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Optical properties and bioavailability of dissolved organic matter along a flow-path continuum from soil pore waters to the Kolyma River, 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 will largely depend upon the composition and amount of carbon released to inland and coastal waters. Here, we measured the 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 absorbance values 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, CDOM absorption at 254 nm showed a strong relationship with dissolved organic carbon (DOC) concentrations across all water types ($r^2 = 0.958, p < 0.01$). 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. 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. 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

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the landscape is therefore critical for understanding potential future feedbacks on 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

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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; Cory et al., 2014); (ii) loss via aggregation of DOM owing to changes in ionic strength when freshwater mixes with sea water (Sholkovitz, 1976); (iii) DOM sorption to particles (Chin et al., 1998); and/or (iv) 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, 2015; Spencer et al., 2015). Here, we complement these studies by providing extensive spa-

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tial characterization of DOM along a flow-path continuum from soil pore waters to the Kolyma River mainstem during mid-summer (July) baseflow. 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. Absorbance values and spectral slopes (calculated within log-transformed absorption spectra) were used to investigate contrasting water types and shifts in DOM quality with increasing water residence time along a land-ocean gradient. 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 methods such as ultraviolet-visible absorption 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, 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

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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 (Fig. 1). Samples were collected over a narrow temporal window from 11–25 July 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 ($n = 9$).

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

We additionally conducted a series of organic matter bioavailability assays to assess the total and relative amounts of bioavailable DOC in soil, stream, and river environments. These assays relied upon 5 day biological oxygen demand (BOD) experiments, with methods similar to those in Mann et al. (2014). The Winkler titration method was used to measure initial ($t = 0$) dissolved oxygen (DO) concentrations (i.e., in situ dissolved oxygen) after a 5 day incubation at 15 °C using water collected in triplicate glass 300 mL BOD bottles, where bottles were kept in the dark in between measurements.

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BOD was calculated as the difference between DO concentrations at $t = 0$ and following incubation. We 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^{-1}, 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; 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 immediately after collection (within ~ 1 day) at the Northeast Science Station in Cherskiy using a using a Thermo Scientific GENESYS 10 UV/Vis Spectrophotometer across wavelengths 800–200 nm (1 nm interval) using a 1 cm quartz cuvette. All sample spectra were blank corrected and referenced against Milli-Q water (18 Ω). Measurements were made after samples had equilibrated to laboratory temperature in order to minimize temperature effects. CDOM absorbance was assumed to be zero across wavelengths greater than 750 nm and the average absorbance between 750 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 absorbance 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

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(Green and Blough, 1994). Several samples with the highest CDOM concentrations (primarily the soil pore waters) were diluted with Milli-Q water before analysis to avoid saturation of the spectra at short wavelengths, where the final CDOM absorbance values 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:

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

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 absorbance at 250 and 365 nm ($a_{250} : a_{365}$); and specific UV absorbance ($SUVA_{254}$), determined by dividing UV absorbance 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, 2009a, b; Mann et al., 2012).

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 (Fig. 2a). Mean (±1 standard deviation) DOC values were 43.35 ± 22.79 mg L^{-1} (soil pore waters), 11.63 ± 2.97 mg L^{-1} (streams), 4.89 ± 1.61 mg L^{-1} (rivers), and 3.61 ± 0.41 mg L^{-1} (mainstem waters). Soil pore waters, in particular, showed highly variable DOC concentrations (ranging from 13.19 to 64.74 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 2.97 to 4.36 mg L^{-1}) during this mid-summer July period (Fig. 2a). Furthermore, DOC concentrations of the four water types sampled were found to be significantly different from one another (two-sample t tests, $p < 0.05$).

Concentrations of bioavailable DOC showed similar patterns to DOC, declining downstream along the flow-path continuum with increasing water residence time in the system (Fig. 2b). Bioavailable DOC concentrations averaged 0.93 ± 0.24 mg L^{-1} (soil pore waters), 0.33 ± 0.15 mg L^{-1} (streams), 0.27 ± 0.17 mg L^{-1} (rivers), and 0.16 ± 0.15 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 (two-samplet tests, $p < 0.05$), 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 (two-sample t tests, $p < 0.05$) and showed relatively similar values among the four water sample types along the flow-path continuum (Fig. 2c), where percentages averaged 3.93 ± 3.81 % (soil pore waters), 3.21 ± 1.94 % (streams), 6.23 ± 4.31 % (rivers), and 4.46 ± 4.55 % (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 (Figs. 3a). CDOM absorption also clearly declined downstream from streams, rivers, to mainstem waters

