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Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin

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[1] High-latitude northern rivers export globally significant quantities of dissolved organic carbon (DOC) to the Arctic Ocean. Climate change, and its associated impacts on hydrology and potential mobilization of ancient organic matter from permafrost, is likely to modify the flux, composition, and thus biogeochemical cycling and fate of exported DOC in the Arctic. This study examined DOC concentration and the composition of dissolved organic matter (DOM) across the hydrograph in Siberia's Kolyma River, with a particular focus on the spring freshet period when the majority of the annual DOC load is exported. The composition of DOM within the Kolyma basin was characterized using absorbance-derived measurements (absorbance coefficient a_{330} , specific UV absorbance (SUVA₂₅₄), and spectral slope ratio S_R) and fluorescence spectroscopy (fluorescence index and excitation-emission matrices (EEMs)), including parallel factor analyses of EEMs. Increased surface runoff during the spring freshet led to DOM optical properties indicative of terrestrial soil inputs with high humic-like fluorescence, SUVA₂₅₄, and low S_R and fluorescence index (FI). Under-ice waters, in contrast, displayed opposing trends in optical properties representing less aromatic, lower molecular weight DOM. We demonstrate that substantial losses of DOC can occur via biological (~30% over 28 days) and photochemical pathways (>29% over 14 days), particularly in samples collected during the spring freshet. The emerging view is therefore that of a more dynamic and labile carbon pool than previously thought, where DOM composition plays a fundamental role in controlling the fate and removal of DOC at a pan-Arctic scale.

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1. Introduction

[2] Arctic biomes contain up to an estimated 50% of the organic carbon stored in soils globally, which is predominantly held within permafrost soils [Dittmar and Kattner, 2003; Tarnocai et al., 2009]. Hydrologic changes attributed to climate change are already underway in the Arctic and include permafrost thaw, shorter snow cover duration and increasing freshwater discharge [Brown, 2000; Guo et al., 2007; McGuire et al., 2009; Peterson et al., 2002; Stone et al., 2002; Striegl et al., 2005; Wu et al., 2005]. The response of Arctic ecosystems to these changes has the potential to mobilize large terrestrial carbon pools and the ability to influence carbon fluxes both to the atmosphere and ocean.

[3] Large quantities of dissolved organic carbon (DOC) are exported from land to the Arctic Ocean, via Arctic rivers, which deliver approximately 10% of the global river discharge [Dittmar and Kattner, 2003; Opsahl et al., 1999]. Arctic rivers exhibit a strong seasonality in discharge with maximum fluxes occurring during the spring thaw and flood event (or "freshet"), generally in the months of May and June. Increased DOC concentrations, associated with elevated discharge during this time, can lead to over 60% of the annual DOC flux occurring over this short period [Holmes et al., 2011; Raymond et al., 2007; Spencer et al., 2009a]. Historically, Arctic riverine DOC was thought refractory in nature owing largely to the apparent conservative mixing behavior observed across the Eurasian continental shelf [Amon and Meon, 2004; Cauwet and Sidorov, 1996; Gordeev et al., 1996] and from studies of its biochemical characteristics [Lobbés et al., 2000]. However, these studies were constrained to late summer after the retreat of sea ice in the coastal zone. More recently, a growing body of evidence suggests a large seasonal variability in the composition of exported dissolved organic matter (DOM) [Spencer et al., 2009a, 2008] coincident with changes in biolability [Holmes et al., 2008], photolability [Osburn et al., 2009],

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and age [Neff *et al.*, 2006; Raymond *et al.*, 2007]. Other studies have also highlighted that the apparent degraded biochemical signature of riverine DOM could be caused by leaching and sorption, as these processes have been shown to shift biochemical signatures toward what have historically been interpreted as degraded [Aufdenkampe *et al.*, 2001; Hernes *et al.*, 2007]. Finally, a number of studies in the Arctic Ocean have reported extensive removal of DOC in the Arctic shelf seas [Alling *et al.*, 2010; Hansell *et al.*, 2004; Letscher *et al.*, 2011]. Therefore, it is now apparent that examining seasonality is of crucial importance to understanding the fate of Arctic river DOC as this determines its composition, and thus underlies its susceptibility to bacterial and photochemical degradation processes.

[4] During the freshet, a large proportion of the DOC pool has been reported to be biologically labile (20%–40%) over timescales of 30 days or less within a range of North American Arctic rivers [Holmes *et al.*, 2008]. By contrast, the DOC exported by these rivers during late summer appears to be largely biologically recalcitrant in nature [Holmes *et al.*, 2008]. The role of photochemical degradation in Arctic DOM has only recently been addressed [Amon and Meon, 2004; Bélanger *et al.*, 2006; Osburn *et al.*, 2009] but its potential role in modifying DOM composition via photobleaching and remineralization of organic C in other aquatic ecosystems is well documented [Miller and Zepp, 1995; Mopper and Kieber, 2002]. Photodegradation can modify DOM function by selectively degrading aromatic and phenolic groups [Hernes and Benner, 2003; Opsahl and Benner, 1998; Spencer *et al.*, 2009b] and can produce, or release, photoproducts that influence DOM bioavailability [Benner and Biddanda, 1998; Bertilsson and Tranvik, 1998; Kieber *et al.*, 1990; Tranvik and Bertilsson, 2001]. The increased aromaticity of allochthonous DOM delivered to coastal regions will lead to intense photobleaching within nearshore environments as light penetration increases, resulting in increased carbon losses and DOM composition changes [Osburn *et al.*, 2009]. Future losses of sea ice, or reductions in ozone levels may contribute to an increasing role for photochemistry in carbon biogeochemistry within Arctic regions [Gibson *et al.*, 2000; Lindsay and Zhang, 2005].

[5] The aim of this study was to investigate variability in DOM quality over the hydrograph on the Kolyma River, and to examine how these changes influenced the fate of exported DOC. Several small tributaries within the Kolyma basin were additionally studied to facilitate discrimination of DOM origin and source. Sample optical properties (absorbance and fluorescence spectroscopy) were used to investigate DOM quality and variability alongside measurements of bulk DOM concentration (DOC and dissolved organic nitrogen, DON). Incubation experiments were conducted to quantify biological and photochemical DOC losses, and relationships between DOC loss and DOM composition were investigated in order to identify the importance of DOM composition on its fate.

2. Methods

2.1. Site Description and Field Sampling

[6] The Kolyma River is the fifth largest river discharging into the Arctic Ocean, draining a watershed area of

650,000 km² [Holmes *et al.*, 2011]. The Kolyma basin represents the Earth's largest river system that is completely underlain by continuous permafrost. These permafrost layers contain vast quantities of ancient organic matter stored in carbon rich Pleistocene age loess, locally known as yedoma [Zimov *et al.*, 2006].

[7] Study sites were located in the vicinity of the Northeast Science Station near Cherskiy, Russia (Figure 1), where mean monthly temperatures range from −33.4 °C during boreal winter conditions in January, to 13.4 °C in July (mean annual −9.9 °C; 1999–2010). Seasonal sampling on the Kolyma River was conducted ~2 km upstream from the town of Cherskiy (Table 1). Water sampling was conducted over a 3 month period and focused on three distinct phases of the hydrologic regime and onset of the Kolyma River freshet: (1) the preflush period between 30 April and 20 May (under-ice sampling), (2) the freshet and ice-out between 21 May and 30 June, and (3) the summer low-flow period from 1 July until the end of the study. Discharge of the Kolyma River was very low during the long winter months but spiked rapidly during the spring freshet causing ice breakup at Cherskiy to start around 25–26 May 2010 (Figure 2). Samples were additionally collected at the mouths of three lowland tributaries to the Kolyma River. Two of these streams (designated Y3 and Y4) drained yedoma rich soils (Table 1) and could be characterized as “blackwater” streams. A single lowland stream that drained a grass and woodland dominated floodplain (designated FP) of the Kolyma River was also studied (Table 1). During the winter months these shallow streams froze completely and as such displayed no winter base flow. Snowmelt caused the opening of the smaller streams around 7–9 May 2010, approximately 2 weeks prior to the Kolyma ice-out event. Sampling was conducted immediately at the onset of flow within these streams, and periodically throughout spring.

[8] Ancillary measurements of water temperature, dissolved oxygen, specific conductivity and pH were collected using a YSI Pro-Plus multiparameter instrument. All samples for DOC and total dissolved nitrogen (TDN) nutrient and optical analyses were filtered on collection through precombusted (550 °C for 8 h) GF/F filters (~0.7 μm, Whatman). DOC/TDN samples were filtered directly into precombusted (550 °C for 8 h) glass vials and stored acidified at pH 2 refrigerated (4 °C) in the dark. Samples for optical analyses were transferred to aged HDPE plastic bottles and stored refrigerated (4 °C) and in the dark until analysis. Most DOC and optical samples were measured within 48 h of collection, but because of logistical constraints some were stored for up to 2 weeks before analysis. Samples for inorganic nutrient analyses (nitrate, ammonium, phosphate and silicate) were acidified and stored refrigerated (4 °C) before being measured on an Astoria Analyzer using established methods [U.S. Environmental Protection Agency, 1984]. Nutrients were stored for up to 3 months and measured after returning to the United States.

