

30 **Abstract**

31           The Kolyma River in Northeast Siberia is among the six largest arctic rivers and drains a  
32 region underlain by vast deposits of Holocene-aged peat and Pleistocene-aged loess known as  
33 yedoma, most of which is currently stored in ice-rich permafrost throughout the region. These  
34 peat and yedoma deposits are important sources of dissolved organic matter (DOM) to inland  
35 waters that in turn play a significant role in the transport and ultimate remineralization of organic  
36 carbon to CO<sub>2</sub> and CH<sub>4</sub> along the terrestrial flow-path continuum. The turnover and fate of  
37 terrigenous DOM during offshore transport will largely depend upon the composition and  
38 amount of carbon released to inland and coastal waters. Here, we measured the optical  
39 properties of chromophoric DOM (CDOM) from a geographically extensive collection of waters  
40 spanning soil pore waters, streams, rivers, and the Kolyma River mainstem throughout a ~250  
41 km transect of the northern Kolyma River basin. During the period of study, CDOM absorbance  
42 values were found to be robust proxies for the concentration of DOM, whereas additional  
43 CDOM parameters such as spectral slopes (*S*) were found to be useful indicators of DOM quality  
44 along the flow-path. In particular, CDOM absorption at 254 nm showed a strong relationship  
45 with dissolved organic carbon (DOC) concentrations across all water types ( $r^2 = 0.958, p < 0.01$ ).  
46 The spectral slope ratio (*S<sub>R</sub>*) of CDOM demonstrated statistically significant differences between  
47 all four water types and tracked changes in the concentration of bioavailable DOC, suggesting  
48 that this parameter may be suitable for clearly discriminating shifts in organic matter  
49 characteristics among water types along the full flow-path continuum across this landscape. The  
50 heterogeneity of environmental characteristics and extensive continuous permafrost of the  
51 Kolyma River basin combine to make this a critical region to investigate and monitor. With  
52 ongoing and future permafrost degradation, peat and yedoma deposits throughout the Northeast

# Résumé des commentaires sur bg-2015-316-manuscript-version1 IL commented.pdf

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There are too few main results provided in the abstract. For example the + or - 4% of DOM that was found to be bioavailable (and the absence of a trend onlong the continuum) is a fundamental discovery. Also interesting is the evidence of increased photolysis. And there are a few other points that could be put forward, at the expense of the usual general blabla.

76 biological processes within streams alter the transport of organic matter to downstream  
77 ecosystems (e.g., Webster and Meyer, 1997), but the fate of terrestrial organic matter in arctic  
78 streams and rivers has only more recently been explored (e.g., Frey and Smith, 2005; Neff et al.,  
79 2006; Holmes et al., 2008; Denfeld et al., 2013; Spencer et al., 2015). Furthermore, a variety of  
80 conceptual and pragmatic issues complicate the study of arctic rivers, including: (i) large  
81 seasonal variations in discharge accompanied by large seasonal variations in nutrient and organic  
82 matter inputs from rivers to the coastal ocean (e.g., McClelland et al., 2012); (ii) the  
83 heterogeneity of vegetation, permafrost extent, topography, and soil attributes within arctic  
84 watersheds (e.g., Frey and McClelland, 2009); and (iii) spatial and temporal inaccessibility  
85 hindering comprehensive sampling; among others.

86 Hydrologic flow-paths and organic matter transport in arctic regions dominated by  
87 permafrost are markedly different than temperate regions with well-drained soils. In particular,  
88 permafrost-dominated watersheds lack deep groundwater flow-paths owing to the permafrost  
89 boundary in soil that prevents deep groundwater movement (Judd and Kling, 2002; Frey et al.,  
90 2007). As a result, the delivery of terrestrial-permafrost organic matter to aquatic ecosystems  
91 may in fact lack significant terrestrial or groundwater processing. Once dissolved organic matter  
92 (DOM) enters aquatic ecosystems, **1 multiple processes remove DOM from the water column:** (i)  
93 photochemical reactions, where DOM is degraded to CO<sub>2</sub> or to compounds bioavailable for  
94 bacterial uptake (**2 Moran and Zepp, 1997; Cory et al., 2014**); (ii) loss via aggregation of DOM  
95 owing to changes in ionic strength when freshwater mixes with sea water (Sholkovitz, 1976);  
96 (iii) **3 DOM sorption to particles** (Chin et al., 1998); and/or (iv) bacterial uptake and utilization of  
97 the bioavailable fraction (Bronk, 2002; Karl and Björkman, 2002; Mann et al., 2014; Spencer et  
98 al., 2015). Measurements of waters along a hydrologic flow-path may indeed give insight into

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is there any papers on precipitation of DOM as a loss process before reaching seawater (when DOM forms microgels?), especially when there is large concentrations of DOM such as in the presence of thaw slumps?

