity<sup>30</sup>. 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)<sup>31</sup> and Jaffé et al (2008)<sup>32</sup>. Potential additional absorbance related to Fe content was  
152 checked on a few samples following the procedure described by Poulin et al<sup>33</sup>. 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 system<sup>34</sup>. From 2 to 4 samples per profile were analyzed. DOM samples were analyzed  
166 through the EA-GIS coupling<sup>35</sup>. 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 $\mu\text{L}$  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  $^{14}\text{C}$  results were corrected for isotopic fractionation  
173 according to the conventions of Stuiver et al (1977)<sup>36</sup> and reported as  $F^{14}\text{C}$  following the  
174 recommendation of Reimer et al. (2004)<sup>37</sup>.

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) <sup>38</sup> 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  $^{14}\text{C}$  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)<sup>39</sup>. Briefly, approximately  
193 1 mg of freeze-dried solid residue was introduced into an 80  $\mu\text{L}$  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 data<sup>40</sup>.

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)<sup>41</sup> 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 biomarkers<sup>42</sup>. The proportion of plant-  
220 derived compounds (%VEG) was calculated using the deoxyC6/C5 ratio<sup>43</sup> and the proportion

221 of plant-derived fatty acids calculated as the proportion of HMW FA among FA excluding n-  
222 C16 and n-C18<sup>39</sup>. Ratios of cinnamyl to vanillyl units (C/V) and of aldehyde to acid moieties  
223 for vanillyl ((Al/Ac)<sub>V</sub>) and syringyl ((Al/Ac)<sub>S</sub>) 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<sup>44,45</sup>.

#### 228 **4. Statistical analysis**

229 Statistical analysis was performed using R<sup>46</sup> and the Rstudio software (Version  
230 1.2.1335), using ggplot<sup>47</sup>, dplyr<sup>48</sup>, dunn.test<sup>49</sup> 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)<sub>V</sub> 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 ( $1.35 \pm 0.06$ )<sup>50</sup>, 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 moieties<sup>30</sup>,  
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  $\text{C}/\text{V}$ <sup>51,52</sup>. The significant correlations of  $(\text{Al}/\text{Ac})_{\text{s}}$  with  $\text{C}/\text{V}$  ( $r^2 = 0.82$ ;  $p = 0.001$ )  
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  $-30 \text{ ‰}$ , 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)<sup>53</sup> 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 Alaska<sup>54</sup>, 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 Siberia<sup>17</sup>, 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)<sup>17</sup> attributed this trend to the  
274 progressive consumption of DOM by heterotrophic bacteria and release of exometabolites by  
275 phytoplankton. Hodgkins et al (2016)<sup>16</sup> 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 <sup>14</sup>C-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 F<sup>14</sup>C of DOM are measured in small  
287 thermokarst bogs (F<sup>14</sup>C = 0.799 ± 0.008 (1800 ± 85 BP)), which correspond to a contribution  
288 of 40 to 60 % permafrost carbon. In large thermokarst bogs, the F<sup>14</sup>C value covers a wide range  
289 of values, depending on sample depth (from F<sup>14</sup>C = 0.842 ± 0.005 (1385 ± 45 BP) to  
290 F<sup>14</sup>C = 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 (F<sup>14</sup>C = 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 ( $F^{14}C = 0.958 \pm 0.008$ ,  $350 \pm 65$  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<sup>7,55</sup>. 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<sup>6,7,11,56</sup>, and lower degradation  
317 states of phenols<sup>6,57</sup>, 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 bogs<sup>58</sup>, 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 DOC<sup>59</sup>, as well as  
328 measurements of the <sup>14</sup>C content of GHGs emitted from permafrost peatlands<sup>60</sup>.

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

331 Our work links the DOM composition with its <sup>14</sup>C content in the context of permafrost  
332 peatlands. Establishing this link between the <sup>14</sup>C-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<sup>5,11,61</sup>, compared to the optical  
336 properties of DOM<sup>5,9,11,18,61,62</sup>. Establishing a relationship between these cheap and widely  
337 measured parameters and <sup>14</sup>C 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 SUVA<sup>9</sup>.

