Editor Comments

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Author Response: We sincerely thank the Editor for her additional comments/edits. We have added statements in **blue** below that detail our response to each comment.

Although you might have not found studies on DOM precipitation (or flocculation might be a better term) specifically related to systems with thaw slumps, I think you will on this process in other systems (try boreal, if not temperate, if not any humic aquatic system on the planet). There is no reason for excluding this loss process. See for example this study on lakes: Wachenfeldt, E. von, D. Bastviken, and L. J. Tranvika (2009), Microbially induced flocculation of allochthonous dissolved organic carbon in lakes. Limnol. Oceanogr. 54: 1811–1818, doi:10.4319/lo.2009.54.5.1811.

This is an excellent suggestion and reference and we have added the following to this section: "(ii) flocculation of terrestrial DOM resulting in the settling of particulate organic matter (Wachenfeldt et al., 2009)"

You wrote: "to the point where A350 at a 1 cm path length was ≤0.02" but I think it needs to be replaced by "to the point where A350 was ≤0.02 for a 1 cm path length"

This change has been made.

You wrote: "In other words, the more abundant "virgin" bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), resulting in the fraction of DOC used relatively constant without any clear pattern overall. If this (or something similar) were not the case, we would expect to see a declining fraction of bioavailable DOC along the flow-path continuum."

I was using the term "virgin" quoted loosely as it's jargon, but you probably need to find a more accurate expression: never exposed, fresh, or something like that. Moreover, I think you need to tone down the sentence, as you do not have direct evidence of this replacement; your results suggest this (use words like may, could, possibly, suggest, etc.). And I don't think "(or something similar)" is necessary.

This is an excellent suggestion to improve this section. We have replaced these sentences to now read the following: "In other words, our results suggest that more abundant newly exposed bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), resulting in the fraction of DOC used relatively constant without any clear pattern overall. If this were not the case, we would expect to see a declining fraction of bioavailable DOC along the flow-path continuum."

Optical properties and bioavailability of dissolved organic matter along a flow-path continuum from soil pore waters to the Kolyma River mainstem, East Siberia

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Abstract

The Kolyma River in Northeast Siberia is among the six largest arctic rivers and drains a region underlain by vast deposits of Holocene-aged peat and Pleistocene-aged loess known as yedoma, most of which is currently stored in ice-rich permafrost throughout the region. These peat and yedoma deposits are important sources of dissolved organic matter (DOM) to inland waters that in turn play a significant role in the transport and ultimate remineralization of organic carbon to CO_2 and CH_4 along the terrestrial flow-path continuum. The turnover and fate of terrigenous DOM during offshore transport largely depends upon the composition and amount of carbon released to inland and coastal waters. Here, we measured the ultraviolet-visible optical properties of chromophoric DOM (CDOM) from a geographically extensive collection of waters spanning soil pore waters, streams, rivers, and the Kolyma River mainstem throughout a ~250 km transect of the northern Kolyma River basin. During the period of study, CDOM absorption coefficients were found to be robust proxies for the concentration of DOM, whereas additional CDOM parameters such as spectral slopes (S) were found to be useful indicators of DOM quality along the flow-path. In particular, the spectral slope ratio (S_R) of CDOM demonstrated statistically significant differences between all four water types and tracked changes in the concentration of bioavailable DOC, suggesting that this parameter may be suitable for clearly discriminating shifts in organic matter characteristics among water types along the full flow-path continuum across this landscape. However, despite our observations of downstream shifts in DOM composition, we found a relatively constant proportion of DOC that was bioavailable (~3–6% of total DOC) regardless of relative water residence time along the flow-path. This may be a consequence of two potential scenarios allowing for continual processing of organic material within the system, namely: (a) aquatic microorganisms are acclimating to a downstream shift in

DOM composition; and/or (b) photodegradation is continually generating labile DOM for continued microbial processing of DOM along the flow-path continuum. Without such processes, we would otherwise expect to see a declining fraction of bioavailable DOC downstream with increasing residence time of water in the system. With ongoing and future permafrost degradation, peat and yedoma deposits throughout the Northeast Siberian region will become more hydrologically active, providing greater amounts of DOM to fluvial networks and ultimately to the Arctic Ocean. The ability to rapidly and comprehensively monitor shifts in the quantity and quality of DOM across the landscape is therefore critical for understanding potential future feedbacks within the arctic carbon cycle.

1. Introduction

There is increasing evidence that inland freshwater ecosystems play a significant role in the global carbon cycle owing to the metabolism of terrestrially-derived organic matter as it moves through fluvial networks from land to ocean (Cole et al., 2007; Battin et al., 2009a, b). Recent research suggests that arctic watersheds may increasingly augment the role of freshwater ecosystems in the global flux of terrestrial carbon to the atmosphere (Walter et al., 2007; Denfeld et al., 2013; Vonk et al., 2013; Hayes et al., 2014; Spencer et al., 2015) and ocean (Frey and Smith, 2005; Frey and McClelland, 2009; Schreiner et al., 2014; Tesi et al., 2014) as a result of climate warming and changing regional hydrology. Terrestrial sources of organic matter generally dominate the energy and carbon fluxes through stream, riverine, and estuarine ecosystems (Mulholland, 1997; Holmes et al., 2008), but the lability and composition of this carbon remain poorly characterized. Headwater and intermediate streams dominate overall channel length in large dendritic drainage basins (e.g., Denfeld et al., 2013), thus the functional

role of streams and intermediate rivers is magnified when assessing landscape controls on carbon and nutrient fluxes to the atmosphere and Arctic Ocean.

Following the publication of the "river continuum concept" (Vannote et al., 1980), there has been much research focused on the delivery and processing of terrestrially-derived organic matter within temperate stream ecosystems. Through these studies, it has been shown that biological processes within streams alter the transport of organic matter to downstream ecosystems (e.g., Webster and Meyer, 1997), but the fate of terrestrial organic matter in arctic streams and rivers has only more recently been explored (e.g., Frey and Smith, 2005; Neff et al., 2006; Holmes et al., 2008; Denfeld et al., 2013; Spencer et al., 2015). Furthermore, a variety of conceptual and pragmatic issues complicate the study of arctic rivers, including: (i) large seasonal variations in discharge accompanied by large seasonal variations in nutrient and organic matter inputs from rivers to the coastal ocean (e.g., McClelland et al., 2012); (ii) the heterogeneity of vegetation, permafrost extent, topography, and soil attributes within arctic watersheds (e.g., Frey and McClelland, 2009); and (iii) spatial and temporal inaccessibility hindering comprehensive sampling; among others.

Hydrologic flow-paths and organic matter transport in arctic regions dominated by permafrost are markedly different than temperate regions with well-drained soils. In particular, permafrost-dominated watersheds lack deep groundwater flow-paths owing to the permafrost boundary in soil that prevents deep groundwater movement (Judd and Kling, 2002; Frey et al., 2007). As a result, the delivery of terrestrial-permafrost organic matter to aquatic ecosystems may in fact lack significant terrestrial or groundwater processing. Once dissolved organic matter (DOM) enters aquatic ecosystems, multiple processes remove DOM from the water column: (i) photochemical reactions, where DOM is degraded to CO_2 or to compounds bioavailable for

bacterial uptake (Moran and Zepp, 1997; Laurion and Mladenov, 2013; Cory et al., 2014); (ii) flocculation of terrestrial DOM resulting in the settling of particulate organic matter (Wachenfeldt et al., 2009); (iii) loss via aggregation of DOM owing to changes in ionic strength when freshwater mixes with sea water (Sholkovitz, 1976); (~~iii~~iv) DOM sorption to particles and sedimentation (Chin et al., 1998); and/or (~~i~~v) bacterial uptake and utilization of the bioavailable fraction (Bronk, 2002; Karl and Björkman, 2002; Mann et al., 2014; Spencer et al., 2015). Measurements of waters along a hydrologic flow-path may indeed give insight into the characteristics of DOM as it is modified through these various processes along the soil-stream-river continuum.

