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Constraining dissolved organic matter sources and temporal variability in a model sub-Arctic lake

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Abstract Circumpolar lakes comprise ~ 1.4 million km^2 of arctic and subarctic landscapes and are vulnerable to change in vegetation, permafrost distribution, and hydrological conditions in response to climate warming. However, the composition and cycling of dissolved organic matter (DOM) is poorly understood for these lakes because most are remote and unstudied. The goal of this study was to assess timescale and source controls on DOM composition in Canvasback Lake, a shallow, sub-Arctic lake in interior Alaska with similar hydrologic and geomorphic characteristics to about a quarter of circumpolar lake ecosystems. Lake dissolved organic carbon (DOC) concentration varied by as much as 16% from the mean (3.34 mg L^{-1} change) through diel cycles in spring 2016 to fall 2017 and was accompanied by minor changes in DOM composition. At the seasonal scale, DOC concentration increased from spring through fall to very high concentrations under ice in winter. Decreases in both condensed aromatic and polyphenolic compound classes and lignin carbon-normalized yield, plus increased relative abundance of aliphatic compounds, suggests that DOM composition shifts from a pulse of allochthonous DOM in the spring to more autochthonous under-ice. These changes highlight the seasonally-dynamic nature of DOM in circumpolar lakes that are poorly captured by single-visit lake surveys and underscores the need to measure DOM properties and fate consistently across multiple timescales (i.e. seasonally) to better constrain

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the role of DOM in lake processes. To further assess DOM sources, a suite of endmember leachates were compared to bulk lake DOM, indicating solely allochthonous inputs are not well reflected in lake DOM, highlighting the role of degradation processes or mixing with autochthonous sources. Thus, Canvasback Lake appears less well connected to terrestrial inputs compared to past studies of northern high-latitude lakes and does not behave as previous boreal lake models suggest.

Keywords Dissolved organic matter · Arctic lake · Carbon cycle · Diel · Lignin · Seasonal

Introduction

Northern circumpolar lakes play a critical role in regional and global carbon (C) cycling because they are sites of intense C turnover and flux (Kling et al. 1991; Tranvik et al. 2009) and cover a large fraction of the landscape (Verpoorter et al. 2014; Muster et al. 2017). Climatic changes are restructuring arctic and subarctic freshwater ecosystems through changes in hydrology, mineral weathering, catchment vegetation cover, and temperature (Striegl et al. 2005; Tank et al. 2016; Pearson et al. 2013; Vonk et al. 2015). Critically, C cycle responses and feedbacks to these changes and the role lakes play in circumpolar C-climate feedbacks remain uncertain (Schuur et al. 2015; Anderson et al. 2017). A primary reason for this uncertainty is because sampling of lake C flux and composition has typically been restricted to single time points due to logistical constraints with few high temporal resolution studies (Schindler et al. 1997; Osburn et al. 2017; Elder et al. 2018). The remoteness of northern high-latitude lakes also makes it difficult to access and study a wide range of lake conditions, leaving many lake types and settings essentially unsampled (Bogard et al. 2019a, b). More intensive studies of C cycling through space and time are required to improve our understanding of the patterns and controls of arctic lake C cycling, and thus their response to environmental changes.

An important step toward understanding arctic lake C cycling more completely lies in better defining the patterns and composition of the dissolved organic matter (DOM) pool. DOM plays an important role in structuring the physical and biogeochemical characteristics of lake ecosystems, including water temperature, toxin cycling, and light attenuation, which indirectly controls biota and overall system productivity (Kirk 1994; Forsström et al. 2015; Solomon et al. 2015). The DOM pool also directly affects food-webs through its role as a source of nutrients and energy (Polis et al. 1997; Solomon et al. 2015). In arctic regions, where extreme seasonal changes in light availability occur, DOM produced during the ice-free season can sustain microbial production within the lake and provides support for the growth of larger heterotrophs (Rautio et al. 2011). Shifts in hydrology, including increasing precipitation and evapotranspiration in Arctic and boreal regions is projected to alter the composition of DOM in these systems, possibly resulting in surface water browning from increased terrestrial DOM inputs (Williamson et al. 2015; de Wit et al. 2016). In contrast, some regions such as western Greenland have been shown to undergo the opposite trend with decadal declines in dissolved organic carbon (DOC) concentration due to prolonged droughts (Saros et al. 2015). The source of DOM has been shown to control its fate in aquatic environments (Spencer et al. 2008; Tank et al. 2011) thus climate induced changes to lake DOM inputs can dramatically alter lake processes.

The composition of DOM is regulated by different processes across multiple timescales, along with lengthening of the ice free and growing seasons (Bring et al. 2016). These changes may impact DOM composition and DOC concentration on seasonal to annual time scales. Seasonal patterns of DOM composition in northern high-latitude lakes and rivers show a strong pulse of DOM during the spring freshet, altering the composition and bio-lability of DOM transported in these systems (Spencer et al. 2008; Tank et al. 2011; Mann et al. 2016). In circumpolar lakes, seasonal changes through the ice-free period also occur due to evapoconcentration in shallow lakes, increasing the DOC concentration and modifying the DOM signature in lakes with long water residence times (Anderson and Stedmon 2007; Kellerman et al. 2015; Larsen et al. 2017). Studies in more accessible landscapes at lower latitudes and in more populated regions have shown that measurements of DOM cycling on diel time scales are important for understanding processes that drive short term ecosystem function (Spencer et al. 2007; Müller et al. 2014;

Watras et al. 2015). These previous studies highlight the need for a comprehensive analysis of changes in DOM over short and mid timescales to assess the role of DOM in lacustrine ecosystem function. To truly understand the role DOM plays in arctic lake processes, measurements need to be integrated over short, diel timescales, to longer, annual timescales.

Given that similar studies have not been conducted for northern high-latitude remote lakes, the goal of this study was to define the sources, patterns, and cycling of lake DOM across multiple timescales (diel to annual) and assess major source inputs of lake DOM in a lake in the Yukon Flats National Wildlife Refuge of interior Alaska, USA. This type of shallow lake environment is representative of approximately one quarter of circumpolar lake area based on having similar slopes, soil properties, and ranges of precipitation (Bogard et al. 2019a). In addition, the lakes in the Yukon Flats are similar to lakes in Southwest Greenland and the Mackenzie River watershed with relatively high DOC concentrations and low chromophoric DOM (CDOM) (Tank et al. 2011; Osburn et al. 2017; Cunada et al. 2018; Bogard et al. 2019a). Currently, most lakes in this region are relatively hydrologically disconnected from surface water flow systems (Bogard et al. 2019a), and projected changes may further impact the hydrologic connectivity of these lakes (Jepsen et al. 2013; Bring et al. 2016). The objectives of this study were twofold: first, we evaluate DOM dynamics at high temporal (diel) resolution during the spring and fall and seasonally in the spring, fall, and winter over two sampling years to assess the timescales of sampling needed to capture the largest variability in lake DOM composition. Second, we assess the major source inputs to lake DOM by comparing endmember leachates of potential DOM sources to lake DOM via CDOM absorbance, FT-ICR MS (Fourier transform ion cyclotron resonance mass spectrometry), and biomarker lignin. Here we use vegetation leachates to assess the dominant sources of DOM and how the source and composition of DOM might change linked to environmental conditions.

Methods

Study site

Samples were collected at Canvasback Lake in the Yukon Flats National Wildlife Refuge, Alaska, approximately 120 km northeast of Fairbanks, Alaska (Fig. 1). Canvasback Lake is a shallow, well-mixed lake with a maximal depth of about 2 m. The Yukon Flats is an arid, low-relief region, with predominantly shallow lakes that do not receive riverine inputs; lakes in this region have been suggested to be representative of approximately one quarter of circumpolar lake area based on geomorphic and climatic similarities (Bogard et al. 2019a). The lake is dominated by submerged macrophytes (predominantly *Myriophyllum* spp.) in the open water region, and emergent bulrush (*Schoenoplectus tabernaemontani*) in littoral zones surrounding the lake. Fish are absent from the lake, and large zooplankton dominate the top of the aquatic food web. Canvasback lake was selected as a model arid, low-relief, northern circumpolar lake because of its comparative accessibility and the representativeness of the Yukon Flats region to other circumpolar lake environments. Canvasback lake has similar characteristics of previously studied lakes in both Northern Canada (Tank et al. 2011; Cunada et al. 2018) and Southwest Greenland (Osburn et al. 2017).

Sample collection

Samples for DOM analyses were collected during the ice free season in spring and fall of 2016 and 2017 at intervals of 2 to 6 h with an additional winter, under-ice sample collected in 2017 (Tables 1 and S1). Surface water samples were collected from an open water area of the lake that was approximately 2 m deep accessed using a small boat. Spring sampling was timed to collect water as close to spring ice out as possible. Based on Sentinel 2 imagery, 2016 ice out occurred around May 10 to May 16 and sampling took place during May 28–29. In 2017 ice out occurred around May 20 and sampling took place during May 24–27. Differences in lake area and vegetation extent between spring and fall in both years and from year to year are readily apparent in Sentinel 2 satellite remote sensing imagery (Fig. S1). Water chemistry parameters including pH, water temperature, percent dissolved oxygen (DO), and specific conductivity were measured using a YSI water quality probe (Xylem Inc., Rye Brook, NY, USA) at the sampling location in fall 2017 and from a raft in the middle of the lake during spring 2016 and 2017. Both locations were in open water areas several meters from shore and thus the differences between the sites would be negligible.

