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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 CO₂ and emitted to the atmosphere, accelerating climate change.
31 Sunlight-driven photoreactions oxidize DOC, converting a portion to CO₂ 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 CO₂ 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 CO₂ abundance of ~400 ppm)
53 [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. CO₂,
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 CO₂ 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 CO₂ 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 CO₂ 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 km²) 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⁻¹ to 3.0 mg-C L⁻¹ 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 λ 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 (m^{-1}) of CDOM at wavelength λ
 141 (nm) and pathlength is the optical pathlength through the flask (m). Percentage transmission
 142 (%T) at wavelength λ 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 ~ 6 cm and inner diameter ~ 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⁻¹ 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_{CPH} 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_{photo}) was calculated as:

$$234$$

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

236

237 where DOC_{initial} is the concentration of DOC in the initial samples and DOC_{final} is the
 238 DOC concentration in the samples after 30 days of irradiation. Percentage DOC_{photo} was then
 239 calculated as DOC_{photo} divided by DOC_{initial} 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}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}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°C to remove carbonates and flame sealed with
 250 pre-combusted CuO under vacuum. 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 CO_2 , both at a concentration of 5% 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}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 ± 0.1). The apparent ^{14}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 ~ 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 (m^{-1})
 281 [Hu *et al.*, 2002]. The percentage loss of a at 320 and 254 nm was calculated:

282

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

283

284

285 The carbon-normalized light absorbance at 254 nm (SUVA₂₅₄; L mg-C⁻¹ m⁻¹) was then
 286 calculated by dividing the Decadic light absorption coefficient at 254 nm (m⁻¹; i.e. the Napierian
 287 absorption coefficient / 2.303) by the DOC concentration (mg-C L⁻¹) [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 SUVA₂₅₄ of photolabile DOC (DOC_{photo} 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_{mod}) [Koch
 309 and Dittmar, 2006; 2016], which indicates the likelihood of a molecular formula representing
 310 aromatic structures, from an AI_{mod} of zero, where formulas are aliphatic, through an intermediate
 311 range, where a molecular formula could indicate aromatic or non-aromatic isomers, to AI_{mod}
 312 values above 0.5, where a molecular formula is highly likely to represent aromatic isomers [Koch
 313 and Dittmar, 2006]. These AI_{mod} values were calculated as:

314

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

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⁻¹ m⁻¹ (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⁻¹ m⁻¹) [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 photoproducted 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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- 597
- 598
- 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 (SUVA₂₅₄) 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 SUVA₂₅₄ 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 μL ; 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.

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