Recent work on the Kolyma River in Northeast Siberia has identified marked variation in annual discharge that is associated with large pulses of organic matter flux to the Arctic Ocean during spring freshet, providing detailed temporal characterization of DOM in the Kolyma River mainstem across the annual hydrograph (e.g., Mann et al., 2012). Furthermore, selective processing and loss of permafrost-derived DOM has been shown to occur via microbial metabolism throughout the Kolyma River basin, as waters move downstream through the fluvial network (Mann et al., 2014; Mann et al., 2015; Spencer et al., 2015). Here, we complement these previous studies by providing extensive spatial characterization of DOM along a flow-path continuum from soil pore waters to the Kolyma River mainstem during mid-summer (July) baseflow. The heterogeneity of environmental characteristics and extensive continuous permafrost of the Kolyma River basin combine to make this a critical region to investigate and monitor. In particular, we measured the ultraviolet-visible absorption spectra (200–800 nm) of chromophoric DOM (CDOM) from a geographically extensive collection of waters throughout a ~250 km transect of the northern Kolyma River basin, including samples of soil pore waters,

streams, rivers, and the Kolyma River mainstem. CDOM absorption and spectral slopes (calculated within log-transformed absorption spectra) were used to investigate contrasting water types and were found to be useful indicators of both the concentration and reactivity of DOM. With ongoing permafrost degradation and subsequent release of a long-term storehouse of organic material into the contemporary carbon cycle, the ability to easily and comprehensively monitor the quantity and quality of DOM across the landscape through investigation of its optical properties is becoming critical for understanding the global significance of the arctic carbon cycle. Here, we explore a full suite of CDOM parameters as well as concentrations of dissolved organic carbon (DOC) and bioavailable DOC as they vary across a full flow-path continuum in the Kolyma River basin in Northeast Siberia.

2. Data and Methods

The Kolyma River in Northeast Siberia is among the six largest arctic rivers and drains a ~650,000 km^2 region underlain by vast deposits of Holocene-aged peat and Pleistocene-aged loess known as yedoma, much of which is currently stored in ice-rich permafrost throughout the region (Holmes et al., 2012; Holmes et al., 2013). These peats and yedoma deposits are important sources of DOM to terrestrial waters that in turn play a significant role in the transport and ultimate remineralization of organic carbon to atmospheric CO_2 and CH_4 (e.g., Walter et al., 2006; Mann et al., 2012; Denfeld et al., 2013; Spencer et al., 2015). The Kolyma River basin and its subwatersheds exhibit extreme hydrologic seasonality, with ice breakup and peak river discharge typically occurring in late May or early June. In this study, sampling took place along the most northern ~250 km of the Kolyma River in the vicinity of Cherskiy, Sakha Republic, Russia (68.767°N, 161.333°E) during the mid-summer period of July 2009 (Figure 1). Samples

were collected over a narrow temporal window from July 11–25, 2009 in order to capture a "snapshot" of observations during the mid-summer period. In total, 47 water samples were collected, including soil pore waters in shallow wetlands (n=9), small streams with watersheds <100 km^2 (n=15), major river tributaries with watersheds 900–120,000 km^2 (n=14), and Kolyma mainstem locations with watersheds >400,000 km^2 (n=9). Although we did not determine residence times directly for our sampled sites, Vonk et al. (2013) estimated that in higher relief areas near Duvannyi Yar (adjacent to the Kolyma River mainstem), the transport time from permafrost thaw to entry into the Kolyma River may be less than one hour. Furthermore, with respect to the mainstem, it has been estimated that water residence times in the Kolyma River from Duvannyi Yar to the river mouth may be ~3–7 days, assuming average mainstem velocities of 0.5–1.5 m/s (Holmes et al., 2012; Vonk et al., 2013). As such, permafrost-derived C may not be easily detectable at the river mouth, as this time is likely comparable to the rapid removal rates of highly labile permafrost C determined through incubation experiments (e.g., Holmes et al., 2012; Vonk et al., 2013).

Samples were collected by hand using a 1 L acid-washed high density polyethylene (HDPE) bottle as a collection vessel, where sample waters were used to rinse the bottle several times before filling. Soil pore waters were collected by depressing the soil surface within the wetlands and allowing the water to slowly seep into the collection vessel. In shallow streams, less than 0.5 m in depth, samples were collected approximately midway below the surface and the bottom. In larger tributaries and rivers, samples were collected at a depth of ~0.5 m. Water samples were then filtered through precombusted (450°C for 6 hours) Whatman 0.7 μm GF/F filters in the field and stored in acid-washed HDPE bottles without headspace to minimize degassing and algal growth. Upon returning to the laboratory (typically within ~1 day), DOC

168 samples were acidified with concentrated HCl to a pH of ≤2 and stored refrigerated and in the
169 dark until analysis via high-temperature combustion using a Shimadzu TOC-VCPH Analyzer
170 (within one month of collection). DOC was calculated as the mean of 3 to 5 injections with a
171 coefficient of variance less than 2%.

172 We additionally conducted a series of organic matter bioavailability assays to assess the
173 total and relative amounts of bioavailable DOC in soil, stream, and river environments. These
174 assays relied upon 5-day biological oxygen demand (BOD) incubations, with methods similar to
175 those in Mann et al. (2014). Water samples were collected in triplicate glass 300 mL BOD
176 bottles and filtered as DOC (above). The samples were initially allowed to equilibrate via
177 filtering in a controlled laboratory environment at 15°C, after which t=0 was the start time of the
178 incubations. The Winkler titration method was used to measure dissolved oxygen (DO)
179 concentrations initially (t=0) (i.e., in situ DO) as well as after 5-day incubations at 15°C , where
180 bottles were kept in the dark in between measurements. At t=0, DO measurements were at
181 concentrations expected at equilibrium with the 15°C laboratory temperature (~8.5–9.0 mg/L).
182 This temperature was only slightly warmer than environmental sampling conditions (i.e., the
183 Kolyma River mainstem samples ranged from 11.40–13.90°C, river samples ranged from 10.70–
184 14.20°C, and stream samples ranged from 4.40–13.80°C). However, we maintained samples at
185 15°C as is standard in the BOD method, which allowed samples to be treated identically in the
186 controlled experiment (in situ temperatures varied depending not only upon location but also
187 date and time of day). Furthermore, bottles were wrapped tightly with paraffin such that
188 physical degassing should have been minimal during the incubations. BOD was then calculated
189 as the difference between DO concentrations at t = 0 and following the 5-day incubations. We
190 assumed 100% of DO consumed was converted to CO_2 via aerobic respiration and that the

carbon source respired was DOM, where resulting BOD measurements were used an analog for bioavailable DOC. The Winkler method we used here has been used extensively and is attractive for a variety of reasons, including: (i) enabling DO to be measured with precision of 0.01 mg/L, thus low respiration rates can be accurately measured; (ii) allowing for convenient replication of assays within habitats; (iii) permitting experimental manipulation of standard bioassays (e.g., N and P amendments, photolysis experiments, alteration of initial microbial consortia, and temperature manipulation; (iv) helping to segregate the relative roles of water column and sediment processes (through comparisons with sediment analyses); and (v) helping to inform more realistic ecosystem-level experiments that are much more laborious and time intensive.