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There are so few studies on DOM photolysis in permafrost aquatic systems, I think it's worth citing (here or elsewhere) the paper by Laurion & Mladenov 2013, especially that it shows a slightly different trend as Cory et al., at least in terms of CO2 production

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and sedimentation?

144 wetlands and allowing the water to slowly seep into the collection vessel. In shallow streams,  
145 less than 0.5 m in depth, samples were collected approximately midway below the surface and  
146 the bottom. In larger tributaries and rivers, samples were collected at a depth of ~0.5 m. Water  
147 samples were then filtered through precombusted (450°C for 6 hours) Whatman 0.7 µm GF/F  
148 filters in the field and stored in acid-washed HDPE bottles without headspace to minimize  
149 degassing and algal growth. Upon returning to the laboratory (typically within ~1 day), DOC  
150 samples were acidified with concentrated HCl to a pH of  $\leq 2$  and stored refrigerated and in the  
151 dark until analysis via high-temperature combustion using a Shimadzu TOC-VCPH Analyzer  
152 (within one month of collection). DOC was calculated as the mean of 3 to 5 injections with a  
153 coefficient of variance less than 2%.

154 We additionally conducted a series of organic matter bioavailability assays to assess the  
155 total and relative amounts of bioavailable DOC in soil, stream, and river environments. These  
156 assays relied upon 5-day biological oxygen demand (BOD) experiments, with methods similar to  
157 those in Mann et al. (2014). The Winkler titration method was used to measure initial ( $t=0$ )  
158 dissolved oxygen (DO) concentrations (i.e., in situ dissolved oxygen) after a 5-day incubation at  
159 15°C using water collected in triplicate glass 300 mL BOD bottles, where bottles were kept in  
160 the dark in between measurements. BOD was calculated as the difference between DO  
161 concentrations at  $t = 0$  and following incubation. We assumed 100% of DO consumed was  
162 converted to CO<sub>2</sub> via aerobic respiration and that the carbon source respired was DOM, where  
163 resulting BOD measurements were used an analog for bioavailable DOC. The Winkler method  
164 we used here has been used extensively and is attractive for a variety of reasons, including: (i)  
165 enabling DO to be measured with precision of 0.01 mg/L, thus low respiration rates can be  
166 accurately measured; (ii) allowing for convenient replication of assays within habitats; (iii)

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(In line with referee 1 comment on oxygen content of water at start and during your incubations) Could there be chemical O<sub>2</sub> consumption, especially from DOC-rich pore water? Was pore water oxitic to start with? (upon in situ sampling)

167 permitting experimental manipulation of standard bioassays (e.g., N and P amendments,  
168 photolysis experiments, alteration of initial microbial consortia, and temperature manipulation;  
169 (iv) helping to segregate the relative roles of water column and sediment processes; and (v)  
170 helping to inform more realistic ecosystem-level experiments that are much more laborious and  
171 time intensive.

172 In order to investigate the optical characteristics of the DOM in these samples, we  
173 additionally measured the ultraviolet-visible absorption spectra of CDOM from this broad  
174 collection of waters. CDOM absorbance was measured immediately after collection (within ~1  
175 day) at the Northeast Science Station in Cherskiy using a using a Thermo Scientific GENESYS  
176 10 UV/Vis Spectrophotometer across wavelengths 800–200 nm (1 nm interval) using a 1 cm  
177 quartz cuvette. All sample spectra were blank corrected and referenced against Milli-Q water  
178 (18 Ω). Measurements were made after samples had equilibrated to laboratory temperature in  
479 order to minimize temperature effects. CDOM absorbance was assumed to be zero across  
180 wavelengths greater than 750 nm and the average absorbance between 750 nm and 800 nm was  
181 subtracted from each spectrum to correct for offsets owing to instrument baseline drift,  
182 temperature, scattering, and refractive effects (Green and Blough, 1994; Helms et al, 2008).

