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Flux and Seasonality of Dissolved Organic Matter From the Northern Dvina (Severnaya Dvina) River, Russia

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Key Points:
- The Northern Dvina is dominated by terrestrial dissolved organic matter inputs throughout the year including even during winter months
- Scaling Northern Dvina dissolved organic carbon and lignin fluxes to similar pan-Arctic regions leads to higher fluxes than past estimates
- Increased lignin fluxes lead to a shorter residence time for terrestrial carbon in the Arctic Ocean compared to past studies

Supporting Information:
- Supporting Information S1

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Abstract Pan-Arctic riverine dissolved organic carbon (DOC) fluxes represent a major transfer of carbon from land-to-ocean, and past scaling estimates have been predominantly derived from the six major Arctic rivers. However, smaller watersheds are constrained to northern high-latitude regions and, particularly with respect to the Eurasian Arctic, have received little attention. In this study, we evaluated the concentration of DOC and composition of dissolved organic matter (DOM) via optical parameters, biomarkers (lignin phenols), and ultrahigh resolution mass spectrometry in the Northern Dvina River (a midsized high-latitude constrained river). Elevated DOC, lignin concentrations, and aromatic DOM indicators were observed throughout the year in comparison to the major Arctic rivers with seasonality exhibiting a clear spring freshet and also some years a secondary pulse in the autumn concurrent with the onset of freezing. Chromophoric DOM absorbance at a_{350} was strongly correlated to DOC and lignin across the hydrograph; however, the relationships did not fit previous models derived from the six major Arctic rivers. Updated DOC and lignin fluxes were derived for the pan-Arctic watershed by scaling from the Northern Dvina resulting in increased DOC and lignin fluxes (50 Tg yr^{-1} and 216 Gg yr^{-1}, respectively) compared to past estimates. This leads to a reduction in the residence time for terrestrial carbon in the Arctic Ocean (0.5 to 1.8 years). These findings suggest that constrained northern high-latitude rivers are underrepresented in models of fluxes based from the six largest Arctic rivers with important ramifications for the export and fate of terrestrial carbon in the Arctic Ocean.

1. Introduction

Northern high-latitude regions store approximately half of all global soil organic carbon (C) in permafrost and peatlands (Schuur et al., 2015; Tarnocai et al., 2009). Arctic rivers connect these large C reservoirs with the ocean and atmosphere (Crawford et al., 2013; Raymond et al., 2007; Striegl et al., 2012) and transport approximately 34 Tg yr^{-1} of dissolved organic carbon (DOC) to the coastal Arctic Ocean annually (Holmes et al., 2012). While the Arctic Ocean accounts for only about 1% of the global ocean volume, it receives over 10% of global freshwater riverine inputs (McClelland et al., 2012; Opsahl et al., 1999). Estuarine-like gradients are observed across the entire Arctic Ocean due to the high input of freshwater and associated terrestrial dissolved organic matter (DOM) (McClelland et al., 2012). Despite past studies highlighting significant removal of terrestrial DOC in the Arctic Ocean, a major fraction of this terrestrial DOC is exported out of the Arctic Ocean (Amon et al., 2003; Kaiser et al., 2017; Letscher et al., 2011). Therefore, the fate of riverine DOC delivered to the Arctic Ocean has implications for the supply of terrestrial DOC to the global oceans (Benner et al., 2005; Spencer et al., 2009). Estimating the current riverine DOC flux to the Arctic Ocean is also fundamentally important for understanding how C fluxes will change due to ongoing and predicted warming in the Arctic. Northern high-latitude regions are warming at a rate twice as fast as the global average, and projected changes from Arctic warming will impact the source, flux, and processing of DOC transported in riverine systems (Drake et al., 2015; Kicklighter et al., 2013; Spencer et al., 2015).

Arctic rivers exhibit marked seasonality, and transport proportionally larger quantities of DOM during the spring freshet (from late April through June) in comparison to the remainder of the year, due to both high DOC concentrations and water fluxes at this time of year (Raymond et al., 2007; Spencer et al., 2009). The composition of the DOM influences its fate whether it will be transported to the coastal ocean or biologically or photochemically mineralized (Hernes & Benner, 2003; Mann et al., 2012). The source of DOM during the freshet has been shown to be predominantly terrestrially derived and aromatic in nature (Amon et al., 2012; Cao et al., 2016; Spencer et al., 2008) while also being younger (Raymond et al., 2007) and more biolabile based on laboratory incubation studies (Holmes et al., 2008). Previous studies investigating the seasonality of DOM composition have focused heavily on the six largest Arctic rivers (i.e., the Ob', Yenisey, Lena, Kolyma, Yukon, and Mackenzie) (e.g., Amon et al., 2012; Mann et al., 2016; Raymond et al., 2007). However, limited data are available for small and medium-sized Arctic rivers and rivers whose watersheds are constrained to northern high-latitude regions, particularly with respect to the Eurasian Arctic.

The current estimate of DOC flux from the pan-Arctic watershed to the Arctic Ocean (34 Tg yr^{-1}) is based on data extrapolated from the six major Arctic rivers (Holmes et al., 2012). These six major rivers encompass 67% of the pan-Arctic watershed, defined as all rivers flowing into the Arctic Ocean and the Bering Sea from the Yukon River north (defined here and throughout as pan-Arctic watershed one or PA1), or 53% of the pan-Arctic watershed when northern Scandinavia, the Canadian Archipelago, and Hudson Bay are also included (defined here and throughout as pan-Arctic watershed two or PA2; Holmes et al., 2012; Mann et al., 2016). Small and medium-sized watersheds accounting for the remaining 33% of the PA1 watershed area (47% of PA2) are more constrained to northern high latitudes and represent areas understudied and potentially undermodeled by scaling from the six largest Arctic rivers. Pan-Arctic flux estimates for DOC are based from the six largest Arctic rivers, with the yields from those watersheds scaled to the remaining 33% of the PA1 watershed area to estimate the total flux to the Arctic Ocean. These estimates assume that the flux from smaller high-latitude constrained watersheds scales linearly with watershed area despite differences in watershed land cover and climate. Previous studies from medium-sized Arctic rivers in Russia suggest that watersheds constrained to high latitudes may have higher C yields compared to estimates from the six largest Arctic rivers (Gordeev et al., 1996). However, this past research did not encompass any sampling during the freshet period of maximum export and so may still represent an underestimate of C yields from these medium-sized rivers.

Improving estimates of riverine DOM fluxes across the pan-Arctic also has importance for calculations of the residence time of terrestrial C in the Arctic Ocean determined from lignin phenols, which are unambiguous tracers of terrestrial C (Fichot et al., 2013; Meyers-Schulte & Hedges, 1986; Opsahl & Benner, 1997). Estimation of lignin biomarker fluxes to the Arctic Ocean has been previously used to calculate Arctic Ocean residence times for terrestrially derived DOM (Mann et al., 2016; Opsahl et al., 1999; Spencer et al., 2009). The diagnostic ratios derived from lignin phenols also provide source information, indicate processes such as phase changes and degradation, and have the ability to distinguish between woody and nonwoody, and angiosperm and gymnosperm sources (Hedges & Mann, 1979; Hernes et al., 2007; Spencer et al., 2016). In conjunction with lignin biomarker analyses, chromophoric DOM (CDOM)-derived parameters have been utilized by a number of studies to assess DOM source and composition exported by Arctic rivers (Spencer et al., 2009; Stedmon et al., 2011; Walker et al., 2013). Additionally, a growing number of studies are utilizing ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) due to the extreme mass accuracy and precision of the technique, to delineate DOM composition and sources in aquatic ecosystems (Kellerman et al., 2015; Kujawinski et al., 2002; Stubbins et al., 2014).

In this study we utilize optical (CDOM), biomarker (lignin phenols), and FT-ICR MS analyses to examine the seasonal changes in DOM composition from the Northern Dvina River (Severnaya Dvina), Russia to determine how DOM composition in this medium-sized and northern high-latitude constrained Arctic river compares with the well-studied six largest Arctic rivers. Furthermore, we examine relationships between CDOM versus DOC and lignin phenols from the Northern Dvina to the six major Arctic rivers to assess the validity of past estimates scaling to the pan-Arctic from solely the major Arctic rivers. Finally, we derive new estimates for DOC and lignin phenol fluxes from the pan-Arctic utilizing the Northern Dvina as a model river for the pan-Arctic watershed not encompassed by the six major Arctic rivers. As a medium-sized and northern high-latitude constrained river the Northern Dvina is more representative of the 33% of the pan-Arctic watershed not encapsulated by the major six Arctic watersheds (Holmes et al., 2013). Taking these new

Figure 1. (a) Map showing the Northern Dvina watershed (yellow) and the six largest Arctic watersheds (blue) with dots for sample locations. The gray and red lines show the estimated area of PA1 and PA2, respectively.

estimates for DOC and lignin phenols derived from incorporating the Northern Dvina, we discuss the ramifications for the fate of terrestrial-derived DOM in the Arctic Ocean.

2. Methods

2.1. Sample Collection

The Northern Dvina watershed encompasses approximately 357,000 km^2 of predominantly low relief peatlands, not underlain by permafrost (Holmes et al., 2013), in Northwestern Russia draining to the White Sea (Figure 1). The Northern Dvina was sampled in Arkhangelsk, Russia about 35 km from the White Sea, upstream of the river delta. Samples were collected between October 2013 and June 2016 from the middle of the channel during low discharge and under ice conditions, and during high discharge events samples were collected from a pier extending out into the river. Seasons were delineated based on hydrology defined as spring (15 April to 14 June, n = 17), summer (15 June to 14 October, n = 4), and winter (15 October to 14 April, n = 17). Between October 2013 and November 2014 five samples were collected throughout the year, and then sampling occurred approximately monthly from November 2014 to March 2016 with intensive sampling occurring during April and May 2016 capturing the spring freshet. During this intensive sampling period samples were collected weekly proceeding peak discharge (March–April 2016), daily to every other day during peak discharge (25 April to 5 May 2016), and weekly during the following month (May–June 2016). All samples were collected at 1 m depth and filtered through precombusted (450°C $>$ 5 h) Whatman GF/F (0.7 μm pore size) filters immediately upon return to the laboratory within 30 min of sampling. Samples were stored in preleached polycarbonate bottles (leached in 1 M HCl for at least 48 h) at −20°C. All samples were then shipped frozen to Florida State University prior to subsequent analyses.

2.2. Dissolved Organic Carbon and Chromophoric Dissolved Organic Matter Analyses

DOC was measured on filtered and acidified (pH 2) samples in amber vials on a Shimadzu TOC-L CPH high-temperature catalytic oxidation total organic carbon analyzer. DOC was calculated using a six-point standard curve on the average of three to seven injections with a coefficient of variance less than 1% and standard deviation ± 0.1.