In order to investigate the optical characteristics of the DOM in these samples, we additionally measured the ultraviolet-visible absorption spectra of CDOM from this broad collection of waters. CDOM absorbance was measured on filtered (precombusted Whatman 0.7 μm GF/F), unacidified waters stored in acid-washed HDPE bottles immediately after collection (within ~1 day) at the Northeast Science Station in Cherskiy using a Thermo Scientific GENESYS 10 UV/Vis Spectrophotometer across wavelengths 800–200 nm (1 nm interval) with a 1 cm quartz cuvette. All sample spectra were blank corrected using Milli-Q water (18 Ω). Measurements were made after samples had equilibrated to the laboratory temperature in order to minimize temperature effects. Null-point adjustments were performed on all spectra, such that CDOM absorbance was assumed to be zero across wavelengths greater than 750 nm and the average absorbance between 750 nm and 800 nm was subtracted from each spectrum to correct for offsets owing to instrument baseline drift, temperature, scattering, and refractive effects (Green and Blough, 1994; Helms et al, 2008). CDOM absorption coefficients were calculated as:

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

where a is the Napierian absorption coefficient (m^{-1}) at a specified wavelength (λ, in nm), $A(\lambda)$ is the absorbance at the wavelength, and l is the cell path length in meters (Green and Blough, 1994). To avoid inner-filtering effects, several highly absorbing samples (primarily the soil pore waters) were diluted with Milli-Q water before analysis (to the point where A_{350} was ≤0.02 ~~at~~ for a 1 cm path length ~~was ≤0.02~~) to avoid saturation of the spectra at short wavelengths, where the final CDOM absorbance and therefore absorption coefficients were corrected for these procedures.

CDOM spectral slopes (S, nm^{-1}) between 290–350 nm ($S_{290–350}$), 275–295 nm ($S_{275–295}$), and 350–400 nm ($S_{350–400}$), calculated within log-transformed absorption spectra, were also utilized to investigate DOM characteristics of contrasting water types, and were calculated as:

$$a(\lambda) = a\,(\lambda_{ref})\, e^{-S\,(\lambda - \lambda ref)} \quad (2)$$

where $a(\lambda)$ is the absorption coefficient at a specified wavelength, λ_{ref} is a reference wavelength, and S is the slope fitting parameter (Hernes et al., 2008; Helms et al., 2008; Spencer et al., 2009a). All slopes are reported here as positive values, such that higher (i.e., steeper) slopes indicate a greater decrease in absorption with increasing wavelength. Additional CDOM parameters investigated here include the spectral slope ratio (S_R), calculated as the ratio between $S_{275–295}$ and $S_{350–400}$; the ratio between CDOM absorption coefficients (a) at 250 nm and 365 nm (a_{250}:a_{365}); and specific UV absorbance ($SUVA_{254}$), determined by dividing UV absorbance (A) at 254 nm by the sample DOC concentration and reported in units of L mg C^{-1} m^{-1} (Weishhar et al., 2003). These 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 provide insights for various DOM characteristics such as molecular weight, source waters, composition, age, and aromatic content for a variety of geographic regions (e.g.,

Weishaar 2003; Neff et al., 2006; Helms et al., 2008; Spencer et al., 2008; Spencer et al., 2009a; Spencer et al., 2009b; Mann et al., 2012). As such, we chose our method for spectral slope calculations to be consistent with previous studies to foster intercomparisons between datasets, however future studies may derive further insight utilizing methods that calculate a continuous spectral slope curve over the full 200–800 nm span (e.g., Loiselle et al., 2009) rather than only specific wavelength intervals as presented here.

3. Results

Total DOC concentrations (and the variance among values within each water type) decreased markedly downstream along the flow-path continuum from soil pore waters to the Kolyma River mainstem (Figure 2a). Mean (±1 standard deviation) DOC values were 43.3 ± 22.8 mg L^{-1} (soil pore waters), 11.6 ± 3.0 mg L^{-1} (streams), 4.9 ± 1.6 mg L^{-1} (rivers), and 3.6 ± 0.4 mg L^{-1} (mainstem waters). Soil pore waters, in particular, showed highly variable DOC concentrations (ranging from 13.2 to 64.7 mg L^{-1}) demonstrating the heterogeneous supply of DOM from terrestrial systems to streams. By contrast, DOC concentrations in the Kolyma mainstem along the ~250 km stretch sampled were remarkably similar (ranging from 3.0 to 4.4 mg L^{-1}) during this mid-summer July period (Figure 2a). Furthermore, DOC concentrations of the four water types sampled were found to be significantly different from one another (one-way ANOVA, $p<0.05$).

Concentrations of bioavailable DOC showed similar patterns to DOC, declining downstream along the flow-path continuum with increasing water residence time in the system (Figure 2b). Bioavailable DOC concentrations averaged 0.9 ± 0.2 mg L^{-1} (soil pore waters), 0.3 ± 0.1 mg L^{-1} (streams), 0.3 ± 0.2 mg L^{-1} (rivers), and 0.2 ± 0.2 mg L^{-1} (mainstem waters), and

showed relative greater variability than DOC within the stream, river and mainstem water types. Concentrations of bioavailable DOC in soil pore waters were statistically different from the other three water types (one-way ANOVA, $p<0.05$), although by contrast, streams, rivers, and mainstem waters were not statistically different from one another ($p>0.05$). Importantly, the percentage of bioavailable DOC (i.e., calculated as the amount of bioavailable DOC divided by total DOC) did not significantly decrease downstream (one-way ANOVA, $p>0.05$) and showed relatively similar values among the four water sample types along the flow-path continuum (Figure 2c), where percentages averaged 3.9 ± 3.8% (soil pore waters), 3.2 ± 1.9% (streams), 6.2 ± 4.3% (rivers), and 4.5 ± 4.5% (mainstem waters).

CDOM absorption spectra (200–800 nm) showed clear separation between soil pore waters, streams, rivers, and the Kolyma mainstem, where soil pore waters exhibited values markedly higher than the other three water sample types (Figure 3a). CDOM absorption also clearly declined downstream from streams, rivers, to mainstem waters when assessing those waters only (Figure 3b). Furthermore, we investigated the potential for utilizing CDOM absorption as a proxy for DOC concentrations in these waters. Our data revealed that independent of water type along the stream-river-mainstem flow-path, CDOM absorption was strongly linearly correlated to DOC concentrations at 254, 350, and 440 nm (Figure 4). In particular, CDOM absorption at 254 nm had the highest predictive capability of DOC (r^2 = 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, $p<0.01$) less strongly predictive (Figure 4).

We additionally investigated the quantitative distribution of the six derived CDOM parameters ($S_{290–350}$, $S_{275–295}$, $S_{350–400}$, a_{250}:a_{365}, $SUVA_{254}$, and S_R) across the four water types (Figure 5; Table 1). In general, four parameters ($S_{290–350}$, $S_{275–295}$, a_{250}:a_{365}, and S_R) showed an

283 increasing pattern along the flow-path continuum, whereas two parameters ($S_{350–400}$ and
284 $SUVA_{254}$) showed a decreasing pattern. In terms of whether the values of the six parameters
285 were statistically significantly different among water sample types, one-way ANOVA tests (at
286 the 0.05 level) revealed inconsistent results. Most commonly, soil pore waters were statistically
287 different from all other water types for four of the parameters ($S_{290–350}$, $S_{275–295}$, a_{250}:a_{365}, and S_R),
288 but no consistent pattern was observed in significant differences across other water types.
289 However, the spectral slope ratio (S_R) was the only CDOM parameter of the six investigated that
290 showed statistically significant differences between all four water types (p<0.05).
291 Lastly, we examined the relationships between CDOM optical properties and DOM
292 bioavailability. To this end, we performed linear regressions between all six of our derived
293 CDOM parameters and bioavailable DOC concentrations to determine the strength of their
294 ability to predict bioavailable DOC. Our results indicated that five of the CDOM parameters
295 ($S_{290–350}$, $S_{275–295}$, a_{250}:a_{365}, $SUVA_{254}$, and S_R) were statistically significant predictors at the 0.05
296 level (Table 2). In particular, S_R showed the strongest relationship with bioavailable DOC
297 concentrations (r^2 value = 0.45, p<0.01). The relationship between bioavailable DOC
298 concentrations and S_R (Figure 6) showed a distinct negative trend (bioavailable DOC mg L^{-1} = -
299 2.204(S_R) + 2.518), with the highest bioavailable DOC concentrations and lowest S_R values for
300 soil pore waters, and lowest bioavailable DOC concentrations and highest S_R values for Kolyma
301 River mainstem waters. We found a clear gradation in the relationship between S_R and
302 bioavailable DOC down the flow-path continuum, as one would also expect by examining these
303 parameters individually (e.g., Figures 2b, 5f). In summary, not only was S_R the only CDOM
304 parameter that showed statistically significant separation between all four water types examined,

but it also had the strongest relationship when compared with concentrations of bioavailable DOC.