2.2. DOC and DOM Analyses

[9] All of the organic and optical measurements were conducted at the Northeast Science station in Cherskiy. DOC and TDN were determined via high-temperature combustion using a Shimadzu TOC-V organic carbon analyzer combined with a nitrogen chemiluminescence

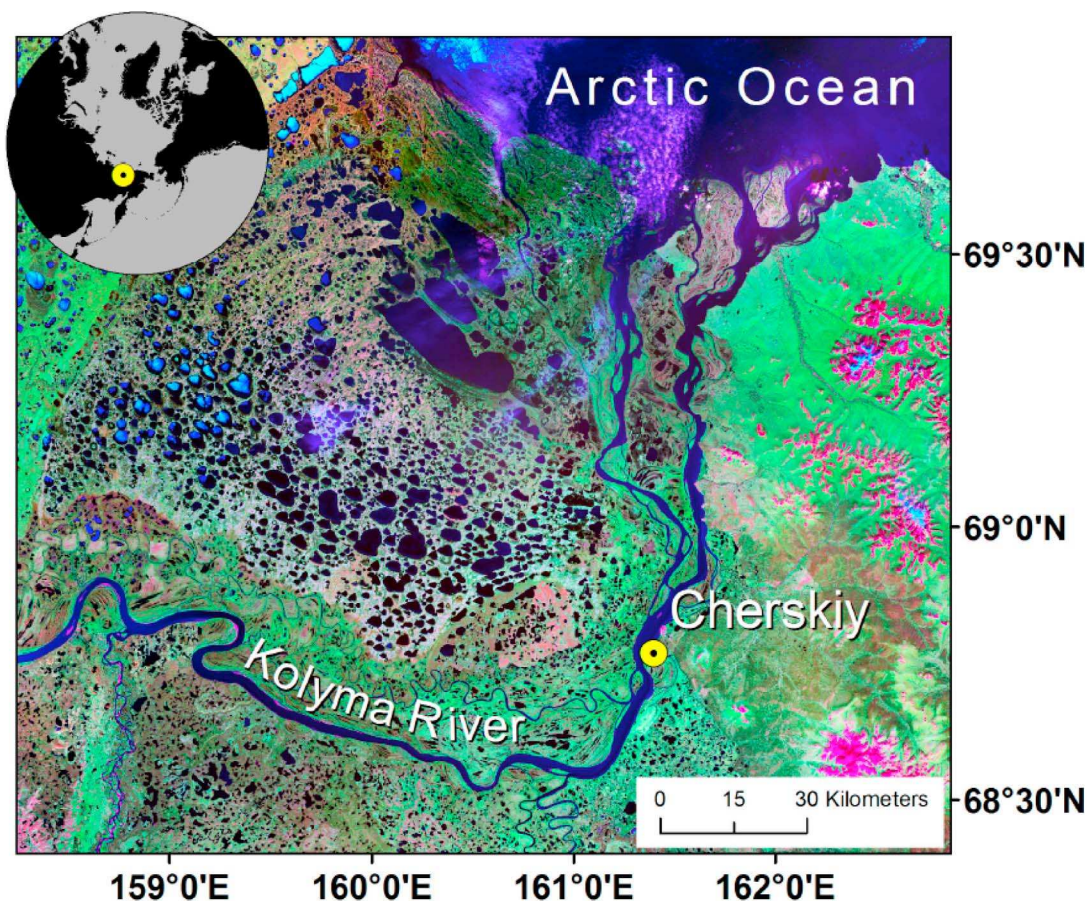


Figure 1. Location of Cherskiy and the Northeast Science station on the Kolyma River, Siberia. Kolyma main stem samples were collected from ~ 2 km upstream from Cherskiy. The yedoma and floodplain tributaries were located within 5 km of Cherskiy.

detection unit (TNM-1). DOC and TDN were calculated as the mean of between three and five injections and the coefficient of variance was always $< 2\%$. DON was calculated by subtracting the dissolved inorganic nitrogen constituents from TDN. A new six-point calibration was generated for each DOC and TDN run, and an internal control standard was measured periodically to account for any baseline drift. The overall precision of independent replicates was $< 5\%$ for both parameters.

[10] UV-visible absorbance measurements were collected at room temperature between 200 and 800 nm on a Shimadzu dual beam UV-1800 spectrophotometer. The spectral slope (S) of each absorbance spectra was determined by applying log linear fits across the wavelengths 275–295 nm ($S_{275-295}$) and 350–400 nm ($S_{350-400}$), and the spectral slope ratio (S_R) calculated as the ratio between the two [Helms *et al.*, 2008]. Specific UV absorbance ($SUVA_{254}$) was determined by dividing the UV absorbance at 254 nm with the sample DOC concentration and is reported in units of $L\ mg^{-1}\ m^{-1}$ [Weishaar *et al.*, 2003].

[11] Three-dimensional fluorescent excitation-emission matrices (EEMs) were generated in S/R mode across an excitation range of 240–450 nm collecting at emission wavelengths of 320–550 nm. EEMs were decomposed into independent fluorescent fractions using parallel factor analysis (PARAFAC) modeling [Bro, 1997; Stedmon *et al.*,

2003] via the DOMFluor toolbox within MATLAB [Stedmon and Bro, 2008]. Matrices across excitation wavelengths from 260 to 450 nm and emission wavelengths from 320 to 550 nm were modeled omitting areas of increased noise. Regions of no fluorescence (where emission is less than excitation) were replaced by “NaN” to minimize the influence of scatter peaks. EEMs were post corrected for laboratory generated instrument specific excitation and emission response, inner filter [McKnight *et al.*, 2001], blank subtraction and Raman normalization using the methods and MATLAB scripts of Cory *et al.* [2010]. EEMs collected from a diverse range of environments within the Kolyma River watershed, including thermokarst lakes and tundra draining streams, were included in the PARAFAC data set to increase variability. Split-half and residual analysis was used to validate a five-component model that explained 99.9% of the fluorescence signatures over 204 EEMs.

Table 1. Site Locations, Stream Type, and Catchment Size

Site Name	Latitude (°N)	Longitude (°E)	Catchment Area (km ²)	Stream Type
Kolyma	68.75	161.29	652,924	mixed
Y4	68.74	161.42	2.85	yedoma
Y3	68.74	161.44	16.84	yedoma
FP	68.74	161.40	1.34	floodplain

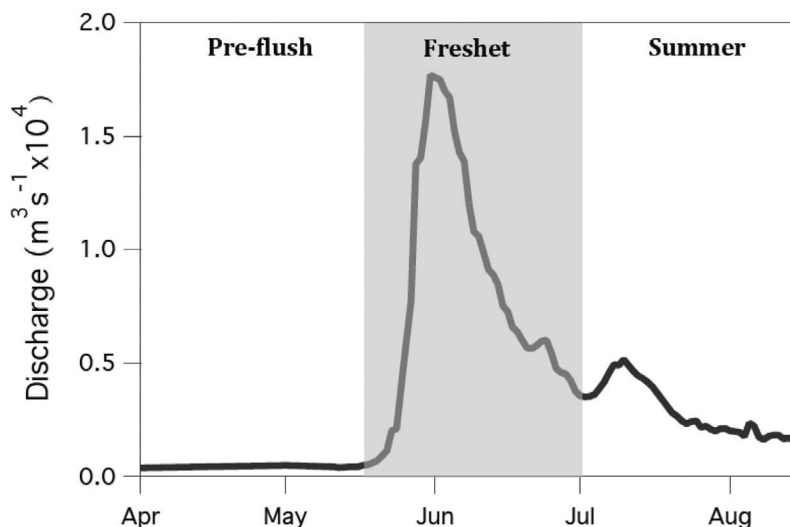


Figure 2. Kolyma River 2010 discharge measured at the Kolymskoye monitoring station.