Absorbance and fluorescence were measured on a Horiba Aqualog in a 10 mm cuvette at a standard temperature of 20°C. Absorbance was measured between 230 and 800 nm, and fluorescence was measured at excitation wavelengths between 230 and 500 nm and emission wavelengths between 230 and 800 nm at 5 nm and 2 nm intervals, respectively. Spectra were blank corrected automatically upon acquisition using the Aqualog software. Absorbance and fluorescence data were processed using Matlab and the drEEM toolbox (Murphy et al., 2013) to normalize the fluorescence data and calculate spectral indices. CDOM parameters reported include the absorption coefficients at 254 and 350 nm (a_{254} and a_{350}, respectively), the spectral slopes between 275–295 nm ($S_{275-295}$) and 350–400 nm ($S_{350-400}$), and their respective spectral slope ratio (S_R; $S_{275-295}$: $S_{350-400}$). The fluorescence index (FI) was calculated as the ratio of the emission intensity of 470 nm to 520 nm at 370 nm excitation, which has been shown to be related to terrestrial versus microbially derived DOM sources (Cory & McKnight, 2005; McKnight et al., 2001). The specific UV absorption at 254 nm ($SUVA_{254}$) was calculated from the decadal absorbance at 254 nm divided by DOC concentration and was used as a proxy for aromaticity (Weishaar et al., 2003).

2.3. Solid Phase Extractions

Solid phase extractions of samples were carried out prior to FT-ICR MS and lignin analyses. All PPL cartridges were soaked in methanol for at least 4 h prior to use and rinsed twice with ultrapure water, once with methanol (high-performance liquid chromatography (HPLC) grade, MilliPore), and twice with acidified ultrapure water (pH2 with 12 M HCl, MilliPore, American Chemical Society (ACS) grade) prior to use. For FT-ICR MS

approximately 40 μg of OC was extracted from samples acidified to pH2 with 12 M HCl (MilliPore, ACS grade) onto 100 mg PPL cartridges (Agilent Technologies, 100 mg, 3 mL PPL). Extracts were eluted with 1 mL methanol (MilliPore, HPLC grade) into 2 mL precombusted (450°C > 5 h) vials and stored frozen (−20°C) prior to further analyses. Approximately 2 mg OC was extracted from 15 acidified samples (pH2 with 12 M HCl, MilliPore, ACS grade) for lignin analysis onto 1 g, 6 mL PPL cartridges (Agilent Technologies), and eluted into 4 mL of methanol (MilliPore, HPLC grade).

2.4. Lignin Phenol Analysis

Lignin-derived phenols were isolated from the dried solid phase extracts followed by cupric oxide oxidation and liquid-liquid extraction modified from Spencer, Aiken, et al. (2010). Briefly, PPL extracts were redissolved in O_2-free 2 M NaOH in a 6 mL Teflon vial (Savillex Corporation) containing 500 mg CuO and amended with 100 mg ferrous ammonium sulfate and 50 mg glucose and reacted in a 155°C oven for 3 h. Following oxidation, the samples were centrifuged and supernatants were decanted into 40 mL vials. Oxidation products were acidified to pH 1 with H_3PO_4 and *t*-cinnamic acid were added as an internal standard. Liquid-liquid extractions of the oxidation products were undertaken by addition of 4 mL ethyl acetate, vortexing, and centrifugation prior to removal of the ethyl acetate. Extracts were pipetted through drying columns containing sodium sulfate into a 4 mL vial. Samples were dried under ultrahigh purity argon between each extraction for a total of three extractions; following the last extraction the sodium sulfate was rinsed with 1 mL of ethyl acetate into the extract vial. Dried ethyl acetate extracts were dissolved in pyridine and derivatized with N/O bis-trimethylsilyltrifluoromethylacetamide at 60°C for 10 min. Lignin phenol monomers were measured as trimethylsilane derivatives using an Agilent 6890N GC/5975 MS and were quantified as the relative response factors of each compound compared to the response of *t*-cinnamic acid and a five-point calibration curve bracketing the concentration range. Blanks were low and did not exceed greater than 2% of the total lignin concentration; in addition, the Dabob Bay sediment standard was analyzed and was within 5% of published values (Hedges et al., 1988). Eight lignin phenols from three phenol groups were quantified: vanillyl (vanillin, acetovanillone, and vanillic acid), syringyl (syringaldehyde, acetosyringone, and syringic acid), and coumaryl (coumaric acid and ferulic acid).

2.5. FT-ICR MS

Solid-phase extraction extracts were introduced into the FT-ICR MS using negative electrospray ionization at a flow rate of 700 nL min^{-1}. A custom-built FT-ICR mass spectrometer equipped with a 21 tesla superconducting magnet (Bruker, USA) was used for the analysis of each sample. Mass spectra were obtained by coadding 100 consecutive scans, and signals greater than 6σ the root mean squared (RMS) baseline noise from mass to charge ratio (*m/z*) 120–1200 were considered for assignment. Molecular formulae were assigned to compounds containing $C_{1-100}H_{4-200}O_{1-25}$ $N_{0-2}S_{0-1}$ with EnviroOrg©,™ (Corilo, 2015) and did not exceed a mass measurement accuracy of 200 ppb. The modified aromaticity index (AI_{mod}) was calculated for each formula (Koch & Dittmar, 2006, 2016). Molecular formulae were classified into compound classes using elemental stochiometries and AI_{mod}. Compound classes included unsaturated, low oxygen ($AI_{mod} < 0.5$, H/C < 1.5, O/C < 0.5), unsaturated high oxygen ($AI_{mod} < 0.5$, H/C < 1.5, O/C ≥ 0.5), aliphatic (H/C ≥ 1.5, $N = 0$), condensed aromatic ($AI_{mod} \geq 0.67$), polyphenolic ($0.67 > AI_{mod} > 0.5$), peptide like (H/C ≥ 1.5, $N > 0$), and sugars (O/C > 0.9).

2.6. Flux and Yield Estimates

DOC and lignin fluxes and yields were calculated from continuous discharge (*Q*) data and DOC and lignin concentrations using Fortran Load Estimator (LOADEST) (Runkel et al., 2004). A minimum of 12 concentration measurements are required for the model across a range of *Q*; we used 38 measurements of DOC and 15 lignin measurements collected between October 2013 and June 2016. LOADEST calculates loads by applying the method of adjusted maximum likelihood estimation while eliminating collinearity by centering *Q* and concentration data. The regression model is automatically selected from one of nine predefined regression models to fit the data based on the Akaike Information Criterion. Fluxes were scaled to the remaining unmeasured portion of the pan-Arctic watersheds (PA1 and PA2) where PA1 included all watersheds draining into the Arctic Ocean including the Bering Sea from the Yukon River, north. PA2 additionally included watersheds in the Canadian Archipelago, in Northern Scandinavia, and those draining into the Hudson Bay (Figure 1).

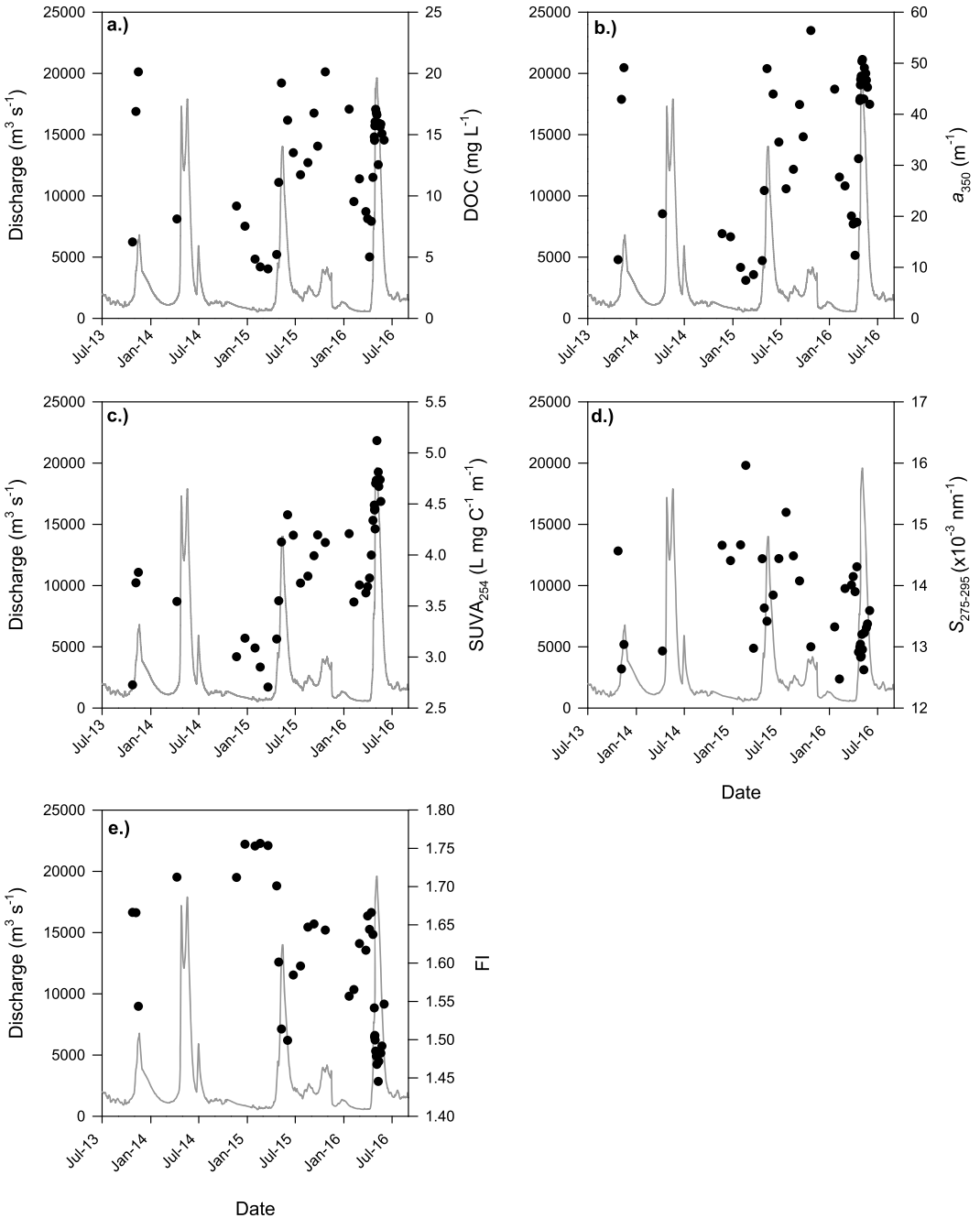

Figure 2. Northern Dvina hydrograph for July 2013 to August 2016 versus (a) DOC, (b) chromophoric dissolved organic matter absorption coefficient at 350 nm (a_{350}), (c) specific UV absorbance at 254 nm ($SUVA_{254}$), (d) spectral slope from 275 to 295 nm ($S_{275-295}$), and (e) fluorescence index (FI). DOC = dissolved organic carbon.

