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## Low photolability of yedoma permafrost dissolved organic carbon

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### Key Points:

- Ancient DOC is released from thawing permafrost soils into arctic rivers
- Sunlight preferentially photomineralizes modern arctic river DOC leaving behind ancient permafrost DOC
- Undetectable photochemical losses of permafrost DOC were accompanied by notable photomodification of DOM optical and molecular signatures

## 27 Abstract

28 Vast stores of arctic permafrost carbon that have remained frozen for millennia are thawing,  
29 releasing ancient dissolved organic carbon (DOC) to arctic inland waters. Once in arctic waters,  
30 DOC can be converted to CO<sub>2</sub> and emitted to the atmosphere, accelerating climate change.  
31 Sunlight-driven photoreactions oxidize DOC, converting a portion to CO<sub>2</sub> and leaving behind a  
32 photomodified pool of dissolved organic matter (DOM). Samples from the Kolyma River, its  
33 tributaries, and streams draining thawing yedoma permafrost were collected. Irradiation  
34 experiments and radiocarbon dating were employed to assess the photolability of ancient  
35 permafrost-DOC in natural and laboratory generated samples containing a mix of modern and  
36 ancient DOC. Photolabile DOC was always modern, with no measurable photochemical loss of  
37 ancient permafrost-DOC. However, optical and ultrahigh resolution mass spectrometric  
38 measurements revealed that both modern river DOM and ancient permafrost-DOM were  
39 photomodified during the irradiations, converting aromatic compounds to less conjugated  
40 compounds. These findings suggest that although sunlight-driven photoreactions do not directly  
41 mineralize permafrost-DOC, photomodification of permafrost-DOM chemistry may influence its  
42 fate and ecological functions in aquatic systems.

## 43 1 Introduction

44 Interactions between anthropogenic climate forcing and natural biogeochemical cycles  
45 have the potential to either offset or amplify global change. Amplification occurs via positive  
46 feedbacks, for example when an increase in atmospheric CO<sub>2</sub> drives the release of further carbon  
47 from vulnerable stores [Gruber *et al.*, 2004]. Arctic permafrost, ground that has been frozen for  
48 millennia, holds the largest of these vulnerable global organic carbon (OC) stores (1,100 to 1,700  
49 Pg; 1 Pg = one billion metric tons) [Schuur *et al.*, 2015; Tarnocai *et al.*, 2009]. By 2100,  
50 permafrost thaw is projected to release 41 to 288 Pg of this ancient permafrost OC [Schuur *et al.*,  
51 2015]. For comparison, current climate change has been driven by the accumulation of ~250 Pg-  
52 C in the present-day atmosphere (based upon an atmospheric CO<sub>2</sub> abundance of ~400 ppm)  
53 [[www.esrl.noaa.gov/gmd/ccgg/trends/](http://www.esrl.noaa.gov/gmd/ccgg/trends/)]. Although it is clear that permafrost OC is vulnerable, to  
54 amplify climate change, permafrost OC needs to be converted to greenhouse gases (e.g. CO<sub>2</sub>,  
55 methane) [Schuur *et al.*, 2015; Vonk and Gustafsson, 2013] and emitted to the atmosphere. As  
56 permafrost thaws, a portion of the OC released enters aquatic ecosystems as DOC where it can  
57 be rapidly converted to CO<sub>2</sub> by bacterial respiration [Mann *et al.*, 2015; Spencer *et al.*, 2015;  
58 Vonk *et al.*, 2013; Ward and Cory, 2015] and outgassed efficiently from inland waters [Vonk and  
59 Gustafsson, 2013].

60 DOC can also be converted to CO<sub>2</sub> by sunlight-driven photoreactions [Mopper *et al.*,  
61 2015; Osburn *et al.*, 2009]. Recent work reported that photochemistry controls the water column  
62 processing of DOC in arctic freshwaters and suggested that photochemistry controls the fate of  
63 permafrost-derived DOC [Cory *et al.*, 2014]. Further studies report that DOC from permafrost  
64 soils in Alaska is photoreactive [Ward and Cory, 2016]. Both the amount of permafrost-derived  
65 DOC and solar irradiance received by arctic freshwaters are increasing, the latter due to  
66 declining ice cover and expansion of thermokarst lakes [Surdu *et al.*, 2014; Williamson *et al.*,  
67 2014]. Consequently, the photochemical conversion of ancient permafrost DOC to CO<sub>2</sub> may also  
68 increase as the Arctic warms. Improved knowledge concerning the photoreactivity of permafrost  
69 DOC is therefore critical to predicting the fate of this climate vulnerable ancient carbon and its  
70 potential contribution to future global change.

71 To expand upon previous permafrost DOC photochemical studies that have solely  
72 focused on sites in Alaska, samples were collected from the Kolyma River Basin, the sixth  
73 largest watershed in the Arctic (~650,000 km<sup>2</sup>) and the largest watershed on Earth completely  
74 underlain by continuous permafrost [Spencer *et al.*, 2015]. The majority of the permafrost  
75 underlying the Kolyma River Basin is Pleistocene-aged yedoma, an organic-rich (1–5% C by  
76 mass) permafrost [Zimov *et al.*, 2006]. Yedoma is of singular importance to the strength of  
77 carbon-permafrost thaw feedbacks with estimates suggesting between a third to one half of all  
78 permafrost OC is stored in yedoma (500 Pg-C) [Zimov *et al.*, 2006]. DOC within yedoma  
79 permafrost thaw water streams in the Kolyma River Basin is typically ≥20,000 years old [Mann  
80 *et al.*, 2015; Spencer *et al.*, 2015; Vonk *et al.*, 2013], while DOC in the larger streams and rivers  
81 of the Kolyma River Basin is predominantly modern [Mann *et al.*, 2015; Neff *et al.*, 2006],  
82 presumably due to inputs of DOC from vegetation and surface soils. In a subversion of standard  
83 age-bioreactivity relationships, where younger material is expected to be more biolabile  
84 [Raymond and Bauer, 2001], the ancient permafrost-derived DOC from this region is highly  
85 biolabile (>50%) compared to the modern DOC (<10%) in the Kolyma River mainstem [Spencer  
86 *et al.*, 2015].

