



RESEARCH ARTICLE

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Key Points:

- Mean annual precipitation exerted a strong control on quantity and quality of lake DOM
- DOM in lakes with low hydrological connectivity experienced substantial microbial and photochemical degradation
- The climatic gradient under which the SW Greenland lakes currently exist may reflect the future changes in Arctic lake C cycling to be expected

Supporting Information:

- Supporting Information S1

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Shifts in the Source and Composition of Dissolved Organic Matter in Southwest Greenland Lakes Along a Regional Hydro-climatic Gradient

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Abstract Dissolved organic matter (DOM) concentration and quality were examined from Arctic lakes located in three clusters across south-west (SW) Greenland, covering the regional climatic gradient: cool, wet coastal zone; dry inland interior; and cool, dry ice-marginal areas. We hypothesized that differences in mean annual precipitation between sites would result in a reduced hydrological connectivity between lakes and their catchments and that this concentrates degraded DOM. The DOM in the inland lake group was characterized by a lower aromaticity and molecular weight, a low soil-like fluorescence, and carbon stable isotope ($\delta^{13}\text{C}\text{-DOC}$) values enriched by $\sim 2\%$ relative to the coastal group. DOC-specific absorbance (SUVA_{254}) and DOC-specific soil-like fluorescence (SUVC_1) revealed seasonal and climatic gradients across which DOM exhibited a dynamic we term “pulse-process”: Pulses of DOM exported from soils to lakes during snow and ice melt were followed by pulses of autochthonous DOM inputs (possibly from macrophytes), and their subsequent photochemical and microbial processing. These effects regulated the dynamics of DOM in the inland lakes and suggested that if circumpolar lakes currently situated in cool wetter climatic regimes with strong hydrological connectivity have reduced connectivity under a drier future climate, they may evolve toward an end-point of large stocks of highly degraded DOC, equivalent to the inland lakes in the present study. The regional climatic gradient across SW Greenland and its influence on DOM properties in these lakes provide a model of possible future changes to lake C cycling in high-latitude systems where climatic changes are most pronounced.

Plain Language Summary Arctic regions are currently experiencing change due to warming climate, and Arctic lakes are natural recorders of this change. We conducted a study of 20 Arctic lakes situated across a climatic gradient in southwest Greenland ranging from cool and wet coastal region to a warm and dry inland region. We found that Arctic carbon cycles are responding to this change by concentrating dissolved organic carbon (DOC), a collection of molecules that form the basis of lake food webs, which may be very old and represent long-term accumulation of carbon in these lake waters. We suspect that the force driving this change is a loss of the connectivity between these lakes and their watersheds. Under this scenario, lakes receive less organic carbon from soils in their surrounding watersheds and perhaps more from fringing aquatic plants. Moreover, earlier loss of lake ice may lead to longer open water periods and the chance for sunlight to convert DOC to carbon dioxide, representing a feedback to regional climate. As global change influences the Arctic broadly, modifications to the hydrologic connectivity of lakes to their watersheds may have important implications for Arctic inland C cycling.

1. Introduction

Arctic terrestrial organic carbon (C) stores are substantial ($\sim 1,400$ Pg; Tarnocai et al., 2009) but are becoming increasingly reactive and mobile as the biogeochemically active layer deepens with regional warming and as soil microbial activity is enhanced (Cory et al., 2013). Coupled with altered hydrology, these processes driven by changes in global climate result in a growing fraction of the C pool being transferred laterally as particulate and dissolved organic matter (DOM) to streams and lakes (Tank et al., 2012). Moreover, transfer of terrestrial C is complemented by an increase in primary production in lakes due to lengthening of the growing season and elevated nutrient availability (derived from melting permafrost and atmospheric deposition; e.g.,

Anderson et al., 2017), which potentially provides a further autochthonous source of DOM. These changing C sources suggest that the optical and chemical properties of the DOM in Arctic lakes will change as Arctic regions undergo warming.

Lakes are an important component of many Arctic landscapes and represent hot spots of biogeochemical processes. Arctic lakes are located in environments undergoing climate change at unprecedented rapidity. Roughly 80% of Arctic lakes are situated in tundra landscapes with continuous permafrost, which is changing rapidly (Vincent et al., 2008). The abundance of lakes at high latitudes is exemplified in the Kangerlussuaq area of SW Greenland where ~15% of the land surface consists of lakes (Anderson et al., 2001). This lake district spans well-defined climate, permafrost, environmental, and limnological gradients from the edge of the Greenland ice sheet to the coast. There are clear gradients in effective precipitation and air temperature that influence vegetation and landscape hydrological connectivity (Anderson et al., 2017). These climatic controls result in distinct differences in limnology, for example, thermal stratification, conductivity, nutrients, and hypolimnetic oxygen availability, but most notably of lake dissolved organic carbon (DOC) concentrations from ice sheet to coast (Anderson & Stedmon, 2007).