4. Discussion and Conclusions

In this study, we present a full suite of DOC, bioavailable DOC, and CDOM parameters throughout the permafrost-dominated Kolyma River basin in Northeast Siberia with the purpose of helping to elucidate the processing of DOM along a full flow-path continuum from soil pore waters to the mainstem. Our findings show that average concentrations of DOC and bioavailable DOC generally decrease as waters travel downstream from soil pore waters, streams, rivers, and ultimately to the Kolyma River mainstem. This pattern suggests the occurrence of rapid in-stream processing of DOM and potential remineralization of DOC to atmospheric CO_2 during this July baseflow period well before these waters reach the Arctic Ocean (e.g., Denfeld et al., 2013; Mann et al., 2015; Spencer et al., 2015). The amount of total DOC putatively lost to remineralization is a relatively small fraction (~3–6% depending upon water type), but on par with similar studies across the Arctic for this time of year (e.g., Holmes et al., 2008). Although this may be a relatively small proportion, it is likely the permafrost-derived, ancient DOC found in headwaters that is contributing to permafrost carbon feedbacks to climate warming (Mann et al., 2015). Moving downstream, the river continuum concept predicts that relative diversity of organic molecules decreases from the headwaters to the river mouth (Vannote et al., 1980). As energetically favorable compounds are converted to living tissue or respired as CO_2, bulk DOM in the Kolyma basin has indeed been shown in previous studies to become less diverse moving from headwaters to mainstem waters before exported to the Arctic Ocean (Spencer et al., 2015).

CDOM parameters presented in this study give further insight into characteristics of DOM along the full flow-path continuum throughout the Kolyma River basin. For instance, the specific ultraviolet absorbance ($SUVA_{254}$) has been shown to be correlated with DOM composition, where $SUVA_{254}$ values are positively correlated with percent aromaticity and molecular size of DOM (and for a given river have been shown to be greatest during spring flood) (e.g., Weishaar et al., 2003; Spencer et al., 2009a; Mann et al., 2012). In this study, we generally found progressively decreasing $SUVA_{254}$ values along the flow-path from soil pore waters towards mainstem waters, suggesting that soil pore waters contain higher molecular weight, aromatic terrestrial DOM that generally becomes lower in molecular weight and aromaticity along the flow-path continuum towards the Kolyma River mainstem. In addition, the a_{250}:a_{365} ratio has been shown to be negatively correlated to aromaticity and molecular size of DOM (Peuravuori and Pihlaja, 1997). In fact (similar to samples from the Yukon River, Alaska (Spencer et al., 2009a)), our data showed that the a_{250}:a_{365} ratio is significantly negatively correlated with $SUVA_{254}$ (a_{250}:a_{365} = -0.947 ($SUVA_{254}$) – 0.947; r^2=0.49, p<0.01). As such, the a_{250}:a_{365} ratio may potentially be utilized as a first-order proxy for $SUVA_{254}$ when DOC concentrations cannot be easily determined.

However, despite our observations of downstream shifts in DOM composition, we find a relatively constant proportion of DOC that was bioavailable (~3–6% of total DOC) regardless of relative water residence time along the flow-path. This suggests that continual microbial processing of organic matter is able to occur with similar rates during transit from headwaters throughout the Kolyma River drainage network to the Arctic Ocean concurrent with ongoing downstream CDOM compositional changes. Microbial demand in headwater streams of the Kolyma River basin is subsidized by significant quantities of DOC specifically derived from

permafrost and aged soils, yet the proportion of permafrost supporting DOC mineralization declines as waters move downstream through the fluvial network (Mann et al., 2015). Thus, our results importantly show that microbial metabolism continues at similar rates independent of dominant DOM source and radiocarbon age.

There may be several reasons for why microbial metabolism maintains this consistent rate along the flow-path, including the possibility that aquatic microorganisms are acclimating to a downstream shift in DOM composition. The higher overall amounts of bioavailable DOC we measured in soil pore waters may reflect a highly bioreactive permafrost or aged surface soil derived fraction of the bulk DOC pool (e.g., Vonk et al., 2013; Mann et al., 2014). Further downstream in larger tributary and Kolyma mainstem waters, it has been shown that lower total amounts of bioavailable DOC is supported almost entirely from predominantly modern radiocarbon aged surface soils and vegetation sources (Mann et al., 2015). Aquatic microorganisms may therefore be readily acclimating to significant shifts in DOM composition caused by selective losses of unique DOM fractions (e.g., Kaplan and Bott, 1983; Spencer et al., 2015) alongside high-internal demand for labile DOM by stream communities in lower order streams, which would otherwise generally be expected to result in decreased DOM lability with increasing water residence time (Stepanauskas et al., 1999a,b; Wikner et al., 1999; Langenheder et al., 2003; Sondergaard et al., 2003; Fellman, 2010; Fellman et al., 2014).

Additional mechanisms such as increasing photodegradation downstream may also account for our observed patterns in downstream DOM. Previous studies have indicated that CDOM spectral slopes (particularly $S_{290–350}$ and $S_{275–295}$) can serve as indicators of DOM source and composition, where a steeper spectral slope typically suggests lower molecular weight material with decreasing aromatic content and a shallower (i.e., lower) slope typically suggests

373 higher molecular weight material with increasing aromatic content (Green and Blough, 1994;
374 Blough and Del Vecchio, 2002; Helms et al., 2008; Spencer et al., 2008; Spencer et al., 2009a).
375 Furthermore, $S_{275–295}$ has been identified as a reliable proxy for dissolved lignin and therefore
376 terrigenous DOM supply across Arctic Ocean coastal waters, as well as photobleaching history
377 (Helms et al., 2008; Fichot et al., 2013). We found a general increase in $S_{290–350}$ and $S_{275–295}$
378 moving downstream through the network, indicative of progressive photodegradation of DOM
379 alongside likely reductions in average DOM molecular weight and aromaticity. We found
380 spectral slopes over longer wavelength regions ($S_{350–400}$) decreased through the network, also
381 suggesting constant photochemical degradation of DOM as waters flowed downstream (e.g.,
382 Helms et al., 2008). The slope ratio (S_R) has also been shown to be a proxy for DOM molecular
383 weight and source, where low ratios typically correspond to more allochthonous, higher
384 molecular weight DOM (Helms et al., 2008; Spencer et al., 2009b; Mann et al., 2012). The
385 advantage of S_R ratios over individual S values is apparent when each spectral slope responds to
386 a process in an opposing manner, emphasizing the response in calculated S_R values. The clear
387 increases in S_R we observed moving downstream in the fluvial network (from a minimum of 0.74
388 in soil pore waters to a maximum of 1.24 in the mainstem) indicate that during July summer
389 conditions, soil pore waters contain higher molecular weight, aromatic terrestrial DOM that
390 generally becomes lower in average molecular weight and aromaticity along the flow-path
391 continuum towards the Kolyma River mainstem. The maximum S_R value of 1.24 we report in
392 the Kolyma River mainstem is markedly higher than the range of S_R (0.82–0.92) reported in
393 Stedmon et al. (2011) for the Kolyma from 2004 and 2005, demonstrating the heterogeneity of
394 DOM properties even in mainstem waters and the necessity for greater temporal resolution in
395 monitoring. Similar to spectral slopes, S_R values may also be indicative of photobleaching

history (e.g., Helms et al., 2008) and our we observed increase in S_R downstream through the network suggests evidence of on-going photochemical degradation of surface water DOM during transit.