3. Results

3.1. Discharge and DOC Concentrations in the Northern Dvina

Discharge (Q) in the Northern Dvina is strongly seasonal with highest Q occurring during the spring freshet period (Figure 2). The spring freshet occurs on the Northern Dvina from late April to early May when discharge reaches its maximum and returns to lower Q throughout the summer months before reaching baseflow during the winter months. Following the spring freshet and through the open water summer months Q is dominated by precipitation events in the summer and fall, which can cause increases in Q much smaller

Table 1
Northern Dvina River DOC, CDOM Data, and the Modified Aromaticity Index From FT-ICR MS

Date	DOC (mg L^{-1})	a_{350} (m^{-1})	$S_{275-295}$ ($\times 10^{-3}$ nm^{-1})	$SUVA_{254}$ (L mg C^{-1} m^{-1})	FI	AI_{mod}
24 Oct 2013	6.23	11.48	14.56	2.72	1.67	0.32
6 Nov 2013	16.88	42.89	12.64	3.73	1.67	0.34
15 Nov 2013	20.12	49.10	13.03	3.83	1.54	0.34
10 Apr 2014	8.10	20.47	12.93	3.54	1.71	0.32
21 Nov 2014	9.16	16.57	14.66	3.00	1.71	0.33
23 Dec 2014	7.52	15.96	14.40	3.18	1.76	0.32
30 Jan 2015	4.83	9.97	14.66	3.09	1.75	0.31
19 Feb 2015	4.19	7.44	15.96	2.90	1.76	0.31
20 Mar 2015	4.03	8.55	12.97	2.70	1.75	0.31
22 Apr 2015	5.21	11.29	14.44	3.17	1.70	0.31
30 Apr 2015	11.09	25.02	13.63	3.55	1.60	0.33
10 May 2015	19.20	48.92	13.41	4.13	1.51	0.34
2 Jun 2015	16.17	43.93	13.84	4.39	1.50	0.36
24 Jun 2015	13.52	34.51	14.44	4.19	1.58	0.36
21 Jul 2015	11.72	25.37	15.20	3.72	1.60	0.33
18 Aug 2015	12.71	29.19	14.48	3.79	1.65	0.34
10 Sep 2015	16.75	41.89	14.07	3.99	1.65	0.34
23 Oct 2015	20.12	56.40	13.00	4.20	1.64	0.36
21 Jan 2016	17.07	44.90	13.32	4.12	1.56	0.36
8 Feb 2016	9.52	27.66	12.47	4.21	1.57	0.36
29 Feb 2016	11.38	25.94	13.95	3.54	1.63	0.35
24 Mar 2016	8.70	20.04	14.01	3.70	1.62	0.34
31 Mar 2016	8.13	18.45	14.14	3.63	1.66	0.34
7 Apr 2016	5.01	12.33	13.90	3.69	1.64	0.35
14 Apr 2016	7.92	18.81	14.30	3.77	1.67	0.34
20 Apr 2016	11.51	31.26	12.91	4.00	1.64	0.36
25 Apr 2016	14.80	42.66	12.99	4.34	1.54	0.37
26 Apr 2016	14.53	43.08	12.98	4.49	1.50	0.37
27 Apr 2016	15.72	45.71	13.04	4.44	1.51	0.37
28 Apr 2016	16.04	46.79	12.83	4.45	1.50	0.37
30 Apr 2016	17.06	47.44	12.84	4.25	1.48	0.37
3 May 2016	16.77	50.35	13.20	4.70	1.48	0.36
5 May 2016	16.60	50.71	12.95	4.73	1.47	0.37
10 May 2016	12.54	42.97	12.62	5.12	1.45	0.38
12 May 2016	15.92	49.08	13.23	4.81	1.47	0.37
20 May 2016	15.85	46.66	13.31	4.67	1.48	0.37
24 May 2016	15.07	45.28	13.37	4.74	1.49	0.37
1 Jun 2016	14.55	41.95	13.59	4.52	1.55	0.36

than observed during spring freshet (Figure 2). Throughout the winter *Q* remains at baseflow (Figure 2). Concentrations of DOC across the year ranged from 4.03 to 20.12 mg L^{-1} (mean = 12.43 mg L^{-1}, n = 38; Figure 2a and Table 1). The mean winter DOC concentration was 9.94 mg L^{-1} (4.03 to 20.12 mg L^{-1}, n = 17), and higher average DOC concentrations were observed between the onset of freezing in late October and through January (mean = 12.74 mg L^{-1}, n = 8), compared to February to mid-April (mean = 7.44 mg L^{-1}, n = 9). The highest average DOC concentrations were observed during the spring freshet period (mean = 14.63 mg L^{-1}, n = 17). During the remainder of the ice-free period of the year (June to October) *Q* was intermediate between baseflow and freshet, and DOC during this portion of the year ranged between 11.72 and 16.75 mg L^{-1} (mean = 13.68 mg L^{-1}, n = 4). The highest observed DOC concentrations occurred concurrent with high *Q* events in November 2013 and October 2015 (20.12 and 20.12 mg L^{-1}, respectively) (Figure 2a and Table 1). Comparable high DOC concentrations were not observed in October/November 2014, but 2014 did not exhibit the prominent October/November peak in *Q* observed in 2013 and 2015. DOC concentrations in the Northern Dvina exceeded the range of seasonal averages (2.6 to 17.5 mg L^{-1}) reported from the six largest Arctic rivers by Mann et al. (2016). However, similar to the six largest Arctic rivers, the average DOC concentration was highest during spring freshet (Raymond et al., 2007; Spencer et al., 2009), but elevated *Q* in the Northern Dvina between October and

November caused an increase in DOC concentrations during that time period not observed in the major Arctic rivers.

3.2. CDOM in the Northern Dvina

The CDOM absorption coefficient at 350 nm (a_{350}) ranged from 7.44 to 56.40 m^{-1} with an average a_{350} of 34.12 m^{-1} (n = 38; Figure 2b and Table 1). Seasonal variations in a_{350} were similar to variations in DOC concentrations with the highest a_{350} values measured in November 2013, October 2015, and during spring freshet when Q was elevated, and the lowest a_{350} values observed under ice during the winter correspond to the lowest DOC concentrations. Low a_{350} values relate to periods when Q was lowest and dominated by groundwater inputs in the late winter, while high a_{350} values occurred when surface runoff was greatest during the spring freshet and fall increased Q period. The maximum a_{350} value in the Northern Dvina was similar to the a_{350} of 58.52 m^{-1} observed in a blackwater tributary of the Yukon River, while the mean was similar to the maximum a_{350} value that was observed in the Yukon River during spring freshet (Spencer et al., 2008). Under ice samples collected just prior to spring freshet were also significantly higher than a_{350} values measured from the Yukon River at the same time of the year (Spencer et al., 2008).

Specific UV absorbance at 254 nm ($SUVA_{254}$) has previously been shown to be a robust proxy for aromaticity (Weishaar et al., 2003). $SUVA_{254}$ values in the Northern Dvina ranged from 2.70 to 5.12 L mg C^{-1} m^{-1} (Figure 2c and Table 1) with the lowest $SUVA_{254}$ values observed when Q was low in late winter and highest $SUVA_{254}$ values during the spring freshet. The average $SUVA_{254}$ for the Northern Dvina was 3.97 L mg C^{-1} m^{-1} (n = 38) indicating that there is predominantly DOM of high aromatic content being exported by the Northern Dvina throughout the year. In comparison to other Arctic watersheds such as the Yukon River (2.0–3.9 L mg C^{-1} m^{-1}; Spencer et al., 2008) Northern Dvina $SUVA_{254}$ values were generally higher. Overall, the Northern Dvina has higher SUVA values (2.70 to 5.12 L mg C^{-1} m^{-1}) than those exhibited in the six major Arctic rivers (1.41 to 3.67 L mg C^{-1} m^{-1}) as well as a higher average $SUVA_{254}$ value compared to the Yenisey River (3.4 L mg C^{-1} m^{-1}) that has previously been described as having the highest $SUVA_{254}$ of the six major Arctic rivers (Stedmon et al., 2011).

Spectral slope from 275 to 295 nm ($S_{275–295}$) has previously been correlated to DOM molecular weight (Helms et al., 2008) and carbon normalized lignin yields (Fichot & Benner, 2012; Spencer, Hernes, et al., 2010), with shallower slopes positively correlated to high molecular weight DOM and relatively high lignin yields. The Northern Dvina $S_{275–295}$ ranged from 12.47 to 15.96 × 10^{-3} nm^{-1} (mean = 13.64 × 10^{-3} nm^{-1}, n = 38; Figure 2d and Table 1) with the steepest values observed in the late fall and winter under ice periods and the shallowest values occurring during the spring freshet. $S_{350–400}$ ranged from 8.66 to 17.73 × 10^{-3} nm^{-1} (mean = 15.77 × 10^{-3} nm^{-1}, n = 38), and S_R was 0.75 to 1.50 (mean = 0.88, n = 38), both exhibited similar trends as $S_{275–295}$. The average $S_{275–295}$ was shallower than the $S_{275–295}$ reported for blackwater sites such as the tropical Epulu River (mean = 14.72 × 10^{-3} nm^{-1}; Spencer, Hernes, et al., 2010) and the Atchafalaya River (mean = 14.85 × 10^{-3} nm^{-1}) and similar to the $S_{275–295}$ observed in the Edisto River (mean = 13.32 × 10^{-3} nm^{-1}) that drains extensive wetlands (Spencer et al., 2012).

In the Northern Dvina, the FI ranged from 1.45 to 1.76 (mean = 1.59, n = 38; Figure 2e and Table 1). The FI minimum corresponded to early May just after the peak of freshet, and the maximum occurred in mid-March during the under ice period when Q was low (Figure 2e). FI showed similar patterns as parameters derived from absorbance with decreases in FI observed during the late fall and spring freshet. FI has been suggested as an indicator of the relative contribution of terrestrial and microbial DOM to the DOM pool; microbially derived DOM has a FI ~1.9, while lower values represent a more terrestrial source of DOM (FI ~1.4 from blackwater rivers; McKnight et al., 2001). FI observed in the Northern Dvina during spring freshet (mean = 1.52, n = 17) was comparable to FI from other blackwater systems such as the Epulu River during the postflush season (mean = 1.43; Spencer, Hernes, et al., 2010).