343 In contrast to studies of permafrost in other geological context<sup>62</sup>, 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 lability<sup>6</sup> (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 composition<sup>10</sup>. 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 acetate<sup>63</sup>, consumed within  
354 days. This explains the low SUVA associated with the older samples, and the high lability<sup>6</sup>. In  
355 the case of high Canadian Arctic ponds<sup>18</sup>, 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 type<sup>20</sup> and the history of permafrost formation<sup>22</sup> 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 aggradation<sup>27</sup>. 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 DOM<sup>64</sup>. This would explain the observed  
365 characteristics of old bulk DOM in our study, and a potentially lower lability of peatland  
366 permafrost DOM<sup>22</sup>. This is in agreement with a recent study in central Siberia showing that  
367 DOM from previously frozen peat was highly refractory<sup>65</sup>. 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 stocks<sup>12</sup>) 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  $^{14}\text{C}$  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 ( $\text{mg L}^{-1}$ )	FI	SUVA ( $\text{L mgC}^{-1} \text{m}^{-1}$ )	$\delta^{13}\text{C}$ -DOC (‰)
Small bogs	10	4.5±0.2	69±40	44.1±10.1	1.35±0.06	5.36±0.60	-27.7±0.3
Large bogs	12	5.0±1.0	82±38	16.7±1.2	1.51±0.06	4.81±0.34	-29.0±0.8
Fens	8	5.7±1.2	47±48	11.0±2.4	1.55±0.06	4.83±0.63	-28.5±1.1
Therm. Lakes	12	4.6±0.9	40±36	14.0±4.2	1.5±0.05	4.88±0.48	-28.8±1.0
Mineral Bog	9	5.4±0.6	44 ±24	12.9±2.3	1.64±0.05	4.28±0.80	-29.4±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)<sub>v</sub>: ratio of aldehyde to acid moieties for vanillyl, (Al/Ac)<sub>s</sub>: aldehyde to acid moieties for syringyl.

	CAR	FA	LMWFA	pcVEG	C/V	S/V	(Al/Ac) <sub>v</sub>	(Al/Ac) <sub>s</sub>
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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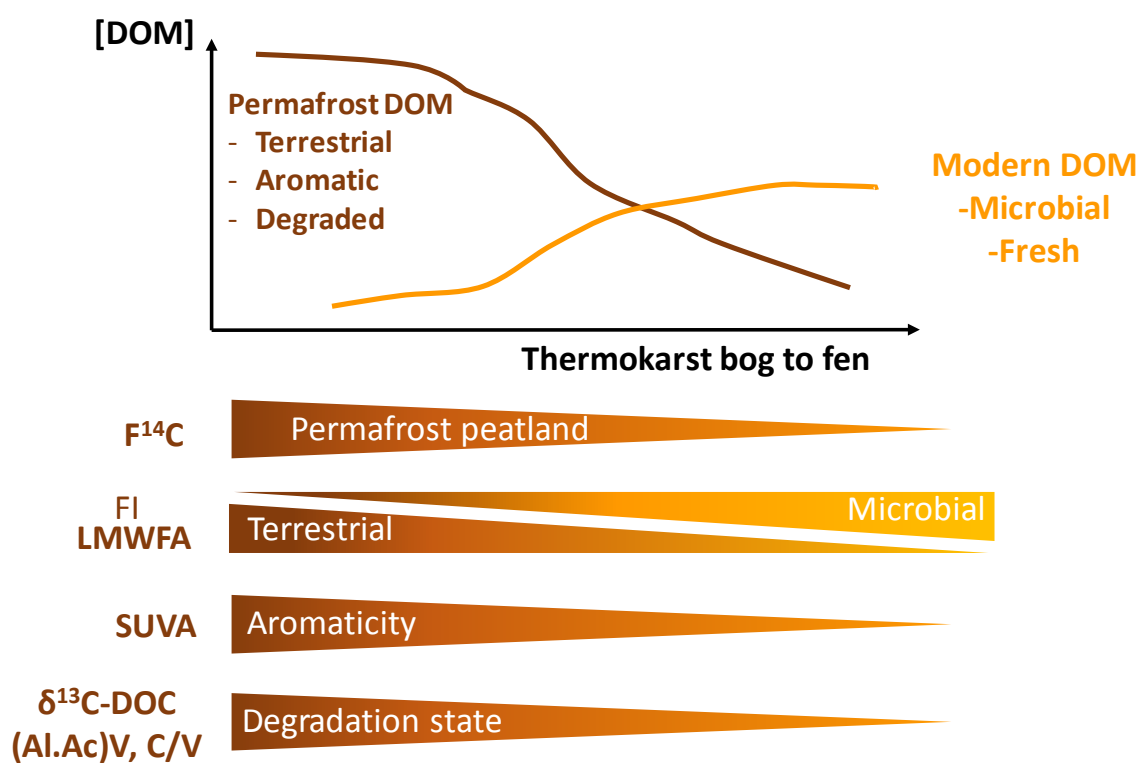
651 **Table 3.** Relationships between radiocarbon content of DOM and SUVA index for this study  
 652 and reported results from the literature.