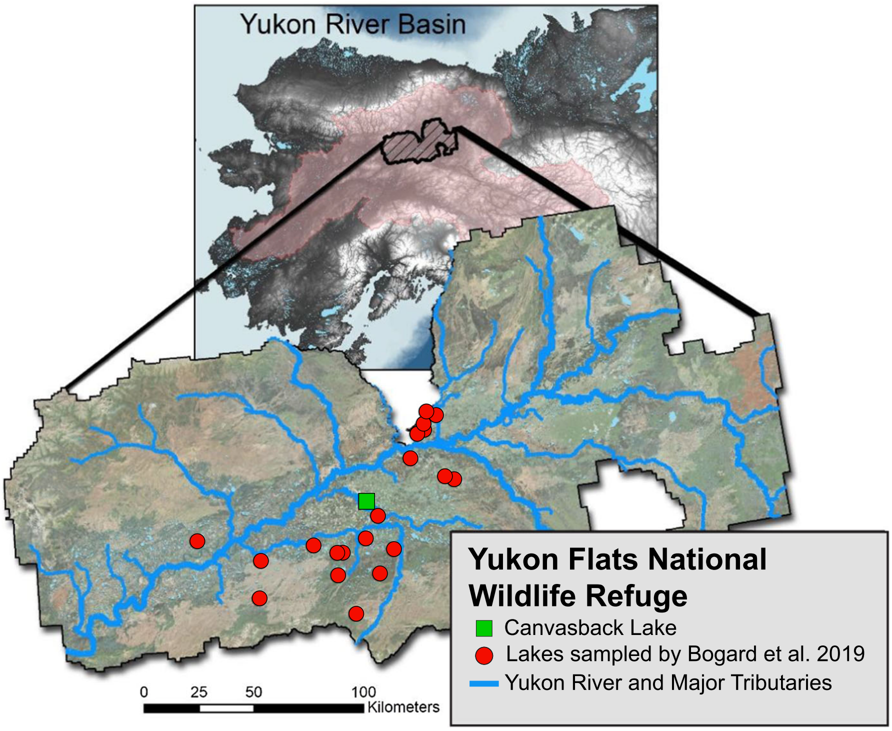

Fig. 1 Map of the Yukon Flats National Wildlife Refuge with Canvasback Lake highlighted (green square) and additional lakes sampled by Bogard et al. (2019a, b) (red dots). (Color figure online)

Table 1 Sampling frequency and mean metadata for seasonal sampling at Canvasback Lake. ND indicates where no data is available

Season	Dates	Number of samples	Mean water temperature (°C)	Mean air temperature (°C)	Mean pH	Mean DO (%)	Mean specific conductivity (µS cm^{-1})
Spring 2016	5/28/16 to 5/29/16	18	14.2	12.4	8.58	105.9	536.6
Fall 2016	9/13/16 to 9/14/16	5	ND	ND	ND	ND	ND
Winter 2017	4/6/17	1	0.04	-0.9	7.53	9.8	1588.0
Spring 2017	5/24/17 to 5/27/17	28	10.7	9.0	8.18	80.6	530.1
Fall 2017	9/5/2017 to 9/8/17	23	11.2	ND	9.68	107.2	647.8

No measurable precipitation occurred during the sampling collection periods (personal observation).

Immediately following collection, samples were filtered through pre-combusted (450 °C, > 4 h) GF/F filters. Samples were stored in 125 mL HDPE bottles pre-leached in 1 M HCl and rinsed three times with filtered sample water, and subsequently frozen within 72 h of collection (− 20 °C).

Representative DOM source materials encompassing aquatic and terrestrial sources from within and surrounding Canvasback Lake were collected in the spring and fall, and were stored frozen (− 20 °C), in the dark. Endmembers were classified into terrestrial sources: mixed feathermosses, peat soil, mineral soil, mixed grasses, and white spruce (*Picea glauca*), and autochthonous and littoral sources: bulrush (*Schoenoplectus tabernaemontani*), water milfoil (*Myriophyllum* spp.), and cyanobateria. The littoral zone around Canvasback Lake is dominated by bulrush, with mainly degraded, dried bulrush from the previous year in the spring, and fresh bulrush in the summer to fall months (Fig. S1). Therefore, spring (dried) and fall (fresh) vegetation samples of bulrush and grasses were obtained to evaluate seasonal impacts on DOM leachates. Throughout the ice-free period, macrophyte growth and mats of cyanobacteria are abundant in Canvasback Lake and were chosen as DOM source materials for leaching representative autochthonous DOM sources.

Prior to leaching, source endmembers were dried at 50 °C for 24 h. DOM from each source material was leached into 500 mL of 0.001 M sodium bicarbonate to buffer the leachate for 24 h in polycarbonate bottles. During the leaching, samples were maintained at 20 °C in the dark on a shaker table (Wickland et al. 2007). Leachates were subsequently filtered through 0.7 µm GF/F filters (pre-combusted, 450 °C, > 4 h) and stored in HDPE bottles in the dark at 4 °C until extraction or analysis (< 24 h).

Dissolved organic carbon and chromophoric dissolved organic matter analyses

Dissolved organic carbon concentrations were measured via high temperature catalytic oxidation using a Shimadzu TOC-L CPH total carbon analyzer (Shimadzu Corp., Kyoto, Japan) on filtered, acidified samples (pH 2 with 12 M HCl). Samples were sparged with CO_2-free air for five minutes on the instrument immediately prior to injection to remove dissolved inorganic carbon. A five-point standard curve and the average of three out of seven injections with a maximum coefficient of variation of 1.0% and standard deviation less than 0.1 mg L^{-1} were used to calculate DOC concentrations.

Chromophoric dissolved organic matter (CDOM) was measured on filtered samples at room temperature in a 10 mm quartz cuvette with a Horiba Aqualog (Horiba Ltd., Kyoto, Japan) between wavelengths 230 and 800 nm at 1 nm intervals. Spectra were blank subtracted upon collection and further processed using the drEEM toolbox (Murphy et al. 2013) in MATLAB (MathWorks Inc., Natick, MA, USA) to calculate spectral parameters. Spectral parameters included the absorption coefficient at 350 nm (a_{350}) used as a proxy for DOC and lignin concentration (Spencer et al. 2009, 2012), and the specific UV absorbance at 254 nm ($SUVA_{254}$) calculated as the DOC normalized absorbance at 254 nm (Weishaar et al. 2003) used as a proxy for aromaticity (Kellerman et al. 2018; Johnston et al. 2018). Values of a_{350} were calculated as Naperian absorption coefficients by multiplying the measured absorbance by 2.303 divided by the pathlength (m) (Hu et al. 2002). $SUVA_{254}$ was calculated from the decadal absorbance at 254 nm divided by DOC concentration (Weishaar et al. 2003).

Dissolved organic matter solid phase extraction

Solid phase extraction was used to isolate and concentrate DOM from filtered, acidified (pH 2) samples prior to FT-ICR MS and lignin analyses using Bond-Elut PPL (Agilent Technologies Inc., Santa Clara, CA, USA) (Dittmar et al. 2008). All cartridges were soaked with methanol for a least 4 h prior to use and subsequently rinsed twice with ultrapure water, once with methanol, and twice with pH 2 ultrapure water. For FT-ICR MS analyses, 40 µg of organic carbon (OC) was isolated onto 100 mg, 3 mL PPL cartridges and eluted with 1 mL methanol into 2 mL precombusted (550 °C, > 4 h) vials and stored frozen at − 20 °C until analysis. Leachates and a representative DOM sample from each sampling season were extracted and analyzed for lignin. For lignin analysis 2 mg OC was extracted onto 1 g, 6 mL PPL cartridges and eluted with 4 mL of methanol following the same PPL preparation described above.

Lignin phenol analysis

Canvasback Lake DOM samples were analyzed for lignin phenol composition at four time points (fall 2016 and winter, spring, and fall 2017) and on all source material leachates. Lignin phenols were used as a unique tracer of vascular plant material, and the concentrations and yields of eight major lignin oxidation products have previously been used as indicators of the contribution of vascular plant DOM to the bulk DOM pool (Hedges and Mann 1979; Spencer et al. 2008). Lignin-derived phenols were measured on solid phase extracts followed by cupric oxide oxidation and liquid–liquid extraction (Spencer et al. 2010; Johnston et al. 2018). PPL extracts were dried and re-dissolved in O_2-free 2 M NaOH and transferred to 6 mL PFA (polyfluoroalkoxy alkane) reaction vessels (Savillex LLC., Eden Prairie MN, USA). 500 mg CuO, 100 mg ferrous ammonium sulfate, and 15 mg glucose were added to each reaction vessel; the reaction vessels were sparged for 10 min with ultra-high purity argon, sealed, and heated at 155 °C for 3 h. After the oxidation samples were centrifuged and supernatants were decanted into 20 mL vials and acidified to pH 1 with 85% H_3PO_4 and amended with 2500 ng of *trans*-cinnamic acid as an internal standard. Triplicate ethyl acetate liquid–liquid extractions were dried under argon, redissolved into pyridine, and derivatized with N/O bis-trimethylsilyltrifluoromethylacetamide with 1% trimethylchlorosilane at 60 °C for 10 min and analyzed on an Agilent 6890N GC/5975 MS (Agilent Technologies Inc., Santa Clara, CA, USA). Lignin phenol responses were calculated from the response ratio of each compound compared to *trans*-cinnamic acid and quantified using a five-point standard curve. Blank concentrations did not exceed 2% of the total lignin concentration in a sample. Lignin phenols were divided into three groups: vanillyl (vanillin, acetovanillone, and vanillic acid), syringyl (syringaldehyde, acetosyringone, and syringic acid), and coumaryl (*p*-coumaric acid and ferulic acid) and reported as the concentration of the sum of the eight lignin phenols, Σ_8 (ug L^{-1}) and as DOC-normalized lignin yield of the eight phenols, Λ_8 (mg (100 mg $OC)^{-1}$). Additionally, vanillyl phenols are ubiquitous in all lignin bearing plants, unlike syringyl (S) and cinnamyl (C) phenols (Hedges and Mann 1979), thus the DOC-normalized lignin yield of the vanillyl phenols (V) was used to evaluate the contribution of vascular plant material to the bulk lignin pool independent of different types of vascular plant tissues (Spencer et al. 2008). To evaluate the vascular plant material sources the C:V and S:V ratios were calculated and compared to previously reported ranges for non-woody and woody and angiosperm and gymnosperm plant tissues (Spencer et al. 2008). A subset of these data are presented in Bogard et al (2019a, b).