[12] Each of the five components identified were related to previously identified DOM fractions (Table 2). Many displayed multiple peaks in the excitation spectra similar to those previously reported for Arctic surface water DOM [Cory and McKnight, 2005; Cory et al., 2007; Walker et al., 2009] (Table 2). Component C1 displayed excitation maxima at <250 nm with another additional pronounced broad maxima at 310 nm (Table 2). C1 emission occurred at short wavelengths (~422 nm) indicating the presence of a relatively low molecular weight, lower aromatic DOM pool [Coble et al., 1990; Coble et al., 1998]. This fluorophore group has previously been described as fulvic-like or low molecular weight humic-like in nature [Fellman et al., 2010a; Sierra et al., 2005]. Similarly, component C3 exhibited emission at shorter wavelengths suggesting it represents a less aromatic DOM pool, although its excitation peak occurred at longer wavelengths (Table 2). An identical component has not been previously reported, although it appears to be related to an unknown humic-like group previously identified in a diverse data set including Arctic EEMs [Cory and McKnight, 2005]. C2 exhibits broader emission spectra at longer wavelengths (redshifted), indicating these fluorophores are more likely to contain conjugated molecules that are more aromatic in nature with higher molecular weight compounds [Coble, 1996; Sierra et al., 2005]. C2

also displays spectra more closely related to the classic peaks defined as “A” and “C” [Coble, 1996] suggesting it may be derived from fresher vascular plant or soil sources [Coble et al., 1998; Fellman et al., 2010a]. These components are commonly referred to as the humic-like fluorophores [Fellman et al., 2010a; Stedmon et al., 2003; Stedmon and Markager, 2005a, 2005b]. Components C4 and C5 displayed excitation and emission spectra closely relating to protein-like DOM fractions. Specifically, C4 and C5 exhibited maxima closely resembling tryptophan-like and tyrosine-like fluorescence, respectively [Fellman et al., 2010a, and references therein]. Replicate EEMs processed and modeled produced fluorescent component loading estimates within 2% for humic and fulvic-like fractions and 5% for protein-like components. The FI, an indicator of DOM aromaticity [McKnight et al., 2001], was also calculated from the corrected EEMs as the ratio of emission intensities at 470/520 nm after excitation at 370 nm [Cory and McKnight, 2005; Cory et al., 2010].

2.3. Biodegradable DOC and Photochemical DOC Loss

[13] Biodegradable DOC (BDOC) was calculated as the difference in DOC before and after 28 days incubation following the procedures of Holmes et al. [2008]. Briefly, sample water was filtered through precombusted GF/F filters

Table 2. Spectral Characteristics of the Five Components Identified Using PARAFAC^a

Component	Excitation λ_{\max} (nm)	Emission λ_{\max} (nm)	Description and Likely Structure	Comparable Previous Studies
C1	<250 (310)	422	low molecular weight, fulvic-like or UV-C humic DOM	Stedmon and Markager [2005a, 2005b] (C3) Walker et al. [2009] (BERC1)
C2	<250 (285)	492	higher aromatic, conjugated, observed from fresh plant sources; humic-like	Stedmon and Markager [2005a, 2005b]
C3	270	448	excitation maxima at longer wavelengths; humic/fulvic-like	Cory and McKnight [2005] (6,7)
C4	280 (<250)	342	amino acids, soluble bound microbial DOM, tryptophan-like aromatic protein	Stedmon and Markager [2005a, 2005b] (C7) Murphy et al. [2008]
C5	265	<320	amino acid; tyrosine-like; aromatic protein	Stedmon and Markager [2005a, 2005b] (C8) Murphy et al. [2008]

^aSecondary excitation maxima are in parentheses. PARAFAC, parallel factor analysis; DOM, dissolved organic material.

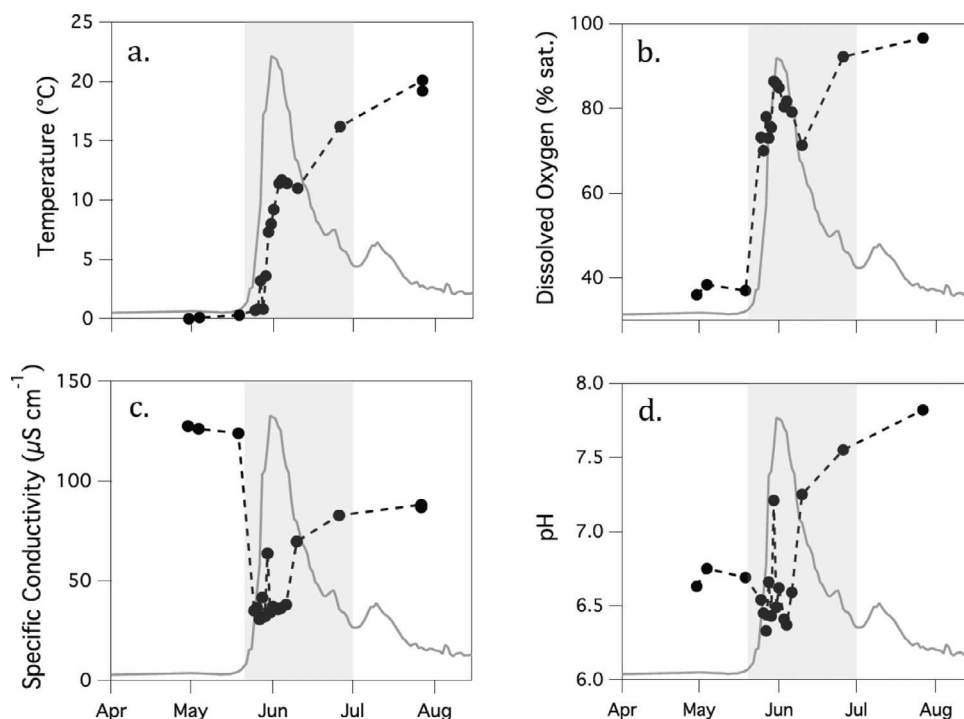


Figure 3. Kolyma River main stem (a) temperature, (b) dissolved oxygen, (c) specific conductivity, and (d) pH measurements over the study period. Kolyma discharge from Figure 2 (gray line) is also shown.

into 60 mL HDPE bottles and incubated in the dark at room temperature ($\sim 20^\circ\text{C}$) for 28 days. Samples were incubated with lids loosely fitted and agitated regularly to maintain oxic conditions. Initial samples were immediately acidified ($\text{pH} \sim 2$, HCl Sigma), stored refrigerated in the dark and analyzed alongside incubated samples acidified after 28 days. All BDOC incubations were run in triplicate and the mean DOC loss was used to derive the percent loss from the initial DOC concentration, defined as BDOC (%). No corrections were made to account for initial sample temperature, and as such these results represent potential lability at summer river water temperatures (Figure 3a). Photochemical DOC degradation was determined as the difference in DOC between dark and light exposed treatments. One liter samples were filtered sequentially through precleaned 0.45 and 0.22 μm filter cartridges into triple sample rinsed, completely filled Tedlar bags (1 L; SKC Inc. 250-01). Bags were secured horizontally across the surface of a lake submerged to a depth of ~ 2 cm for 14 days. The environmental conditions of the lake closely matched those within the river ($\pm 2^\circ\text{C}$) during the incubation period. Dark controls were treated identically except for being covered prior to exposure with a dark bag blocking all light exposure. In order to aid comparison, all samples were irradiated under natural sunlight conditions simultaneously ensuring identical light exposure. Samples collected earlier were filtered and stored in cool and dark conditions until the beginning of the experiment with no discernable DOC loss observed in stored samples ($< 2\%$). DOC losses were measured after 3 and 14 days of exposure and the % DOC loss ($\text{DOC}_{\text{photo}}$) calculated. Experiments were started on the 10 June during the

summer solstice period providing 24 h of sunlight for the full 14 day incubation period.

3. Results

3.1. Hydrology and Biogeochemical Setting

[14] The Kolyma River displayed rapid changes in its biogeochemical characteristics over the spring freshet period. Preflush, under-ice Kolyma waters were cold (0°C – 1°C) and exhibited low dissolved oxygen saturation ($< 40\%$; Figures 3a and 3b). Preflush waters also had high specific conductivity indicating the presence of increased concentrations of soluble salts, indicative of elevated groundwater supply (Figure 3c). With the onset of the freshet, Kolyma water temperature and oxygen saturation increased rapidly with accompanying decreases in specific conductivity and pH (Figures 3a–3d). Nitrate concentrations rapidly declined during the study period, with high concentrations measured under-ice declining to very low concentrations by early summer (Figure 4a). Silicate concentrations were high under ice, dropped dramatically with the onset of the freshet, and then steadily increased over the remainder of spring and into summer (Figure 4b). No discernable patterns in phosphate or ammonium concentrations were apparent during the freshet period (Figures 4c and 4d).

[15] Stream runoff from tributaries in the 2 weeks prior to the ice-out on the Kolyma led to large accumulations of DOC rich water pooling onto the surface of the Kolyma River ice, exposing it to intense photochemical irradiation. Extensive runoff and melt from tributary streams also aided mechanical fracturing and break up of the ice on the Kolyma River main stem.