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when assessing those waters only (Fig. 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 (Fig. 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 (Fig. 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 (Fig. 5). In general, four parameters ($S_{290-350}$, $S_{275-295}$, $a_{250} : a_{365}$, and S_R) showed an increasing pattern along the flow-path continuum, whereas two parameters ($S_{350-400}$ and $a_{250} : a_{365}$) showed a decreasing pattern. Spectral slope and other CDOM parameters for soil pore waters, streams, rivers, and mainstem waters averaged: (a) 15.35×10^{-3}, 17.08×10^{-3}, 17.17×10^{-3}, and $18.10 \times 10^{-3}\,\mathrm{nm}^{-1}$, respectively, for $S_{290-350}$ (Fig. 5a); (b) 15.27×10^{-3}, 17.39×10^{-3}, 17.79×10^{-3}, and $18.57 \times 10^{-3}\,\mathrm{nm}^{-1}$, respectively, for $S_{275-295}$ (Fig. 5b); (c) 18.65×10^{-3}, 18.89×10^{-3}, 18.19×10^{-3}, and $17.50 \times 10^{-3}\,\mathrm{nm}^{-1}$, respectively, for $S_{350-400}$ (Fig. 5c); (d) 5.47, 6.44, 6.27, and 6.53, respectively, for $a_{250} : a_{365}$ (Fig. 5d); (e) 3.52, 2.9, 2.77, and 2.56 $\mathrm{L\,mg\,C^{-1}\,m^{-1}}$, respectively, for $SUVA_{254}$ (Fig. 5e); and (f) 0.82, 0.92, 0.98, and 1.06, respectively, for S_R (Fig. 5f). In terms of whether the values of the six parameters were statistically significantly different among water sample types, two-sample *t* tests (at the 0.05 level) revealed inconsistent results. Most commonly, soil pore waters were statistically different from all other water types for four of the parameters ($S_{290-350}$, $S_{275-295}$, $a_{250} : a_{365}$, and S_R), but no consistent pattern was observed in significant differences across other water types. However, the spectral slope ratio (S_R) was the only parameter of the six that showed statistically significant differences between all four water types ($p < 0.01$).

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Lastly, we examined the relationships between CDOM optical properties and DOM bioavailability. To this end, we performed linear regressions between all six of our derived CDOM parameters and bioavailable DOC concentrations to determine the strength of their ability to predict bioavailable DOC. Our results indicated that five of the CDOM parameters ($S_{290-350}$, $S_{275-295}$, $a_{250} : a_{365}$, $SUVA_{254}$, and S_R) were statistically significant predictors at the 0.05 level (Table 1). In particular, S_R showed the strongest relationship with bioavailable DOC concentrations (r^2 value $= 0.45, p < 0.01$). The relationship between bioavailable DOC concentrations and S_R (Fig. 6) showed a distinct negative trend (bioavailable DOC $mg\,L^{-1} = -2.204(S_R) + 2.518$), with the highest bioavailable DOC concentrations and lowest S_R values for soil pore waters, and lowest bioavailable DOC concentrations and highest S_R values for Kolyma River mainstem waters. We found a clear gradation in the relationship between S_R and bioavailable DOC down the flow-path continuum, as one would also expect by examining these parameters individually (e.g., Figs. 2b and 5f). In summary, not only was S_R the only CDOM 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; Spencer et al.,

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2015; Mann et al., 2015). In general, 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 to become less diverse moving from headwaters to mainstem waters before exported to the Arctic Ocean (Spencer et al., 2015).

Despite these downstream shifts in DOM composition however, we find a relatively constant proportion of DOC that was bioavailable (∼ 4.4 % total DOC averaged across all samples) regardless of relative water residence time. This suggests that continual microbial processing of organic matter occurs over 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.

The higher overall amounts of bioavailable DOC we measured in soil pore waters may reflect a highly bioreactive permafrost or aged surface soil derived DOC fraction (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 must therefore readily adapt to significant shifts in DOM composition caused by selective losses of unique DOM fractions (Kaplan and Bott, 1983; Spencer et al., 2015) alongside high-internal demand for labile DOM by stream communities in lower order streams, which is generally 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).