FT-ICR MS analyses

Dissolved organic matter chemical composition was evaluated via 21 T FT-ICR MS (Hendrickson et al. 2015; Smith et al. 2018) on PPL extracts in methanol. Samples were introduced into the magnet cell by negative electrospray ionization at a flow rate of 700 ng min^{-1}. Mass spectra from 100 consecutive scans were accumulated and signals greater than 6σ root mean squared baseline noise were considered for assignment with a mass to charge ratio (*m/z*) from 120 to 1200. Mass error did not exceed 200 ppb (Savory et al. 2011). Formulae were assigned using EnviroOrg (Corilo 2015) for compounds containing $C_{1-100}H_{4-200}O_{1-25}$ $N_{0-2}S_{0-1}$. Compound classes were assigned to each molecular formula based on the elemental ratios and modified aromaticity index (Koch and Dittmar 2006, 2016). The modified aromaticity index (AI_{mod}) is related to the degree of aromaticity of DOM and contribution of terrestrial DOM (Johnston et al. 2018; Kellerman et al. 2018).The compound classes included highly unsaturated and phenolic ($AI_{mod} < 0.5$, $H/C < 1.5$), aliphatic ($H/C \geq 1.5$, $N = 0$), polyphenolic ($0.67 > AI_{mod} > 0.5$), condensed aromatic ($AI_{mod} \geq 0.67$), peptide-like ($H/C \geq 1.5$, $N > 0$), and sugar-like ($O/C > 0.9$) compounds following O'Donnell et al. (2016). The abundance of each compound class is reported as percent of relative abundance. The term compound is used here to describe peaks detected by FT-ICR MS, while assigned molecular formulae may represent multiple isomers that describe the underlying molecular compounds comprising DOM.

Numerical analyses

A principal component analysis (PCA) was performed on all reported data from seasonal sampling (spring 2016, fall 2016, spring 2017, and fall 2017). All variables were range normalized to one prior to the PCA to standardize the data. Significant differences among seasons and sample years were determined using a two-tailed t-test. Results were reported as significant at $p < 0.05$ and highly significant at $p < 0.001$. The significance of linear regressions were determined using a two-tailed t-test and reported as statistically significant at $p < 0.05$. Endmember mixing models of leachate lignin yields were used as a qualitative approximation of the proportion of vascular plant material comprising the bulk DOM pool. The lignin yield of the leachates were considered 100% vascular plant material. The percentage of vascular plant material in bulk DOM samples was estimated from the endmember model within the range of vascular plant material leachates. The PCA was performed using JMP Pro 12 (SAS Institute Inc., Cary, NC, USA), all other statistical analyses were performed in SigmaPlot (SYSTAT Software Inc., San Jose, CA, USA).

Table 2 Summary statistics of DOM parameters for each sampling season, the ice-free sampling period of each year, and the total of all sampling periods

	2016			2017				Total		
	Spring (n = 18)	Fall (n = 5)	Ice-free season (n = 23)	Winter (n = 1)	Spring (n = 28)	Fall (n = 23)	Ice-free season (n = 52)	Spring (n = 46)	Fall (n = 28)	All season (n = 74)
DOC (mg L^{-1})										
Mean	21.55	25.07	22.32	124.80	20.35	25.10	22.49	20.82	25.09	23.80
Min	20.06	24.80	20.06		18.60	23.67	18.60	18.60	23.67	18.60
Max	22.36	25.51	25.51		21.94	25.59	25.59	22.36	25.59	124.80
*a*350 (m^{-1})										
Mean	9.85	10.81	10.06	23.25	9.50	11.54	10.42	9.63	11.41	10.48
Min	9.32	10.61	9.32		9.12	10.84	9.12	9.12	10.61	9.12
Max	10.14	10.96	10.96		10.01	11.96	11.96	10.14	11.96	23.25
$SUVA_{254}$ (L mg C^{-1} m^{-1})										
Mean	2.63	2.64	2.63	1.20	2.71	2.73	2.72	2.68	2.72	2.67
Min	2.57	2.59	2.57		2.56	2.63	2.56	2.56	2.59	1.20
Max	2.68	2.66	2.68		2.95	2.80	2.95	2.95	2.80	2.95
Weighted average mass (Da)										
Mean	442.1	447.5	443.3	453.3	431.7	435.9	433.6	435.9	438.0	436.9
Min	435.1	431.7	431.7		410.9	418.6	410.9	410.9	418.6	410.9
Max	453.1	454.4	454.4		453.7	458.7	458.7	453.7	458.7	458.7
AImod										
Mean	0.263	0.263	0.263	0.242	0.275	0.273	0.274	0.270	0.271	0.270
Min	0.260	0.262	0.260		0.268	0.271	0.268	0.260	0.262	0.242
Max	0.267	0.264	0.267		0.281	0.276	0.281	0.281	0.276	0.281
Highly unsaturated and phenolic (%RA)										
Mean	86.93	87.50	87.07	87.39	85.94	85.75	85.85	86.34	86.06	86.25
Min	86.02	86.83	86.01		85.36	85.12	85.12	85.36	85.12	85.12
Max	87.75	87.90	87.90		88.56	86.98	88.56	88.56	87.90	88.56
Polyphenolic (%RA)										
Mean	6.05	6.09	6.05	3.92	7.00	7.11	7.05	6.62	6.93	6.70
Min	5.80	5.96	5.80		6.41	6.87	6.41	5.80	5.96	3.92
Max	6.42	6.17	6.42		7.48	7.40	7.48	7.48	7.40	7.48
Condensed aromatic (%RA)										
Mean	1.38	1.36	1.37	0.60	1.65	1.78	1.71	1.54	1.70	1.59
Min	1.12	1.27	1.12		1.12	1.40	1.12	1.12	1.27	0.60
Max	1.55	1.53	1.55		1.88	1.99	1.99	1.88	1.99	1.99
Aliphatic (%RA)										
Mean	4.70	3.63	4.46	6.88	4.21	4.09	4.16	4.40	4.01	4.29
Min	4.00	3.42	3.42		2.96	3.17	2.96	2.96	3.17	2.96
Max	5.18	3.93	5.18		5.01	4.80	5.01	5.18	4.80	6.88

Results

Chemical characteristics of Canvasback lake

During the ice-free sampling seasons the water temperature in Canvasback Lake ranged from 10.0 to 15.0 °C (mean = 11.8 ± 1.53 °C, n = 68; Tables 1 and S2) and under-ice was 0.04 °C. The mean pH, calculated as the negative $\log_{10}$ of mean of the hydrogen ion concentration, of the lake was 8.47 ± 0.66 (8.02 to 9.78, n = 68; Tables 1 and S2) during the ice-free sampling seasons and was 7.53 under-ice. The specific conductivity was significantly greater under ice compared to the mean ice-free sampling seasons (1588.0 and 571.6 ± 57.7 $\mu S\ cm^{-1}$, respectively; Tables 1 and S2), and the percent DO was nearly ten-fold lower under ice compared to the ice-free sampling seasons (9.8 and 96.3 ± 13.6%, respectively; Tables 1 and S2).

Seasonal changes in DOC concentration and DOM composition

Dissolved organic carbon concentrations increased between spring and fall in 2016 and 2017 (Table 2). The mean DOC concentration of all samples collected in the spring was 20.82 ± 0.90 mg L^{-1} (18.60 to 22.36 mg L^{-1}, n = 46) and increased significantly ($p < 0.001$) to a mean concentration of 25.09 ± 0.39 mg L^{-1} (23.67 to 25.59 mg L^{-1}, n = 28) in the fall (Fig. 2a, b). In addition, spring DOC concentrations exhibited higher variability compared to fall concentrations (SD = 0.90 and 0.39 mg L^{-1}, respectively). One sample was collected under-ice in 2017 (due to sampling constraints diel sampling was not feasible during the winter) and had a DOC concentration of 124.80 mg L^{-1} (Table 2). This DOC concentration is approximately five times higher than the DOC concentrations observed during the ice-free periods of the year.