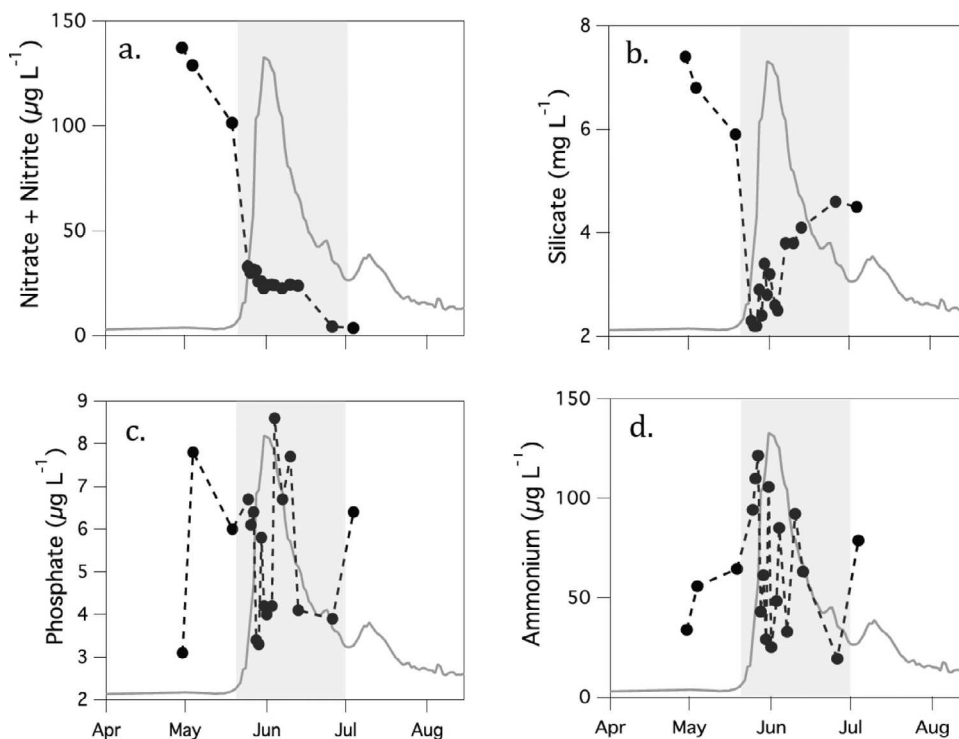


Figure 4. Nutrient concentrations of (a) nitrate, (b) ammonium, (c) phosphate, and (d) silicate in the Kolyma main stem over the study period. Kolyma discharge from Figure 2 (gray line) is also shown.

3.2. DOC Concentration and BDOC

[16] Preflush DOC concentrations in waters collected under the ice from the Kolyma main stem were low, ranging from 2.0–2.7 mg L⁻¹ (mean = 2.4 mg L⁻¹, n = 3; Figure 5a). DOC concentrations peaked during the spring freshet and reached a maximum of 14.2 mg L⁻¹ coincident with ice breakup on the 25–26 May 2010 (Figure 5a). Kolyma DOC concentrations quickly declined over the preceding days after ice-out and continued to steadily decrease over the months afterward, reaching 4.0 mg L⁻¹ by the end of July 2010. DOC concentration during the freshet period ranged from 5.8–14.2 mg L⁻¹ (mean = 10.2 mg L⁻¹, n = 15) with maximum DOC concentrations observed up to 4–5 days prior to peak discharge (Figure 5a). DOC concentrations were intermediate during summer conditions (mean = 4.4 mg L⁻¹, n = 2; Figure 5a). DON concentrations were highly correlated to DOC and thus followed the same trend during the study period ($r = 0.92$; $p < 0.001$; n = 18). DON ranged from ~0.1 mg L⁻¹ under the ice (mean = 0.09 mg L⁻¹, n = 3) during preflush conditions to 0.6 mg L⁻¹ (mean = 0.37 mg L⁻¹, n = 14) during the freshet (Figure 5b).

[17] DOC concentrations within the yedoma streams ranged from 13.1 to 63.5 mg L⁻¹ (mean = 25.9 mg L⁻¹, n = 19) over the study period. The highest concentrations in both streams were measured 1 week after ice breakup (Figure 5c). DOC concentrations varied less in the stream draining the floodplain catchment ranging from only 9.1 to 17.1 mg L⁻¹ (mean = 11.8 mg L⁻¹, n = 6) over the study duration. Both yedoma streams displayed consistently higher DOC concentrations than the floodplain stream throughout the sampling period (Figure 5c).

[18] Kolyma BDOC rates mirrored DOC concentration with lowest or negligible losses (0.1%) observed in early season under-ice samples, and highest losses (20.4%) associated directly with the ice-out period (Table 3). Highest BDOC losses of ~20% were observed in the first two days of the spring freshet. BDOC losses then declined for the remainder of the freshet period ranging between 1–11% (mean = 7.4%; n = 10; Table 3). BDOC losses in under-ice Kolyma samples ranged from 0.1–9.5% increasing immediately prior to the Kolyma ice breakup.

3.3. CDOM Optical Properties

[19] SUVA₂₅₄ can act as a proxy for DOM aromaticity with higher SUVA₂₅₄ values representing a more aromatic organic matter pool [Weishaar *et al.*, 2003]. SUVA₂₅₄ in the Kolyma main stem ranged between 2.1 and 4.2 L mg⁻¹ m⁻¹ over the study period, reaching highest values during the spring flush (mean = 3.9 L mg⁻¹ m⁻¹; n = 15; Figure 6a). Summer conditions were characterized by intermediate SUVA₂₅₄ values (mean = 2.9 L mg⁻¹ m⁻¹; n = 2) whereas lowest SUVA₂₅₄ values were observed in preflush, under-ice samples (mean = 2.1 L mg⁻¹ m⁻¹; n = 3; Figure 6a).

[20] The spectral slope ratio (S_R) has been shown to be correlated to DOM molecular weight and source with increases in the ratio characterizing decreasing molecular weight and a shift from DOC rich black waters to optically clearer waters [Helms *et al.*, 2008; O'Donnell *et al.*, 2010; Spencer *et al.*, 2009b]. Kolyma main stem S_R ranged from 0.78 to 1.13 during the study period, the highest values observed in preflush samples (mean = 0.99; n = 3) indicating the presence of primarily low molecular weight material and lower amounts of aromatic functional groups (moieties) (Figure 6b). The S_R peaked immediately before ice-out

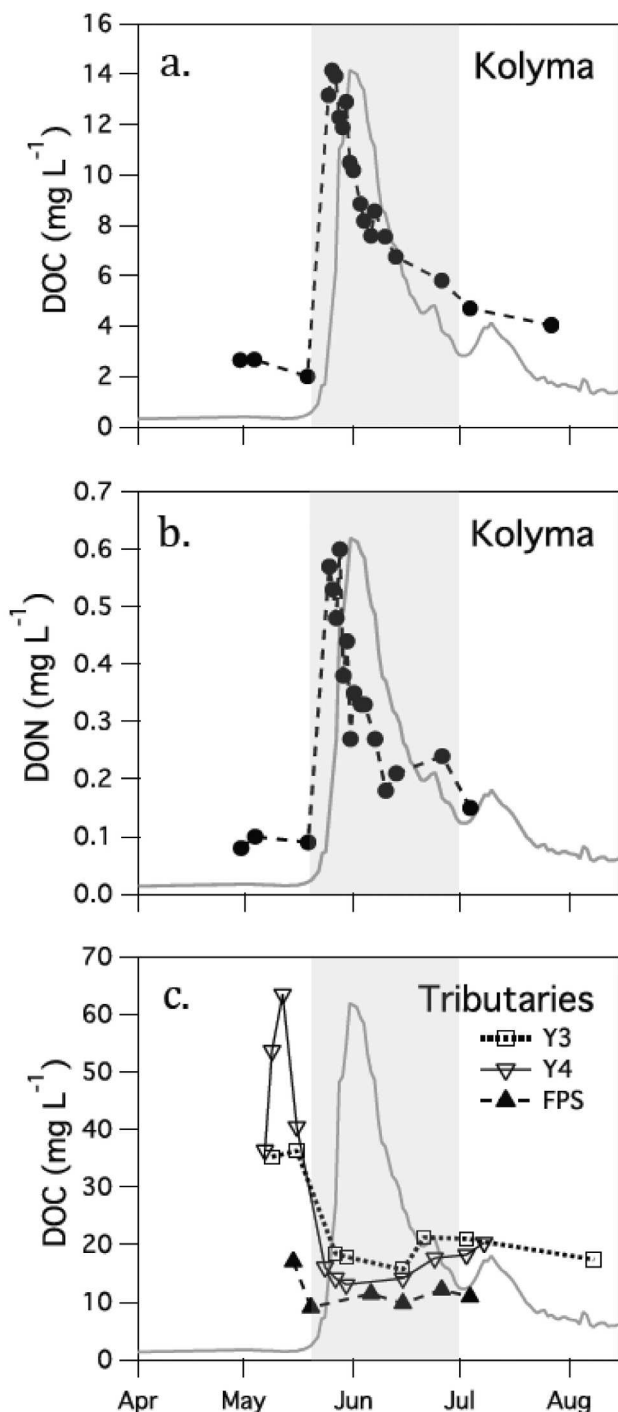


Figure 5. Concentrations of (a) dissolved organic carbon (DOC) and (b) dissolved organic nitrogen (DON) over the 2010 spring freshet in the Kolyma River. (c) DOC concentrations of three tributaries of the Kolyma. Y3 and Y4 both represent streams draining organic-rich yedoma catchments. The FP site drains a floodplain catchment of the Kolyma main stem. Kolyma discharge from Figure 2 (gray line) is also shown.