183 CDOM absorption coefficients were calculated as:

$$184 \quad a(\lambda) = 2.303A(\lambda)/l \quad (1)$$

185 where  $a$  is the Napierian absorbance coefficient ( $\text{m}^{-1}$ ) at a specified wavelength ( $\lambda$ , in nm),  $A(\lambda)$   
186 is the absorbance at the wavelength, and  $l$  is the cell path length in meters (Green and Blough,  
187 1994). Several samples with the highest CDOM concentrations (primarily the soil pore waters)  
588 were diluted with Milli-Q water before analysis to avoid saturation of the spectra at short  
189 wavelengths, where the final CDOM absorbance values were corrected for these procedures.

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how if only water is incubated in BOD?

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**T** Nombre : 2      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 13:52:21 -04'00'  
I guess in separate bottles where no acidification was done? (i.e. not the same as DOC)

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isn't this the same?

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**T** Nombre : 4      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-12-21 11:51:04  
this is called null-point adjustment

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**T** Nombre : 5      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 14:08:45 -04'00'  
what was the criteria for diluting? ABS<X at Xnm



190 CDOM spectral slopes ( $S$ ,  $\text{nm}^{-1}$ ) between 290–350 nm ( $S_{290-350}$ ), 275–295 nm ( $S_{275-295}$ ),  
 191 and 350–400 nm ( $S_{350-400}$ ), calculated within log-transformed absorption spectra, were also  
 192 utilized to investigate DOM characteristics of contrasting water types, and were calculated as:  
 193 
$$a(\lambda) = a(\lambda_{ref}) e^{-S(\lambda - \lambda_{ref})} \quad (2)$$
  
 194 where  $a(\lambda)$  is the absorption coefficient at a specified wavelength,  $\lambda_{ref}$  is a reference wavelength,  
 195 and  $S$  is the slope fitting parameter (Hernes et al., 2008; Helms et al., 2008; Spencer et al.,  
 196 2009a). All slopes are reported here as positive values, such that higher (i.e., steeper) slopes  
 197 indicate a greater decrease in absorption with increasing wavelength. Additional CDOM  
 198 parameters investigated here include the spectral slope ratio ( $S_R$ ), calculated as the ratio between  
 199  $S_{275-295}$  and  $S_{350-400}$ ; the ratio between DOM absorbance at 250 nm and 365 nm ( $a_{250}:a_{365}$ ); and  
 200 specific UV absorbance ( $SUVA_{254}$ ), determined by dividing UV absorbance at 254 nm by the  
 201 sample DOC concentration and reported in units of  $\text{L mg C}^{-1} \text{ m}^{-1}$  (Weishaar et al., 2003). These  
 202 six CDOM parameters ( $S_{290-350}$ ,  $S_{275-295}$ ,  $S_{350-400}$ ,  $a_{250}:a_{365}$ ,  $SUVA_{254}$ , and  $S_R$ ) have been shown to  
 203 provide insights for various DOM characteristics such as molecular weight, source waters,  
 204 composition, age, and aromatic content for a variety of geographic regions (e.g., Weishaar 2003;  
 205 Neff et al., 2006; Helms et al., 2008; Spencer et al., 2008; Spencer et al., 2009a; Spencer et al.,  
 206 2009b; Mann et al., 2012).

207

### 208 3. Results

209 Total DOC concentrations (and the variance among values within each water type)  
 210 decreased markedly downstream along the flow-path continuum from soil pore waters to the  
 211 Kolyma River mainstem (Figure 2a). Mean ( $\pm 1$  standard deviation) DOC values were  $3.35 \pm$   
 212  $22.79 \text{ mg L}^{-1}$  (soil pore waters),  $11.63 \pm 2.97 \text{ mg L}^{-1}$  (streams),  $4.89 \pm 1.61 \text{ mg L}^{-1}$  (rivers), and

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I suggest you consider applying Loiselle method for spectral slope calculations in the future, to avoid any effects of slope variations within the chosen wavebands, and more importantly to generate the spectral slope signature which has the potential to bring even more insights. Moreover, the use of a linear fit on log-transformed data could be problematic as it does not give the same weight to all data over the waveband

Nombre : 2      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 14:17:21 -04'00'

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please be careful throughout the ms to distinguish between absorption coefficients (a) and absorbance (A). As you know, SUVA<sub>254</sub> for example is calculated with A while other indices could be with a (for ex. apparently your a<sub>250</sub>:a<sub>365</sub>)

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does the second digit really mean something considering analytical errors?