Similar to DOC, the absorption coefficient at 350 nm (a_{350}) varied seasonally with significantly ($p < 0.001$) lower a_{350} observed in the spring (mean = 9.63 ± 0.31 m^{-1}, n = 46; Table 2) compared to the fall (mean = 11.41 ± 0.35 m^{-1}, n = 28; Table 2). During the winter, under-ice period a_{350} was 23.25 m^{-1}, nearly two times higher than the maximum value observed throughout the ice-free periods of 2016 and 2017 (Table 2). $SUVA_{254}$, a proxy for aromaticity, ranged from 2.56 to 2.95 L mg C^{-1} m^{-1} (mean = 2.68 ± 0.07 L mg C^{-1} m^{-1}, n = 46; Fig. 2c) in the spring and 2.59 to 2.80 L mg C^{-1} m^{-1} (mean = 2.72 ± 0.05 L mg C^{-1} m^{-1}, n = 28; Fig. 2d) in the fall, and was 1.20 L mg C^{-1} m^{-1} in the winter, under-ice sample (Table 2). Annually, $SUVA_{254}$ was significantly higher ($p < 0.001$) during the ice-free season in 2017 (mean = 2.72 ± 0.06 L mg C^{-1} m^{-1}, n = 52) compared to 2016 (mean = 2.63 ± 0.03 L mg C^{-1} m^{-1}, n = 23).

Seasonal and annual changes in DOM chemodiversity (number of molecular formulae) were evaluated via FT-ICR MS. The weighted average mass between the spring and fall of 2016 (mean = 442.1 ± 4.7 and 447.5 ± 9.1 Da, respectively) and 2017 (mean = 431.7 ± 9.6 and 435.9 ± 11.2 Da, respectively) did not vary greatly between seasons but varied annually with higher weighted average mass of assigned molecular formulae observed in 2016 compared to 2017. The highest weighted average mass was observed during the winter, under-ice period (453.3 Da). Similar to annual differences between the weighted mass average, AI_{mod} did not vary between spring and fall (mean = 0.270 ± 0.002 and 0.271 ± 0.004, respectively, Fig. 2e, f; Table 2), but decreased to 0.242 during the under-ice period. In the open water season AI_{mod} was higher in 2017 (mean = 0.274 ± 0.003, n = 50, Fig. 2e, f) compared to 2016 (mean = 0.263 ± 0.002, n = 23, Fig. 2e, f) consistent with the higher $SUVA_{254}$ observed in 2017.

The highly unsaturated and phenolic compound class represented the vast majority of assigned molecular formulae across all seasons (mean = 86.25 ± 0.84%, n = 74). Major compound classes presented in Table 2 show an increased relative abundance of condensed aromatic and polyphenolic compounds, typically associated with terrestrial DOM (D'Andrilli et al. 2015; Kellerman et al. 2018), in the fall (mean = 1.70 ± 0.21 and 6.93 ± 0.42%, respectively) compared to the spring (mean = 1.54 ± 0.21 and 6.62 ± 0.55%, respectively) and winter (0.60 and 3.92%, respectively). The relative abundance of the aliphatic compound class was higher in the winter under-ice sample (6.88%) compared to the spring (mean = 4.40 ± 0.53%, n = 45) and fall (mean = 4.01 ± 0.50%, n = 28).

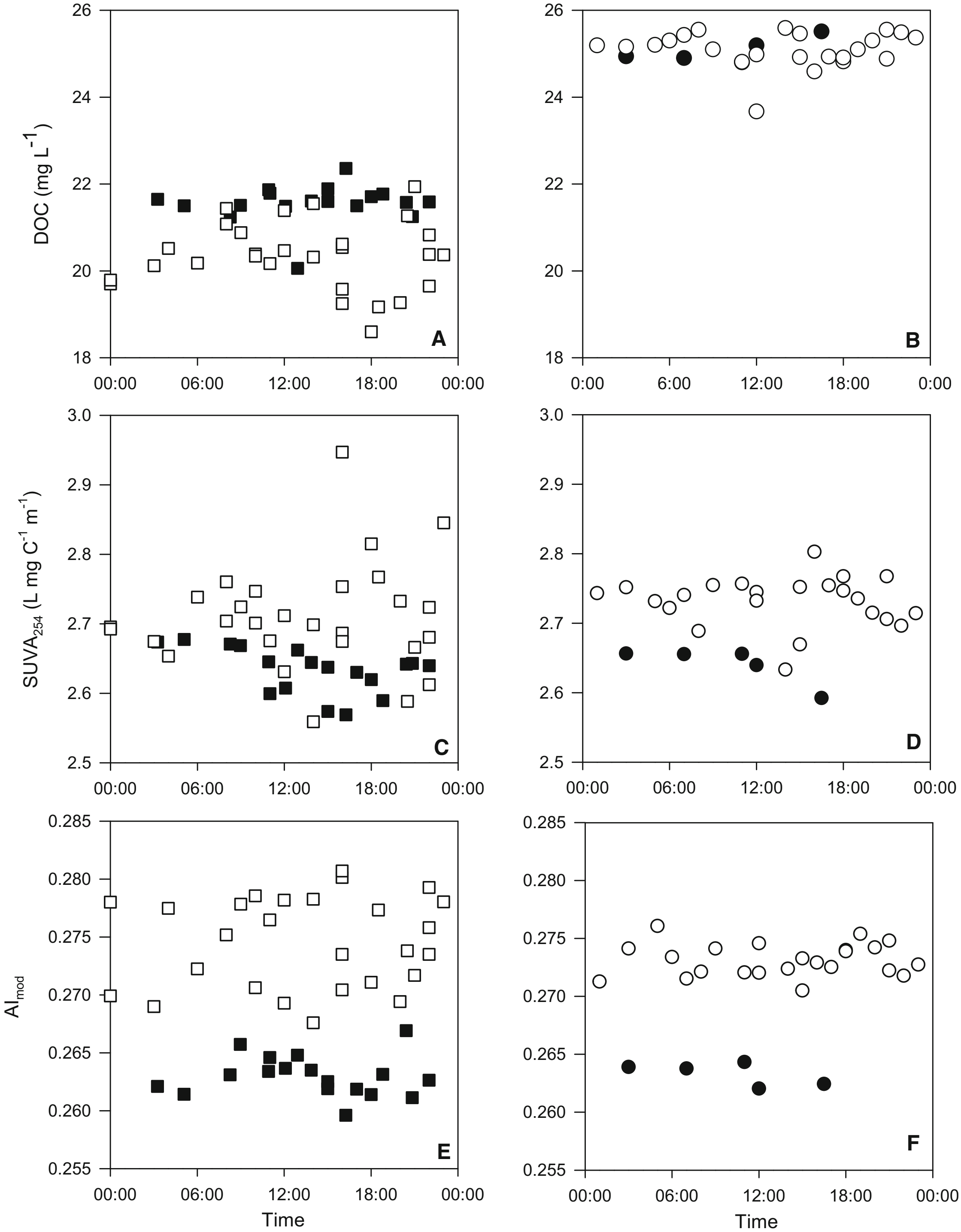

Fig. 2 DOM properties versus time of day for spring (left panels, squares) and fall (right panels, circles) for 2016 and 2017 (closed and open symbols, respectively). Parameters include DOC concentration (**a**, **b**), SUVA$_{254}$, a proxy for aromaticity (**c**, **d**), and the modified aromaticity index (AI$_{mod}$; **e**, **f**)

Lignin concentrations, the sum of the eight lignin phenols (Σ_8), reached a maximum under-ice (90.48 µg L^{-1}) and were low throughout the ice-free period (mean = 35.58 µg L^{-1}, n = 3). The lignin yields of the eight lignin phenols (Λ_8) represent a DOC normalized lignin concentration and are therefore indicative of lignin contribution to the bulk DOC pool (Opsahl and Benner 1997). The Λ_8 reached a maximum in the spring (Λ_8 = 0.16 mg (100 mg OC)$^{-1}$) and was lowest during the under-ice period (Λ_8 = 0.07 mg (100 mg OC)$^{-1}$, Table 3) despite the highest Σ_8 observed during this time.

The C:V and S:V ratios ranged from 0.55 to 0.85 and 1.26 to 1.70, respectively, reflecting a range typical of non-woody angiosperms through all sampling seasons (Table 3; Fig. S2). The ratio of acid to aldehyde of vanillyl and syringyl phenols ($Ad{:}Al_v$ and $Ad{:}Al_s$, respectively) are indicators of degradation of plant tissue, as well as may be impacted due to phase changes from leaching and sorption (Opsahl and Benner, 1995; Hernes et al. 2007). Low variations in $Ad{:}Al_v$ and $Ad{:}Al_s$ were observed during the ice-free season (mean = 0.90 and 0.78, respectively) and increased under ice to 1.27 and 1.18, respectively (Table 3), coinciding with an increase in DOC concentration during the under-ice period.

Diel changes in DOC concentration and DOM composition

Overall, we observed larger diel changes in DOC concentrations in spring than in fall. In spring 2017, DOC concentrations varied by 3.34 mg L^{-1} (18.60 to 21.94 mg L^{-1}, n = 28) over the 80-h sampling period (Fig. 2a). Over the 38-hr sampling period in spring 2016, a smaller range of DOC concentrations was observed (20.06 to 22.36 mg L^{-1}, n = 18). Fall variability in DOC concentration was comparatively low, with a 1.92 mg L^{-1} (23.67 to 25.59 mg L^{-1}, n = 28) range in DOC concentration across both years (Fig. 2b). Fall 2017 DOC exhibited a weak diel cycle with increasing DOC concentrations through the daylight hours from 06:00 to 18:00. Over the three-day sampling period DOC concentrations decreased on average 0.42 mg L^{-1} (Table S1) between 06:00 and 18:00 (n = 14). The small sample size (n = 5) from fall 2016 precludes identification of any possible diel signal in 2016.