3.3. Lignin Phenol Concentration and Composition in the Northern Dvina

Lignin concentrations (Σ_8) were measured as the sum of the eight lignin phenols (three vanillyl phenols, three syringyl phenols, and two cinnamyl phenols). Σ_8 ranged between 13.3 and 90.7 μg L^{-1} with a mean of 37.5 μg L^{-1} (n = 15; Figure 3a and Table 2). The lowest Σ_8 value (13.3 μg L^{-1}) was observed prior to freshet in the late winter. During spring freshet Σ_8 quickly increased to 68.8 μg L^{-1}, and the maximum Σ_8 value

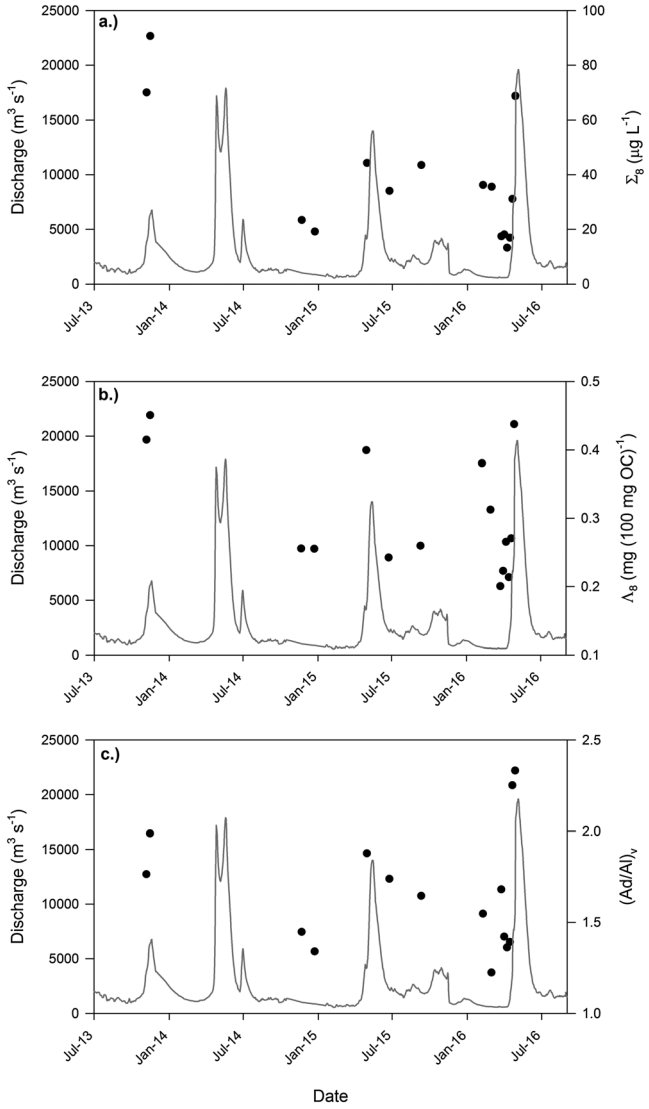

Figure 3. Northern Dvina hydrograph for July 2013 to August 2016 versus lignin phenol parameters: (a) lignin phenol concentration (Σ_8), (b) carbon normalized lignin yield (Λ_8), and (c) acid to aldehyde ratio of the vanillyl phenols ($(Ad/Al)_v$).

(90.7 μg L^{-1}) was observed during the late fall November 2013 sample concurrent with a peak in *Q* (Figure 3a and Table 2). The following November 2014 there was a less pronounced increase in *Q* that corresponded to a much lower observed lignin concentration at that time of year (23.4 μg L^{-1}). Compared to other rivers, Σ_8 was similar to the concentrations observed in the Yukon River (mean = 32.38 μg L^{-1}), but unlike the Northern Dvina, the maximum concentration in the Yukon was observed during spring freshet (Mann et al., 2016). The average Σ_8 was similar to concentrations reported for blackwater river tributaries to the Yukon River (Spencer et al., 2008).

The carbon normalized lignin yield (Λ_8) is used to determine relative contributions of vascular plant material to organic matter (Hedges & Mann, 1979; Hernes et al., 2007). Λ_8 ranged from 0.20 to 0.45 mg (100 mg $OC)^{-1}$ with a mean of 0.30 mg (100 mg $OC)^{-1}$ (*n* = 15; Figure 3b and Table 2). The maximum Λ_8 values occurred in November 2013 during the fall high *Q* event and during the spring freshet samples from April 2016. Λ_8 was lowest in March 2016 corresponding to low DOC concentrations and baseflow *Q* during the late winter. The average Λ_8 was similar to the average carbon normalized lignin yields reported for the Mackenzie River (mean = 0.28 mg (100 mg $OC)^{-1}$; Amon et al., 2012) and the Yukon River (mean = 0.32 mg (100 mg $OC)^{-1}$; Mann et al., 2016).

The acid to aldehyde lignin phenol ratios have been related to degradation and processing of lignin with higher values of acid to aldehyde ratios indicative of more degraded DOM (Hedges & Ertel, 1982). High lignin phenol acid to aldehyde ratios have also been attributed to phase changes such as leaching and sorption (Hernes et al., 2007; Spencer et al., 2016). The $(Ad/Al)_v$ ranged between 1.22 and 2.33 (mean = 1.66, *n* = 15; Figure 3c and Table 2), suggesting highly degraded or processed vascular plant material is transported in the Northern Dvina throughout the year. The highest $(Ad/Al)_v$ was observed during spring freshet when the ratio exceeded 2. $(Ad/Al)_s$ ranged from 0.80 to 1.80 (mean = 1.20, *n* = 15; Table 2) with the maximum values observed during spring freshet and the minimum observed in late December after the onset of freezing, similar to the pattern observed in the $(Ad/Al)_v$ ratios. The $(Ad/Al)_v$ ratios from the six major Arctic rivers were lower on average compared to the Northern Dvina (Mann et al., 2016). The Yukon River exhibited the highest average $(Ad/Al)_v$ (mean = 1.48) among the major Arctic rivers (Mann et al., 2016) compared to a mean $(Ad/Al)_v$ of 1.66 from the Northern Dvina.

The ratios of cinnamyl to vanillyl (C:V) and syringyl to vanillyl (S:V) phenols are an indicator of lignin source. Syringyl phenols are uniquely found in angiosperms and cinnamyl phenols are present only in nonwoody tissue, while vanillyl phenols are ubiquitous in all vascular plant tissue. Thus, the ratios of the syringyl and cinnamyl phenol concentrations to the vanillyl phenol concentrations allow the discrimination of lignin sources between angiosperm, gymnosperm, woody, and nonwoody tissues (Hedges & Mann, 1979). The C:V and S:V ratios ranged from 0.12 to 0.19 (mean = 0.16; *n* = 15) and 0.23 to 0.39 (mean = 0.32; *n* = 15), respectively (Table 2). The ratios did not show any trends with *Q* or seasonality and suggest that the DOM inputs to the Northern Dvina are predominantly from gymnosperm sources mixing with a smaller proportion of angiosperm sources. However, as suggested by the (Ad/Al) ratios (Table 2) this material has also likely undergone extensive degradation or phase changes that precludes the determination of sources solely from phenol ratios (Hernes et al., 2007). A previous study of the Mezen River to the east of the Northern Dvina with similar vegetation reported similar C:V (mean = 0.19) and S:V (mean = 0.30) ratios (Lobbes et al., 2000). The ratios differed from the Yukon River where C:V (mean = 0.27) and S:V (mean = 0.59) were higher in comparison to the Northern Dvina (Spencer et al., 2008).

Table 2
Northern Dvina River Lignin Phenol Diagnostic Parameters

Date	DOC (mg L^{-1})	Σ_8 (μg L^{-1})	Λ_8 (mg (100 mg OC)$^{-1}$)	C:V	S:V	$(Ad/Al)_v$	$(Ad/Al)_s$
6 Nov 2013	16.88	70.0	0.41	0.13	0.29	1.76	1.16
15 Nov 2013	20.12	90.7	0.45	0.12	0.25	1.99	1.19
21 Nov 2014	9.16	23.4	0.26	0.14	0.27	1.45	0.86
23 Dec 2014	7.52	19.2	0.26	0.13	0.23	1.34	0.80
30 Apr 2015	11.09	44.3	0.40	0.16	0.33	1.88	1.40
24 Jun 2015	13.52	34.1	0.24	0.15	0.30	1.74	1.40
10 Sep 2015	16.75	43.5	0.26	0.13	0.25	1.65	1.20
8 Feb 2016	9.52	36.2	0.38	0.15	0.34	1.55	1.09
29 Feb 2016	11.38	35.6	0.31	0.17	0.37	1.22	0.81
24 Mar 2016	8.70	17.4	0.20	0.19	0.36	1.68	1.58
31 Mar 2016	8.13	18.1	0.22	0.18	0.39	1.42	0.96
7 Apr 2016	5.01	13.3	0.27	0.19	0.38	1.36	1.05
14 Apr 2016	7.92	16.9	0.21	0.19	0.38	1.39	1.03
20 Apr 2016	11.51	31.1	0.27	0.18	0.34	2.25	1.76
27 Apr 2016	15.72	68.8	0.44	0.14	0.33	2.33	1.80

3.4. Northern Dvina DOM Composition by FT-ICR MS

An average of 6,532 unique molecular formulae were assigned (min = 4,686, max = 8,382, n = 38; supporting information Table S1) with no seasonal pattern to the number of unique formulae assigned to each sample. Van Krevelen plots of representative samples from each season show the seasonal variation of chemodiversity in the Northern Dvina (Figures 4a–4d). The percentage of assigned molecular formulae was calculated for different compound classes and examined across the hydrograph (Figure 5a). Condensed aromatic and polyphenolic compounds are derived from terrestrial sources (Kellerman et al., 2015; Koch & Dittmar, 2006) and ranged from 5.03 to 9.85% (mean = 7.75%, n = 38) and 14.24 to 17.92% (mean = 16.50%, n = 38), respectively (supporting information Table S1). During the spring freshet, the percentage of assigned formula of condensed aromatic and polyphenolic compounds increases with increased Q compared to the remainder of the year and plateaus at high discharge, ranging from 6.46 to 9.85% (mean = 8.60%, σ = 0.92, n = 17) and 15.01 to 17.92% (mean = 16.95%, σ = 0.75, n = 17), respectively (Figure 5b). The highest variability in chemodiversity of condensed aromatic (min = 5.03, max = 8.69, mean = 6.94, σ = 1.08, n = 17) and polyphenolic (min = 14.24%, max = 17.69%, mean = 16.06%, σ = 1.16, n = 17) compounds occurs in the winter, under ice period, evidenced by higher standard deviations during the winter months compared to the standard deviation from samples from spring freshet. The period of high Q prior to the onset of freezing may account for some of this variability. The remainder of the year during the ice-free period displays lower variability in percentage of assigned formula compared to freshet and under ice periods and exhibits intermediary values of percentage of assigned formulae for both condensed aromatic (min = 7.04%, max = 8.25%, mean = 7.57%, σ = 0.52, n = 4) and polyphenolic compounds (min = 15.84%, max = 17.47%, mean = 16.45%, σ = 0.73, n = 4). Unlike condensed aromatic and polyphenolic compounds, aliphatic compounds did not vary in relation to Q (min = 5.38%, max = 8.91%, mean = 7.01%, σ = 0.90, n = 38; Figure 5a). Sugars and peptide-like compounds exhibited low chemodiversity throughout the year and ranged from 0.50 to 2.18% (mean = 1.54%, n = 38) and 0 to 0.22% (mean = 0.09%, n = 38), respectively (supporting information Table S1). The remainder of the assigned formulae were in the highly unsaturated and phenolic compound class and ranged from 63.15 to 73.29% (mean = 67.12%, n = 38; supporting information Table S1). Additionally, the modified aromaticity index (AI_{mod}) is a conservative measurement of the presence of aromatic and condensed aromatic structures in a DOM sample (Koch & Dittmar, 2006). AI_{mod} was highest during peak discharge in the spring (min = 0.31, max = 0.38, mean = 0.35, n = 38; Figures 5c and 5d), further suggesting a relative increase in high molecular weight, aromatic DOM exported during the freshet period (Figures 5c and 5d and Table 1).