213  $3.61 \pm 0.41 \text{ mg L}^{-1}$  (mainstem waters). Soil pore waters, in particular, showed highly variable  
214 DOC concentrations (ranging from 13.19 to  $64.74 \text{ mg L}^{-1}$ ) demonstrating the heterogeneous  
215 supply of DOM from terrestrial systems to streams. By contrast, DOC concentrations in the  
216 Kolyma mainstem along the ~250 km stretch sampled were remarkably similar (ranging from  
217  $2.97$  to  $4.36 \text{ mg L}^{-1}$ ) during this mid-summer July period (Figure 2a). Furthermore, DOC  
218 concentrations of the four water types sampled were found to be significantly different from one  
219 another (1 two-sample t-tests,  $p < 0.05$ ).

220 Concentrations of bioavailable DOC showed similar patterns to DOC, declining  
221 downstream along the flow-path continuum with increasing water residence time in the system  
222 (Figure 2b). Bioavailable DOC concentrations averaged  $0.93 \pm 0.24 \text{ mg L}^{-1}$  (soil pore waters),  
223  $0.33 \pm 0.15 \text{ mg L}^{-1}$  (streams),  $0.27 \pm 0.17 \text{ mg L}^{-1}$  (rivers), and  $0.16 \pm 0.15 \text{ mg L}^{-1}$  (mainstem  
224 waters), and showed relative greater variability than DOC within the stream, river and mainstem  
225 water types. Concentrations of bioavailable DOC in soil pore waters were statistically different  
226 from the other three water types (two-sample t-tests,  $p < 0.05$ ), although by contrast, streams,  
227 rivers, and mainstem waters were not statistically different from one another (2  $p < 0.05$ ).


228 Importantly, the percentage of bioavailable DOC (i.e., calculated as the amount of bioavailable  
229 DOC divided by total DOC) did not significantly decrease downstream (two-sample t-tests,  
230  $p < 0.05$ ) and showed relatively similar values among the four water sample types along the flow-  
231 path continuum (Figure 2c), where percentages averaged  $3.93 \pm 3.81\%$  (soil pore waters),  $3.21 \pm$   
232  $1.94\%$  (streams),  $6.23 \pm 4.31\%$  (rivers), and  $4.46 \pm 4.55\%$  (mainstem waters).

233 CDOM absorption spectra (200–800 nm) showed clear separation between soil pore  
234 waters, streams, rivers, and the Kolyma mainstem, where soil pore waters exhibited values  
235 markedly higher than the other three water sample types (Figures 3a). CDOM absorption also

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an ANOVA would be better suited to test the "water type" effect all at once instead of pair by pair

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 Nombre : 2      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 15:16:02 -04'00'  
then I guess you mean >

236 clearly declined downstream from streams, rivers, to mainstem waters when assessing those  
237 waters only (Figure 3b). Furthermore, we investigated the potential for utilizing CDOM  
238 absorption as a proxy for DOC concentrations in these waters. Our data revealed that  
239 independent of water type along the stream-river-mainstem flow-path, CDOM absorption was  
240 strongly linearly correlated to DOC concentrations at 254, 350, and 440 nm (Figure 4). In  
241 particular, CDOM absorption at 254 nm had the highest predictive capability of DOC ( $r^2 =$   
242  $0.958, p < 0.01$ ), with CDOM absorption at 350 nm ( $r^2 = 0.855, p < 0.01$ ) and 440 nm ( $r^2 = 0.667,$   
243  $p < 0.01$ ) less strongly predictive (Figure 4).