Little diel variability was observed in a_{350} through the sampling periods, with ranges varying less than 10% from the mean of each season. Similarly, the contribution of aromatic DOM, assessed using $SUVA_{254}$, did not exhibit a regular diel pattern (Fig. 2c, d). Over the diel period, $SUVA_{254}$ rarely exceeded a variance of 0.25 L mg C^{-1} m^{-1} from the mean. The largest variability in $SUVA_{254}$ was observed during spring 2017 with an approximately 0.5 L mg C^{-1} m^{-1} range throughout the diel period (Fig. 2c). Although a regular diel pattern was not discernable in this dataset, the high springtime variability observed in this study and in a previous study of planktonic community respiration (Bogard et al. 2019b) indicates that changes to DOM composition can occur over short time scales in Canvasback Lake.

Molecular level changes in DOM composition based on compound classes throughout the diel cycle are shown in Table S1. The greatest range in weighted average mass of assigned molecular formulae occurred in spring 2017 (410.9 to 453.7 Da, n = 27); variability through the sampling period was also high in fall 2017, ranging from 418.6 to 458.7 Da (Table 2). Similar to $SUVA_{254}$, the AI_{mod} displayed little distinct diel variability. The greatest variability of AI_{mod} occurred in spring 2017, with a range of 0.268 to 0.281 (n = 27; Table 2). All other seasons displayed low variability in AI_{mod} through the diel cycle (Table 2).

Diel variability in the contribution of highly unsaturated and phenolic compounds was low compared to the other compound classes. The high overall contribution of highly unsaturated and phenolic compounds (mean = 86.24 ± 0.84%) was similar to ranges observed in aquifers and Antarctic lakes (Kellerman et al. 2018) and compared to past studies examining boreal soil leachates (O'Donnell et al. 2016). We recorded little diel change in the condensed aromatics and polyphenolic compound classes associated with terrestrially derived DOM (D'Andrilli et al. 2015). The highest variation occurred in polyphenolic compounds, with a 1.1% relative abundance (6.41 to 7.48%) change in spring 2017 (Table 2) likely reflecting the timing of ice out when terrestrial DOM could be supplied to the lake via runoff. The aliphatic compound class, typically associated with more biolabile DOM (Spencer et al. 2015; D'Andrilli et al. 2015), showed changes of up to 2% relative abundance (2.96 to 5.01%) throughout the diel sampling period, particularly in 2017 (Table 2; Fig. 3). In

Table 3 Representative DOM sources to Canvasback Lake and average seasonal sample DOC concentration and optical, FT-ICR MS, and lignin parameters

Source material type or Sample date	DOC (mg L^{-1})	*a*350 (m^{-1})	SUVA$_{254}$ (L mg C^{-1} m^{-1})	Weighted average mass (Da)	AI$_{mod}$	Highly unsaturated and phenolic (%RA)	Polyphenolic (%RA)	Condensed aromatic (%RA)
Terrestrial sources								
Feathermoss	37.80	35.34	2.91	448.26	0.288	59.23	13.05	5.04
Peat Soil	26.96	49.20	5.83	454.91	0.414	59.41	22.25	11.33
Mineral Soil	12.91	19.48	4.77	436.58	0.412	61.49	20.40	12.65
Fresh Grass	1115.00	304.57	0.74	432.28	0.181	55.83	3.04	2.74
Dried Grass	222.80	308.72	4.91	449.18	0.241	58.16	8.56	2.83
White spruce	364.50	139.87	0.96	460.46	0.316	71.26	12.90	1.26
Autochthonous and littoral sources								
Fall Bulrush	1387.00	262.27	0.41	459.16	0.201	65.96	3.77	0.21
Spring Bulrush	243.90	158.98	2.13	421.21	0.227	67.22	5.93	1.01
Macrophyte	117.70	44.52	1.45	405.21	0.175	48.83	5.56	1.46
Cyanobacteria	291.70	103.05	1.23	393.59	0.214	69.58	9.28	0.32
DOM samples								
13-Sep-16	30.07	10.68	2.18	455.22	0.256	87.91	5.59	1.09
6-Apr-17	124.80	23.25	1.20	453.31	0.242	87.39	3.92	0.60
25-May-17	21.87	9.73	2.64	435.43	0.265	86.18	6.46	1.61
6-Sep-17	25.43	11.39	2.69	435.22	0.267	85.35	6.91	1.71

Source material type or Sample date	Aliphatic (%RA)	Peptide -like (%RA)	Sugar -like (%RA)	Σ_8 (μg L^{-1})	Λ_8 mg (100 mg OC)$^{-1}$)	V (mg (100 mg OC)$^{-1}$)	C/V	S/V	(Ad/Al)$_V$	(Ad/Al)$_S$
Terrestrial sources										
Feathermoss	20.76	1.03	0.89	76.36	0.20	0.12	0.18	0.44	1.75	1.97
Peat Soil	6.00	0.13	0.88	210.72	0.78	0.60	0.08	0.21	1.79	1.67
Mineral Soil	3.70	0.13	1.63	54.77	0.42	0.30	0.27	0.13	0.95	1.79
Fresh Grass	23.62	13.47	1.30	10,348.70	0.93	0.27	1.78	0.68	0.52	1.85
Dried Grass	27.79	1.82	0.84	1807.05	0.81	0.31	0.88	0.73	1.04	1.63
White spruce	14.12	0.00	0.46	2437.38	0.67	0.35	0.91	0.01	0.98	3.27
Autochthonous and littoral sources										
Fall Bulrush	29.18	0.00	0.87	12,729.00	0.92	0.35	0.76	0.86	1.61	1.45
Spring Bulrush	20.16	5.07	0.61	4350.77	1.78	0.46	1.28	1.59	1.10	0.84
Macrophyte	31.72	11.94	0.49	105.17	0.09	0.02	3.16	1.35	0.74	1.04

Table 3 continued

Source material type or Sample date	Aliphatic (%RA)	Peptide-like (%RA)	Sugar-like (%RA)	Σ_8 (μg L^{-1})	Λ_8 mg (100 mg OC)$^{-1}$	V (mg (100 mg OC)$^{-1}$)	C/V	S/V	$(Ad/Al)_V$	$(Ad/Al)_S$
Cyanobacteria	15.99	4.45	0.38	480.36	0.16	0.07	1.13	0.13	1.28	0.86
DOM samples										
13-Sep-16	3.95	0.96	0.49	37.67	0.13	0.04	0.85	1.70	0.99	0.86
6-Apr-17	6.88	0.99	0.22	90.48	0.07	0.03	0.55	1.26	1.27	1.18
25-May-17	3.91	0.82	1.02	39.08	0.16	0.05	0.77	1.48	0.97	0.82
6-Sep-17	4.77	0.38	0.89	30.00	0.12	0.04	0.63	1.43	0.75	0.67

ND indicates where no data is available

Σ_8, lignin phenol concentration; Λ_8, carbon-normalized lignin yield; V, DOC normalized yield of vanillyl phenols; C:V, cinnamyl to vanillyl phenol ratio; S:V, syringyl to vanillyl phenol ratio; $(Ad{:}Al)_v$, vanillic acid to vanillin ratio; $(Ad{:}Al)_s$, syringic acid to syringaldehyde ratio

2017, consistent changes over the sampling period in the relative abundance of aliphatic compounds were observed. Through the spring sampling period, a relative decrease in aliphatic compounds was observed over the 88-hour period, while a relative increase was observed through the fall, 70-hour sampling period (Fig. 3). A significant linear relationship ($p < 0.001$) between the relative abundance of aliphatic compounds and the time of sampling was present in both seasons. This increase occurred irrespective of the time of day when the samples were collected, but rather displayed an increase through the multiday sampling period (Fig. 3). In 2016 the trend of changing aliphatic relative abundance was not observed through the sampling period in either season but the data-set for both spring and fall in 2016 versus 2017 was much more limited both in terms of sample number and duration.

A principal component analysis (PCA) incorporating all data from the open water period shows the distinct differences between sampling seasons and years. Together principal components (PC) 1 and 2 account for 71.2% of the variability within the dataset (Table S3; Fig. 4). The separation along PC1 appears to reflect interannual differences in the indicators of terrestrial DOM contribution (e.g. SUVA$_{254}$, polyphenolic and condensed aromatic percent relative abundance, and AI$_{mod}$). The separation along PC2 reflected seasonal differences in aliphatic percent relative abundance (higher in spring) and DOC concentration and a_{350} (higher in fall). The PCA also reflected variability over shorter, diel timescales, as variations along both PC1 and PC2 also reflect the changes in relative abundance of aliphatic compounds within each sampling period.