CDOM parameters presented in this study give further insight into characteristics of DOM along the full flow-path continuum throughout the Kolyma River basin. 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 slope typically suggests higher molecular weight material with increasing aromatic content (Green and Blough, 1994; Blough and Del Vecchio, 2002; Helms et al., 2008; Spencer et al., 2008, 2009a). Furthermore, $S_{275-295}$ has been identified as a reliable proxy for dissolved lignin and therefore terrigenous DOM supply across Arctic Ocean coastal waters, as well as photobleaching history (Helms et al., 2008; Fichot et al., 2013). We found a general increase in $S_{290-350}$ and $S_{275-295}$ moving downstream through the network, indicative of progressive photodegradation of DOM alongside likely reductions in average DOM molecular weight and aromaticity. We found spectral slopes over longer wavelength regions ($S_{350-400}$) decreased through the network, also suggesting constant photochemical degradation of DOM as waters flowed downstream (e.g., Helms et al., 2008). The slope ratio (S_R) has also been shown to be a proxy for DOM molecular weight and source, where low ratios typically correspond to more allochthonous, higher molecular weight DOM (Helms et al., 2008; Spencer et al., 2009b; Mann et al., 2012). The advantage of S_R ratios over individual S values is apparent when each spectral slope responds to a process in an opposing manner, emphasizing the response in calculated S_R values. The clear increases in S_R we observed moving downstream in the fluvial network (from a minimum of 0.74 in soil pore waters to a maximum of 1.24 in the mainstem) indicate that during July summer conditions, soil pore waters contain higher molecular weight, aromatic terrestrial DOM that generally becomes lower in average molecular weight and aromaticity along the flow-path continuum towards the Kolyma River mainstem. The maximum S_R value of 1.24 we report in the Kolyma River mainstem is markedly higher than the range of S_R (0.82–0.92)

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reported in Stedmon et al. (2011) for the Kolyma from 2004 and 2005, demonstrating the heterogeneity of DOM properties even in mainstem waters and the necessity for greater temporal resolution in monitoring.

The specific ultraviolet absorbance ($SUVA_{254}$) has also 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 (similar to spectral slope parameters) 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 terms of the remaining CDOM parameter investigated here, the $a_{254} : a_{365}$ 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 $a_{254} : a_{365}$ ratio is significantly negatively correlated with $SUVA_{254}$ ($a_{254} : a_{365} = -0.947$ ($SUVA_{254}$) $- 0.947$; $r^2 = 0.49$, $p < 0.01$). As such, the $a_{254} : a_{365}$ ratio may potentially be utilized as a first-order proxy for $SUVA_{254}$ when DOC concentrations cannot be easily determined.

In this study, we have provided new and important findings with regards to the spatial distribution of DOM concentration, bioavailability, and optical properties during midsummer hydrologic conditions throughout the Kolyma River basin in Northeast Siberia. Freshwater DOC measurements across the network were strongly positively correlated to CDOM absorption at 254 nm ($r^2 = 0.958, p < 0.01$), confirming the utility of simple CDOM optical measurements for estimating carbon concentrations in arctic freshwaters (Spencer et al., 2008, 2009a; Stedmon et al., 2011) and across water types within the Kolyma River basin in particular. Furthermore, the optical parameter S_R proved to be the only CDOM compositional measure that showed statistically significant separation between all four water types examined during the study period, suggesting that

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this parameter may be useful for easily distinguishing characteristics and processes occurring in organic matter among water types along the full flow-path continuum. The significant increase in S_R values we observed downstream through the network suggests evidence of on-going photochemical degradation of surface water DOM during transit. Additionally, of all the CDOM parameters, S_R values were most closely related to concentrations of bioavailable DOC ($r^2 = 0.454$, $p < 0.01$), suggesting that this value may be correlated with the rate of decline in bioavailable DOC through the network. However, biological degradation has previously been shown to typically slightly decrease S_R values (Helms et al., 2008), which indicates that the relationship observed here may be a consequence of co-variance with photodegradation of DOM, or demonstrate that S_R values reflect a range of physical and biological processes. 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 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). 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. 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
$S_{290-350}$	0.3560	0.00025
$S_{275-295}$	0.4497	0.00002
$S_{350-400}$	0.0443	0.23987
$a_{250} : a_{365}$	0.2645	0.00220
$SUVA_{254}$	0.1980	0.01376
S_R	0.4540	0.00002