244 We additionally investigated the quantitative distribution of the six derived CDOM  
245 parameters ( $S_{290-350}$ ,  $S_{275-295}$ ,  $S_{350-400}$ ,  $a_{250}:a_{365}$ ,  $SUVA_{254}$ , and  $S_R$ ) across the four water types  
246 (Figure 5). In general, four parameters ( $S_{290-350}$ ,  $S_{275-295}$ ,  $a_{250}:a_{365}$ , and  $S_R$ ) showed an increasing  
247 pattern along the flow-path continuum, whereas two parameters ( $S_{350-400}$  and  $a_{250}:a_{365}$ ) showed a  
248 decreasing pattern. Spectral slope and other CDOM parameters for soil pore waters, streams,  
249 rivers, and mainstem waters averaged: (a)  $15.35 \times 10^{-3} \text{ nm}^{-1}$ ,  $17.08 \times 10^{-3} \text{ nm}^{-1}$ ,  $17.17 \times 10^{-3} \text{ nm}^{-1}$   
250  $^{-1}$ , and  $18.10 \times 10^{-3} \text{ nm}^{-1}$ , respectively, for  $S_{290-350}$  (Figure 5a); (b)  $15.27 \times 10^{-3} \text{ nm}^{-1}$ ,  $17.39 \times 10^{-3}$   
251  $\text{ nm}^{-1}$ ,  $17.79 \times 10^{-3} \text{ nm}^{-1}$ , and  $18.57 \times 10^{-3} \text{ nm}^{-1}$ , respectively, for  $S_{275-295}$  (Figure 5b); (c)  $18.65 \times$   
252  $10^{-3} \text{ nm}^{-1}$ ,  $18.89 \times 10^{-3} \text{ nm}^{-1}$ ,  $18.19 \times 10^{-3} \text{ nm}^{-1}$ , and  $17.50 \times 10^{-3} \text{ nm}^{-1}$ , respectively, for  $S_{350-400}$   
253 (Figure 5c); (d) 5.47, 6.44, 6.27, and 6.53, respectively, for  $a_{250}:a_{365}$  (Figure 5d); (e)  $3.52 \text{ L mg}$   
254  $\text{ C}^{-1} \text{ m}^{-1}$ ,  $2.94 \text{ L mg C}^{-1} \text{ m}^{-1}$ ,  $2.77 \text{ L mg C}^{-1} \text{ m}^{-1}$ , and  $2.56 \text{ L mg C}^{-1} \text{ m}^{-1}$ , respectively, for  $SUVA_{254}$   
255 (Figure 5e); and (f) 0.82, 0.92, 0.98, and 1.06, respectively, for  $S_R$  (Figure 5f). In terms of  
256 whether the values of the six parameters were statistically significantly different among water  
257 sample types, two-sample t-tests (at the 0.05 level) revealed inconsistent results. Most  
258 commonly, soil pore waters were statistically different from all other water types for four of the

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**T** Nombre : 1      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-12-21 11:52:48  
I guess you mean SUVA254??

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**T** Nombre : 2      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-12-21 11:53:03  
give this in a table instead, but here you could highlight the most interesting differences or averages that you will be discussing (if any is discussed)

259 parameters ( $S_{290-350}$ ,  $S_{275-295}$ ,  $a_{250}:a_{365}$ , and  $S_R$ ), but no consistent pattern was observed in  
260 significant differences across other water types. However, the spectral slope ratio ( $S_R$ ) was the  
261 only parameter of the six that showed statistically significant differences between all four water  
262 types ( $p < 0.01$ ).

263 Lastly, we examined the relationships between CDOM optical properties and DOM  
264 bioavailability. To this end, we performed linear regressions between all six of our derived  
265 CDOM parameters and bioavailable DOC concentrations to determine the strength of their  
266 ability to predict bioavailable DOC. Our results indicated that five of the CDOM parameters  
267 ( $S_{290-350}$ ,  $S_{275-295}$ ,  $a_{250}:a_{365}$ ,  $SUVA_{254}$ , and  $S_R$ ) were statistically significant predictors at the 0.05  
268 level (Table 1). In particular,  $S_R$  showed the strongest relationship with bioavailable DOC  
269 concentrations ( $r^2$  value = 0.45,  $p < 0.01$ ). The relationship between bioavailable DOC  
270 concentrations and  $S_R$  (Figure 6) showed a distinct negative trend (bioavailable DOC  $\text{mg L}^{-1} = -$   
271  $2.204(S_R) + 2.518$ ), with the highest bioavailable DOC concentrations and lowest  $S_R$  values for  
272 soil pore waters, and lowest bioavailable DOC concentrations and highest  $S_R$  values for Kolyma  
273 River mainstem waters. We found a clear gradation in the relationship between  $S_R$  and  
274 bioavailable DOC down the flow-path continuum, as one would also expect by examining these  
275 parameters individually (e.g., Figures 2b, 5f). In summary, not only was  $S_R$  the only CDOM  
276 parameter that showed statistically significant separation between all four water types examined,  
277 but it also had the strongest relationship when compared with concentrations of bioavailable  
278 DOC.