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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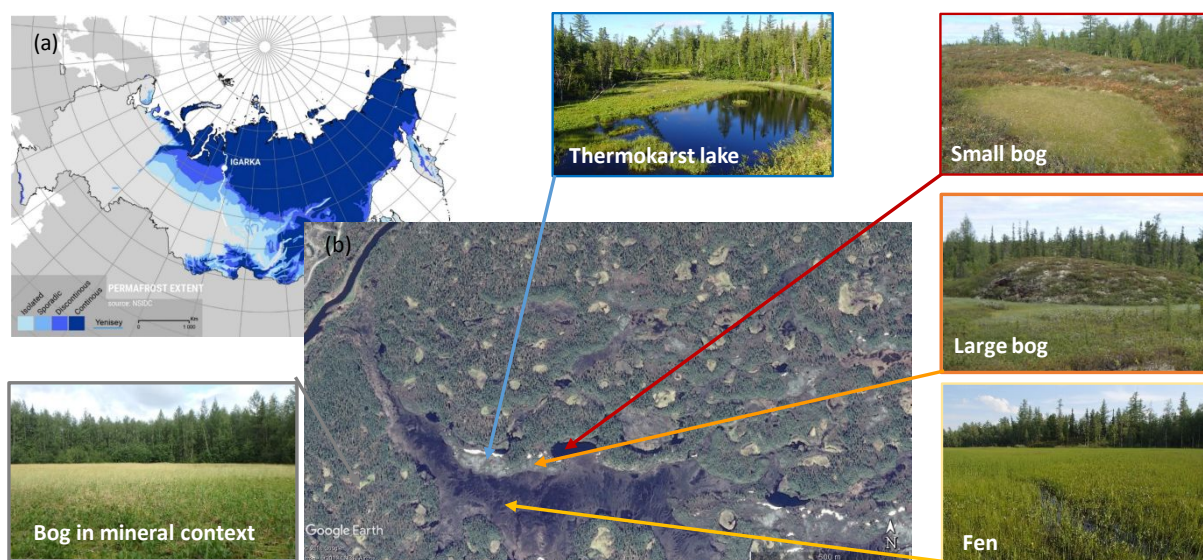
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**Graphical abstract.**