(1.13; Figure 6b) potentially representing inputs of low molecular weight DOM from increasing ice melt. Lowest S_R values were observed at the peak of the freshet, indicating the rapid input of higher molecular weight, aromatic terrestrial material (Figure 6b). The S_R values then increased throughout the remainder of the study period demonstrating a gradual shift toward lower molecular weight and less aromatic DOM throughout the open water season.

[21] Fluorescence index (FI) values ranged from 1.38 to 1.51, with the highest values observed in under-ice samples (mean = 1.50; $n = 3$; Figure 6c). These results indicate that preflush Kolyma waters have lower aromaticity and are more microbial in source, or represent more heavily degraded material [Cory *et al.*, 2007; McKnight *et al.*, 2001]. The lowest FIs were measured during the freshet period on the Kolyma main stem (mean = 1.41, $n = 14$) demonstrating that DOM composition during this period is more aromatic in nature and primarily derived from terrestrial soils and vascular plant sources [McKnight *et al.*, 2001; Spencer *et al.*, 2010].

3.4. Fluorescence and PARAFAC Modeling

[22] The onset of the spring freshet resulted in an increased contribution, and relative intensity of the humic-like fluorophore (C2) in the Kolyma. This increase led to a shift in the overall DOM fluorescence signal to higher emissions indicating the presence of a more conjugated, aromatic DOM (Figures 7a and 7b). Following the spring freshet, C2 fluorescence intensity and contribution, slowly declined resulting in a blueshift (lowering of emission) in the fluorescence signature. C2 and C3 fluorescence intensities also generally increased with increasing discharge suggesting an allochthonous source linked to extensive surface runoff. Thus, it appears that component C2 acts as an indicator of allochthonous inputs from surface soil and litter layer derived materials. Conversely, C1 (fulvic-like) fluorescence intensities displayed the opposite trend to those of C2 and C3, generally decreasing with increasing discharge and DOC concentration suggesting this fraction was less associated with surface runoff and terrestrial supply. An increased intensity and relative contribution ($\geq 20\%$) of the protein-like fractions (C4 and C5) was observed in the under-ice samples, peaking immediately prior to ice breakup upon the Kolyma River (Figure 7b). With peak freshwater discharge, protein-like fraction contributions to the total fluorescence pool declined to low levels ($\sim 10\%$). Protein-like DOM intensity (C4) also increased throughout the summer possibly indicating increasing relative autochthonous DOM contributions [Stedmon *et al.*, 2003; Stedmon and Markager, 2005b].

3.5. DOC Photomineralization

[23] Natural sunlight exposure resulted in DOC concentration losses of between 0.5–1.8 and 1.0–3.4 mg L⁻¹ over the 3 and 14 day incubation periods, respectively. DOC losses calculated as a percentage of initial DOC concentration ($\text{DOC}_{\text{photo}}$) were highest in Kolyma main stem samples collected during the first stages of the spring flush with over 13% of the DOC pool proving susceptible to photomineralization over just three days (Table 3). $\text{DOC}_{\text{photo}}$ losses increased up to a maximum of $\sim 30\%$ after 14 days of natural irradiation (Table 3). These losses represent maximal

Table 3. Initial Sample Characteristics of Waters Used in Biolability and Photolability Experiments^a

Date	Initial DOC (mg L ⁻¹)	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	S _R	FI	C1 (R.U.)	C2 (R.U.)	C3 (R.U.)	C4 (R.U.)	C5 (R.U.)	BDOC (% C Loss)	DOC _{photo} (% C Loss)
30 Apr 2010	2.7	2.15	0.91	1.51	8.03	7.01	4.53	1.84	0.29	0.1	–
19 May 2010	2.0	2.15	1.13	–	–	–	–	–	–	9.5	–
24 May 2010	12	4.04	0.78	1.39	7.07	8.34	4.61	1.51	0.45	18.5	24.8 (13.1)
25 May 2010	13.2	3.94	0.78	1.40	7.07	8.41	4.65	1.38	0.35	20.4	–
27 May 2010	13.9	4.00	0.78	1.38	7.11	8.46	4.69	1.20	0.25	8.3	25.0 (13.2)
28 May 2010	12.3	3.91	0.79	1.40	7.88	7.25	4.57	1.75	0.33	9.8	–
29 May 2010	11.9	4.07	0.79	1.40	7.43	7.91	4.61	1.55	0.31	8.3	29.9 (9.1)
30 May 2010	12.9	3.98	0.80	1.40	7.52	7.77	4.60	1.61	0.31	7.2	20.5 (7.6)
31 May 2010	10.5	4.16	0.80	1.40	7.42	7.94	4.61	1.50	0.36	7.4	–
1 Jun 2010	10.2	4.06	0.82	1.40	7.47	7.89	4.63	1.50	0.30	7.0	–
3 Jun 2010	8.9	3.99	0.82	1.42	7.58	7.7	4.63	1.55	0.34	8.7	19.3 (10.0)
4 Jun 2010	8.2	4.02	0.83	1.41	7.61	7.67	4.62	1.57	0.34	11.4	–
6 Jun 2010	7.6	3.86	0.82	–	–	–	–	–	–	5.1	–
7 Jun 2010	8.6	3.91	0.83	1.43	7.88	7.25	4.57	1.75	0.33	1.2	12.2 (5.4)

^aBiodegradable dissolved organic carbon (BDOC) loss is the percent loss of carbon after 28 days incubation in the dark. DOC_{photo} is the percent loss of carbon after 14 days of irradiation (3 day results are in parentheses). R.U., Raman units.

surface removal rates and as such, are unlikely to accurately portrait natural degradation. DOC_{photo} losses from this study, although not directly comparable with, are within the range of those reported previously on Mackenzie River estuarine samples, collected during the summer months and exposed to up to 12 days natural irradiation (1%–6%) [Amon and Meon, 2004]. They also compare well with the 10–30% losses observed in samples collected from over the hydrograph in the Mackenzie River and Beaufort Sea after three days under natural light [Osburn *et al.*, 2009].

[24] Photochemical degradation of DOM led to changes in DOM composition through photobleaching and production processes. Photobleaching of DOM led to losses in the absorbance coefficient (a_{330}) and FI, and overall decreases in SUVA₂₅₄ across the freshet (Table 4). The slope of the absorbance spectra over short wavelengths 275–295 nm ($S_{275-295}$) became steeper with light exposure, whereas $S_{350-400}$ consistently became shallower (Table 4). This resulted in overall increases in the slope ratio (S_R) between $S_{275-295}$ and $S_{350-400}$, as has been previously reported resulting with photobleaching [Helms *et al.*, 2008; Spencer *et al.*, 2009b]. These results are therefore indicative of a DOM pool becoming less aromatic in nature with decreasing average molecular weight upon irradiation. Additionally, photodegradation led to losses in humic and fulvic-like fluorescence (C2 and C3), and increased protein-like fluorescence (C4 and C5) suggesting higher molecular weight compounds were broken down and smaller, lower molecular weight fractions were photochemically produced (Table 4).