3.5. Terrestrial DOM Fluxes to the Arctic Ocean

The Northern Dvina is estimated to export 1.19 Tg of DOC annually (Table 3). This is a similar flux of DOC as observed from the much larger watersheds of the Mackenzie (1.78 × 10^6 km^2, 1.38 Tg yr^{-1}) and Yukon (0.83 × 10^6 km^2, 1.47 Tg yr^{-1}) Rivers (Holmes et al., 2012). The DOC yield was estimated at

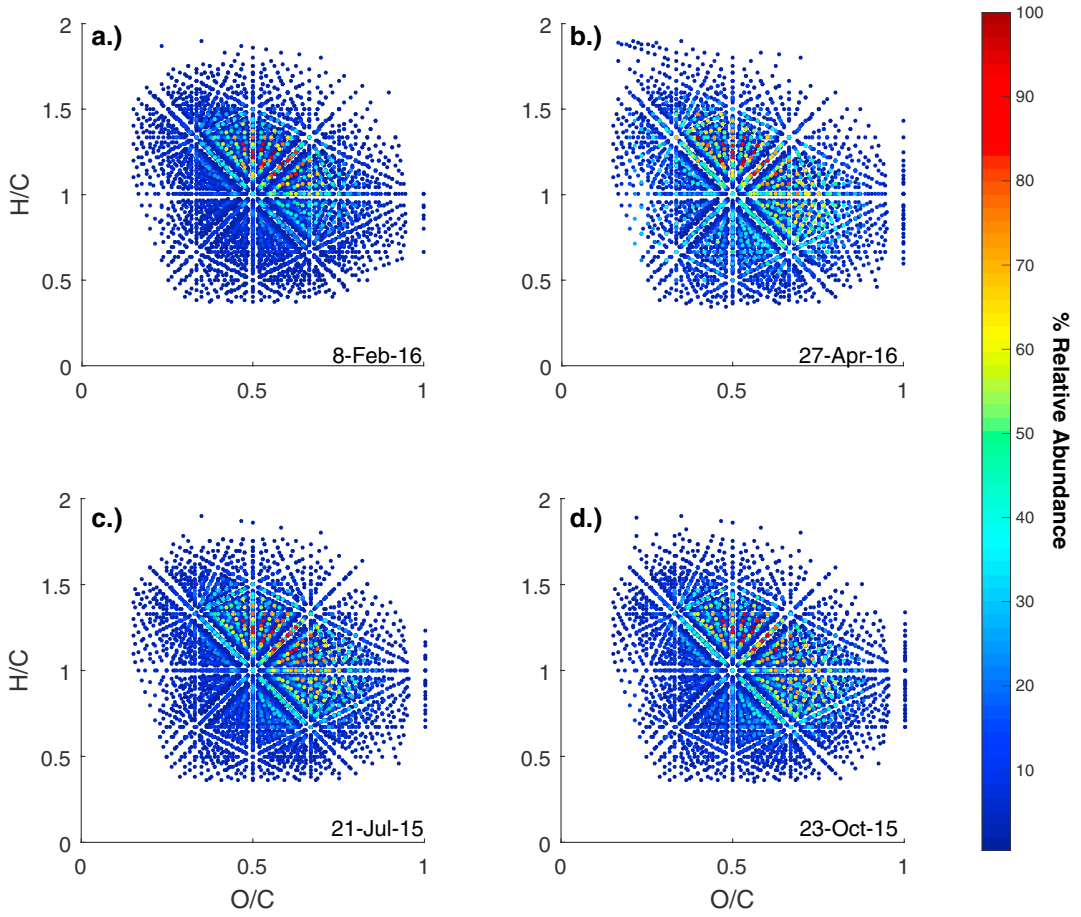

Figure 4. Van Krevelen plots of representative samples for each season: (a) winter under ice, (b) spring freshet, (c) summer, and (d) fall.

3,329 kg km^2 yr^{-1}. The highest yield observed from the major Arctic rivers was from the Lena River where the DOC yield was 2,338 kg km^2 yr^{-1} (Holmes et al., 2012). Lignin flux from the Northern Dvina was 4.60 Gg yr^{-1} (Table 3) and a yield of 12.87 g km^2 yr^{-1}. Mann et al. (2016) calculated lignin fluxes from the six major Arctic rivers based on a_{350}. The lignin flux estimated from the Northern Dvina was comparable to the fluxes from the Mackenzie (5.2 Gg yr^{-1}) and Yukon (4.6 Gg yr^{-1}) Rivers despite its much smaller watershed size.

4. Discussion

4.1. CDOM Parameters for Tracing Arctic Riverine DOM

The absorption coefficient at 350 nm has been used in previous studies as a proxy for DOC and lignin concentrations (Hernes & Benner, 2003; Spencer et al., 2008, Spencer, Hernes, et al., 2010; Mann et al., 2016). In this study examining the Northern Dvina, a_{350} exhibited similar patterns with Q as DOC concentrations (Figures 2a and 2b) and was strongly correlated to DOC concentration ($r^2 = 0.94$, $p < 0.01$; Figure 6a). The linear regression between a_{350} and DOC has a slightly steeper slope in comparison to the relationship between a_{350} and DOC for the six largest Arctic rivers (Figure 6a, Mann et al., 2016), indicating that the Northern Dvina transports comparatively more CDOM per unit DOC than the six largest Arctic rivers. This is also evidenced by the high average $SUVA_{254}$ and shallower $S_{275-295}$ values (Figures 2c and 2d) observed in the Northern Dvina compared to the six largest Arctic rivers, indicating that the Northern Dvina is a more organic-rich blackwater system that transports a comparatively high proportion of CDOM. The relationship between CDOM and DOC from the Rio Grande (Figure 6a, black dashed line; Spencer et al., 2012), a river dominated by autochthonous inputs, shows that the major Arctic rivers (gray dashed line; Mann et al., 2016) and the Northern Dvina transport significantly more CDOM per unit DOC due to the dominance of allochthonous inputs in the Arctic rivers.

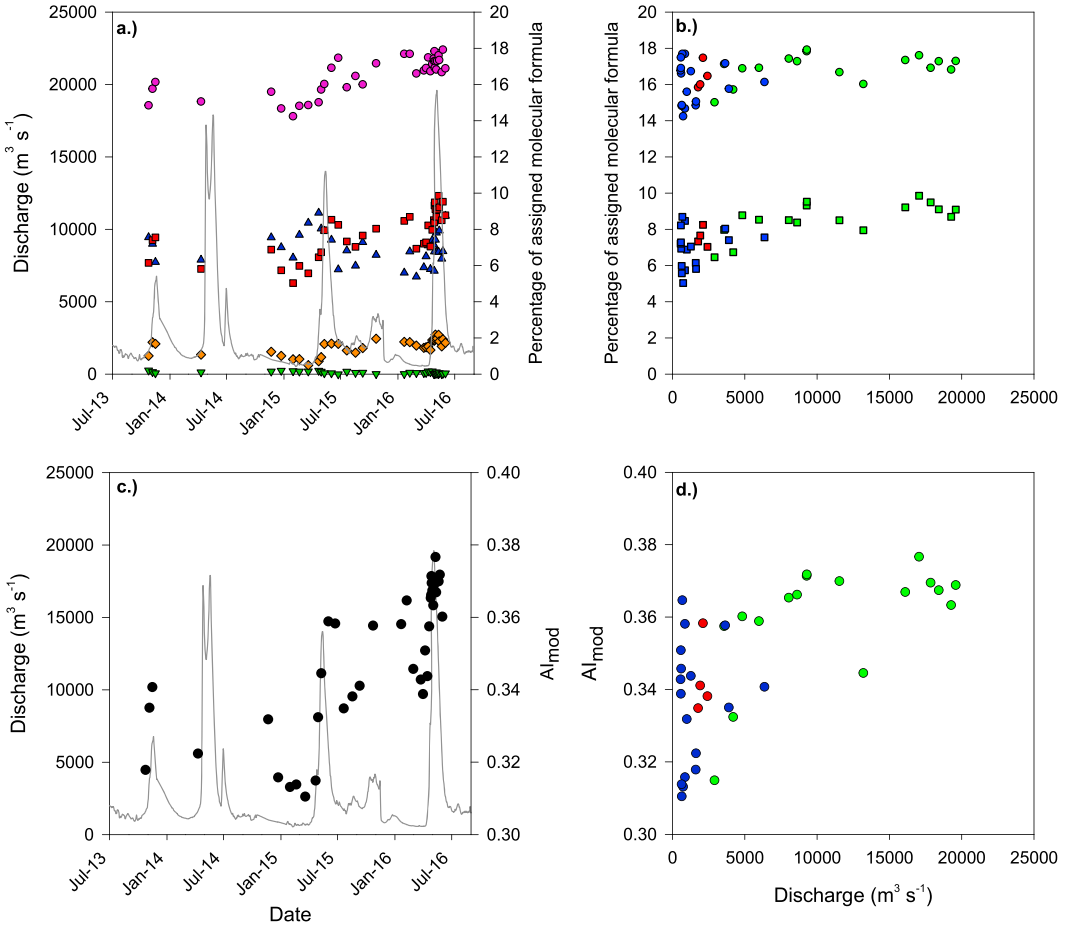

Figure 5. (a) Percentage of assigned formula of major compound classes and discharge versus date. Compound classes include polyphenolics (purple circles), condensed aromatics (red squares), aliphatics (blue triangles), sugars (orange diamonds), and peptide-like (green inverted triangles). (b) Polyphenolics (circles) and condensed aromatics (squares) versus discharge where color indicates season: blue (15 October to 14 April), green (15 April to 14 June), and red (15 June to 14 October). (c) Aromaticity index (AI_{mod}) and discharge versus date. (d) AI_{mod} versus discharge where color indicates season: blue (15 October to 14 April), green (15 April to 14 June), and red (15 June to 14 October).

The shift in the slope of the relationships between CDOM and DOC from the autochthonous-dominated Rio Grande to the six major Arctic rivers and finally to the Northern Dvina in Figure 6a clearly shows the increasing contribution of CDOM per unit DOC in the Northern Dvina. Thus, it is apparent that by employing the CDOM versus DOC relationship derived from the six largest Arctic rivers, DOC concentrations would be systematically overestimated if extrapolated to the Northern Dvina (e.g., DOC derived from a_{350} at 50 m^{-1} for six major Arctic rivers: 19.34 mg L^{-1} and Northern Dvina: 17.97 mg L^{-1}; Figure 6a) due to the high relative proportion of CDOM mobilized from the Northern Dvina.