Photodegradation may indeed play an important and direct role in our observed consistent fraction of bioavailable DOC along the flow-path. Previous studies in the Arctic underscore the importance of residence times as well as a significant combined role for photo- and biological degradation along the flow-path in Arctic watersheds (Cory et al., 2007; Merck et al., 2012; Cory et al., 2013; Laurion and Mladenov, 2013). These previous results show that the photochemical "pretreatment" of stream DOM that occurs during export into lakes and coastal zones may impact the ability of microorganisms to mineralize DOM. Therefore, the residence times and flow-paths of waters should greatly influence the ultimate fate of DOM (e.g., DOM vs. CO_2) exported to the adjacent ocean. In our case, we find that our increasing S_R values downstream suggest important photodegradation processes are occurring along the flow-path continuum, where this photodegradation may potentially release significant quantities of labile DOM for continued microbial processing of DOM further downstream in these stream networks. In other words, our results suggest that ~~the~~ more abundant ~~"virgin"~~newly exposed bioavailable molecules upstream are replaced downstream by photobleached smaller molecules (originating from aromatic compounds), resulting in the fraction of DOC used relatively constant without any clear pattern overall. If this ~~(or something similar)~~ were not the case, we would expect to see a declining fraction of bioavailable DOC along the flow-path continuum.

In this study, we have provided new and important findings with regards to the spatial distribution of DOM concentration, bioavailability, and optical properties during mid-summer hydrologic conditions throughout the Kolyma River basin in Northeast Siberia. Freshwater DOC

419 measurements across the network were strongly positively correlated to CDOM absorption at
420 254 nm ($r^2 = 0.958$, $p<0.01$), confirming the utility of simple CDOM optical measurements for
421 estimating carbon concentrations in arctic freshwaters (Spencer et al., 2008, 2009a; Stedmon et
422 al., 2011) and across water types within the Kolyma River basin in particular. Furthermore, the
423 optical parameter S_R proved to be the only CDOM compositional measure that showed
424 statistically significant separation between all four water types examined during the study period,
425 suggesting that this parameter may be useful for easily distinguishing characteristics and
426 processes occurring in organic matter among water types along the full flow-path continuum.
427 The significant increase in S_R values we observed downstream through the network suggests
428 evidence of on-going photochemical degradation of surface water DOM during transit.
429 Additionally, of all the CDOM parameters, S_R values were most closely related to concentrations
430 of bioavailable DOC ($r^2 = 0.454$, $p<0.01$), suggesting that this value may be correlated with a
431 decline in bioavailable DOC through the network. However, biological degradation has
432 previously been shown to typically slightly decrease S_R values (Helms et al., 2008), which
433 indicates that the opposite relationship observed here may instead be a consequence of co-
434 variance with photodegradation of DOM, or demonstrate that S_R values may reflect a broader,
435 more complex range of physical and biological processes than previously recognized. Garnering
436 further insight from our measurements, the relatively constant proportion of DOC that was
437 bioavailable regardless of relative water residence time along the flow-path may be a
438 consequence of two potential scenarios allowing for continual processing of organic material
439 within the system, namely: (a) aquatic microorganisms are acclimating to a downstream shift in
440 DOM composition; and/or (b) photodegradation is continually generating labile DOM for
441 continued microbial processing of DOM along the flow-path continuum. Without such

processes, we would otherwise expect to see a declining fraction of bioavailable DOC downstream with increasing residence time of water in the system.

Unlike many previous studies that focus on only mainstem rivers in the Arctic, we focus here on a variety of waters along a full flow-path continuum, showing that CDOM metrics (in particular, S_R) reflect important compositional differences in DOM of waters along the transit from headwaters to the Arctic Ocean. The range in DOM properties of waters travelling downstream through the Kolyma Basin often spanned wider ranges than DOM compositional differences reported annually among the six major arctic rivers. For example, S_R values across the major arctic rivers over the years 2004 and 2005 spanned a minimum of 0.79 in the Yenisey River, to a maximum value of 1.11 in the Mackenzie River (Stedmon et al., 2011), compared to the range of 0.74–1.24 for waters in our study within a single basin. It is therefore essential that changes taking place in the quality of CDOM exported by these rivers be examined throughout entire river basins in order to adequately assess climate driven shifts in terrigenous carbon supply and reactivity. Future work that includes both photo- and microbial degradation experiments may further elucidate the ability for S_R to serve as a direct proxy for these processes along a flow-path gradient. Our overall results thus far demonstrate promise for utilizing ultraviolet-visible absorption characteristics to easily, inexpensively, and comprehensively monitor the quantity and quality of DOM (over broad ranges) across permafrost landscapes in the Arctic. This is particularly critical for remote arctic landscapes such as those in Northeast Siberia, where the future fate of organic carbon currently frozen in permafrost soils (and whether it ultimately is released as CO_2 and CH_4) is tightly linked to the lability of this material.

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Table 1. Mean spectral slope and other CDOM parameters for soil pore waters, streams, rivers, and the Kolyma River mainstem.

	$S_{290–350}$ ($\times 10^{-3}$ nm^{-1})	$S_{275–295}$ ($\times 10^{-3}$ nm^{-1})	$S_{350–400}$ ($\times 10^{-3}$ nm^{-1})	a_{250}:a_{365}	$SUVA_{254}$ (L mg C^{-1} m^{-1})	S_R
Soil pore waters	15.35	15.27	18.65	5.47	3.52	0.82
Streams	17.08	17.39	18.89	6.44	2.94	0.92
Rivers	17.17	17.79	18.19	6.27	2.77	0.98
Kolyma Mainstem	18.10	18.57	17.50	6.53	2.56	1.06

Table 2. Relationships between bioavailable DOC and each of the six CDOM metrics investigated. S_R shows the highest r-squared value, with a *p*-value of 0.00002.

	r^2	*p*-value
$\boldsymbol{S_{290\text{-}350}}$	0.3560	0.00025
$\boldsymbol{S_{275\text{-}295}}$	0.4497	0.00002
$\boldsymbol{S_{350\text{-}400}}$	0.0443	0.23987
$\boldsymbol{a_{250}}$**:**$\boldsymbol{a_{365}}$	0.2645	0.00220
$\mathbf{SUVA_{254}}$	0.1980	0.01376
$\boldsymbol{S_R}$	0.4540	0.00002

Figure Legends

Figure 1. The northern reaches of the Kolyma River in East Siberia and the locations of the 47 water samples collected throughout the region in this study (including soil pore waters, streams, rivers, and the Kolyma River mainstem).

Figure 2. Concentrations of (a) dissolved organic carbon (DOC), (b) bioavailable DOC, and (c) percentage of total DOC that is bioavailable for the four water sample types. The mean (hollow squares), median (horizontal lines), ±1 standard deviation (gray boxes), and total range (whiskers) for each sample population are shown.

Figure 3. Chromophoric dissolved organic carbon (CDOM) absorption spectra from 200–800 nm for (a) all samples; and (b) streams, rivers, and the Kolyma River mainstem only.