4. Discussion

4.1. Temporal Trends in DOM Concentration and Composition

[25] DOM concentration and composition varied significantly throughout the study period. Increasing snowmelt and surface runoff at the onset of the spring thaw lead to rapid inputs of allochthonous organic matter with high DOC and DON concentrations (Figure 5). Maximum DOC and DON concentrations were measured a few days prior to peak freshwater discharge, suggesting either a large pool of DOM was readily mobilized with the onset of the freshet, or that a dilution effect occurred with increased discharge. Kolyma

main stem DOM during the freshet exhibited signatures associated with increased DOM molecular weight and aromaticity as indicated by high SUVA₂₅₄, and low S_R and FI ratios (Figure 6). These findings are consistent with increasing snowmelt runoff leaching organic carbon within the upper shallow organic-rich surface layer because of the impermeability of frozen ground [Balcarczyk *et al.*, 2009; Holmes *et al.*, 2008; O'Donnell *et al.*, 2010]. Positive relationships between C2 fluorescence and SUVA₂₅₄ ($r = 0.86$, $p < 0.001$), as well as inverse linear relationships with S_R and FI ($r = -0.93$ and -0.78 , $p < 0.001$, respectively), demonstrate that the C2 (humic-like) DOM fraction may reflect the compositional shift in Kolyma DOM caused by terrestrial inputs of higher molecular weight aromatic compounds (C2; Figure 7). Increasing terrestrial DOM inputs, as indicated by C2 fluorescence, also correlated strongly with DOC concentration ($r = 0.93$, $p < 0.001$) reinforcing the organic rich nature of this material. The initial change in DOM composition occurred prior to maximum discharge rates, indicating that the rapid input of a large terrestrial DOM pool is likely to have led to the early spike in DOC concentration (Figure 6). DOC concentrations within snowmelt-dominated catchments have previously been reported to be production limited during high flow, leading to a peak on the rising limb of the hydrograph and tapering off despite little change in the hydrological routing over this time [Boyer *et al.*, 1997; Hornberger *et al.*, 1994]. Similar seasonal trends in DOC concentration and DOM composition were observed in each of the smaller streams studied. Consistently higher DOC concentrations within waters draining the yedoma catchments, to those from the floodplain draining stream, may indicate floodplain regions have limited soil DOC availability, a difference in hydrologic flow path or limited wetland area [Finlay *et al.*, 2006; Laudon *et al.*, 2004].

[26] Post freshet conditions were characterized by a steady decline in DOM molecular weight and aromaticity (decreasing SUVA₂₅₄, and increasing FI, S_R ; Figure 6) indicating reductions in terrestrial runoff and the depletion in surface horizon DOC stored from the antecedent winter [Neff *et al.*, 2006; Spencer *et al.*, 2009a; Striegl *et al.*, 2005]. An increase in the fluorescence signature C1 (fulvic-like), with concomitant decrease of C2 (humic-like) over the next weeks also suggested a shift in DOM source possibly

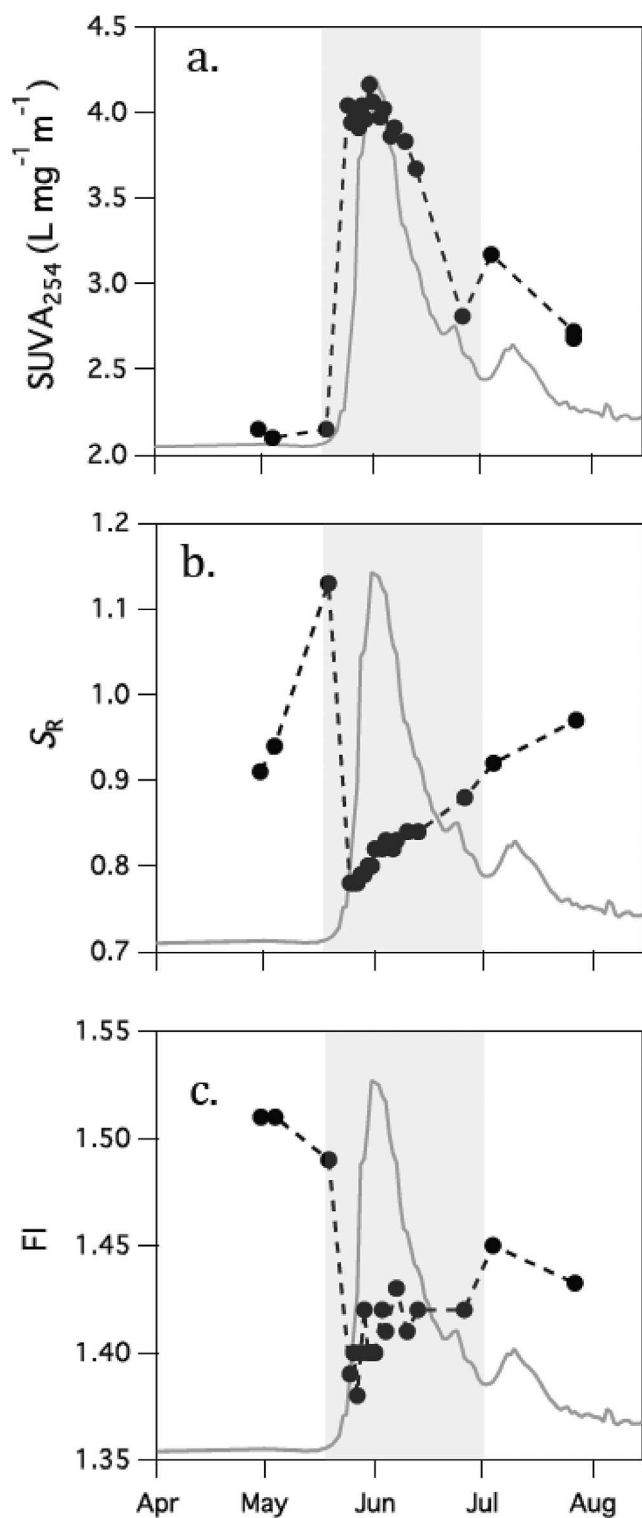


Figure 6. Optical indices: (a) $SUVA_{254}$, (b) S_R , and (c) fluorescence index (FI) calculated over the 2010 Kolyma freshet. Kolyma discharge from Figure 2 (gray line) is also shown.

through increased contributions from deeper soil horizons via deepening of the active layer (Figure 7). Additional waters, collected during this study from a tundra ground-water seep, displayed increased C1 and depleted C2

contributions providing evidence that deeper hydrological flow paths may have contributed to the observed patterns. Cryosol soils within Siberian permafrost have also been shown to contain higher proportions of fulvic to humic acids, and consequently are likely composed of low molecular weight, less aromatic DOM in comparison to organic rich surface horizons [Kimble, 2004]. The presence of elevated contributions of C1 fluorescence in the Kolyma early in the season, before ice melt occurred, also provides evidence that ground waters contribute increased fulvic-like DOM relative to humic-like fractions. These waters were also characterized by low $SUVA_{254}$, and high FI and S_R values indicative of the presence of low molecular weight material of lower aromaticity (Figure 6). A period of increased protein-like, and very low humic and fulvic-like fractions, was observed prior to the peak in discharge. We propose this was caused by an increased supply of DOM from ice melt as previous studies have shown that DOM fluorescence derived from ice is dominated by protein-like fluorescence [Fellman *et al.*, 2010b; Hood *et al.*, 2009; Lafrenière and Sharp, 2004].

[27] Longer hydrologic residence times and increased microbial processing of the DOM pool could also have contributed to the observed shift [McKnight and Aiken, 1998; Striegl *et al.*, 2005]. These findings agree well with previous studies that suggest winter base flow DOM is less aromatic and composed of fewer hydrophobic compounds in favor of hydrophilic compounds [O'Donnell *et al.*, 2010; Striegl *et al.*, 2005, 2007].

[28] Results from this study therefore suggest that optical proxies may prove useful in tracing changes in the hydrological flow paths and DOM compositional changes, within Arctic carbon cycles. The seasonal trends in S_R observed here for example, are highly comparable to those reported for the Yukon River [Spencer *et al.*, 2009a, 2008] further highlighting the potential to derive information about DOM composition via these techniques across the Arctic.

4.2. Linking DOM Composition to Biolability and Photoreactivity

[29] DOC transported during the spring flush in the Kolyma River displayed different composition and lability compared to the rest of the open water season and preflush, as has been previously reported in the North American Arctic [Holmes *et al.*, 2008; Osburn *et al.*, 2009; Spencer *et al.*, 2008]. The contribution of C2 (humic-like) fluorescence was positively correlated with BDOC within the Kolyma River over the study period (Table 5 and Figure 8a; $r^2 = 0.53$, $p < 0.01$). DOC derived from surface biomass, litters and the organic rich surface horizon is therefore likely responsible for driving the increased DOC biomineralization observed over the freshet period. These findings compare well with recent studies that show DOC exported during the freshet from Arctic rivers is younger and has an elevated lignin carbon-normalized yield in comparison to the rest of the year [Raymond *et al.*, 2007; Spencer *et al.*, 2008], underpinning that “fresh” terrestrially derived DOC is exceptionally biolabile at this time of maximum export. Highly aromatic humic-like DOM has often previously been considered recalcitrant and unavailable for biodegradation [Geller, 1986; Fellman *et al.*, 2008]. Our results, however, suggest that surface soils mobilized during the freshet,