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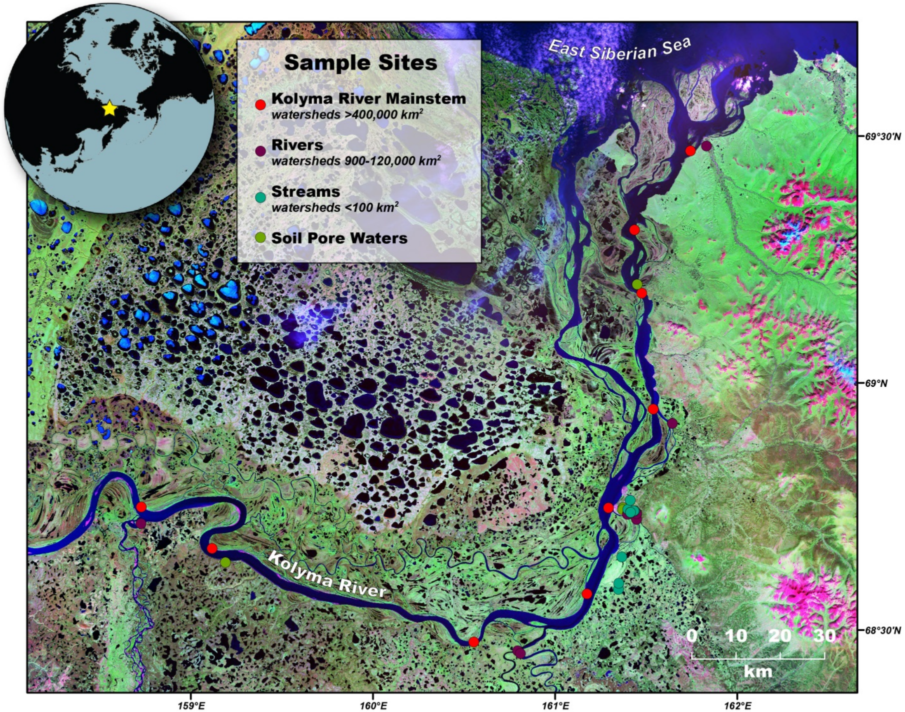

Figure 1. The northern reaches of the Kolyma River in East Siberia and the locations of the 47 water samples collected throughout the region in this study (including soil pore waters, streams, rivers, and the Kolyma River mainstem).

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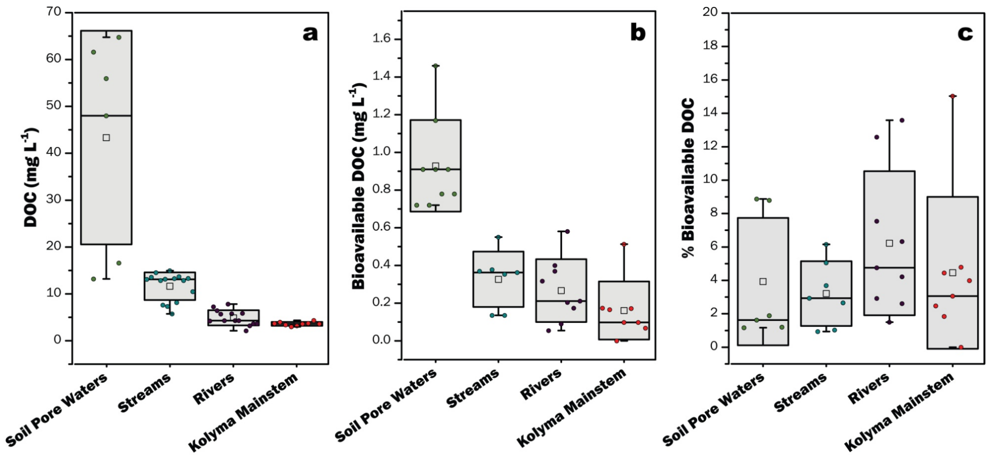

Figure 2. Concentrations of **(a)** dissolved organic carbon (DOC), **(b)** bioavailable DOC, and **(c)** percentage of total DOC that is bioavailable for the four water sample types. The mean (hollow squares), median (horizontal lines), ±1 standard deviation (gray boxes), and total range (whiskers)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