Figure 4. Relationships between DOC and CDOM absorption at 254, 350, and 440 nm for streams, rivers, and the Kolyma River mainstem.

Figure 5. The six presented CDOM metrics, (a) $S_{290–350}$, (b) $S_{275–295}$, (c) $S_{350–400}$, (d) a_{250}:a_{365}, (e) $SUVA_{254}$, and (f) S_R, show the separation between soil pore, stream, river, and Kolyma mainstem waters. The mean (hollow squares), median (horizontal lines), ±1 standard deviation (gray boxes), and total range (whiskers) for each sample population are shown.

753

754 **Figure 6.** The CDOM metric S_R shows a relatively strong relationship with concentrations of

755 bioavailable DOC present in the sampled waters, with an r-squared value of 0.4540 and *p*-value

756 <0.01.

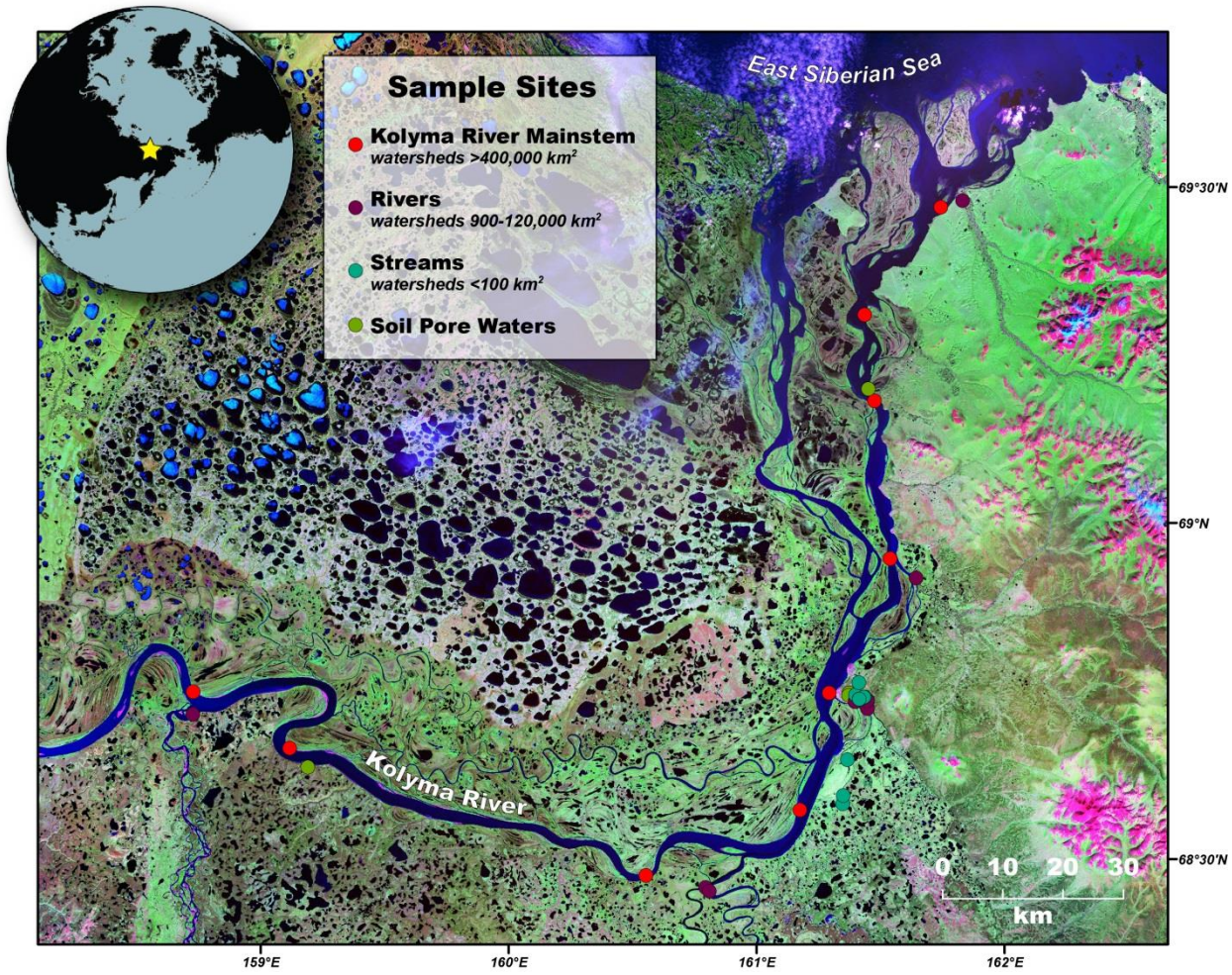
Sample Sites
Kolyma River Mainstem
watersheds >400,000 km²
Rivers
watersheds 900-120,000 km²
Streams
watersheds <100 km²
Soil Pore Waters
East Siberian Sea
Kolyma River
69°30'N
69°N
68°30'N
159°E
160°E
161°E
162°E
0 10 20 30
km

Figure 1.

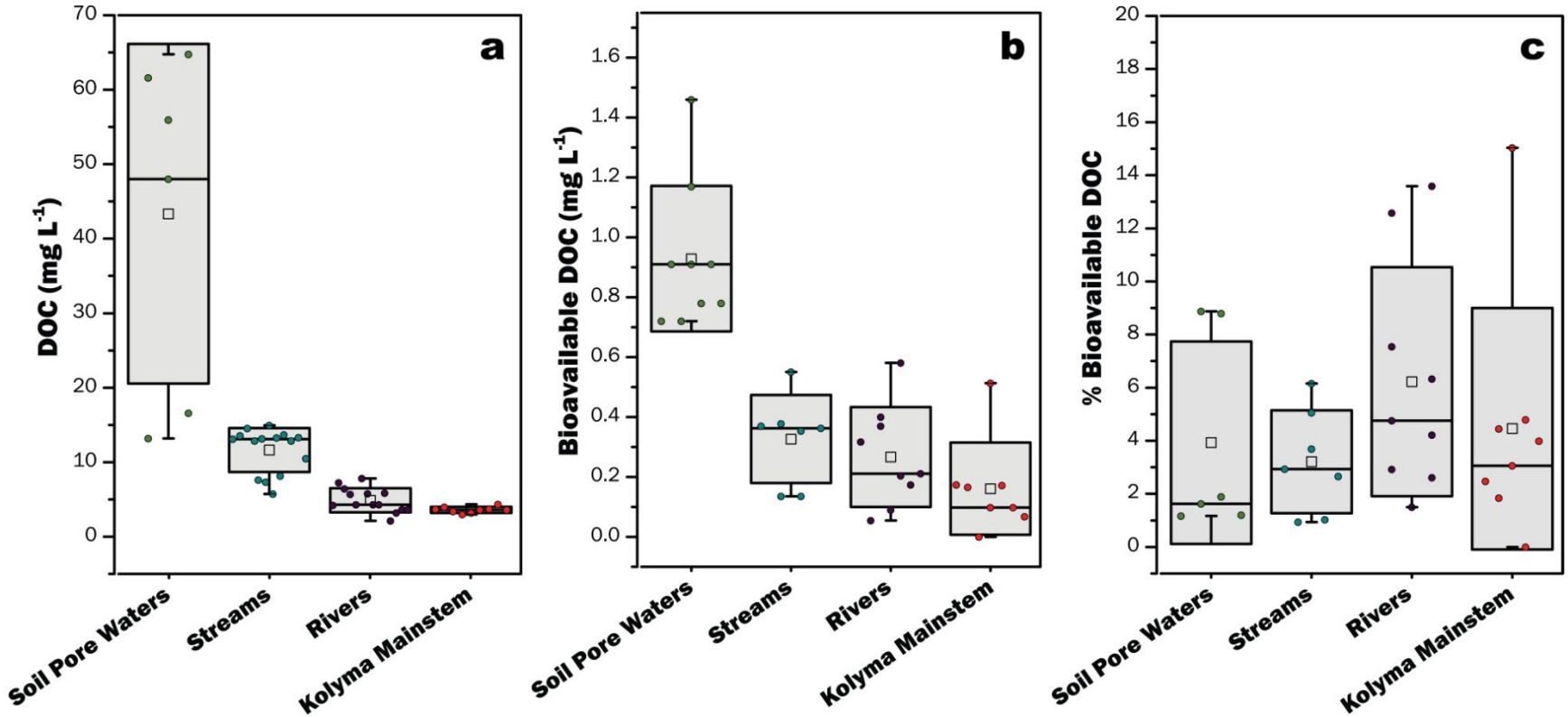
a
DOC (mg L-1)
70
60
50
40
30
20
10
0
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem
b
Bioavailable DOC (mg L-1)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem
c
% Bioavailable DOC
20
18
16
14
12
10
8
6
4
2
0
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem

Figure 2.