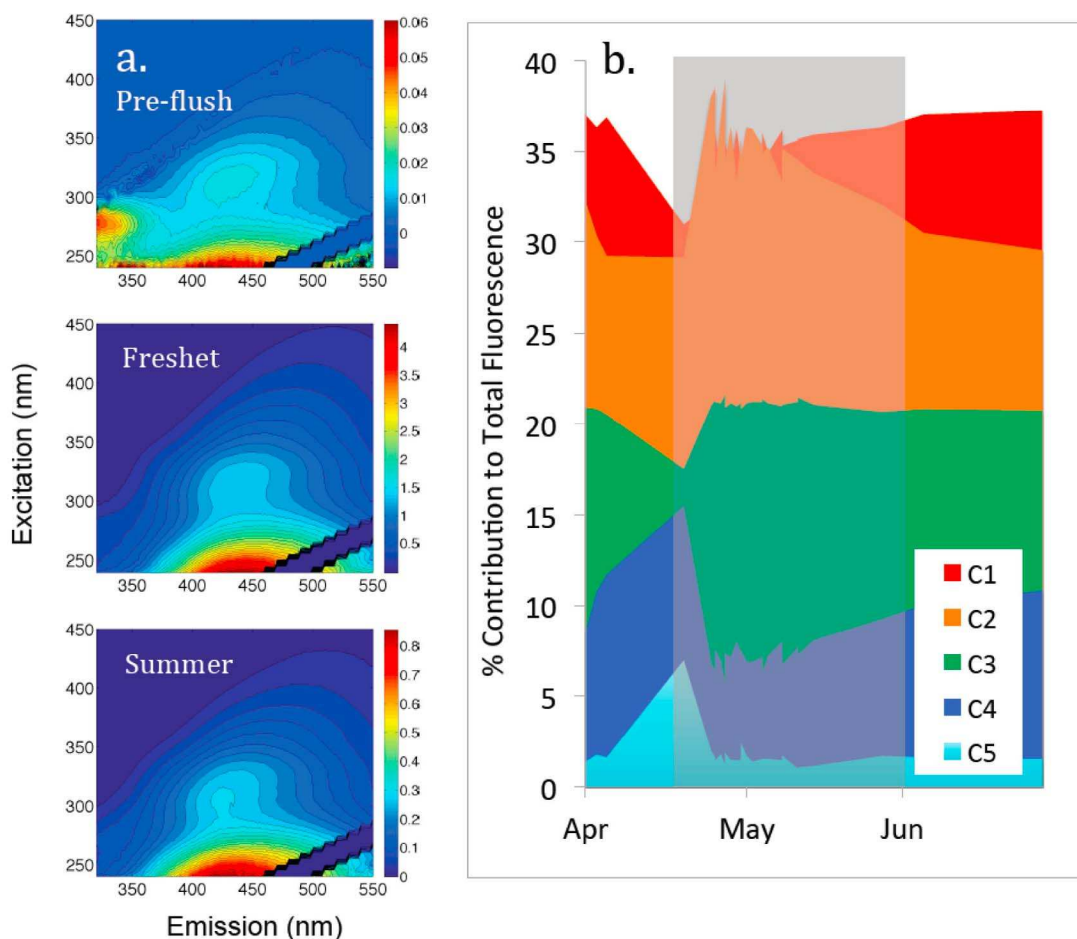


Figure 7. Dissolved organic matter (DOM) compositional change within the Kolyma River over the freshet. (a) Representative EEMs collected under preflush (under-ice), freshet and summer conditions. Changes in the overall intensity and emission maxima within the EEMs demonstrate shifts in the concentration and composition of the DOM pool. (b) Stacked percent contribution of each parallel factor analysis component (see Table 2) to the overall fluorescence signal.

although highly aromatic and displaying high average molecular weight, are readily biodegradable over short times scales, probably because of their exceptional freshness and limited degradation history. During the remainder of the freshet period, BDOC losses remained relatively constant indicating a supply of moderately biolabile allochthonous organic material. This pattern suggests a highly biolabile surface pool, likely derived from the

previous fall's vegetation input to the litter layer which has been frozen in place, is quickly depleted and washed out leading to an increasingly refractory pool for export [Inamdar *et al.*, 2006; McGlynn and McDonnell, 2003; Spencer *et al.*, 2010].

[30] In contrast, the fulvic-like component C1 negatively correlated with BDOC in the Kolyma River main stem (Table 5 and Figure 8b, $r^2 = 0.58$, $p < 0.01$), indicating

Table 4. Changes in the Optical Properties of Kolyma Freshet Samples (K1–K6) After 14 Days of Natural Irradiation^a

Date	Δa_{330} (m^{-1})	$S_{275-295}$ ($\times 10^{-3} \text{ nm}^{-1}$)	$S_{350-400}$ ($\times 10^{-3} \text{ nm}^{-1}$)	ΔS_R	ΔSUVA_{254} ($\text{L mg}^{-1} \text{ m}^{-1}$)	ΔFI	ΔC1 (%)	ΔC2 (%)	ΔC3 (%)	ΔC4 (%)	ΔC5 (%)
24 May 2010	-12.1	-3.23	+1.75	+0.30	-0.33	-0.08	+0.6	-4.3	-4.7	+30.0	+55.4
27 May 2010	-11.9	-3.05	+1.41	+0.26	-1.32	-0.15	+12.3	-16.6	-11.7	+26.0	+114.3
29 May 2010	-9.1	-3.02	+1.18	+0.24	-1.70	-0.11	+2.7	-6.9	-5.0	+35.0	+75.9
30 May 2010	-9.4	-3.12	+0.61	+0.22	-0.99	-0.11	-1.9	-3.8	-4.2	+44.5	+107.4
3 Jun 2010	-8.1	-3.62	+1.24	+0.28	+0.04	-0.10	-0.5	-3.9	-4.5	+37.1	+72.1
7 Jun 2010	-5.3	-2.92	+0.64	+0.20	-0.06	-0.08	-1.2	-3.2	-2.6	+32.2	+50.7

^aPositive changes in S represent a steepening of the spectral slope. Fluorescence component losses are calculated as a percent change from initial values. FI, fluorescence index.

Table 5. Pearson's Correlation Coefficients r Between Bacterial and Photochemical DOC Losses and Initial Optical Properties^a

DOC Type	DOC (mg L ⁻¹)	DON (mg L ⁻¹)	NH ₄ -N (μg L ⁻¹)	NO ₃ /NO ₂ (μg L ⁻¹)	PO ₄ -P (μg L ⁻¹)	SiO ₂ (mg L ⁻¹)	FI (L mg ⁻¹)	S ₂₇₅₋₂₉₅ (nm ⁻¹)	S ₃₅₀₋₄₀₀ (nm ⁻¹)	S _R	SUVA _{A254} (L mg ⁻¹ m ⁻¹)	C1 (R.U.)	C2 (R.U.)	C3 (R.U.)	C4 (R.U.)	C5 (R.U.)
Bacterial DOC (%)	0.47	0.64*	0.61*	-0.34	0.37	-0.58*	-0.59	-0.25	0.11	-0.21	0.32	-0.76**	0.73**	0.52	-0.54	0.60*
Photochemical DOC _{photo} (%)	0.69	0.60	0.57	0.59	-0.46	-0.83*	-0.77	-0.89*	0.38	-0.85*	0.96**	-0.75	0.75	0.49	-0.58	-0.03

^aIncubation periods are 28 and 14 days for bacterial and photochemical DOC losses, respectively. A single asterisk (*) indicates correlations significant at $p < 0.05$; a double asterisk (**) indicates correlations significant at $p < 0.01$. R.U., Raman units.

heterotrophic bacteria were less able to utilize this fraction of the DOC. This may suggest DOC inputs from deeper flow paths that are inherently a more degraded fraction and less biolabile, or that longer hydraulic residence times have led to the remineralization of labile C compounds before catchment export. Furthermore, stream water chemistry particularly during the early phases of snowmelt could be affected by differential rates of melting throughout the catchment region, resulting in different proportions of organic matter contributions from varying regions. The bioavailability of