Table 3
Annual Fluxes of DOC and Lignin for the Pan-Arctic Watershed (Outlined in Figure 1) Scaled From the Northern Dvina and Residence Times of the Arctic Ocean From Previous Studies and Using the Updated Estimates From This Study

		DOC flux (Tg yr^{-1})		Lignin flux (Gg yr^{-1})		Residence time		
	Watershed area (10^6 km^2)	Holmes et al., 2012	This study	Mann et al., 2016	This study	Opsahl et al., 1999	Mann et al., 2016	This study
Northern Dvina	0.36	—	1.19	—	4.60	—	—	—
Pan-Arctic 1	16.8	27.31	36.95	155.50	171.26	—	—	0.6–2.3 years
Pan-Arctic 2	20.5	34.06	50.06	185.30	216.82	1.5–6 years	0.6–2.5 years	0.5–1.8 years

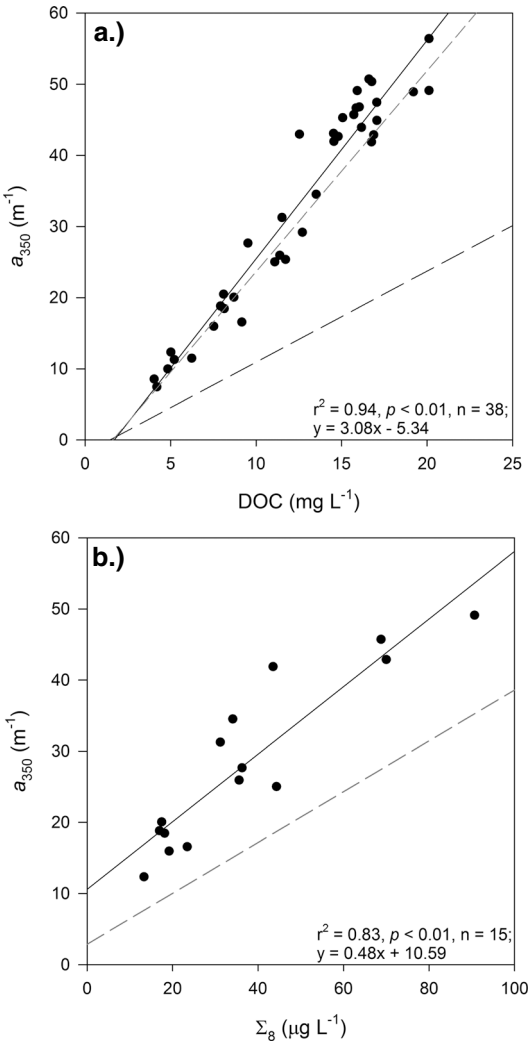

Figure 6. (a) Relationship between a_{350} and DOC for the Northern Dvina, (black dots, solid line; r^2 = 0.94) compared to the six largest Arctic rivers (gray dashed line), and the Rio Grande (black dashed line). (b) Relationship between a_{350} and Σ_8 for the Northern Dvina (black dots, solid line; r^2 = 0.82) and the six largest Arctic rivers (gray dashed line). DOC = dissolved organic carbon.

In addition to DOC, robust optical proxies have been identified for lignin phenol concentrations (Benner & Kaiser, 2010; Hernes et al., 2009; Osburn & Stedmon, 2011; Spencer et al., 2009). As an unambiguous marker of terrestrial plant material, lignin is used to evaluate the export of terrestrial DOM in aquatic systems. Lignin phenol concentrations were significantly correlated to a_{350} (r^2 = 0.83, $p < 0.01$; Figure 6b) in the Northern Dvina, similar to relationships observed in the Yukon River and the other major Arctic rivers (Mann et al., 2016; Spencer et al., 2008). However, the comparatively steeper slope of the linear regression highlights that the Northern Dvina transports more CDOM per unit lignin than the other major Arctic rivers (Figure 6b). This suggests a CDOM-rich source within the Northern Dvina watershed that is relatively poor in lignin, and similar results have been shown in past studies examining DOM sourced from wetland environments (Mann et al., 2014). Within the Northern Dvina watershed extensive wetland regions are found throughout the basin that likely result in a similar phenomenon (Pokrovsky et al., 2010). While there was a significant correlation between Σ_8 and a_{350}, no relationship was observed in the Northern Dvina between Λ_8 and $S_{275-295}$ as found in past Arctic focused studies (Fichot et al., 2013; Mann et al., 2016). $SUVA_{254}$ and FI are both linked to DOM aromaticity and source, but similar to $S_{275-295}$ no relationship was found in the Northern Dvina between these optical parameters and Λ_8. However, there was a significant correlation between aromatic DOM indicators, $SUVA_{254}$ and AI_{mod} (r^2 = 0.88, $p < 0.05$; AI_{mod} = 0.23 + (0.03*$SUVA_{254}$); Koch & Dittmar, 2006; Weishaar et al., 2003). This shows the ability to utilize simple optical parameters such as $SUVA_{254}$ as potential surrogates for more complex (i.e., time consuming), expensive, and analytically intensive measurements such as ultrahigh resolution mass spectrometry data. Linking CDOM to both DOC and lignin concentrations in the Northern Dvina (Figure 6) shows great potential for future studies to harness in situ CDOM technologies providing high temporal resolution measurements (Pellerin et al., 2012; Spencer et al., 2007) to allow for improved flux estimates from this fluvial system.

4.2. Drivers of DOM Composition in the Northern Dvina

Examination of DOM composition via CDOM parameters, biomarker (lignin phenol), and FT-ICR MS indicates a predominantly terrestrial source of DOM throughout the year in the Northern Dvina (Figures 2–5). Clear differences were observed seasonally with respect to composition, particularly the mobilization of terrestrial derived aromatic DOM (Figures 2c–2e, 3a and 3b, and 5a–5d). $SUVA_{254}$, AI_{mod}, and $S_{275-295}$ (Figures 2c and 2d, 5c, and Table 1), indicators of aromatic DOM, and lignin yield (Figure 3b and Table 2), an indicator of vascular plant material, show increases in aromatic, terrestrial DOM during the spring freshet in mid-April to mid-June. During the spring freshet period the Northern Dvina displays relatively similar characteristics as other major Arctic rivers with an increase in DOC concentration and relative increasing contribution of aromatic DOM (Raymond et al., 2007; Striegl et al., 2007) showing mobilization of a largely terrestrial DOM source during the freshet period. Compound classes, measured via FT-ICR MS, showed little variation in the sugars and peptide-like compounds, both more likely to be found from autochthonous DOM production, compared to polyphenolic and condensed aromatic compounds that have terrestrial sources and showed variability throughout the year (Figure 5a; Koch & Dittmar, 2006). The high observed contributions of condensed aromatic and polyphenolic compounds during the spring freshet also indicate the dominance of a largely terrestrial DOM source at this time of year (Figures 5a and 5b). Interestingly, the high $(Ad/Al)_v$ ratios observed during the spring freshet period (Figure 3c) suggest that at this time of maximum DOM export the DOM may be highly degraded (Opsahl & Benner, 1995). Alternatively, the elevated $(Ad/Al)_v$ signature may be a reflection of the physical processes

mobilizing the lignin into the dissolved phase, especially extensive leaching at this time of year (Hernes et al., 2007; Spencer et al., 2016).

The remainder of the ice-free period, from June to October, displayed a similar trend to other Arctic rivers where DOC, CDOM, and lignin were at intermediary values (Holmes et al., 2012; Spencer et al., 2008; Stedmon et al., 2011) but with higher overall $SUVA_{254}$ values (Stedmon et al., 2011). The average $SUVA_{254}$ value (Table 1 and Figure 2c) was similar to values observed in blackwater tributaries to the Yukon River such as the Tolovana and Black Rivers in interior Alaska (Spencer et al., 2008). Molecular indicators of terrestrial DOM, polyphenolic and condensed aromatic compounds, are intermediate at this time as well and have lower variability compared to other seasons (Figure 5b), indicating a consistent DOM source throughout the summer ice-free period. The high $SUVA_{254}$ and Σ_8 (Figures 2c and 3a) values indicate that a high proportion of aromatic DOM is transported throughout the summer months compared to other Arctic rivers (Mann et al., 2016; Spencer et al., 2008). The end of the ice-free, summer period is marked by elevated *Q* during 2013 and 2015 prior to the onset of freezing. This elevated *Q* event corresponds to the maximum DOC, a_{350}, and $SUVA_{254}$ (Figures 2a–2c and Table 1) observations over the sampling period, while AI_{mod} is elevated but does not exceed the values observed during spring freshet (Figure 5d and Table 1). Additionally, lignin concentrations and yields (Figure 3a and 3b and Table 2) reach a maximum during this time, and similarly $(Ad/Al)_v$ ratio is also elevated indicating that during the late autumn there is an increase in overall DOC and terrestrial, aromatic DOM being transported akin to a secondary pulse after the spring freshet (Figure 3c). Elevated allochthonous DOM inputs during this end of summer period in 2013 and 2015 are likely due to extensive precipitation events within the watershed mobilizing fresh organic material from litter layers that have freshly formed at the onset of autumn and had little time for degradation. In comparison to the major Arctic rivers, the Northern Dvina watershed is marked by a later onset of freezing and increased *Q* during the late autumn period prior to the onset of freezing (Shiklomanov & Lammers, 2014). Finally, rapid onset of freezing in the watershed may explain the increased relative contribution of aromatic DOM observed at this time (Figures 2c–2e, 3b, and 5c) compared to major Arctic rivers, although increases in DOC have also been noted in the Yukon at this time and may be attributed to exclusion of water and associated concentrated DOM from soil pore waters as well as ice formation on the river (Ågren et al., 2012; Belzile et al., 2002; Guo et al., 2012). Within the Northern Dvina watershed extensive wetlands (Pokrovsky et al., 2012) may undergo surface freezing causing the movement of DOM-rich pore water out of organic-rich soils and into the river, thus extensively mobilizing allochthonous DOM during this time of year.

Following the late autumn elevated *Q* events, *Q* returned to baseflow throughout the winter months (Figure 2). The concentrations of DOC and aromatic indicators ($SUVA_{254}$, Λ_8, and AI_{mod}) remain relatively high through this period (Figures 2c, 3b, and 5c), unlike in other Arctic rivers where baseflow is a period of low DOC concentrations and relatively low terrestrial DOM inputs (Belzile et al., 2002; Mann et al., 2016; Stedmon et al., 2011). The domination of allochthonous DOM throughout the year in the Northern Dvina is likely as a result of the extensive wetland inputs in this well-constrained high-latitude watershed. Ongoing mobilization of DOM from wetland soils through the winter months through ice exclusion processes likely is responsible for this terrestrially derived DOM mobilization at low *Q* (Ågren et al., 2012). Ultimately, this relatively high loading of allochthonous DOM in the winter months at low *Q* naturally leads to a higher DOC and lignin flux than would be expected if simply scaling flux estimates from the major Arctic rivers do not exhibit this phenomenon. Taken in conjunction with the higher relative DOC and lignin loadings in comparison to the six major Arctic rivers described above in relation to CDOM relationships, it becomes apparent that scaling from the major rivers to the remainder of the pan-Arctic watershed may lead to underestimates in terms of DOC and lignin fluxes.