Canvasback lake representative source leachate DOM composition

The DOC concentrations from leachates ranged from 12.91 to 1387.00 mg L^{-1} (mean = 382.03 mg L^{-1}, n = 10; Table 3) with the fresh, fall plant material from bulrush and grass leaching more DOC (1387.00 and 1115.00 mg L^{-1}, respectively) compared to their spring counterparts (243.90 and 222.80 mg L^{-1}, respectively). The average a_{350} for all leachates was 142.60 m^{-1} (18.48 to 308.72 m^{-1}, n = 10; Table 3). Unlike DOC concentrations, the fresh, fall material from bulrush and grass (262.27 and 304.57 m^{-1},

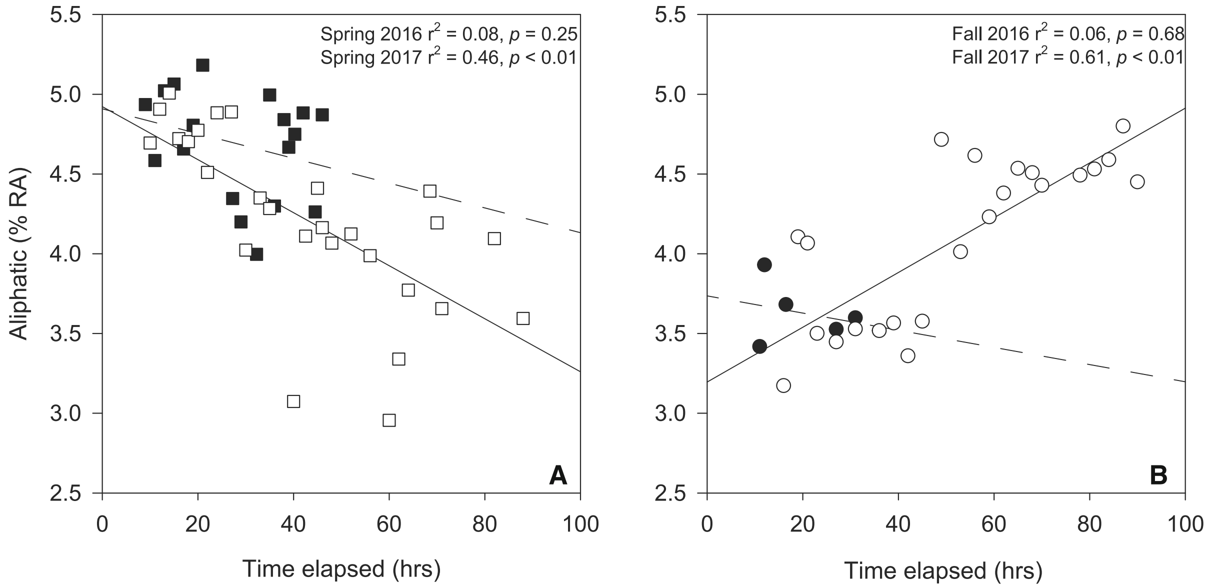

Fig. 3 The relationship between relative abundance of the aliphatic compound class versus the time elapsed through the sampling period: **a** spring (2016—closed squares, dashed line; 2017—open squares, solid line) and **b** fall (2016—closed circles, dashed line; 2017—open circles, solid line). p-values were determined based on a two-tailed t-test and correlations were considered significant at $p < 0.05$

respectively) exhibited a_{350} values similar to dried spring material (158.98 and 308.72 m^{-1}, respectively). Leachate $SUVA_{254}$ values ranged from 0.41 to 5.83 L mg C^{-1} m^{-1} (mean = 2.53 L mg C^{-1} m^{-1}, n = 10; Table 3). The lowest $SUVA_{254}$ values were observed in fall plant material (bulrush, fall grass, and white spruce), whilst the highest $SUVA_{254}$ was observed in peat soil (Table 3), exhibiting a value characteristic of highly aromatic DOM (Weishaar et al. 2003). The mean $SUVA_{254}$ of the leachates was similar to the mean value observed in Canvasback lake (mean = 2.69 L mg OC^{-1} m^{-1}, n = 74; Table S1).

Molecular indicators of DOM composition assessed via FT-ICR MS varied across source types and between seasons (Table 3). Macrophyte and cyanobacteria leachates had the lowest weighted average mass (405.21 and 393.59 Da, respectively), while the white spruce leachate had the highest weighted mass average (460.46 Da). Lake DOM fell within the range of leachate weighted average masses (435.22 to 455.22 Da). In terrestrial sources of DOM, AI_{mod} ranged from 0.181 in fall grass to 0.414 in peat soil, and in the autochthonous and littoral leachates AI_{mod} was generally lower and ranged from 0.175 in the macrophyte to 0.227 in the spring bulrush (Table 3). Lower AI_{mod} was observed for both the fall grass and bulrush (0.181 and 0.201, respectively) compared to the spring plant material (0.241 and 0.227, respectively).

The leachates contained lower relative abundances of highly unsaturated and phenolic compounds (mean = 61.70%; Table 3; Fig. S3) compared to Canvasback Lake bulk DOM (mean = 86.24%, n = 74). Leachates also had higher relative abundances of biolabile aliphatic, sugar-like, and peptide-like compound classes (3.70 to 31.72%, 0.37 to 1.63%, and 0 to 13.47%, respectively; Table 3; Fig. S3) compared to Canvasback Lake DOM. The high relative abundance of the sum of the aliphatic, sugar-like, and peptide-like compound classes leached from the littoral and autochthonous sources (mean = 30.22%) were not reflected in the bulk DOM pool (mean = 6.32%; Table 3; Fig. S3). These littoral and autochthonous leachates also contained low proportions of aromatic DOM (mean = 6.14 and 0.75% for polyphenolics and condensed aromatics, respectively; Fig. S3) compared to terrestrial leachate sources (mean = 13.37 and 5.98%, respectively; Fig. S3). The proportions of polyphenolic and condensed aromatic compounds found in littoral and autochthonous sources were similar to lake bulk DOM (6.74 and 1.60%, respectively; Fig. S3).

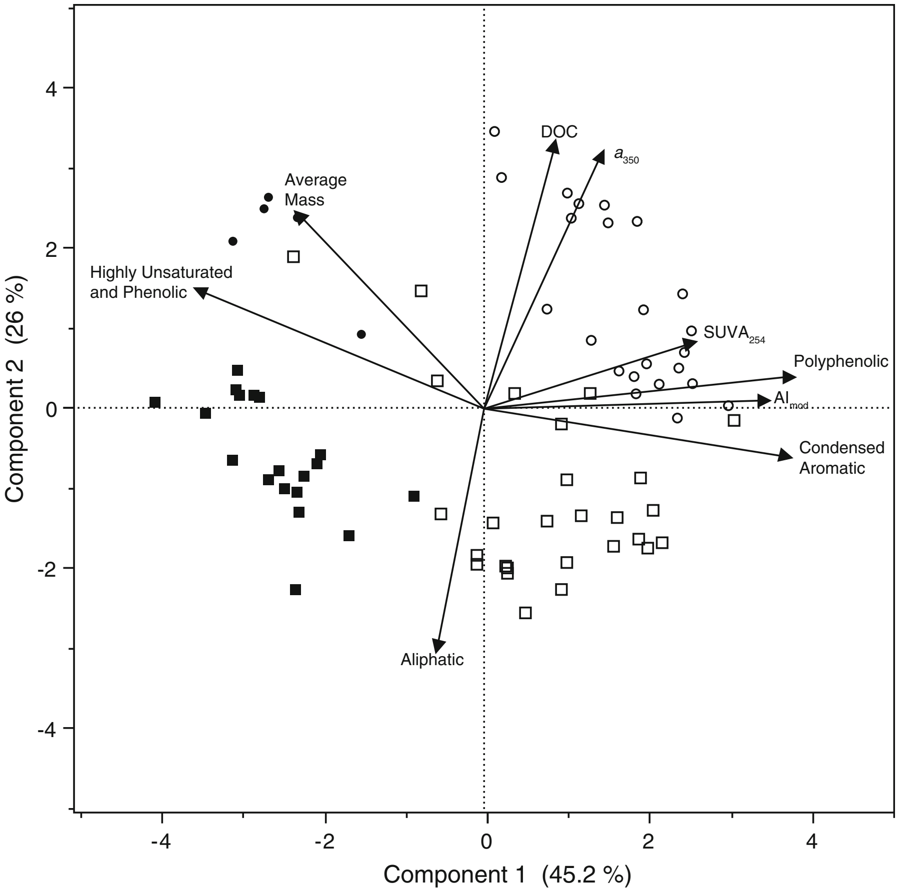

Fig. 4 Principal components analysis score plot of the DOC concentration, optical, and FT-ICR MS parameters for principal components (PC) 1 and 2. Symbols represent sampling season including Spring 2016 (closed squares), Fall 2016 (closed circles), Spring 2017 (open squares), and Fall 2017 (open circles)

Lignin concentrations in leachates ranged from 54.77 ug L^{-1} (mineral soil) to 12,729.00 ug L^{-1} (fall bulrush), and from 30.00 to 90.48 ug L^{-1} in lake DOM. Leachate Λ_8 values ranged from 0.09 in macrophyte and cyanobacteria to 1.78 mg (100 mg OC)$^{-1}$ in bulrush and grasses (Table 3). The Λ_8 observed in lake DOM was low compared to nearly all of the source leachates, ranging from 0.07 to 0.16 mg (100 mg OC)$^{-1}$. To evaluate source contributions, the DOC-normalized yield of only the vanillyl phenols (V) was used. Bulk lake DOM had low V yields (mean = 0.04 mg (100 mg OC)$^{-1}$), n = 4) compared to all terrestrial leachate sources (Table 3; Fig. 5). The higher V from the cyanobacteria compared to the macrophyte leachate (Table 3; Fig. 5) is likely due to the mat being saturated with water when collected and subsequently dried, concentrating the lignin remaining in the water in the leached material. A simple endmember mixing model using the DOC-normalized lignin yield of the vanillyl phenols (V) was performed to evaluate the percent contribution of terrestrial, vascular plant material to the lake DOM (Fig. 5). The lignin analysis included three sources that are not traditionally considered lignin bearing (feathermoss, macrophytes, and cyanobacteria) so are excluded from the endmember mixing model estimates but are shown on Fig. 5 to highlight that other, non-lignin sources contribute to the DOM pool. Based on the mixing model, Canvasback Lake DOM contains a small proportion (approximately 5 to 15% based on the mixing model) vascular plant derived material and varies seasonally with the lowest V in the winter, under-ice period, and highest in spring 2017, just following spring freshet.