87 In this study, we determined whether ancient, yedoma permafrost-derived DOC is  
88 degraded by sunlight in the absence of microbes. To do this, we collected freshwaters from the  
89 same sites within the Kolyma River Basin that were sampled by Spencer *et al.* [2015]. These  
90 sites included a yedoma permafrost thaw stream (Duvanni Yar), small streams (Y3, Y4), a large  
91 tributary (Pantileikha River), and the Kolyma River mainstem (Table 1). We sterile filtered and  
92 irradiated the samples under a solar simulator for 30 days. We report and discuss the  
93 concentration and radiocarbon age of initial and photolabile DOC, along with colored dissolved  
94 organic matter (CDOM) light absorbance and ultra-high resolution mass spectrometry data of  
95 initial and photomodified DOM.

96

## 97 **2 Materials and Methods**

### 98 **2.1 Sample Handling**

99 Fieldwork was conducted out of the Northeast Science Station, Cherskiy, Russia (Fig. 1).  
100 Water samples were collected from five sites (Table 1) in September (2014), when annual  
101 maxima in permafrost thaw and active layer depth occur [Spencer *et al.*, 2015]. Samples (2 L) were  
102 collected in precleaned (acid soaked and ultrapure water rinsed) high-density polyethylene  
103 plasticware and kept on ice and in the dark until return to the laboratory (<6 hours) where they  
104 were filtered through pre-cleaned (acid soaked, ultrapure water rinsed, and sample flushed) 0.2  
105 μm capsule filters (Whatman Polycap TC) to remove particulates before freezing. Samples were  
106 returned frozen to the Skidaway Institute of Oceanography, Savannah, Georgia, USA (~24 hour  
107 transit time). Once at Skidaway, samples were transferred to -20°C freezers and stored in the  
108 dark until the photochemical experiments were conducted (January 2015).

### 109 **2.2 Photochemical Experimental Details**

110 Samples were thawed at the Skidaway Institute of Oceanography and refiltered through  
111 0.2 μm GHP syringe filters (Acrodisc). Dissolved organic carbon (DOC) concentrations were  
112 determined for all samples. For the photochemical experiments, the permafrost thaw water  
113 stream sample was diluted from a concentration of 98.7 mg-C L<sup>-1</sup> to 3.0 mg-C L<sup>-1</sup> to prevent the

114 possibility of high photochemical oxygen demand and other non-photochemical artefacts (e.g.  
 115 precipitation) that could have occurred at such elevated DOC concentrations. All other samples  
 116 were irradiated at natural DOC concentrations (Table 1). In addition to irradiating natural waters,  
 117 approximately carbon-normalized mixtures of yedoma permafrost thaw water and Kolyma River  
 118 mainstem water were produced generating a series of samples with varying ratios of modern and  
 119 ancient DOC (Table 2). Aliquots of natural waters and the mixtures were transferred to 100 mL  
 120 pre-combusted, UV-C sterilized spherical quartz irradiation flasks.

121 The current study did not seek to quantify real world rates of photoreactions. To  
 122 determine environmentally relevant rates, spectrally-resolved irradiations and a careful  
 123 accounting of wavelength specific absorbed photon doses are required to determine the apparent  
 124 quantum yield spectra that are the starting point for photochemical models [Hu *et al.*, 2002;  
 125 Powers *et al.*, 2016; Stubbins *et al.*, 2011; Stubbins *et al.*, 2006]. The current study was instead  
 126 designed to determine the fraction of DOM that is susceptible to photodegradation (i.e. the  
 127 photolabile fraction) under broadband simulated sunlight [Stubbins and Dittmar, 2015; Stubbins  
 128 *et al.*, 2010]. The broadband irradiation source was a solar simulator fitted with 12 UVA-340  
 129 bulbs (Q-Panel), which provide non-collimated light with a spectral shape and flux closely  
 130 approximating natural sunlight from 295 to 365 nm [Stubbins *et al.*, 2008], the main wavelength  
 131 range for environmental photochemical reactions involving CDOM [Mopper *et al.*, 2015]. The  
 132 integrated irradiance quantified in the solar simulator was  $\sim 14.4 \pm 0.7 \text{ W m}^{-2}$  as determined using  
 133 a spectroradiometer (OL756, Optronic Laboratories) fitted with a quartz fiber optic cable and 2”  
 134 diameter integrating sphere and calibrated with a NIST standard lamp (OL752-10 irradiance  
 135 standard) [Powers and Miller, 2015].

136 Absorbance (A) at wavelength  $\lambda$  within the flasks is calculated as:

$$137$$

$$138 \quad A_{(\lambda)} = a_{(\lambda)} \div 2.303 \times \text{pathlength} \quad (1)$$

139

140 where  $a$  is the Napierian light absorption coefficient ( $\text{m}^{-1}$ ) of CDOM at wavelength  $\lambda$   
 141 (nm) and pathlength is the optical pathlength through the flask (m). Percentage transmission  
 142 (%T) at wavelength  $\lambda$  is then calculated as:

$$143$$

$$144 \quad \%T_{(\lambda)} = 10^{(2-A_{(\lambda)})} \quad (2)$$

145

146 For our study, the outer diameter of the flasks was  $\sim 6$  cm and inner diameter  $\sim 5.5$  cm, the  
 147 discrepancy being due to the thickness of the flasks' quartz walls. The inner diameter determines  
 148 the pathlength that light will travel through the sample once the flasks are filled. Even with this  
 149 information, calculating the average pathlength of a sphere within which liquid sample is placed  
 150 is non-trivial due to variability in the amount of light reflected, which is dependent upon the  
 151 angle of incidence [Bolton, 2000], variation in the pathlength through the sphere due to refraction  
 152 of light as it travels from air, through the curved quartz surface and into the water, which is  
 153 dependent upon wavelength and the angle of incidence [Bolton, 2000], and the additional  
 154 uncertainties due to the variable angles of incidence that result from the use of a non-collimated  
 155 light source. Consequentially, careful and arduous actinometrical tests would have been required