4.3. Improving Estimates of Riverine DOM Flux to the Arctic Ocean

Recent estimates of Arctic riverine DOC fluxes have been scaled linearly from the six major Arctic rivers despite the large differences in the range of latitude drained by the largest watersheds versus smaller, well-constrained high-latitude rivers (Holmes et al., 2012, 2013). Here we utilize the Northern Dvina to scale to the unmeasured portion of the pan-Arctic watershed as a more appropriate model for the constrained high-latitude northern watersheds that are not encompassed by the six major Arctic rivers. The DOC and lignin yields derived for the Northern Dvina were scaled to the remaining unmeasured portion of the pan-Arctic watershed for both PA1 and PA2 (Figure 1; 33 and 47%, respectively). The estimated DOC flux to the Arctic

Ocean by scaling the unmeasured portion from the Northern Dvina increased the estimate of DOC flux from 27 Tg yr^{-1} to 36.95 Tg yr^{-1} for PA1 and from 34 Tg yr^{-1} to 50.06 Tg yr^{-1} for PA2 (Table 3; Holmes et al., 2012). Previous studies have suggested that the undersampling of high-latitude peatland-dominated watersheds leads to a conservative estimate of DOC flux due to the relatively high DOC yield from these watersheds (Raymond et al., 2007; Striegl et al., 2007; Suzuki et al., 2006). These past suggestions appear to be supported by the inclusion of the Northern Dvina watershed here as a more appropriate model for the constrained high-latitude northern watersheds as it leads to a significant increase in the DOC flux estimates.

Lignin fluxes to the Arctic Ocean have also been scaled linearly from the six largest Arctic rivers (Mann et al., 2016). By scaling the remaining portions of PA1 and PA2 from the Northern Dvina the lignin flux estimates increase from the Mann et al. (2016) study from 155.5 to 171.26 Gg yr^{-1} for PA1 and 185.3 to 216.82 Gg yr^{-1} for PA2 (Table 3). Lignin, as a unique tracer of terrestrial plant inputs, has previously been used to estimate the residence time of terrestrial C in the Arctic Ocean and thus the export of terrestrial C to the North Atlantic Deep Waters (Mann et al., 2016; Opsahl et al., 1999; Spencer et al., 2009). The updated residence time of terrestrial C in the Arctic Ocean using the scaled flux estimates from the Northern Dvina is 6 months to 1.8 years. This updated estimate decreases and narrows the range for residence time of terrestrial C in the Arctic Ocean compared to previous estimates from Mann et al. (2016) (7 months to 2.5 years) and Opsahl et al. (1999) (1.5 to 6 years; Table 3). The higher lignin flux estimates compared to previous studies and shorter residence time of terrestrial C have implications for the supply of terrestrial C to the North Atlantic deep waters as well as the efficient removal of DOM from the Arctic Ocean. Constraining residence time estimates are essential for understanding the reactivity of terrestrial C in the Arctic Ocean where photochemical or microbial processes must remove a large portion of the DOM or it is transported to the North Atlantic deep waters (Benner et al., 2005; Dittmar & Kattner, 2003). In the Northern Dvina, seasonality is markedly different than the seasonality observed in the six largest Arctic rivers leading to higher fluxes and thus shorter Arctic Ocean terrestrial C residence times than would be predicted from simply scaling from the six major rivers (Mann et al., 2016; Spencer et al., 2009). Additionally, the relationship between CDOM and DOC and lignin concentrations (Figure 6) also emphasizes that this constrained northern high-latitude system is not completely represented by the six largest Arctic rivers. This highlights the importance of including well-constrained northern high-latitude rivers such as the Northern Dvina River in estimates of fluxes and residence time calculations to improve both our calculations for supply of DOC to the Arctic Ocean as well as our understanding of the removal mechanisms of terrestrial DOC in the Arctic Ocean.

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References

Ågren, A. M., Haei, M., Blomkvist, P., Nilsson, M. B., & Laudon, H. (2012). Soil frost enhances stream dissolved organic carbon concentrations during episodic spring snow melt from boreal mires. *Global Change Biology*, *18*(6), 1895–1903. https://doi.org/10.1111/j.1365-2486.2012.02666.x

Amon, R. M. W., Budéus, G., & Meon, B. (2003). Dissolved organic carbon distribution and origin in the Nordic Seas: Exchanges with the Arctic Ocean and the North Atlantic. *Journal of Geophysical Research*, *108*(C7), 3221. https://doi.org/10.1029/2002JC001594

Amon, R. M. W., Rinehart, A. J., Duan, S., Louchouarn, P., Prokushkin, A., Guggenberger, G., et al. (2012). Dissolved organic matter sources in large Arctic rivers. *Geochimica et Cosmochimica Acta*, *94*, 217–237. https://doi.org/10.1016/j.gca.2012.07.015

Belzile, C., Gibson, J. A. E., & Vincent, W. F. (2002). Colored dissolved organic matter and dissolved organic carbon exclusion from lake ice: Implications for irradiance transmission and carbon cycling. *Limnology and Oceanography*, *47*(5), 1283–1293. https://doi.org/10.4319/lo.2002.47.5.1283

Benner, R., & Kaiser, K. (2010). Biological and photochemical transformations of amino acids and lignin phenols in riverine dissolved organic matter. *Biogeochemistry*, *102*(1–3), 209–222. https://doi.org/10.1007/s10533-010-9435-4

Benner, R., Louchouarn, P., & Amon, R. M. W. (2005). Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic. *Global Biogeochemical Cycles*, *19*, GB2025. https://doi.org/10.1029/2004GB002398

Cao, X., Aiken, G. R., Spencer, R. G. M., Butler, K., Mao, J., & Schmidt-Rohr, K. (2016). Novel insights from NMR spectroscopy into seasonal changes in the composition of dissolved organic matter exported to the Bering Sea by the Yukon River. *Geochimica et Cosmochimica Acta*, *181*, 72–88. https://doi.org/10.1016/j.gca.2016.02.029

Corilo, Y. (2015). *EnviroOrg*. Tallahassee, FL: Florida State University.

Cory, R. M., & McKnight, D. M. (2005). Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environmental Science & Technology*, *39*(21), 8142–8149. https://doi.org/10.1021/es0506962

Crawford, J. T., Striegl, R. G., Wickland, K. P., Dornblaser, M. M., & Stanley, E. H. (2013). Emissions of carbon dioxide and methane from a headwater stream network of interior Alaska. *Journal of Geophysical Research: Biogeosciences*, *118*, 482–494. https://doi.org/10.1002/jgrg.20034

Dittmar, T., & Kattner, G. (2003). The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: A review. *Marine Chemistry*, *83*(3–4), 103–120. https://doi.org/10.1016/S0304-4203(03)00105-1

Drake, T. W., Wickland, K. P., Spencer, R. G. M., McKnight, D. M., & Striegl, R. G. (2015). Ancient low-molecular-weight organic acids in permafrost fuel rapid carbon dioxide production upon thaw. *Proceedings of the National Academy of Sciences of the United States of America*, *112*(45), 13,946–13,951. https://doi.org/10.1073/pnas.1511705112

Fichot, C. G., & Benner, R. (2012). The spectral slope coefficient of chromophoric dissolved organic matter (S275–295) as a tracer of terrigenous dissolved organic carbon in river-influenced ocean margins. *Limnology and Oceanography*, *57*(5), 1453–1466. https://doi.org/10.4319/lo.2012.57.5.1453

Fichot, C. G., Kaiser, K., Hooker, S. B., Amon, R. M. W., Babin, M., Bélanger, S., et al. (2013). Pan-Arctic distributions of continental runoff in the Arctic Ocean. *Scientific Reports*, *3*(1). https://doi.org/10.1038/srep01053

Gordeev, V. V., Martin, J. M., Sidorov, I. S., & Sidorova, M. V. (1996). A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean. *American Journal of Science*, *296*(6), 664–691. https://doi.org/10.2475/ajs.296.6.664

Guo, L., Cai, Y., Belzile, C., & Macdonald, R. W. (2012). Sources and export fluxes of inorganic and organic carbon and nutrient species from the seasonally ice-covered Yukon River. *Biogeochemistry*, *107*(1–3), 187–206. https://doi.org/10.1007/s10533-010-9545-z

Hedges, J. I., Clark, W. A., & Come, G. L. (1988). Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography*, *33*(5), 1116–1136. https://doi.org/10.4319/lo.%201988.33.5.1116

Hedges, J. I., & Ertel, J. R. (1982). Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry*, *54*(2), 174–178. https://doi.org/10.1021/ac00239a007

Hedges, J. I., & Mann, D. C. (1979). The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta*, *43*(11), 1803–1807. https://doi.org/10.1016/0016-7037(79)90028-0

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography*, *53*(3), 955–969. https://doi.org/10.4319/lo.2008.53.3.0955

Hernes, P. J., & Benner, R. (2003). Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research*, *108*(C9), 3291. https://doi.org/10.1029/2002JC001421

Hernes, P. J., Bergamaschi, B. A., Eckard, R. S., & Spencer, R. G. M. (2009). Fluorescence-based proxies for lignin in freshwater dissolved organic matter. *Journal of Geophysical Research*, *114*, G00F03. https://doi.org/10.1029/2009JG000938

Hernes, P. J., Robinson, A. C., & Aufdenkampe, A. K. (2007). Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". *Geophysical Research Letters*, *34*, L17401. https://doi.org/10.1029/2007GL031017

Holmes, R. M., Coe, M. T., Fiske, G. J., Gurtovaya, T., McClelland, J. W., Shiklomanov, A. I., et al. (2013). Climate change impacts on the hydrology and biogeochemistry of Arctic rivers. In C. R. Goldman, M. Kumagai, & R. D. Robarts (Eds.), *Climatic change and global warming of inland waters: Impacts and mitigation for ecosystems and societies* (pp. 3–26). Chichester, UK: John Wiley.