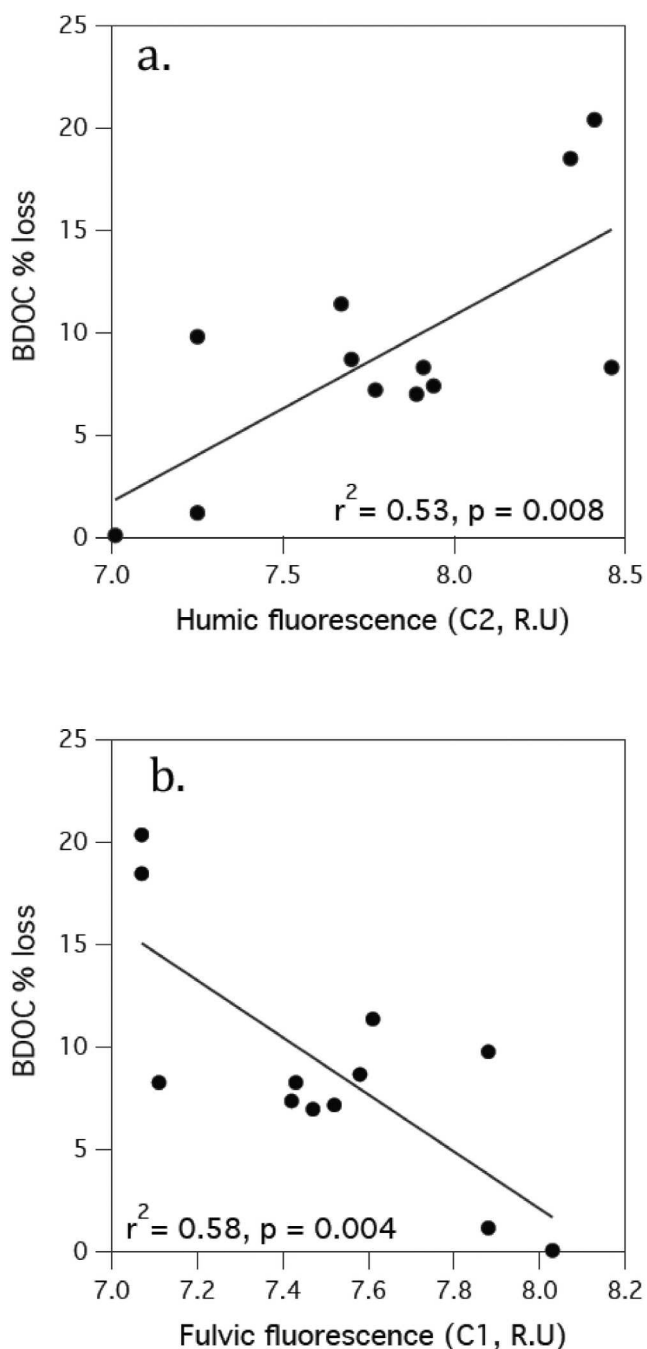


Figure 8. Relationships between percent biodegradable DOC (BDOC) loss over 28 days and initial sample (a) C2 fluorescence and (b) C1 fluorescence.

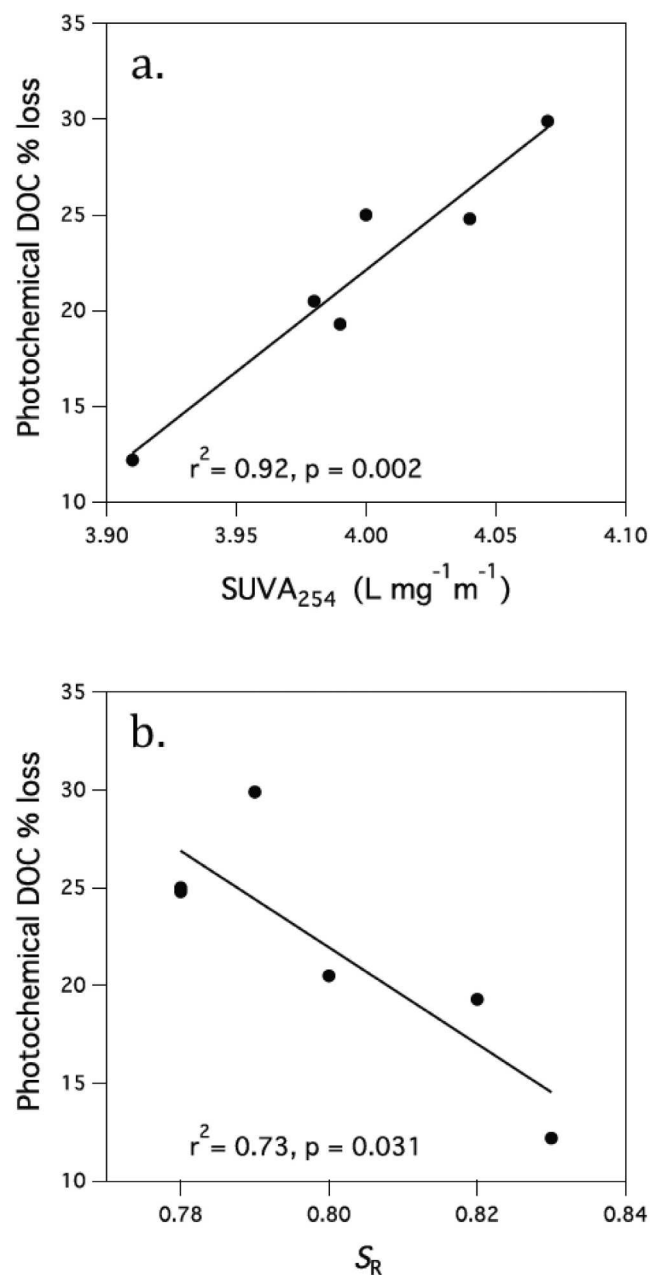


Figure 9. Relationships over the course of 14 days between percent photochemical DOC loss and (a) $SUVA_{254}$ and (b) S_R .

inorganic and organic nitrogen sources may also influence the biodegradation of carbon as demonstrated by positive correlations between DON, NH_4^+N and BDOC (%) (Table 5). Nitrogen additions have previously been shown to stimulate DOM bioremineralization in North American Arctic rivers during the freshet period [Holmes *et al.*, 2008]. Low nutrient levels within the river (Figures 4a, 4c, and 4d) may therefore limit the maximum biolability observed during the freshet within the Kolyma.

[31] The photochemical removal of DOC we measured likely represents the maximum remineralization rate possible over such short times exposure times, as we measured

surface irradiated samples under 24 h sunlight conditions. Despite this, losses of up to 30% of the DOC pool under natural light conditions (e.g., low Sun angles, cloud) still demonstrate a significant removal mechanism for terrestrial DOC in the Arctic. Photochemical DOC removal may be limited by self-shading in highly colored waters and by water column light attenuation with depth, making estimates of total natural removal rates challenging. Maximum photochemical DOC losses, however, probably occur within coastal and open ocean regions where dilution of terrestrial inputs leads to maximum light penetration.

[32] The photo reactivity of freshet DOM (DOC_{photo}) exposed to identical light treatments differed in response to varying DOM composition. Significant correlations between indices relating to DOM aromaticity and molecular weight ($SUVA_{254}$ and S_R) with DOC_{photo} demonstrated that increasing molecular weight and aromaticity led to higher photochemically mediated DOC loss (Table 5 and Figures 9a and 9b). Aromatic compounds have previously been shown to be preferentially lost via photodegradation processes with major losses in aromatic moieties and enrichment in the ^{13}C -DOC signature upon irradiation [Opsahl and Zepp, 2001; Spencer *et al.*, 2009b; Stubbins *et al.*, 2010]. Decreases in $SUVA_{254}$ and a steepening in the S_R were observed during irradiations consistent with the loss of aromatic compounds (Table 5). Photodegradation of spring flush derived DOM also led to an absolute and relative loss in C2 and C3 fluorescence consistent with the notion that these fractions represent more conjugated, complex DOM associated with surface soils and vegetation sources. Photochemical exposure led to an absolute (and relative) increase in protein-like fluorescent fractions (C4 and C5; Table 4), providing evidence for the production of low molecular weight compounds (Table 4). The photo-production and photochemically recalcitrant nature of these moieties has previously been suggested as a mechanism explaining a positive correlation between fulvic acid nitrogen content and residence time across a diverse range of Arctic surface waters [Cory *et al.*, 2007].

[33] The effect of climate change on future fluxes of DOC from Arctic rivers is not entirely clear, with conflicting evidence for both increases and decreases in flux [Striegl *et al.*, 2007; Guo *et al.*, 2007]. Warmer air temperatures, however, will likely lead to increased permafrost thaw and active layer deepening, driving the freshwater system to transition from a surface water-dominated system to a groundwater-dominated system [Frey and McClelland, 2009]. If our under-ice and late summer conditions were indicative of these deeper, older DOM sources, our results would indicate that an increase in sub-surface flow will result in the export of relatively lower amounts of DOC that is more biologically and photochemically recalcitrant.

5. Conclusions

[34] The composition and lability of DOM within the Kolyma River varied dramatically over the hydrograph, with maximum biological and photochemical lability observed during the spring freshet period. These results from the Russian Arctic followed similar trends in biolability to those previously reported within rivers draining the North

American Arctic [Holmes *et al.*, 2008], implying that large proportions of the annual DOC flux mobilized across the entire Arctic are readily available for biological remineralization and removal. Changes in the composition of the exported organic matter appear to be able to explain much of variability in the biological and photochemical susceptibility of terrestrial DOM. The emerging view is therefore that of a far more dynamic and labile carbon pool over a pan-Arctic scale, particularly during the historically under sampled freshet period. Understanding the fate of terrestrial carbon within the Arctic is crucial not only for our understanding of coastal and oceanic biogeochemical processes, but also in determining the effects of future perturbations brought about by climatic change. Future studies will need to identify the mechanisms controlling degradation rates of Arctic DOC particularly in ancient carbon pools.

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