156 to determine wavelength specific average pathlengths for our spherical flasks and even then,  
157 estimates of photon flux and pathlength would have included uncertainties. Keeping these  
158 caveats in mind, it is possible to estimate whether the samples placed within the flasks were  
159 optically thin for given wavelengths over the range of pathlengths light can travel through the  
160 flasks. The following considerations are for 320 nm, a wavelength that absorbed light under the  
161 solar simulator and was efficiently photobleached (94 to 98% loss; Table 1). At the start of the  
162 experiment, samples ranged in Napierian light absorption coefficient from 3.5 to 74 m<sup>-1</sup> at 320  
163 nm (Table 1). Assuming that 5.5 cm is the maximum pathlength that light can take through the  
164 spherical irradiation flask, this equates to absorbance values (A; optical densities) ranging from  
165 0.08 to 1.8. At this maximum pathlength, none of the samples were optically thin (<90% of light  
166 was transmitted) at 320 nm with %T ranging from 82.5 for permafrost thaw water to 1.7 for Y3.  
167 The shortest pathlength through the sphere is approximately zero cm and at this pathlength all  
168 samples were optically thin. As the irradiation progressed, all samples photobleached, reducing  
169 light absorbance and increasing transmission. As the experiments were designed to mimic near-  
170 total photobleaching, by the end of the experiment, all samples were optically thin at 320 nm  
171 (>90%T for the maximum possible pathlength of 5.5 cm).

172 The samples were irradiated between 25°C and 30°C. One day of irradiation using this  
173 solar simulator is approximate to 18 hours of solar irradiance during July at the Cherskiy field  
174 station based upon irradiance modeled using the System for Transfer of Atmospheric Radiation  
175 (STAR) [Ruggaber *et al.*, 1994]. Every three days the flasks were swirled to mix the sample and  
176 switched between fixed points to account for any variation in the light flux under the solar  
177 simulator. For the permafrost and Kolyma River samples, a further four 100 mL flasks were  
178 filled and irradiated to allow a time series of CDOM photobleaching to be recorded. This time  
179 series allowed photobleaching to be tracked through the experiment until ≥94% of CDOM  
180 absorbance at 320 nm was lost. After 30 days of irradiation, ≥94% of CDOM absorbance at 320  
181 nm was lost for all samples and samples were sub-sampled with a pre-combusted Pasteur pipette  
182 for analysis of DOC concentration (collected in pre-combusted glass vials and immediately  
183 acidified to pH 2 with hydrochloric acid), CDOM (refrigerated in pre-combusted glassware),  
184 radiocarbon (frozen in pre-cleaned polycarbonate bottles), and ultrahigh resolution Fourier  
185 transform ion cyclotron mass spectrometry (FT-ICR MS; frozen in pre-cleaned polycarbonate  
186 bottles).

### 187 **2.3 Assessment of Potential Microbial Contamination in Photochemical Experiments**

188 Permafrost thaw water DOC from our sampling site is highly biolabile [Drake *et al.*,  
189 2015; Mann *et al.*, 2015; Spencer *et al.*, 2015; Vonk *et al.*, 2013]. Permafrost thaw DOC at other  
190 sites in the Arctic, for instance in Alaska, has also been found to be highly biolabile [Abbott *et al.*,  
191 2014; Ward and Cory, 2015]. However, previous studies of permafrost-derived DOC  
192 photolability have not sterile filtered samples (i.e. they used 0.7 µm GF/F filters) [Cory *et al.*,  
193 2014; Ward and Cory, 2016], leaving uncertainty about the direct photolability of permafrost  
194 thaw DOC. Therefore, extra care was taken to ensure that the light irradiation experiments in the  
195 current study detailed only photochemical effects and not combined photo+bio effects as might  
196 be expected if samples were not sterile. Samples were 0.2 µm filtered immediately prior to  
197 irradiations to minimize the possibility of microbial contamination. Prior to filling with sample,  
198 glassware was also sterilized under UV-C light in a laminar flow hood. Filling of the glassware  
199 with samples was conducted in the laminar flow hood with the UV light turned off.

200 To ascertain whether these precautions were effective in preventing microbial  
 201 contamination, samples were collected at the end of the photochemical experiments and analyzed  
 202 for bacterial abundance using flow cytometry. Samples for flow cytometry were preserved with  
 203 0.1% glutaraldehyde solution (final concentration) and frozen at -80°C. Ultrapure water and 0.2  
 204 µm-filtered sample were run as blanks. Samples were vortexed, and stained for 30 min with Sybr  
 205 Green I (Thermo Fisher Scientific), a nucleic acid (NA) binding stain [Marie *et al.*, 1997].  
 206 Bacterial cells were counted using a flow cytometer (BD FACSCalibur) equipped with a 15 mW  
 207 air-cooled argon-ion laser tuned for blue excitation (ex 488 nm), with emission (em) detectors at  
 208 535, 585 and 650 nm. Runs were calibrated with fluorescent polystyrene beads (1 µm,  
 209 Spherotech) added to each sample to ensure instrument reproducibility and provide a  
 210 fluorescence reference. Data were acquired using BD Cell Quest Pro software (v. 4.0.1) and  
 211 analyzed with FlowJo software (v.10).

212 Counts in samples (Table 3) were below those of the ultrapure water (10 counts) and  
 213 Sample Blank (66 counts) in all samples except Y3. Blank counts reflect background noise. The  
 214 counts recorded for Y3 are still within the typical range for river water blanks (0.2 µm filtered  
 215 samples; e.g., 7 to 758 counts for samples from the Connecticut River Basin run on the same  
 216 instrument and using the same settings in the same month. River Water Blank Counts Mean =  
 217 212; n = 24). Based upon this data, we conclude that all samples were sterile. Of major  
 218 significance are the extremely low counts (count = 2; Table 3) observed for the highly biolabile,  
 219 100% permafrost thaw sample, indicating that this sample was sterile, as were the other mixtures  
 220 in the photo-priming experiment (Table 3). These results add confidence to our assertion that our  
 221 experiments assessed the direct photolability of permafrost thaw DOC in the absence of  
 222 biological artifacts.