279

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281

would it be more valuable to use stepwise regressions?



#### 282 4. Discussion and Conclusions

283 In this study, we present a full suite of DOC, bioavailable DOC, and CDOM parameters  
284 throughout the permafrost-dominated Kolyma River basin in Northeast Siberia with the purpose  
285 of helping to elucidate the processing of DOM along a full flow-path continuum from soil pore  
286 waters to the mainstem. Our findings show that average concentrations of DOC and bioavailable  
287 DOC generally decrease as waters travel downstream from soil pore waters, streams, rivers, and  
188 ultimately to the Kolyma River mainstem. This pattern suggests the occurrence of rapid in-  
289 stream processing of DOM and potential 212 mineralization of DOC to atmospheric CO<sub>2</sub> during  
290 this July baseflow period well before these waters reach the Arctic Ocean (e.g., Denfeld et al.,  
291 2013, Spencer et al., 2015, Mann et al., in press). In general, the river continuum concept  
292 predicts that relative diversity of organic molecules decreases from the headwaters to the river  
293 mouth (Vannote et al. 1980). As energetically favorable compounds are converted to living  
394 tissue or respired as CO<sub>2</sub>, bulk DOM in the Kolyma basin has indeed been shown to become less  
295 diverse moving from headwaters to mainstem waters before exported to the Arctic Ocean  
296 (Spencer et al. 2015).

297 Despite these downstream shifts in DOM composition however, we find a relatively  
298 constant proportion of DOC that was bioavailable (~4.4% total DOC averaged across all  
299 samples) regardless of relative water residence time. This suggests that continual microbial  
300 processing of organic matter 412 occurs over similar rates during transit from headwaters throughout  
301 the Kolyma River drainage network to the Arctic Ocean concurrent with ongoing downstream  
302 CDOM compositional changes. Microbial demand in headwater streams of the Kolyma River  
303 basin is subsidized by significant quantities of DOC specifically derived from permafrost and  
304 aged soils, yet the proportion of permafrost supporting DOC mineralization declines as waters

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1 Nombre : 1 Auteur : Sujet : Commentaire sur le texte Date : 2015-12-21 11:54:28  
(In line with referees 1 & 2) What is the residence time (or transit time) of the water from soil to mainstem?

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1 Nombre : 2 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:47:45 -04'00'  
you found in average 3-6% of total DOC putatively lost to remineralization; worth discussing that it's only a small fraction that is remineralized. It's only this fraction that is remineralized "well before waters reach the Arctic Ocean", right?

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1 Nombre : 3 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:49:17 -04'00'  
from which index can you say this? are you talking about your own study?

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1 Nombre : 4 Auteur : Sujet : Commentaire sur le texte Date : 2015-09-24 16:56:22 -04'00'  
can you be more specific/explicit on why your results indicate so?  
And is this (unchange in % bioavailable DOC) supporting the last sentence of previous paragraph?

305 move downstream through the fluvial network (Mann et al., in press). Thus, our results  
306 importantly show that microbial metabolism continues at similar rates independent of dominant  
307 DOM source and radiocarbon age.

308 The higher overall amounts of bioavailable DOC we measured in soil pore waters may  
309 reflect a **highly bioreactive** permafrost or aged surface soil derived DOC fraction (e.g., Vonk et  
310 al. 2013, Mann et al. 2014). Further downstream in larger tributary and Kolyma mainstem  
311 waters, it has been shown that lower total amounts of bioavailable DOC is supported almost  
312 entirely from predominantly modern radiocarbon aged surface soils and vegetation sources  
313 (Mann et al., in press). Aquatic microorganisms must therefore readily **adapt** to significant shifts  
314 in DOM composition caused by selective losses of unique DOM fractions (Kaplan and Bott,  
315 1983; Spencer et al. 2015) alongside high-internal demand for labile DOM by stream  
316 communities in lower order streams, **which is generally expected to result in decreased DOM**  
317 **lability with increasing water residence time** (Stepanauskas et al., 1999a,b; Wikner et al., 1999;  
318 Langenheder et al., 2003; Sondergaard et al., 2003; Fellman, 2010; Fellman et al., 2014).