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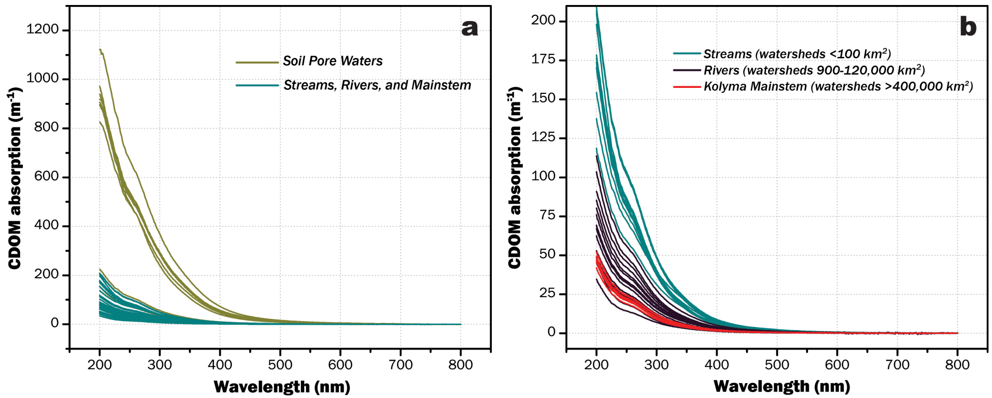

Figure 3. Chromophoric dissolved organic carbon (CDOM) absorption spectra from 200–800 nm for **(a)** all samples; and **(b)** streams, rivers, and the Kolyma River mainstem only.

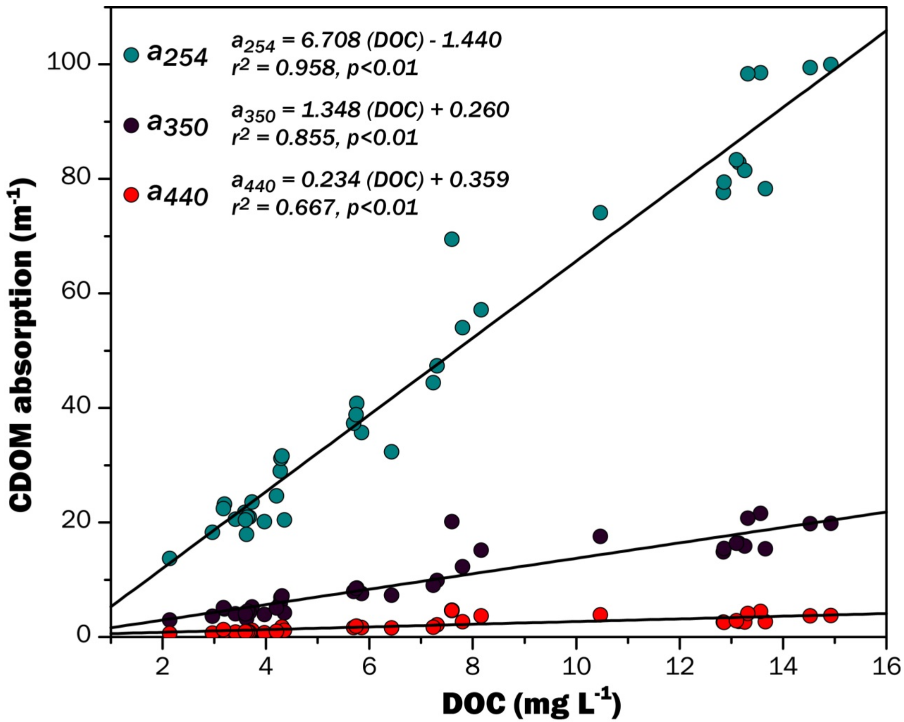

Figure 4. Relationships between DOC and CDOM absorption at 254, 350, and 440 nm for streams, rivers, and the Kolyma River mainstem.