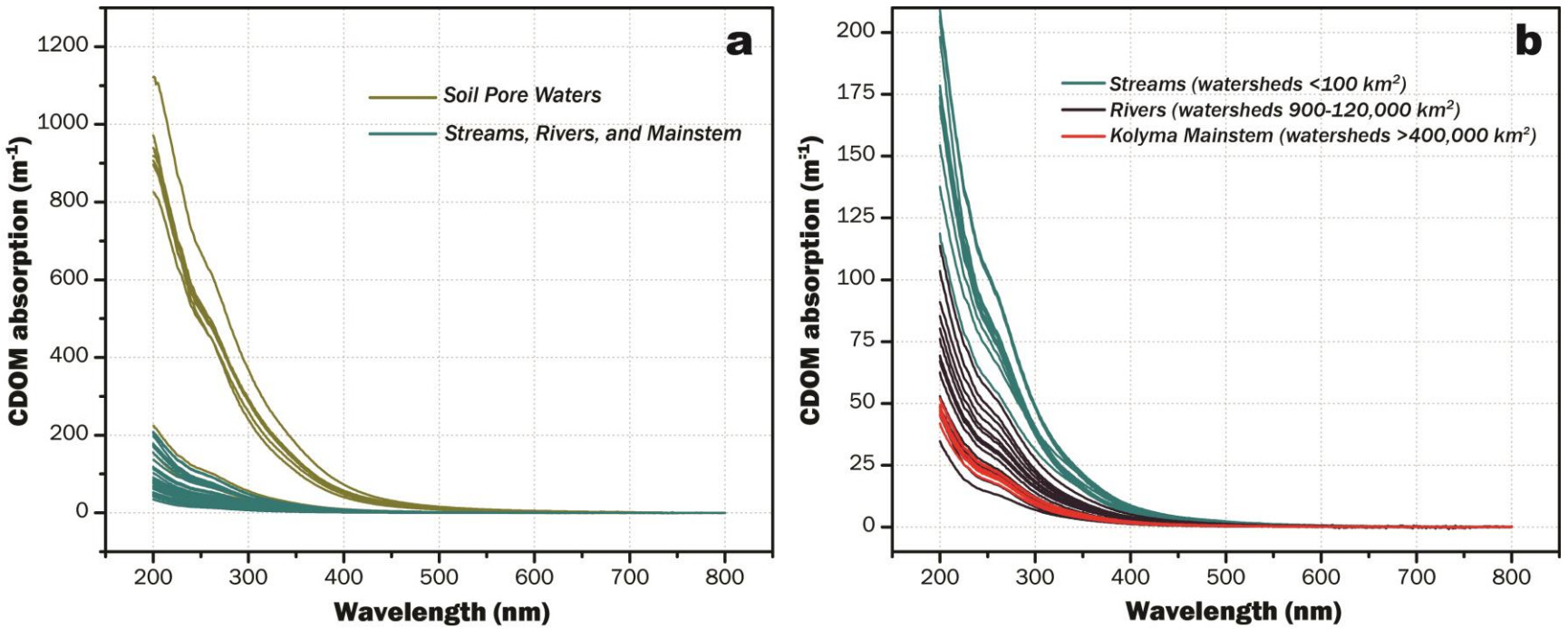
a
Soil Pore Waters
Streams, Rivers, and Mainstem
CDOM absorption (m-1)
Wavelength (nm)
b
Streams (watersheds <100 km2)
Rivers (watersheds 900-120,000 km2)
Kolyma Mainstem (watersheds >400,000 km2)
CDOM absorption (m-1)
Wavelength (nm)

Figure 3.

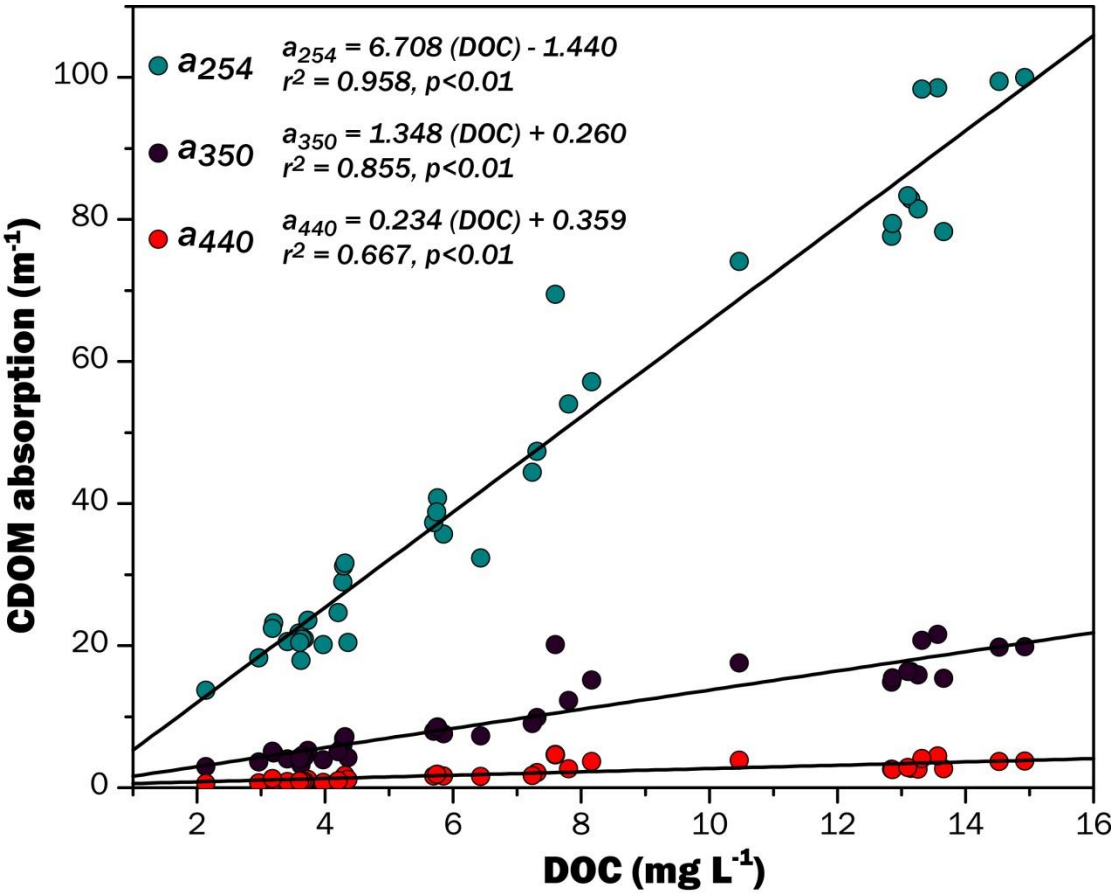
a254
a350
a440
a254 = 6.708 (DOC) - 1.440
r2 = 0.958, p<0.01
a350 = 1.348 (DOC) + 0.260
r2 = 0.855, p<0.01
a440 = 0.234 (DOC) + 0.359
r2 = 0.667, p<0.01
CDOM absorption (m-1)
DOC (mg L-1)
0
20
40
60
80
100
2
4
6
8
10
12
14
16

Figure 4.

