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Low photolability of yedoma permafrost dissolved organic carbon

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20 **Key Points:**

21 - Ancient DOC is released from thawing permafrost soils into arctic rivers

22 - Sunlight preferentially photomineralizes modern arctic river DOC leaving behind ancient
23   permafrost DOC

24 - Undetectable photochemical losses of permafrost DOC were accompanied by notable
25   photomodification of DOM optical and molecular signatures

26

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_2 and emitted to the atmosphere, accelerating climate change.
31 Sunlight-driven photoreactions oxidize DOC, converting a portion to CO_2 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_2 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_2 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. CO_2,
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_2 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_2 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_2 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^2) 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

2 Materials and Methods

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).

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

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

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 Naperian 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
191 al.*, 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       $$DOC_{photo} = DOC_{initial} - DOC_{final} \tag{3}$$

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 $\delta^{13}C$ analyses were conducted at the University of California, Davis Stable Isotope
242 Facility and ^{14}C analyses at the Laboratory for Ion Beam Physics, Eidgenossische Technische
243 Hochschule (ETH) Zürich. $\delta^{13}C$-DOC samples were analyzed using an O.I. Analytical Model
244 1010 TOC analyzer (precision of ±0.2%) interfaced to a PDZ Europa 20–20 IRMS (Sercon Ltd).
245 $\delta^{13}C$-DOC measurements were calibrated against the $\delta^{13}C$ 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°C/5 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 (~30 μg-
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 ($F^{14}C$) 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 μg-C; $F^{14}C$ of 0.3 ± 0.1). The apparent ^{14}C age of the photolabile DOC fraction ($[DOC]_{photo}$)
260 was calculated using measurements of initial DOC ($[DOC]_{initial}$) and final DOC concentrations
261 ($[DOC]_{final}$) alongside the associated change in isotopic composition using a simple mass
262 balance:

263

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

264

265 Individual errors associated with DOC concentration and isotope measurements were
266 propagated to assess error on $F^{14}C_{photo}$ 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 ($F^{14}C$) 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⁻
281 ¹) [*Hu et al.*, 2002]. The percentage loss of *a* at 320 and 254 nm was calculated:

282

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

284

285   The carbon-normalized light absorbance at 254 nm (SUVA$_{254}$; 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 SUVA$_{254}$ 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   $AI_{mod} = (1 + C - 0.5O - S - 0.5(N+P+H)) \, / \, (C - 0.5O - S - N - P)$ (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), photoproduced (>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 photoproduced.

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), photoproduced (>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_{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 photoproduced 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.

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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

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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±4.5 µL 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 photoproduced 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, photoproduced, 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