## 223 **2.4 Quantification of Dissolved Organic Carbon**

224 Samples acidified to pH 2 by addition of hydrochloric acid (p.a.) were analyzed for non-  
 225 purgable organic carbon using a Shimadzu TOC-V<sub>CPH</sub> analyzer fitted with a Shimadzu ASI-V  
 226 autosampler. Potassium hydrogen phthalate standards were analyzed. In addition to standards,  
 227 aliquots of deep seawater reference material, Batch 10, Lot# 05-10, from the Consensus  
 228 Reference Material Project (CRM) were analyzed to check the precision and accuracy of the  
 229 DOC analyses. Analyses of the CRM deviated by less than 5% from the reported value for these  
 230 standards (41 to 44 µM-DOC) [<http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.htm>].  
 231 Routine minimum detection limits in the investigator's laboratory using the above configuration  
 232 are 34±4 µg-C and standard errors are typically 1.7±0.5 % of the DOC concentration [Stubbins  
 233 and Dittmar, 2012]. The photolabile fraction of DOC (DOC<sub>photo</sub>) was calculated as:

$$234$$

$$235 \quad \text{DOC}_{\text{photo}} = \text{DOC}_{\text{initial}} - \text{DOC}_{\text{final}} \quad (3)$$

236

237 where DOC<sub>initial</sub> is the concentration of DOC in the initial samples and DOC<sub>final</sub> is the  
 238 DOC concentration in the samples after 30 days of irradiation. Percentage DOC<sub>photo</sub> was then  
 239 calculated as DOC<sub>photo</sub> divided by DOC<sub>initial</sub> multiplied by 100.

## 240 **2.5 Stable and Radiocarbon Analysis**

241  $\delta^{13}\text{C}$  analyses were conducted at the University of California, Davis Stable Isotope  
 242 Facility and  $^{14}\text{C}$  analyses at the Laboratory for Ion Beam Physics, Eidgenössische Technische  
 243 Hochschule (ETH) Zürich.  $\delta^{13}\text{C}$ -DOC samples were analyzed using an O.I. Analytical Model  
 244 1010 TOC analyzer (precision of  $\pm 0.2\%$ ) interfaced to a PDZ Europa 20–20 IRMS (Sercon Ltd).  
 245  $\delta^{13}\text{C}$ -DOC measurements were calibrated against the  $\delta^{13}\text{C}$  values of KHP and IHSS Suwannee  
 246 River humic acid in ultrapure water. Waters for  $^{14}\text{C}$ -DOC analyses were freeze-dried (Christ  
 247 Alpha 2-4, LSC with a low-carbon vacuum hybrid pump, Vacubrand RC-6; Martin Christ, Labex  
 248 Instrument AB, Sweden) directly in pre-combusted ( $850^\circ\text{C}/5\text{ h}$ ) quartz tubes. Samples were  
 249 fumigated with hydrochloric acid for 24 hrs at  $60^\circ\text{C}$  to remove carbonates and flame sealed with  
 250 pre-combusted CuO under vacuum.  $\text{CO}_2$  gas was cryogenically captured and quantified ( $\sim 30\ \mu\text{g}$ -  
 251 C) before measurement using an accelerator mass spectrometer (AMS) fitted with a gas  
 252 accepting ion source (MICADAS, Ionplus AG) [Mann *et al.*, 2015]. Combusted NIST SRM  
 253 4990C oxalic acid was used as a standard for normalization, and blanks were determined using  
 254 radiocarbon-free  $\text{CO}_2$ , both at a concentration of 5%  $\text{CO}_2$  in He. The modern oxalic acid standard  
 255 was measured to 3 ‰ relative error and the blank value was 39,400 (years before present, yBP).  
 256 Samples were run until they were fully consumed giving relative errors of 1–4%.

257 Radiocarbon contents are reported as fraction modern ( $F^{14}\text{C}$ ) and  $^{14}\text{C}$  age (yBP) [Reimer  
 258 *et al.*, 2004; Stenström *et al.*, 2011]. All radiocarbon values were corrected for a procedural blank  
 259 ( $0.6\ \mu\text{g-C}$ ;  $F^{14}\text{C}$  of  $0.3 \pm 0.1$ ). The apparent  $^{14}\text{C}$  age of the photolabile DOC fraction ( $[\text{DOC}]_{\text{photo}}$ )  
 260 was calculated using measurements of initial DOC ( $[\text{DOC}]_{\text{initial}}$ ) and final DOC concentrations  
 261 ( $[\text{DOC}]_{\text{final}}$ ) alongside the associated change in isotopic composition using a simple mass  
 262 balance:

$$[\text{DOC}]_{\text{photo}} \times F^{14}\text{C}_{\text{photo}} = [\text{DOC}]_{\text{initial}} \times F^{14}\text{C}_{\text{initial}} - [\text{DOC}]_{\text{final}} \times F^{14}\text{C}_{\text{final}} \quad (4)$$

264

265 Individual errors associated with DOC concentration and isotope measurements were  
 266 propagated to assess error on  $F^{14}\text{C}_{\text{photo}}$  and apparent age of the photolabile DOC (Table 1 and 3).  
 267 A paired t-test was used to assess the statistical significance of the change in fraction modern  
 268 ( $F^{14}\text{C}$ ) between the initial and final sample means.