DOM source leachates exhibited a range of C:V and S:V ratios corresponding to the different plant types

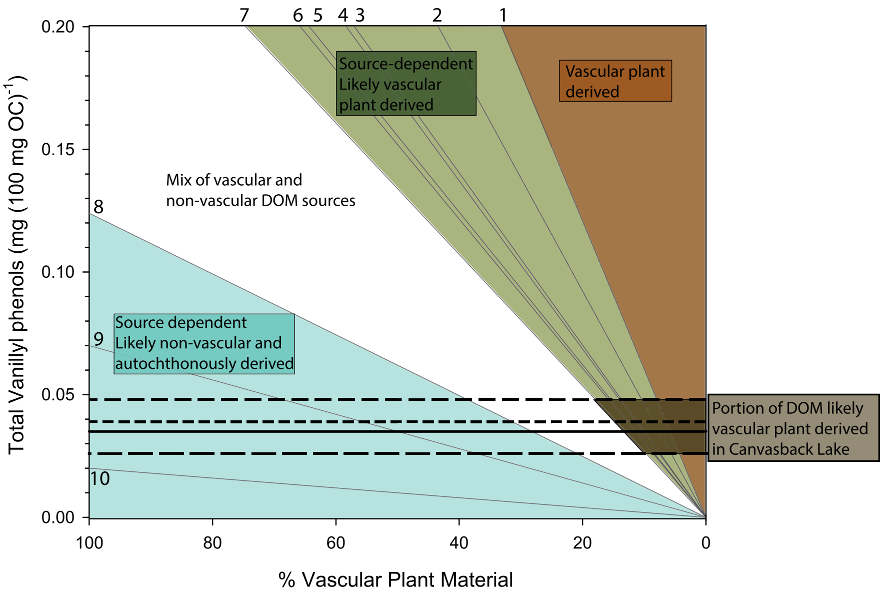

Fig. 5 Carbon-normalized lignin yield of vanillyl phenols (V) endmember mixing model showing the approximate contribution of vascular plant material to the DOM pool. Sloped lines with represent individual source leachates and horizontal lines represent V measured in seasonal samples. Terrestrial sources include peat soil (1), white spruce (4), spring grass (5), mineral soil (6), fall grasses (7), and feathermoss (8); autochthonous and littoral sources including spring bulrush (2), fall bulrush (3), cyanobacteria (9), and macrophyte (10). Horizontal lines represent DOM samples from each season: fall 2016 (solid line), winter 2017 (long dash), spring 2017 (dashed), fall 2017 (short dash). Colored regions indicate the likely source range for each category: red-brown (vascular plant derived), green (source-dependent; likely vascular plant derived), white (mixture of vascular and non-vascular sources), and blue (source dependent; likely non-vascular plant or autochthonously derived). The shaded brown area represents the range of vascular plant material comprising Canvasback Lake bulk DOM

leached (Fig. S2). Notably, macrophyte leachate contained a high proportion of cinnamyl phenols suggestive of a non-terrestrially derived source of cinnamyl phenols. The C:V and S:V ratios of Canvasback Lake lignin corresponded with the expected range of nonwoody angiosperm plant tissues (0.55 to 0.85 and 1.25 to 1.70, respectively; Table 3) similar to the ratios observed in the C:V ratios observed in the spring and fall bulrushes and S:V of the aquatic macrophytes. The mean Ad:Al$_v$ and Ad:Al$_s$ were 1.17 and 1.64, respectively, for leached material (0.52 to 1.79 and 0.84 to 3.27, respectively, n = 10, Table 3). In Canvasback Lake DOM, Ad:Al$_v$ and Ad:Al$_s$ ranged from 0.75 to 1.27 and 0.67 to 1.18, respectively (Table 3), within the range of ratios observed in leachate DOM.

Discussion

Our results characterize temporal variability and cycling of DOM for a shallow, macrophyte dominated lake in an under-sampled, flat, arid, remote northern region. The observations for Canvasback Lake demonstrate that the sources and composition of DOM display temporal variability reflecting both short (diel) and longer term (seasonal and interannual) changes in environmental controls on DOM dynamics. Seasonal scale variability appears to be the largest driver of DOM composition in Canvasback Lake, highlighting the need for sampling lakes seasonally when evaluating patterns of DOM cycling. Additionally, source endmember leachates show little persistence of allochthonous DOM in this lake, with autochthonous production appearing to supply a major portion of DOM. The low persistence of allochthonous DOM suggests that the well-studied lakes in other boreal regions are not representative of the relatively hydrologically disconnected Canvasback Lake and that this lake is more similar to lakes in arid, western Greenland (Saros et al. 2015; Osburn et al. 2017).

Defining the seasonality of dissolved organic matter variability

Variability of DOM composition and DOC concentration occurred across both seasonal and, to a lesser extent, diel time scales (Fig. 4), similar to previous studies of streams, rivers (Spencer et al. 2007; Nimick et al. 2011; Pellerin et al. 2012) and lakes (Müller et al. 2014; Watras et al. 2015). In the spring, the proximity to the freshet appeared to play an important role in DOC concentration and DOM composition with a 1.2 mg L^{-1} difference in average DOC concentration between spring 2016 and 2017 (Fig. 2a) accompanied by lower AI_{mod} in 2016 compared to 2017 (mean = 0.263 and 0.275, respectively) (Table 2; Fig. 2e). These differences underscore the non-linear response of the supply and processing of DOM to Canvasback Lake through time following ice out, whereby aliphatic, biolabile compounds that were either leached into the lake water or accumulated under-ice were rapidly depleted in the spring (Fig. 3a) and that meltwater following ice out provides additional aromatic, allochthonous sourced DOM to the lake. This conclusion that Canvasback Lake and likely other lakes in the region receive a pulse of allochthonous sourced DOM during the spring is consistent with patterns seen in large Arctic rivers during freshet (Holmes et al. 2008; Mann et al. 2012; Wickland et al. 2012). The fall DOC concentrations were similar between the two years (Table 2; Fig. 2b) showing a similarity between DOC concentrations late in the ice-free period of the year when plant growth dominates the littoral and riparian zones of the lake and represents a major source of DOM to the lake.

However, in contrast to the spring 2017 sampling, in the fall the percent relative abundance of aliphatic compounds was significantly positively correlated with time through the sampling period (Fig. 3b). This suggests that in the fall there is an accumulation of aliphatic compounds potentially tied to leaching of fresh plant material with high relative abundances of aliphatic compounds (Fig. S3) and/or a decrease in microbial activity as the daylength becomes shorter and air temperature becomes colder (Adams et al. 2010). Previous studies of ecosystem respiration rates at this site are consistently high in both the spring and fall, suggesting that this may be due to plant decomposition and DOM leaching rather than a decrease in microbial processes (Bogard et al. 2019a).

Throughout the later spring and summer period, longer-term, seasonal scale buildup of DOC and CDOM is likely related to warmer conditions, plus extreme day length and photic periods that sustain increased productivity in the lake and littoral and riparian vegetation growth (Bogard et al. 2019a). Earlier research revealed intense net autotrophic ecosystem metabolism (i.e., net OM production) that lasted from May until mid September in 2016 (Bogard et al. 2019a). This suggests that in situ production of DOM follows strong seasonal patterns and is a major control on DOM composition within the lake (i.e. not allochthonous inputs).

A nearly fivefold increase in DOC concentration under-ice compared to spring 2017 samples (124.80 and 21.87 mg L^{-1}, respectively) shows that this lake undergoes intense freeze exclusion of DOM and liquid water loss (Ågren et al. 2012; Müller et al. 2013). Formation of approximately 1 m of ice on a 2 m deep lake results in a substantial loss of liquid water to ice in winter. The lower lignin yield (0.07 and 0.16 mg $(100\ \mathrm{mg\ OC})^{-1}$, respectively), $SUVA_{254}$ (1.20 and 2.71 L mg C^{-1} m^{-1}, respectively) and relative abundances of polyphenolic (3.92 and 6.46%, respectively) and condensed aromatic (0.60 and 1.61%, respectively) compound classes demonstrate that under-ice, there is a reduced contribution of allochthonous sources to the DOM pool (Table 3). This lower contribution of allochthonous DOM under-ice is also similar to the decrease seen in the major Arctic rivers (Striegl et al 2005, 2007; Spencer et al. 2008; O'Donnell et al. 2010; Mann et al. 2016). The presence of iron could cause a significant overestimate of $SUVA_{254}$ (Poulin et al. 2014), however, the similar trends seen between $SUVA_{254}$ and other terrestrial DOM proxies indicates that error introduced by iron on absorbance data would not impact the conclusions of this study. Further, these results suggest that much of the intense spring DOM dynamics are driven by both internally-derived OM inputs, and a spring influx of allochthonous OM, however, allochthonous contribution remains relatively low through the ice-free period in comparison to the OM dynamics observed in more fluvially-dominated systems in other northern landscapes (Spencer et al. 2008). In Canvasback and other similar lakes in the study region, intense autotrophic growth that initiates shortly after ice-out (Bogard et al. 2019a) is strongly in line with our observation that internally derived materials are a major source of the lake's OM.

Seasonal variations of nearly 20% between spring and fall averages in DOC concentration with accompanying changes in DOM composition (i.e. decreases in aliphatic compounds from spring to fall) along with increased evapoconcentration through the ice-free season could lead to different conclusions when evaluating DOM sources and processing in lakes. This is supported by a recent study that found that six to seven and two to three samples, respectively, were needed to capture changes in CO_2 and CDOM across circumpolar lakes in Sweden in order to accurately assess lake carbon cycling (Klaus et al. 2019).