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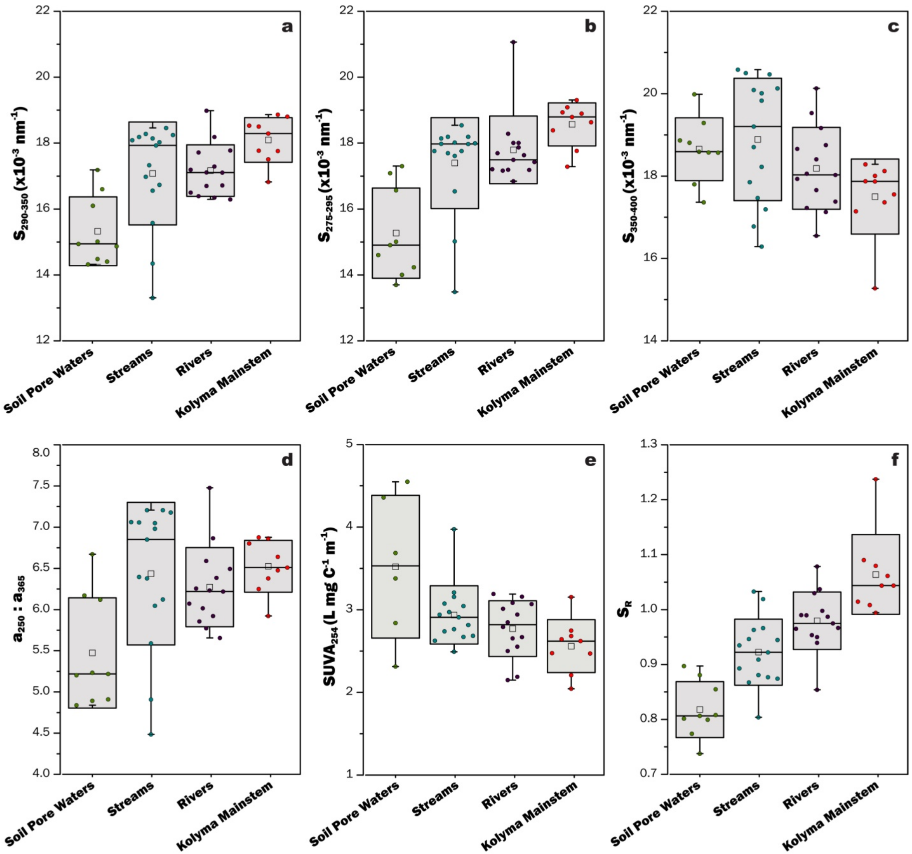

Figure 5. The six presented CDOM metrics, **(a)** $S_{290-350}$, **(b)** $S_{275-295}$, **(c)** $S_{350-400}$, **(d)** a_{250} : a_{365}, **(e)** $SUVA_{254}$, and **(f)** S_R, show the separation between soil pore, stream, river, and Kolyma main stem waters. The mean (hollow squares), median (horizontal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

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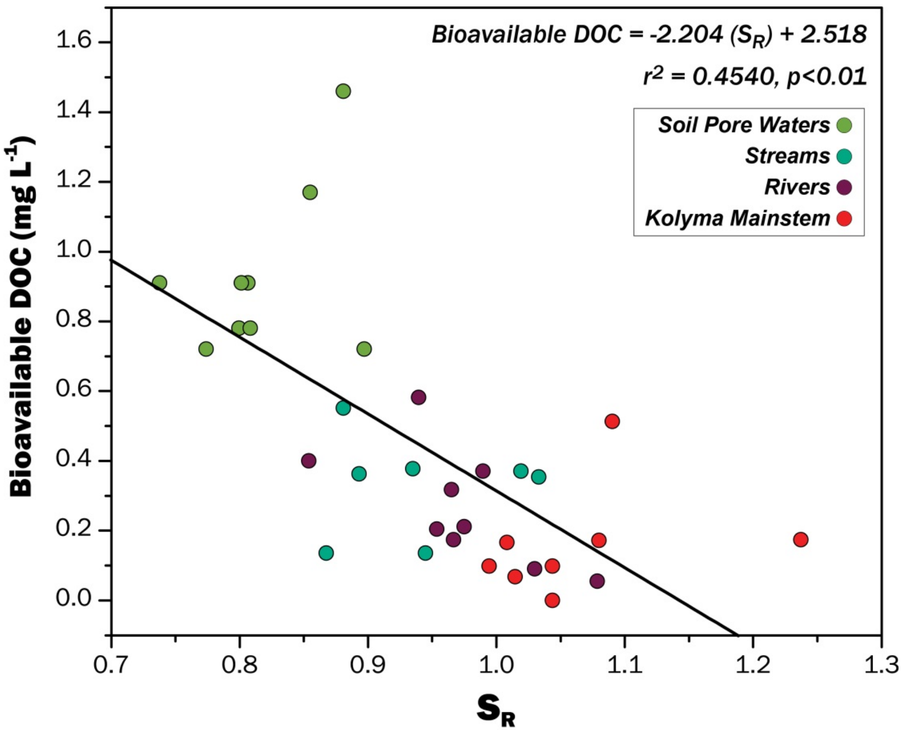

Figure 6. The CDOM metric S_R shows a relatively strong relationship with concentrations of bioavailable DOC present in the sampled waters, with an r squared value of 0.4540 and p value < 0.01.

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