## 269 **2.6 Spectrophotometric Analysis of Colored Dissolved Organic Matter**

270 Following irradiation, aliquots were transferred from the flasks to combusted glass vials,  
 271 which were then capped with Teflon septa and placed in the dark for approximately 8 hours in  
 272 order to return to room temperature. Subsequently, each aliquot was transferred to a 1 cm quartz  
 273 absorbance cuvette (Starna Cells) using a pre-combusted Pasteur pipette. The cuvette was then  
 274 situated in the light path of an Agilent 8453 ultraviolet-visible spectrophotometer and a sample  
 275 CDOM absorbance spectrum was recorded. An aliquot of temperature equilibrated ultrapure  
 276 water was run immediately before and after the samples, as well as every  $\sim 10$  samples, to  
 277 provide a blank. Blank corrected absorbance spectra were then corrected for offsets due to  
 278 scattering and instrument drift by subtraction of the average absorbance between 700 and 800 nm  
 279 [Stubbins *et al.*, 2011]. Data output from the spectrophotometer were in the form of  
 280 dimensionless absorbance (A) and were converted to the Napierian absorption coefficient,  $a$  ( $\text{m}^{-1}$ )  
 281 [Hu *et al.*, 2002]. The percentage loss of  $a$  at 320 and 254 nm was calculated:

282



$$\% \text{ Photolabile } a_{(\lambda)} = (\text{Initial } a_{(\lambda)} - \text{Final } a_{(\lambda)}) \div \text{Initial } a_{(\lambda)} \times 100 \quad (5)$$

284

285 The carbon-normalized light absorbance at 254 nm (SUVA<sub>254</sub>; L mg-C<sup>-1</sup> m<sup>-1</sup>) was then  
 286 calculated by dividing the Decadic light absorption coefficient at 254 nm (m<sup>-1</sup>; i.e. the Napierian  
 287 absorption coefficient / 2.303) by the DOC concentration (mg-C L<sup>-1</sup>) [Weishaar *et al.*, 2003].  
 288 This calculation was performed for the initial and photodegraded DOM samples, and for the  
 289 fraction of DOC and CDOM absorbance lost during irradiation. Individual errors associated with  
 290 DOC concentration and absorbance measurements were propagated to assess error in the  
 291 apparent SUVA<sub>254</sub> of photolabile DOC (DOC<sub>photo</sub> in Table 1).

## 292 2.7 Fourier Transform Ion Cyclotron Mass Spectrometry

293 Samples were analyzed via ultrahigh resolution FT-ICR MS without prior extraction or  
 294 isolation, allowing the broadest possible analytical window for electrospray ionization FT-ICR  
 295 MS. Samples were diluted 1:1 with ultrapure water and analyzed in negative mode electrospray  
 296 ionization using a 15 Tesla FT-ICR MS (Bruker Solarix) at the University of Oldenburg,  
 297 Germany [Spencer *et al.*, 2015]. 500 broadband scans were accumulated for the mass spectra.  
 298 After internal calibration, mass accuracies were within an error of <0.2 ppm. Molecular formulas  
 299 were assigned to detected masses with signal to noise ratios greater than five, based on published  
 300 rules [Singer *et al.*, 2012; Stubbins *et al.*, 2010]. Compounds detected in the procedural blank  
 301 (ultrapure water) were removed. Detection limits were standardized between samples by  
 302 adjusting the dynamic range of each sample to that of the sample with the lowest dynamic range  
 303 (dynamic range = average of the largest 20% of peaks assigned a formula divided by the signal  
 304 to noise threshold intensity; standardized detection limit = average of largest 20% of peaks  
 305 assigned a formula within a sample divided by the lowest dynamic range within the sample set)  
 306 [Stubbins *et al.*, 2014]. Peaks below this detection limit were removed to prevent false negatives  
 307 for the occurrence of a formula within samples with low dynamic range.

308 For each molecular formula, we calculated the modified Aromaticity Index (AI<sub>mod</sub>) [Koch  
 309 and Dittmar, 2006; 2016], which indicates the likelihood of a molecular formula representing  
 310 aromatic structures, from an AI<sub>mod</sub> of zero, where formulas are aliphatic, through an intermediate  
 311 range, where a molecular formula could indicate aromatic or non-aromatic isomers, to AI<sub>mod</sub>  
 312 values above 0.5, where a molecular formula is highly likely to represent aromatic isomers [Koch  
 313 and Dittmar, 2006]. These AI<sub>mod</sub> values were calculated as:

314

$$315 \text{ AI}_{\text{mod}} = (1 + \text{C} - 0.5\text{O} - \text{S} - 0.5(\text{N} + \text{P} + \text{H})) / (\text{C} - 0.5\text{O} - \text{S} - \text{N} - \text{P}) \quad (5)$$

316

317 The main goal of the FT-ICR MS analyses in the current study was to determine the  
 318 molecular signatures of photomodification. In order to do this, FT-ICR MS formulas were  
 319 classified as photolabile (>30% reduction in peak intensity), photoproduct (>30% increase in  
 320 peak intensity), and photorefractory (<30% change in peak intensity). The choice of the  
 321 percentage change in normalized signal intensity (i.e. 30%) is somewhat arbitrary. However,  
 322 similar molecular trends were apparent when different percentages were utilized, indicating that  
 323 the inferences made with the choice of 30% differences represent robust trends in molecular  
 324 photomodification. In defining these groupings, it should be remembered that electrospray  
 325 ionization is selective, and that this selectivity results in one peak's intensity changing relative to

326 increases or decreases in other peak intensities. Therefore, a molecular formula that appeared to  
327 be produced during the irradiation may have been present in the sample all along, but emerged  
328 from the background as other peaks were removed during photodegradation. Alternatively, a  
329 molecular formula identified as labile, may also still be present at the end of the experiment, but  
330 may not show up if photoproducts with high ionization efficiencies are photoproducted.

331

### 332 **3 Results and Discussion**

#### 333 **3.1 Photostability of Ancient, Yedoma Permafrost-derived DOC**

334 The DOC in yedoma permafrost thaw streams was verified as being ancient permafrost-  
335 derived DOC (20,000 yBP) and showed no measurable photochemical loss (Table 1). By  
336 contrast, irradiation of river samples containing modern DOC resulted in significant DOC losses  
337 (26 to 40%; Table 1). These trends in DOC photolability (i.e. percentage DOC loss during  
338 photodegradation) contrast with trends in DOC biolability which was much higher in samples  
339 from the same permafrost thaw stream (~62% biolabile) than for the Kolyma River (~7%  
340 biolabile) [Spencer *et al.*, 2015].