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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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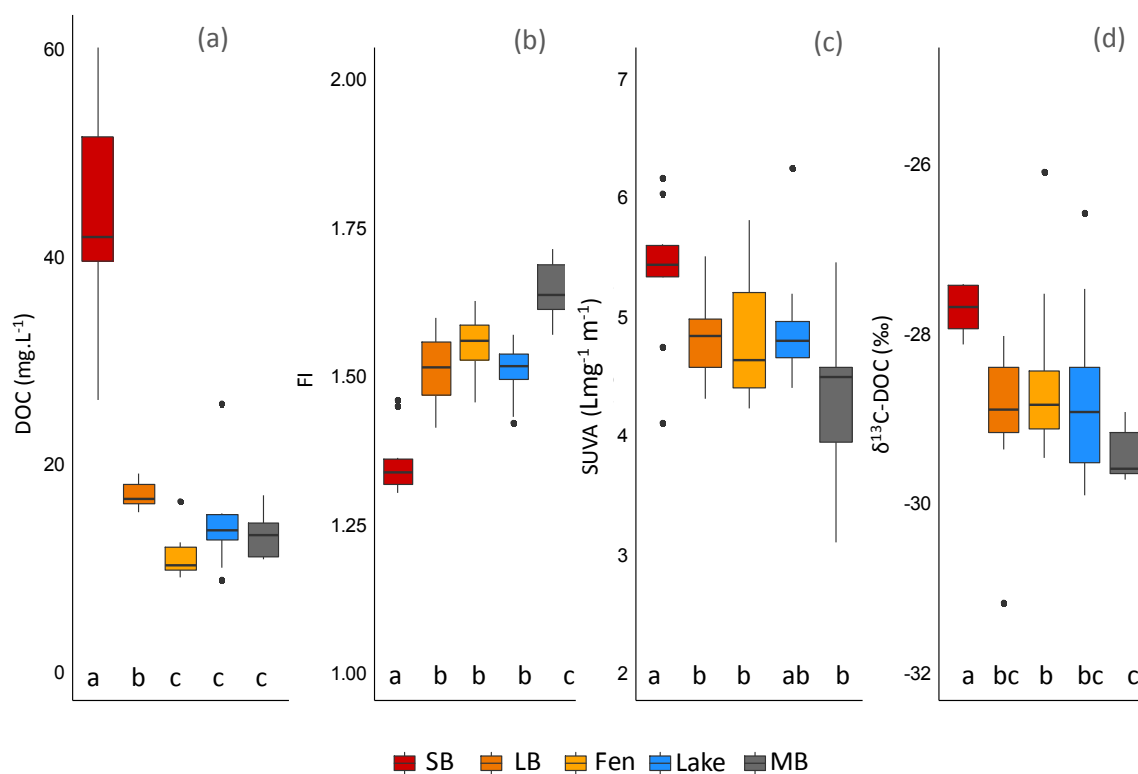
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688 **Figure 2.** (a) DOC concentration, (b) Fluorescence Index (FI), (c) Specific UV Absorbance  
 689 (SUVA) and (d)  $\delta^{13}\text{C}$  of DOM of the different sample types. The black line is the  
 690 median. The lower and upper levels of 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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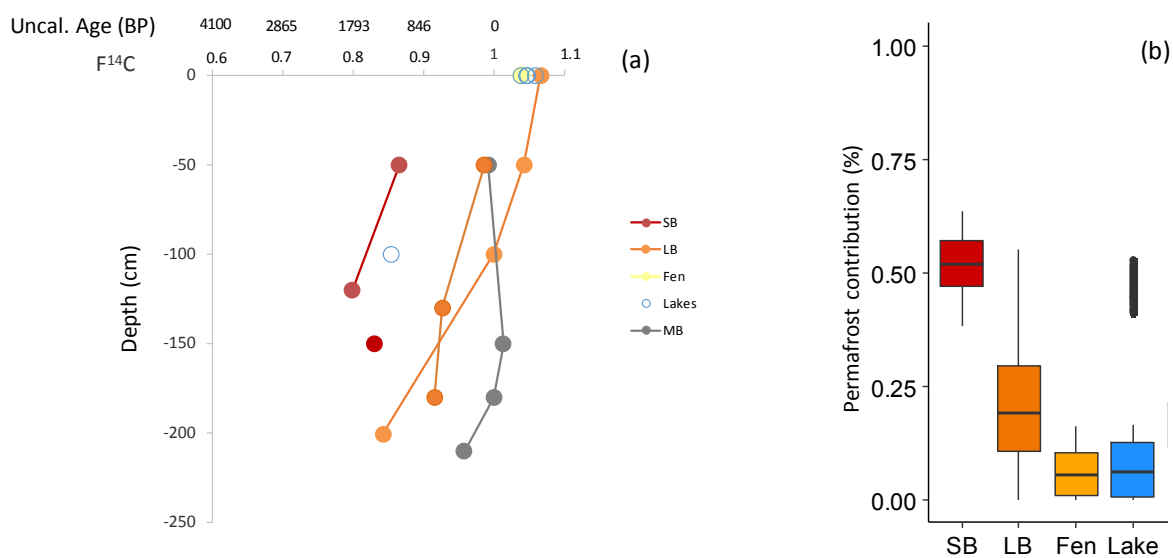
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704 **Figure 3.** (a) Profiles of radiocarbon content of selected samples of DOM in thermokarst bogs profiles,