Small relative variability in diel dissolved organic matter characteristics

Principal components 1 and 2 of the PCA (Table S3; Fig. 4) strongly reflected variability in DOM composition across longer timescales (seasonal, interannual), with a clear nesting of smaller-scale DOM diel changes within larger seasonal and interannual patterns. Variation along PC1 reflects interannual differences (i.e., from open to closed symbols) in aromatic DOM content, and accumulation of terrestrial DOM ($SUVA_{254}$, percent relative abundance of polyphenolic and condensed aromatic compound classes). Variability along PC2 reflected seasonal differences in DOC concentrations and availability of aliphatic compounds. Although diel variability was not the most important timescale structuring the PCA axes, short time scale changes were still reflected within the higher variability of PCA scores, particularly for the spring sampling seasons (Fig. 4). Therefore, for Canvasback Lake, sampling at seasonal and interannual scales appears to capture most (> 70%) of the variability observed in DOM composition and DOC concentration. While diel sampling might be useful for understanding mechanistic drivers of short timescale changes: the net change of DOC, for example, is 80 mg L^{-1} over the seasonal scale while over the diel scale the maximum change observed was 3 mg L^{-1}. However, these diel changes have been linked to planktonic community respiration, which varied 17-fold through the diel period (Bogard et al. 2019b). These data suggest that diel sampling does not add significantly to our interpretation of DOM composition and cycling gathered from seasonal sampling.

Leachate DOM persistence through time

A majority of endmember source leachates contain more energy-rich aliphatic compounds compared to lake bulk DOM (Fig. S3; Table 3), suggesting rapid turnover of the biolabile pool sourced from leachate DOM. Autochthonous sources including cyanobacteria, aquatic macrophytes, and spring and fall bulrush showed high relative abundances (20.82–44.15%; Fig. S3) of biolabile compounds (sum of aliphatic, sugar-like, and peptide-like compounds) (D'Andrilli et al. 2015). The abundant growth in the lake of organisms that generate this more biolabile DOM suggests that they may be large contributors to the bulk DOM pool. This is supported by the high rates of primary production measured in the spring and summer in Canvasback lake (Bogard et al. 2019a). However, the high relative abundance of the aliphatic, sugar-like, and peptide-like compounds detected in the leachates was absent in bulk lake DOM (Table 3). It is likely that these compounds are rapidly metabolized, a hypothesis consistent with the high rates of ecosystem respiration measured throughout the entire ice-free period (Bogard et al. 2019a).

Lake bulk DOM was dominated by highly unsaturated and phenolic compounds (over 85% of assigned molecular formulae) that appeared to persist in the environment over much longer timeframes than the biolabile pool. The abundance of highly unsaturated and phenolic compounds in the bulk DOM compared to leachate DOM suggests a degradation pathway (microbial, photochemical or both combined) from more biolabile to more stable compounds, or an overall persistence of highly unsaturated and phenolic compounds with rapid cycling of biolabile compounds (Rossel et al. 2013; D'Andrilli et al. 2016). This is also evident when comparing the composition of spring and fall bulrush leachates where the fresh, fall material was collected during the growing season and the dried, spring material was collected in the spring from growth from the previous year. Bulrush collected in spring that had been subjected to previous degradative processing had much higher $SUVA_{254}$ compared to the fall material (2.13 and 0.41 L mg C^{-1} m^{-1}, respectively); higher AI_{mod} (0.227 and 0.201), relative abundances of condensed aromatics (1.01 and

0.21%), and polyphenolics (5.93 and 3.77%); and lower weighted average mass (421.21 and 459.16 Da). The feathermoss, peat soil, and mineral soil also follow this trend from fresher, more aliphatic containing DOM to more aromatic containing DOM with depth in the soil column. This is consistent with previous findings from boreal soil leachates showing a lower abundance of the aliphatic compound class and higher condensed aromatic and polyphenolic compound classes with increasing depth (O'Donnell et al. 2016). These suggest that increasing degradation pathways lead to leachate DOM that initially appears more similar to lake DOM, with much of the fresh biolabile signal being degraded prior to being leached.

The hydrologic connectivity of shallow lakes in the Yukon Flats region is generally low (Anderson et al. 2013) and there is little surface runoff in this arid region, decreasing the role of allochthonous sources to the lake and driving the chemodiversity of the lake toward a more autochthonous endmember. Carbon-normalized lignin yields, an indicator of the contribution of terrestrial C to the total DOC pool, support this conclusion, showing low terrestrial inputs to Canvasback Lake throughout the year (0.07–0.16 mg(100 mg OC)$^{-1}$; Table 3) in comparison to values seen in fluvial ecosystems that receive extensive surface inputs in the Yukon River Basin (0.17–0.48 mg (100 mg OC)$^{-1}$; Spencer et al. 2008). Chemodiversity patterns were consistent with lignin yield patterns. The condensed aromatic and polyphenolic compounds were more abundant in mineral and peat soil leachates (33.05 and 33.59%, respectively) and feathermoss and dried grass leachates (18.1 and 11.4% relative abundance) than in the lake bulk DOM (7.7%). This suggests that these external sources were only minor sources of DOM to the lake. It is possible that their signal is diminished by degradative processes such as photodegradation of aromatic compounds toward more highly unsaturated and phenolic compounds (Stubbins et al. 2010). Yet this is unlikely given that contributions from photo-chemical degradation of allochthonous DOM decline in systems with weak hydrologic connectivity to the landscape (Lapierre and Giorgio 2014).

The average V and Λ_8 for lake DOM were generally low (0.037 and 0.12 mg (100 mg OC)$^{-1}$, respectively) compared to other lake systems (Osburn et al. 2011) and Arctic rivers (Amon et al. 2012; Mann et al. 2016). Canvasback Lake contained a small proportion of vascular plant material (~ 5–15%) based on the endmember mixing model. In comparison, the average V yield of the Yukon River was 0.15 mg (100 mg OC)$^{-1}$ (Spencer et al. 2008), or approximately 20–50% vascular plant material when this endmember model was applied (Fig. 5). The decrease in lignin yield during the winter is consistent with decreases under-ice observed in the six largest Arctic rivers (Amon et al. 2012; Mann et al. 2016) and, while DOC and Σ_8 both increase under-ice, Σ_8 is not concentrated as efficiently, accounting for the decrease in V under-ice. This suggests that during the under-ice period it is unlikely that there are additional lignin sources from leaching of mineral or peat soils into the lake, but rather an enrichment of autochthonous DOM from microbial processes under-ice (Fig. 5). Ultimately, comparison between Canvasback Lake and the nearby Yukon River highlights that this lacustrine system receives much less allochthonous DOM compared to riverine systems.

Implications for lake dissolved organic matter cycling

By accounting for the variability of DOM composition and DOC concentration across diel to annual time scales, we show that the hydrologically-isolated Canvasback Lake receives small contribution of allochthonous DOM compared to boreal and arctic rivers (Spencer et al. 2008; Johnston et al. 2018), or more hydrologically connected lakes in other high-latitude regions (Tranvik et al. 2009; Lapierre et al. 2013). Low terrestrial C inputs to Canvasback Lake, despite littoral and riparian vegetation leachates having high lignin yields, suggests that these sources of DOM do not persist in the lake either by degradation or lack of supply to the lake, and that lake DOM is dominated by persistent, highly unsaturated and phenolic compounds (Tables 2, 3 and Fig. S3). The relatively high abundance of aliphatic compounds identified in the source leachates but not in the lake DOM further supports this conclusion. Overall, these findings add to the growing understanding that some remote, hydrologically isolated lakes are active processors of DOM produced within the lakes and thus may play a minor regional role in cycling allochthonous terrestrial C (Tank et al. 2011; Osburn et al. 2011; Bogard et al. 2019a).

This study further highlights the need for seasonally-resolved sampling to accurately characterize C dynamics in this dynamic circumpolar lake system for process-based evaluations of DOM cycling. Over large spatial scales the importance of seasonal sampling may be less critical compared to studies evaluating the regional sources and cycling of DOM. Although diel-scale variability in DOM characteristic was small relative to that over longer timescales, PCA results showed that a great deal of variability in DOM content and composition in Canvasback Lake is observed across seasons. For instance, DOC accumulated in the lake from spring to fall with little change in Λ_8 (Table 3), with a fivefold increase in concentration and $\sim$ 50% decrease in Λ_8 over the annual cycle in 2017. This variability reflected seasonal shifts in DOM source input that are important to account for in evaluating the lake DOM cycling and composition and similar to a recent study of CO_2 and CDOM variability through seasonal to annual timescales in Swedish lakes (Klaus et al. 2019). The under-ice period showed the most pronounced change in DOM composition, however, from spring to fall the buildup of CDOM and loss of aliphatic DOM shows shifting DOM processing through the ice-free period following the shift from autotrophy to heterotrophy reported in Bogard et al. (2019a, b). Although it is unclear how lake C cycling will respond as the Yukon Flats region undergoes changes related to warming induced drought, wildfire frequency, and hydrologic shifts linked to permafrost thaw (Prowse et al. 2006; Walvoord et al. 2012; Bring et al. 2016; Pastick et al. 2018; Rey et al. 2019), this study serves as an important baseline to evaluate future changes, and underscores the importance of accounting for seasonal variability when assessing the role of lake DOM sources and lability in relation to regional-scale arctic C cycling.

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