341 An isotope balance approach (Equation 4) was applied to calculate the apparent age of  
342 DOC lost during the irradiations of permafrost thaw stream and other Kolyma River Basin  
343 waters. The mean  $F^{14}C$  of final samples were significantly lower (older) than initial samples ( $t =$   
344  $2.61$ , degrees freedom = 7;  $p < 0.05$ ).  $F^{14}C$  values for  $DOC_{photo}$  indicated that photolabile DOC was  
345 always modern (Table 1). This contrasts with results from biodegradation experiments with  
346 waters from the same field sites, where microbes preferentially utilized ancient DOC [Mann *et*  
347 *al.*, 2015; Spencer *et al.*, 2015].

348 In the current study, samples were irradiated for 30 days under a solar simulator. The  
349 areal light dose received was equivalent to approximately 22.5 days of natural solar irradiance at  
350 the latitude of the Kolyma River (see methods). This timeframe is approximately equivalent to  
351 the transit time of water from the Kolyma River source to the sea [Holmes *et al.*, 2012].  
352 However, the similarity in these timeframes should not be interpreted as a similarity in the light  
353 dose received by the irradiated samples and CDOM in the Kolyma River as it is carried toward  
354 the ocean. In the river, the water column mixes and the photochemical potency of the solar  
355 irradiance dose received and absorbed in the top few centimeters of the surface is effectively  
356 diluted throughout the depth of the water column. In our experimental setup, samples received  
357 much higher photon doses per unit volume as they were trapped in a spherical flask with a 5.5  
358 cm internal diameter. As the samples in our experiments photobleached, they also became  
359 optically thin, increasing the penetration of light into the flask and increasing the photon dose  
360 absorbed per unit CDOM. Consequently, the light dose absorbed per unit CDOM over 30 days in  
361 our experiments is likely only experienced by Kolyma River CDOM in nature once the CDOM  
362 has been exported to and diluted within the coastal ocean. Even at this point, CDOM derived  
363 from the Kolyma River would need to remain in low color, stratified waters for many months to  
364 receive a photon dose approaching those absorbed by CDOM in our experiments. Furthermore,  
365 the permafrost thaw stream sample had the lowest initial absorbance of all the samples collected  
366 (Table 1). Therefore, permafrost-DOM received a greater photon dose per unit CDOM than  
367 received by the optically thicker river water samples. Based upon these considerations, the  
368 stability of permafrost-derived DOC under the unnaturally high photon dose conditions of our

369 experiments, suggest that permafrost-derived DOC will be highly resistant to  
370 photomineralization in natural waters.

371 The contrasting rapid and preferential loss of ancient permafrost DOC during bio-  
372 incubations and undetectable loss of ancient permafrost DOC during photochemical irradiations  
373 indicate that microbial processes are likely responsible for the loss of permafrost-derived DOC  
374 from arctic freshwaters, at least for permafrost DOC derived from the organic-rich yedoma that  
375 is the greatest store of climate-vulnerable ancient permafrost organic carbon [Zimov *et al.*, 2006].

### 376 **3.2 Dissolved Organic Matter Photomodification**

377 The aromatic molecules comprising the CDOM pool are the primary light absorbing  
378 chromophores and initiators of photoreactions in natural waters [Mopper *et al.*, 2015]. The  
379 permafrost thaw sample had the lowest carbon-normalized CDOM absorbance ( $SUVA_{254}$ ), a  
380 proxy for aromaticity [Weishaar *et al.*, 2003], of the samples studied (Table 1), consistent with  
381 previous studies that also report low CDOM absorbance levels for permafrost-derived DOM  
382 [Abbott *et al.*, 2014; Mann *et al.*, 2014]. The low  $SUVA_{254}$  of permafrost-derived DOM likely  
383 partly explains its low photolability. Although permafrost-derived DOC was not significantly  
384 photolabile (i.e. DOC loss was below detection limits), 78% of permafrost-derived CDOM was  
385 photobleached (Table 1). Consistent with previous studies [Mopper *et al.*, 2015; Osburn *et al.*,  
386 2009; Spencer *et al.*, 2009; Stubbins *et al.*, 2012], CDOM was also preferentially photobleached  
387 (78 to 89%) relative to DOC (0 to 40%) in all samples (Table 1). The preferential loss of CDOM  
388 relative to DOC during photodegradation resulted in photolabile DOM apparent  $SUVA_{254}$  values  
389 ranging from 5.7 to 12.2 L mg-C<sup>-1</sup> m<sup>-1</sup> (Table 1). These calculated  $SUVA_{254}$  values for the  
390 organic matter lost during photodegradation exceed the maximum values normally observed in  
391 natural waters (~5 L mg-C<sup>-1</sup> m<sup>-1</sup>) [Mann *et al.*, 2014; Spencer *et al.*, 2012], indicating that  
392 irradiation resulted in the loss of an organic matter pool that was enriched in colored, aromatic  
393 moieties.

394 The molecular signatures accompanying the apparent photomodification of DOM in  
395 permafrost thaw and Kolyma mainstem waters were determined by FT-ICR MS [Dittmar and  
396 Stubbins, 2014]. Molecular formulas were classified as photolabile (>30% reduction in signal  
397 intensity), photoproduct (>30% increase in signal intensity), and photorefractory (<30% change  
398 in signal intensity). Consistent with previous results for river [Stubbins *et al.*, 2010] and ocean  
399 DOM [Stubbins and Dittmar, 2015], aromatic formulas ( $AI_{mod} > 0.5$ ) were highly photolabile and  
400 aliphatics ( $AI_{mod} < 0.1$ ) were the main photoproducts within both permafrost and Kolyma River  
401 DOM (Fig. 2a,b), indicating that the preferential photochemical loss of CDOM is driven by the  
402 photomodification of colored aromatic compounds to non-aromatic, transparent DOM.  
403 Furthermore, these results suggest that the photobleaching of permafrost CDOM that occurred  
404 without significant DOC losses may have been driven by the photo-induced cleavage of aromatic  
405 ring structures in CDOM to form non-colored, non-aromatic DOM photoproducts as exemplified  
406 by aliphatic compounds.