319 CDOM parameters presented in this study give further insight into characteristics of  
320 DOM along the full flow-path continuum throughout the Kolyma River basin. Previous studies  
321 have indicated that CDOM spectral slopes (particularly  $S_{290-350}$  and  $S_{275-295}$ ) can serve as  
322 indicators of DOM source and composition, where a steeper spectral slope typically suggests  
323 lower molecular weight material with decreasing aromatic content and a **shallower** slope  
324 typically suggests higher molecular weight material with increasing aromatic content (Green and  
325 Blough, 1994; Blough and Del Vecchio, 2002; Helms et al., 2008; Spencer et al., 2008; Spencer  
326 et al., 2009a). Furthermore,  $S_{275-295}$  has been identified as a reliable proxy for dissolved lignin  
327 and therefore terrigenous DOM supply across Arctic Ocean coastal waters, as well as

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**T** Nombre : 1      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 16:59:15 -04'00'  
why "highly bioreactive" if simply more in quantity but not more reactive in percentage bioavailable?

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**T** Nombre : 2      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 17:00:38 -04'00'  
is it an adaptation or an acclimation? (depend on transit time, see question above)

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**T** Nombre : 3      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-12-21 11:56:03  
unless photolysis generates labile molecules, which needs time (exposure to light).  
And that is what you are discussing in next paragraph, but unfortunately you do not make the link with lability (smaller molecules are known to be more labile than aromatic large molecules). Maybe the more abundant "virgin" bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), making the % used relatively constant or without any clear pattern overall?


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**T** Nombre : 4      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-24 17:07:32 -04'00'  
is this the correct word?


374 evidence of on-going photochemical degradation of surface water DOM during transit.  
375 Additionally, of all the CDOM parameters,  $S_R$  values were most closely related to concentrations  
176 of bioavailable DOC ( $r^2 = 0.454$ ,  $p < 0.01$ ), suggesting that this value may be correlated with the  
377 rate of decline in bioavailable DOC through the network. However, biological degradation has  
178 previously been shown to typically slightly decrease  $S_R$  values (Helms et al., 2008), which  
379 indicates that the relationship observed here may be a consequence of co-variance with  
380 photodegradation of DOM, or demonstrate that  $S_R$  values reflect a range of physical and  
381 biological processes. Unlike many previous studies that focus on only mainstem rivers in the  
382 Arctic, we focus here on a variety of waters along a full flow-path continuum, showing that  
383 CDOM metrics (in particular,  $S_R$ ) reflect important compositional differences in waters along the  
384 transit from headwaters to the Arctic Ocean. The range in DOM properties of waters travelling  
385 downstream through the Kolyma Basin often spanned wider ranges than DOM compositional  
386 differences reported annually among the six major arctic rivers. For example,  $S_R$  values across  
387 the major arctic rivers over the years 2004 and 2005 spanned a minimum of 0.79 in the Yenisey  
388 River, to a maximum value of 1.11 in the Mackenzie River (Stedmon et al., 2011). It is therefore  
389 essential that changes taking place in the quality of CDOM exported by these rivers be examined  
390 throughout entire river basins in order to adequately assess climate driven shifts in terrigenous  
391 carbon supply and reactivity.

392 Future work that includes both photo- and microbial degradation experiments may further  
393 elucidate the ability for  $S_R$  to serve as a direct proxy for these processes along a flow-path  
394 gradient. Our overall results thus far demonstrate promise for utilizing ultraviolet-visible  
395 absorption characteristics to easily, inexpensively, and comprehensively monitor the quantity and  
396 quality of DOM (over broad ranges) across permafrost landscapes in the Arctic. This is


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 Nombre : 1      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-25 15:26:32 -04'00'  
being correlated to the bioavailable portion of DOM does not mean it is related to the **rate** of decline of this fraction, does it?

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 Nombre : 2      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-12-21 11:58:04  
this sentence needs to be clarified

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 Nombre : 3      Auteur :      Sujet : Commentaire sur le texte      Date : 2015-09-25 16:13:41 -04'00'  
in DOM