Holmes, R. M., McClelland, J. W., Peterson, B. J., Tank, S. E., Bulygina, E., Eglinton, T. I., et al. (2012). Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas. *Estuaries and Coasts*, *35*(2), 369–382. https://doi.org/10.1007/s12237-011-9386-6

Holmes, R. M., McClelland, J. W., Raymond, P. A., Frazer, B. B., Peterson, B. J., & Stieglitz, M. (2008). Lability of DOC transported by Alaskan rivers to the Arctic Ocean. *Geophysical Research Letters*, *35*, L03402. https://doi.org/10.1029/2007GL032837

Kaiser, K., Benner, R., & Amon, R. M. W. (2017). The fate of terrigenous dissolved organic carbon on the Eurasian shelves and export to the North Atlantic. *Journal of Geophysical Research: Oceans*, *122*, 4–22. https://doi.org/10.1002/2016JC012380

Kellerman, A. M., Kothawala, D. N., Dittmar, T., & Tranvik, L. J. (2015). Persistence of dissolved organic matter in lakes related to its molecular characteristics. *Nature Geoscience*, *8*(6), 454–457. https://doi.org/10.1038/ngeo2440

Kicklighter, D. W., Hayes, D. J., McClelland, J. W., Peterson, B. J., McGuire, A. D., & Melillo, J. M. (2013). Insights and issues with simulating terrestrial DOC loading of Arctic river networks. *Ecological Applications*, *23*(8), 1817–1836. https://doi.org/10.1890/11-1050.1

Koch, B. P., & Dittmar, T. (2006). From mass to structure: An aromaticity index for high-resolution mass data of natural organic matter. *Rapid Communications in Mass Spectrometry*, *20*(5), 926–932. https://doi.org/10.1002/rcm.2386

Koch, B. P., & Dittmar, T. (2016). From mass to structure: An aromaticity index for high-resolution mass data of natural organic matter. *Rapid Communications in Mass Spectrometry*, *30*(1), 250–250. https://doi.org/10.1002/rcm.7433

Kujawinski, E. B., Freitas, M. A., Zang, X., Hatcher, P. G., Green-Church, K. B., & Jones, R. B. (2002). The application of electrospray ionization mass spectrometry (ESI MS) to the structural characterization of natural organic matter. *Organic Geochemistry*, *33*(3), 171–180. https://doi.org/10.1016/S0146-6380(01)00149-8

Letscher, R. T., Hansell, D. A., & Kadko, D. (2011). Rapid removal of terrigenous dissolved organic carbon over the Eurasian shelves of the Arctic Ocean. *Marine Chemistry*, *123*(1-4), 78–87. https://doi.org/10.1016/j.marchem.2010.10.002

Lobbes, J. M., Fitznar, H. P., & Kattner, G. (2000). Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean. *Geochimica et Cosmochimica Acta*, *64*(17), 2973–2983. https://doi.org/10.1016/S0016-7037(00)00409-9

Mann, P. J., Davydova, A., Zimov, N., Spencer, R. G. M., Davydov, S., Bulygina, E., et al. (2012). Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin. *Journal of Geophysical Research*, *117*, G01028. https://doi.org/10.1029/2011JG001798

Mann, P. J., Spencer, R. G. M., Dinga, B. J., Poulsen, J. R., Hernes, P. J., Fiske, G., et al. (2014). The biogeochemistry of carbon across a gradient of streams and rivers within the Congo Basin: Aquatic C biogeochemistry in Congo Basin. *Journal of Geophysical Research: Biogeosciences*, *119*, 687–702. https://doi.org/10.1002/2013JG002442

Mann, P. J., Spencer, R. G. M., Hernes, P. J., Six, J., Aiken, G. R., Tank, S. E., et al. (2016). Pan-Arctic trends in terrestrial dissolved organic matter from optical measurements. *Frontiers in Earth Science*, *4*, 25. https://doi.org/10.3389/feart.2016.00025

McClelland, J. W., Holmes, R. M., Dunton, K. H., & Macdonald, R. W. (2012). The Arctic Ocean estuary. *Estuaries and Coasts*, *35*(2), 353–368. https://doi.org/10.1007/s12237-010-9357-3

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., & Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, *46*(1), 38–48. https://doi.org/10.4319/lo.2001.46.1.0038

Meyers-Schulte, K. J., & Hedges, J. I. (1986). Molecular evidence for a terrestrial component of organic matter dissolved in ocean water. *Nature*, *321*(6065), 61–63. https://doi.org/10.1038/321061a0

Murphy, K., Stedmon, C. A., Graeber, D., & Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. PARAFAC. *Analytical Methods*, *5*(23), 6557–6566. https://doi.org/10.1039/C3AY41160E

Opsahl, S., & Benner, R. (1995). Early diagenesis of vascular plant tissues: Lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta*, *59*(23), 4889–4904. https://doi.org/10.1016/0016-7037(95)00348-7

Opsahl, S., & Benner, R. (1997). Distribution and cycling of terrigenous dissolved organic matter in the ocean. *Nature*, *386*(6624), 480–482. https://doi.org/10.1038/386480a0

Opsahl, S., Benner, R., & Amon, R. M. W. (1999). Major flux of terrigenous dissolved organic matter through the Arctic Ocean. *Limnology and Oceanography*, *44*(8), 2017–2023. https://doi.org/10.4319/lo.1999.44.8.2017

Osburn, C. L., & Stedmon, C. A. (2011). Linking the chemical and optical properties of dissolved organic matter in the Baltic–North Sea transition zone to differentiate three allochthonous inputs. *Marine Chemistry*, *126*(1–4), 281–294. https://doi.org/10.1016/j.marchem.2011.06.007

Pellerin, B. A., Saraceno, J. F., Shanley, J. B., Sebestyen, S. D., Aiken, G. R., Wollheim, W. M., & Bergamaschi, B. A. (2012). Taking the pulse of snowmelt: In situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry*, *108*(1–3), 183–198. https://doi.org/10.1007/s10533-011-9589-8

Pokrovsky, O. S., Viers, J., Shirokova, L. S., Shevchenko, V. P., Filipov, A. S., & Dupré, B. (2010). Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary. *Chemical Geology*, *273*(1-2), 136–149. https://doi.org/10.1016/j.chemgeo.2010.02.018

Pokrovsky, O. S., Viers, J., Dupré, B., Chabaux, F., Gaillardet, J., Audry, S., et al. (2012). Biogeochemistry of carbon, major and trace elements in watersheds of northern Eurasia drained to the Arctic Ocean: The change of fluxes, sources and mechanisms under the climate warming prospective. *Comptes Rendus Geoscience*, *344*(11–12), 663–677. https://doi.org/10.1016/j.crte.2012.08.003

Raymond, P. A., McClelland, J. W., Holmes, R. M., Zhulidov, A. V., Mull, K., Peterson, B. J., et al. (2007). Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest Arctic rivers. *Global Biogeochemical Cycles*, *21*, GB4011. https://doi.org/10.1029/2007GB002934

Runkel, R. L., Crawford, C. G., & Cohn, T. A. (2004). Load estimator (LOADEST): A FORTRAN program for estimating constituent loads in streams and rivers. In *In Techniques and Methods Book 4* (Chap. A5, 69 pp.). Denver, CO: U.S. Geological Survey.

Schuur, E. A. G., McGuire, A. D., Schädel, C., Grosse, G., Harden, J. W., Hayes, D. J., et al. (2015). Climate change and the permafrost carbon feedback. *Nature*, *520*(7546), 171–179. https://doi.org/10.1038/nature14338

Shiklomanov, A. I., & Lammers, R. B. (2014). River ice responses to a warming Arctic—Recent evidence from Russian rivers. *Environmental Research Letters*, *9*(3), 35,008. https://doi.org/10.1088/1748-9326/9/3/035008

Spencer, R. G. M., Aiken, G. R., Butler, K. D., Dornblaser, M. M., Striegl, R. G., & Hernes, P. J. (2009). Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska. *Geophysical Research Letters*, *36*, L06406. https://doi.org/10.1029/2008GL036831

Spencer, R. G. M., Aiken, G. R., Dyda, R. Y., Butler, K. D., Bergamaschi, B. A., & Hernes, P. J. (2010). Comparison of XAD with other dissolved lignin isolation techniques and a compilation of analytical improvements for the analysis of lignin in aquatic settings. *Organic Geochemistry*, *41*(5), 445–453. https://doi.org/10.1016/j.orggeochem.2010.02.004

Spencer, R. G. M., Aiken, G. R., Wickland, K. P., Striegl, R. G., & Hernes, P. J. (2008). Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska: Yukon River basin DOM dynamics. *Global Biogeochemical Cycles*, *22*, GB4002. https://doi.org/10.1029/2008GB003231

Spencer, R. G. M., Butler, K. D., & Aiken, G. R. (2012). Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA. *Journal of Geophysical Research*, *117*, G03001. https://doi.org/10.1029/2011JG001928

Spencer, R. G. M., Hernes, P. J., Dinga, B., Wabakanghanzi, J. N., Drake, T. W., & Six, J. (2016). Origins, seasonality, and fluxes of organic matter in the Congo River. *Global Biogeochemical Cycles*, *30*, 1105–1121. https://doi.org/10.1002/2016GB005427

Spencer, R. G. M., Hernes, P. J., Ruf, R., Baker, A., Dyda, R. Y., Stubbins, A., & Six, J. (2010). Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. *Journal of Geophysical Research*, *115*, G03013. https://doi.org/10.1029/2009JG001180

Spencer, R. G. M., Mann, P. J., Dittmar, T., Eglinton, T. I., McIntyre, C., Holmes, R. M., et al. (2015). Detecting the signature of permafrost thaw in Arctic rivers. *Geophysical Research Letters*, *42*, 2830–2835. https://doi.org/10.1002/2015GL063498

Spencer, R. G. M., Pellerin, B. A., Bergamaschi, B. A., Downing, B. D., Kraus, T. E. C., Smart, D. R., et al. (2007). Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). *Hydrological Processes*, *21*(23), 3181–3189. https://doi.org/10.1002/hyp.6887

Stedmon, C. A., Amon, R. M. W., Rinehart, A. J., & Walker, S. A. (2011). The supply and characteristics of colored dissolved organic matter (CDOM) in the Arctic Ocean: Pan Arctic trends and differences. *Marine Chemistry*, *124*(1–4), 108–118. https://doi.org/10.1016/j.marchem.2010.12.007

Striegl, R. G., Dornblaser, M. M., Aiken, G. R., Wickland, K. P., & Raymond, P. A. (2007). Carbon export and cycling by the Yukon, Tanana, and Porcupine Rivers, Alaska, 2001–2005. *Water Resources Research*, *43*, W02411. https://doi.org/10.1029/2006WR005201

Striegl, R. G., Dornblaser, M. M., McDonald, C. P., Rover, J. R., & Stets, E. G. (2012). Carbon dioxide and methane emissions from the Yukon River system. *Global Biogeochemical Cycles*, *26*, GB0E05. https://doi.org/10.1029/2012GB004306

Stubbins, A., Lapierre, J.-F., Berggren, M., Prairie, Y. T., Dittmar, T., & del Giorgio, P. A. (2014). What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada. *Environmental Science & Technology*, *48*(18), 10598–10606. https://doi.org/10.1021/es502086e

Suzuki, K., Konohira, E., Yamazaki, Y., Kubota, J., Ohata, T., & Vuglinsky, V. (2006). Transport of organic carbon from the Mogot experimental watershed in the southern mountainous taiga of eastern Siberia. *Hydrology Research*, *37*(3), 303–312. https://doi.org/10.2166/nh.2006.015

Tarnocai, C., Canadell, J. G., Schuur, E. A. G., Kuhry, P., Mazhitova, G., & Zimov, S. (2009). Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochemical Cycles*, *23*, GB2023. https://doi.org/10.1029/2008GB003327

Walker, S. A., Amon, R. M. W., & Stedmon, C. A. (2013). Variations in high-latitude riverine fluorescent dissolved organic matter: A comparison of large Arctic rivers. *Journal of Geophysical Research: Biogeosciences*, *118*, 1689–1702. https://doi.org/10.1002/2013JG002320

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology*, *37*(20), 4702–4708. https://doi.org/10.1021/es030360x