### 407 **3.3 Potential Influence of Photomodification upon DOC Biolability**

408 Photomodification can alter DOC biolability. For instance, experiments irradiating low  
409 biolability DOC from colored, aromatic-rich freshwaters generally report an increase in DOC  
410 biolability after irradiation [Cory *et al.*, 2014; Miller and Moran, 1997]; while photodegradation  
411 of highly biolabile DOC can decrease its biolability [Bittar *et al.*, 2015]. Thus, for the colored,  
412 modern DOM samples irradiated here, it is likely that photomodification increased DOC

413 biolability as observed for other arctic freshwaters [Cory *et al.*, 2014]. The aliphatic compounds  
414 that are enriched in permafrost-derived DOM relative to Kolyma River DOM ( $AI_{\text{mod}} < 0.1$  Fig.  
415 2a,b;  $H/C > 1.5$  Fig. 2C&D) are highly biolabile [Spencer *et al.*, 2015]. These classes of aliphatic  
416 compounds were photorefractory or photoproducts in the current experiments (Fig. 2).  
417 Therefore, we may expect the photomodification and accompanying photoproduction of  
418 aliphatics to also enhance the biolability of permafrost DOC. However, until direct  
419 measurements of the enhanced microbial utilization of radiocarbon depleted DOC post-  
420 irradiation are made, it remains unclear whether photomodification of highly biolabile  
421 permafrost DOC will result in an increase or decrease in its biolability.

### 422 **3.4 Photochemical Priming**

423 When CDOM absorbs sunlight, secondary photochemical or photosensitization reactions  
424 can lead to the indirect photodegradation of organic compounds [Chin *et al.*, 2004].  
425 Consequently, we hypothesized that sunlight absorbed by relatively photolabile, aromatic-rich,  
426 modern DOM, could lead to the indirect photomineralization of relatively aromatic-poor, ancient  
427 permafrost-derived DOM as the latter mixes into arctic fluvial networks. We term this potential  
428 indirect photomineralization “photo-priming”.

429 To test for photo-priming, carbon-normalized mixtures of permafrost thaw and Kolyma  
430 River waters were irradiated. The photobleaching of CDOM absorbance, the percentage of  
431 photolabile DOC, and the percentage of photolabile molecular formulas all increased linearly  
432 with the proportion of Kolyma River DOC in the mixture (Fig. 3a-c). Concurrently, the fraction  
433 of modern DOC in each mixture decreased significantly during the irradiations (Fig. 3d; paired t-  
434 test (df 7)  $t = 2.61$ ,  $p < 0.05$ ), highlighting that modern DOC was consistently photomineralized.  
435 Where the loss of DOC during irradiations was above detection limits (0 to 39% permafrost-  
436 derived DOC mixtures), the photomineralized DOC was consistently modern (Table 2) clearly  
437 showing that no significant loss of ancient permafrost-derived DOC occurred either through  
438 direct photochemical reactions or secondary, photo-priming reactions (Table 2). Thus, yedoma  
439 permafrost-derived DOC is unlikely to undergo photomineralization as it mixes into arctic rivers  
440 containing modern, colored DOM.

441

### 442 **4. Conclusions**

443 Delineating the controls on the fate of thawed permafrost-derived DOC is critical to  
444 assessing how the Arctic carbon cycle will impact the aquatic ecosystems of the Arctic and their  
445 role in global climate change. Although photochemistry appears to be quantitatively important  
446 for the mineralization of modern arctic DOC to  $CO_2$  [Cory *et al.*, 2014], photochemistry does not  
447 appear to have a significant, direct influence upon the fate of ancient yedoma permafrost-derived  
448 DOC. Due to the high biolability of yedoma permafrost-derived DOC [Abbott *et al.*, 2014; Drake  
449 *et al.*, 2015; Mann *et al.*, 2015; Spencer *et al.*, 2015; Vonk *et al.*, 2013], we suggest that  
450 microbial activity, rather than sunlight, will control the strength of the positive feedback between  
451 climate change, carbon mobilization to inland waters due to yedoma permafrost thaw, and the  
452 release of ancient permafrost-derived  $CO_2$  to the atmosphere.

453

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461

462

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- 599

600 **Table 1** | Initial dissolved organic carbon (DOC) concentration, fraction modern ( $F^{14}C$ ), apparent  
 601 radiocarbon age in years before present (yBP), colored dissolved organic matter (CDOM) light  
 602 absorption coefficient at 254 nm ( $a_{254}$ ), and specific ultraviolet light absorbance of DOM at 254  
 603 nm ( $SUVA_{254}$ ) for a permafrost thaw water stream, two small order streams underlain by  
 604 permafrost (Y3, Y4), a large tributary (Pantileikha River), and the Kolyma River mainstem, all  
 605 within the Kolyma River Basin, as well as the percentage photolabile DOC ( $DOC_{photo}$ ) and  $a_{254}$ ,  
 606 and the  $F^{14}C$ , apparent age, and  $SUVA_{254}$  of  $DOC_{photo}$  that was lost from each sample during 30  
 607 days of irradiation in a solar simulator and the decimal degrees latitude and longitude for each  
 608 site. Modern is defined as  $F^{14}C$  that is not significantly different from 1.0.