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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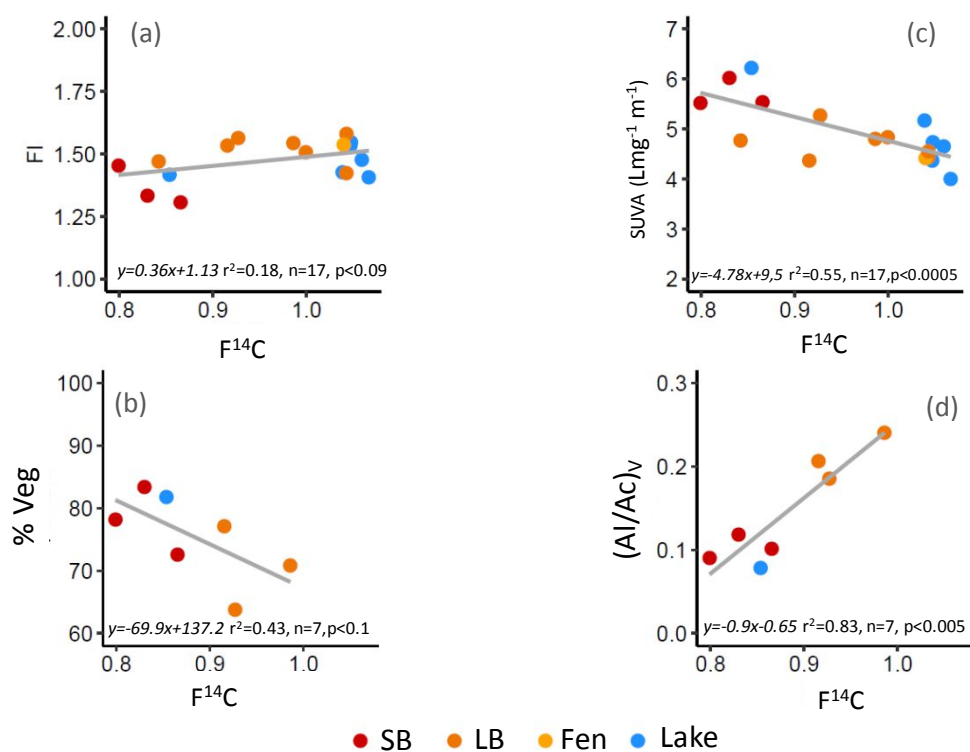
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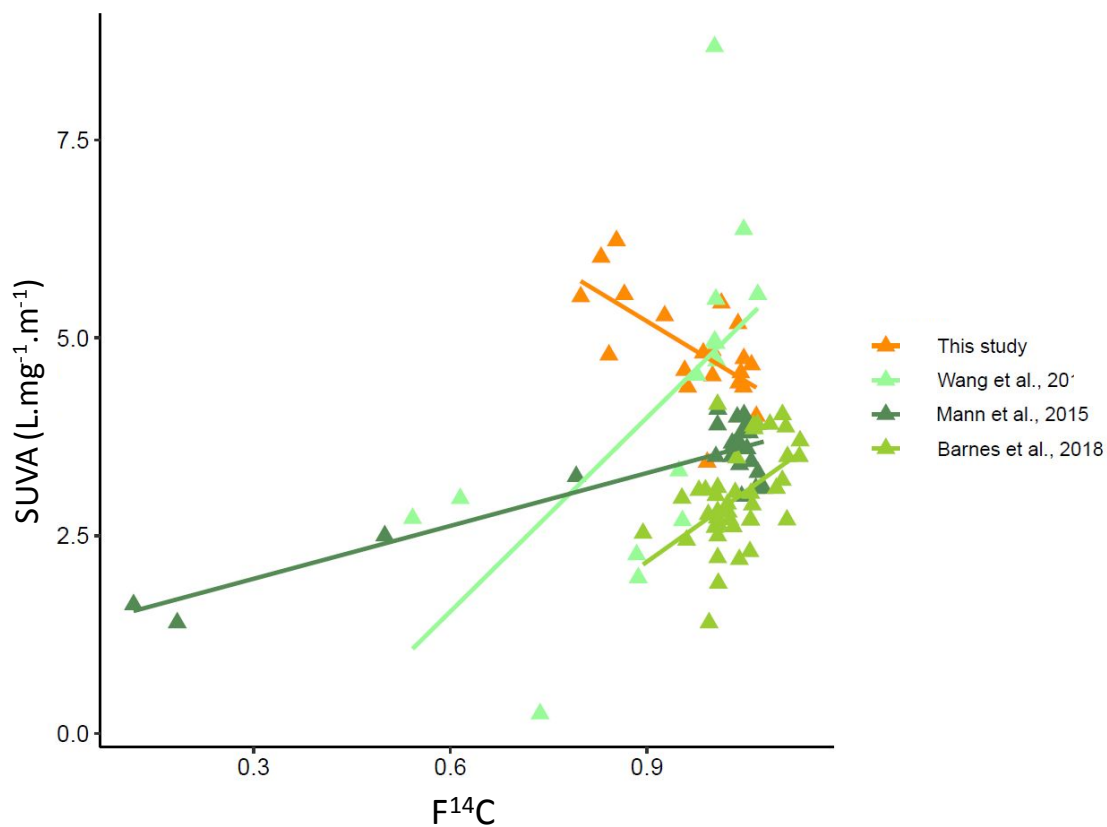
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719 **Figure 4.** Relationship between radiocarbon content of DOM with (a) FI (Fluorescence Index), (b),  
 720 SUVA (Specific UV Absorbance), (c) percentage of vegetation origin of DOM, (d)  
 721  $(Al/Ac)_v$ : ratio of aldehyde to acid moieties 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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