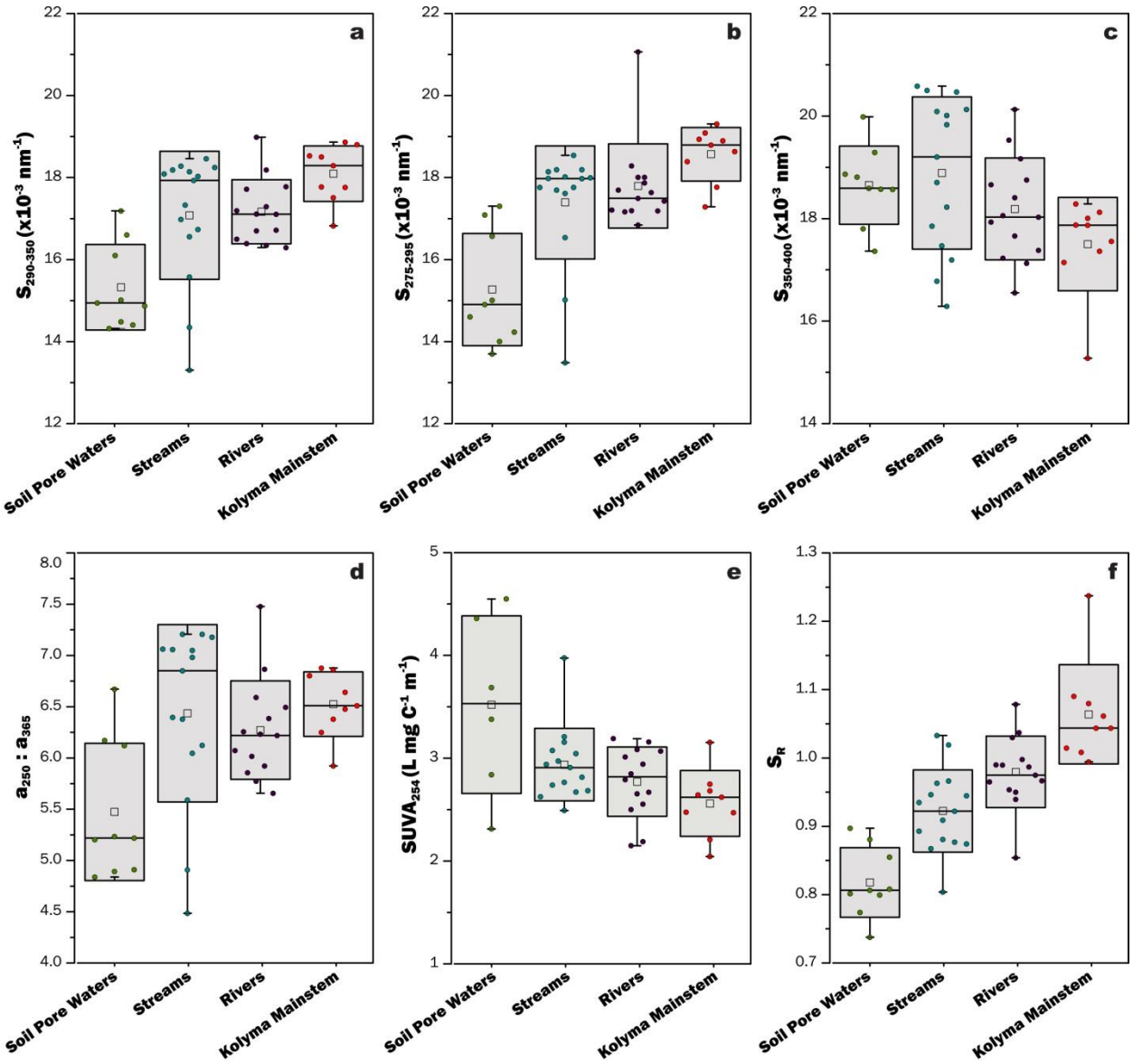
a
b
c
d
e
f
$S_{290-350}$ (x10^{-3} nm^{-1})
$S_{275-295}$ (x10^{-3} nm^{-1})
$S_{350-400}$ (x10^{-3} nm^{-1})
a_{250} : a_{365}
$SUVA_{254}$ (L mg C^{-1} m^{-1})
S_R
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem

Figure 5.

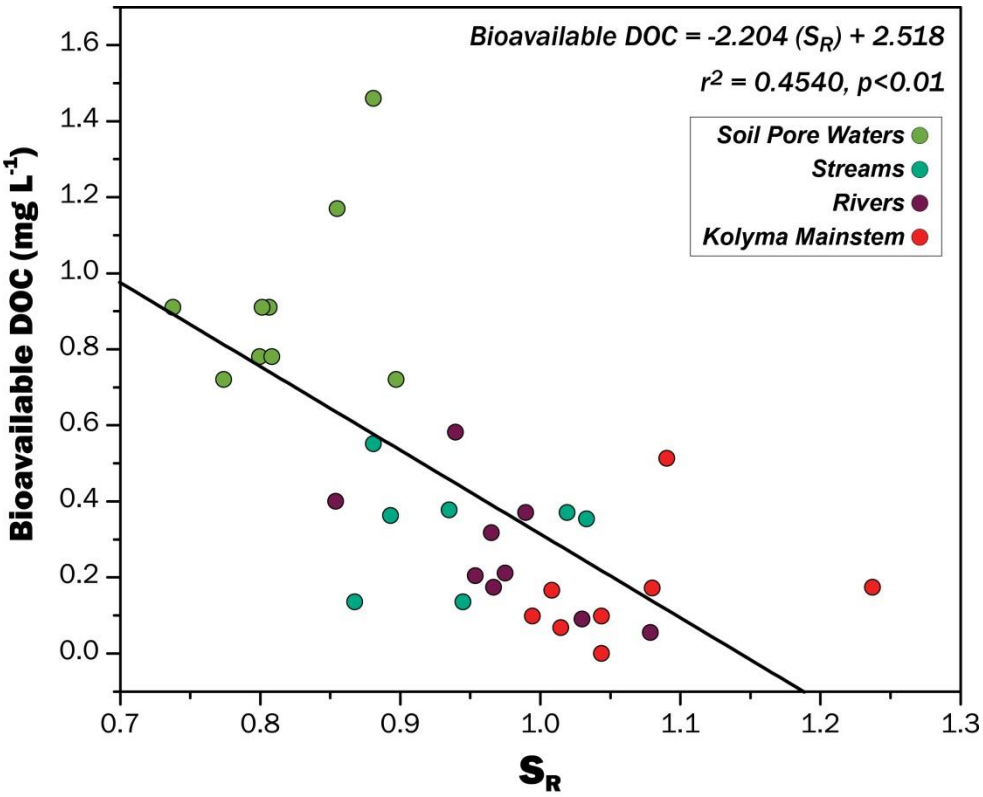
Bioavailable DOC = -2.204 (S_R) + 2.518
r² = 0.4540, p<0.01
Soil Pore Waters
Streams
Rivers
Kolyma Mainstem
Bioavailable DOC (mg L⁻¹)
S_R
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.7
0.8
0.9
1.0
1.1
1.2
1.3

Figure 6.