	Permafrost Thaw* Water Stream	Y3	Y4	Pantileikha River	Kolyma River Mainstem
Latitude:	68.6305:	68.7592:	68.7424:	68.7120:	68.7891:
Longitude	159.1501	161.4477	161.4137	161.4942	161.3132
Initial DOC ( $mg-C L^{-1}$ )	3.0±0.1	24.4±0.6	21.4±0.7	12.1±0.5	4.8±0.1
% $DOC_{photo}$	-3±4 %	40±2 %	28±3 %	31±4 %	26±2%
Initial $a_{320}$ ( $m^{-1}$ )	3.5	74	58	34	11
% Photolabile $a_{320}$	94 %	98 %	97 %	97 %	98 %
Initial $a_{254}$ ( $m^{-1}$ )	11	188	151	88	30
% Photolabile $a_{254}$	78 %	89 %	85 %	87 %	86 %
Initial $SUVA_{254}$ ( $L mg-C^{-1} m^{-1}$ )	1.7	3.3	3.1	3.1	2.7
$SUVA_{254}$ of $DOC_{photo}$ ( $L mg-C^{-1} m^{-1}$ )	NA	7.4±0.3	9.3±1.5	8.6±1.2	8.8±0.8
$F^{14}C$ of Initial DOC	0.087±0.01	1.06±0.01	1.05±0.01	1.05±0.01	0.993±0.002
$F^{14}C$ of $DOC_{photo}$	NA	1.04±0.06	1.0±0.1	1.0±0.1	0.93±0.09
$^{14}C$ Age of Initial DOC	20,000 yBP	Modern	Modern	Modern	Modern
$^{14}C$ Age of $DOC_{photo}$	NA	Modern	Modern	Modern	Modern

609 \*The permafrost thaw water sample was diluted from 98.7  $mg-C L^{-1}$  to 3.0  $mg-C L^{-1}$  to prevent  
 610 artifacts that could have occurred at elevated DOC concentrations.

611

612 **Table 2** | Percentages of dissolved organic carbon (DOC) derived from permafrost thaw water or  
 613 Kolyma River water and DOC apparent age in years before present (yBP) within Kolyma River  
 614 water:permafrost thaw stream water mixtures, as well as the percentage, fraction modern ( $F^{14}C$ )  
 615 and apparent age of the photolabile DOC ( $DOC_{photo}$ ) lost during 30 day irradiations in a solar  
 616 simulator. \*DOC loss in mixtures with less than 61% Kolyma River DOC was within analytical  
 617 error introducing uncertainties into estimates of the  $F^{14}C$  and apparent age of  $DOC_{photo}$  in these  
 618 samples. Modern is defined as  $F^{14}C$  that is not significantly different from 1.0.

% Permafrost DOC	100%	98%	92%	66%	39%	17%	3%	1%	0%
% Kolyma River DOC	0%	2%	8%	34%	61%	83%	97%	99%	100%
$^{14}C$ Age of Initial DOC	20,000	17,100	12,400	7,380	3,580	1,510	Modern	Modern	Modern
% $DOC_{photo}$	*-3±4%	*3±3%	*3±4%	*4±3%	14±3%	22±3%	25±3%	27±2%	26±2%
$F^{14}C$ of $DOC_{photo}$	0.1±0.1	0.9±1.2	1.6±2.2	2.0±1.9	1.1±0.2	0.9±0.1	1.0±0.1	1.0±0.1	0.9±0.1
$^{14}C$ Age of $DOC_{photo}$	-	Modern*	Modern*	Modern*	Modern	Modern	Modern	Modern	Modern

619

620

621 **Table 3** | Raw and volume corrected counts for irradiated samples, process blanks and ultrapure  
 622 water blanks based upon flow cytometry.

623

Sample Type	% Permafrost DOC	Counts	Counts per mL*
Permafrost Thaw Stream	100%	2	49
Permafrost/Kolyma Mix	98%	29	711
Permafrost/Kolyma Mix	92%	0	0
Permafrost/Kolyma Mix	66%	6	151
Permafrost/Kolyma Mix	39%	7	173
Permafrost/Kolyma Mix	17%	6	144
Permafrost/Kolyma Mix	3%	3	74
Permafrost/Kolyma Mix	1%	0	0
Kolyma River Mainstem	0%	2	49
Pantileikha River	-	3	73
Y4	-	14	348
Y3	-	206	4951
Sample Blank	-	66	1628
Ultrapure Water Blank	-	10	245

624 \*Sample volumes varied from 39.8 to 41.6  $\mu\text{L}$ ; the average flow rate was  $15.9 \pm 4.5 \mu\text{L min}^{-1}$ .

625

626

627 **Figure captions:**

628

629 **Figure 1:** Study site and sample locations. Individual site latitude and longitude are provided in  
630 Table 1. Upper right panel is a map centered on the north pole with land in black and sea  
631 in grey.

632

633 **Figure 2: Panels a and b)** Bar charts grouping the percentage of photoresistant, photo-labile,  
634 and photoproducted molecular formulas by modified aromaticity index. **a:** permafrost  
635 thaw water stream. **b:** Kolyma River mainstem. **Panels c and d)** van Krevelen diagrams  
636 where each dot represents one molecular formula, and where color indicates the change  
637 in normalized signal intensity in mass spectra caused by 30 days of photo-modification in  
638 a solar simulator for, **c:** permafrost thaw water stream, and **d:** Kolyma River mainstem.  
639 Tables embedded in Panels c and d present the number of total, photoproducted, photo-  
640 labile, and photorefractory molecular formulas.

641 **Figure 3:** Results from 30 day photochemical irradiations of mixtures of yedoma permafrost  
642 thaw stream and Kolyma River mainstem water. **a:** Loss of colored dissolved organic  
643 matter (CDOM) light absorption ( $a$ ) at 254 nm. **b:** Percentage photo-labile dissolved  
644 organic carbon (DOC). **c:** Percentages of photo-labile molecular formulas. **d:** Fraction  
645 modern ( $F^{14}C$ ) for DOC in the mixtures before and after irradiation. Light and dark green  
646 regions on a to c indicate the 95% confidence of fit and prediction respectively. Error  
647 bars are drawn at 1 standard deviation. d has no error bars as each sample was analyzed  
648 only once via ultrahigh resolution Fourier ion cyclotron resonance mass spectrometry.

649