Sobek et al. (2007) suggested a hierarchical regulation of DOC in lakes in which climate and topographic characteristics set a range of DOC concentrations for a region of lakes. Catchment and lake properties, such as the proportion of wetland and water residence time, influence DOC within a particular lake. Specifically, lakes with high hydrological connectivity are expected to have comparatively high DOC concentrations as a result of allochthonous C inputs. In this study, we define *hydrological connectivity* with respect to lake DOM cycling, as water-mediated transfer of organic matter to a lake from its landscape (Tetzlaff et al., 2007). Currently, the presence of continuous permafrost means that the hydrological connectivity of SW Greenland lakes to their watersheds via subsurface linkages between tundra soils and lakes is limited. Therefore, we expect that surface runoff dominates and is closely linked to mean annual precipitation (m.a.p.) (Anderson et al., 2017). We anticipate that hydrological connectivity exhibits seasonal variability across the precipitation gradient in which the SW Greenland lakes are situated, strengthening as spring snowmelt runs into the lakes, but weakening as summer progresses, where evapoconcentration in the inland lakes becomes important as indicated by their higher conductivity (Anderson et al., 2001, 2017; Anderson & Stedmon, 2007).

DOC concentrations of Greenland lakes are well described and appear to fit the hierarchical regulation suggested by Sobek et al. (2007) (Anderson & Stedmon, 2007). However, DOM characteristics are not well described, and yet they are important to understand with respect to DOM processing and reactivity as the lakes in the Kangerlussuaq area respond to rapid regional warming (Anderson et al., 2017). Moreover, recent work has shown coherent declines in mean lake DOC concentrations across SW Greenland over the past 10 years, which suggests an alteration, or perhaps an acceleration, of Arctic lake C cycling in this area of rapid global environmental change (Anderson et al., 2017; Saros et al., 2015).

The aim of this paper is to examine the potential sources of DOM in the Arctic lakes of Greenland using chromophoric DOM (CDOM) absorption and fluorescence across well-defined limnological and climate gradients. We summarize observations made over 10 years and place our findings in context of hydrological connectivity of these lakes to their watersheds. We extend the Sobek paradigm to DOM quality by hypothesizing that lakes with higher m.a.p., and thus stronger hydrological connectivity, have DOM characteristics consistent with that of soil-derived DOM. We further hypothesized that lakes with lower m.a.p., and thus weaker hydrological connectivity, accumulate heavily degraded DOM resulting from microbial and/or photochemical processing of both soil-derived and internally produced organic matter. Thus, we expect these lakes to have higher concentrations of DOM but also DOM that is less reactive than that present in lakes with lower concentrations of fresher DOM. Our results are viewed in the context of a rapidly changing Arctic climate and suggest alterations to lake C cycling at northern latitudes that may occur under drier climatic scenarios.

2. Methods

2.1. Study Area

The lakes in this study are located across an approximately 130 km transect ranging from the coast of SW Greenland inland through the Kellyville (Central) region toward the edge of the ice sheet. This transect represented a longitudinal gradient of mean summer temperatures and m.a.p. across SW Greenland that we define

as a cool-wet Coastal region near 53°W (8°C, 410 mm), containing low Arctic maritime vegetation. Evaporation is an important climatic variable in a warm-dry Central region near 51°W (11°C, 183 mm) and a cool-dry Ice margin region near 50°W (8°C, 269 mm) (Nielsen, 2010). Two lakes of the Ice margin region are fed by glacial meltwater. The ages of the lakes range from 10,000 years (Coastal group) to 8,000 years (Central group) to ~4–5,000 years (Ice margin group) (Bennike & Björck, 2002). Locations and physical properties of the lakes grouped by these regions can be found in Tables S1 and S2. The primary sampling strategy was determined by prior knowledge of the regional limnology (Anderson et al., 2001; Whiteford et al., 2016): we sampled lake clusters with distinctive limnology to provide regional replication when determining lake DOM characteristics, across the longitudinal climatic gradient. The data set contained 20 lakes sampled intensively during 2009, 2013, and 2014 (Table S1), along with data from 29 lakes sampled in 2002 and 2003 (Anderson & Stedmon, 2007) (Table S2).

2.2. Sampling Methods

Water sampling for DOM absorbance and fluorescence, and DOC concentrations was conducted between June and August for all years, with additional under-ice water sampling conducted in April 2014. Sampling was not consistent between years; e.g., Coastal lakes were not sampled in 2003, 2009, or 2014 while in 2013, no under-ice samples were taken. Therefore, we were not able to critically address seasonality effects (see Table S1 for sampling dates). Sampling details for lakes sampled in 2002 and 2003 can be found in Anderson and Stedmon (2007) but were consistent with subsequent sampling in 2009, 2013, and 2014. Sampling was conducted via a small rubber boat at approximately the deepest part of each lake. Surface water samples in this study were collected from the epilimnion of each lake via Van Dorn samplers and filtered through precombusted (450°C, 6 h) Whatman GFF glass fiber filters (0.7 μm nominal mesh size) and stored frozen until analysis, generally from 3 to 6 months after collection. For the 2002 and 2003 lake samples, filtration was achieved through 0.45 μm porosity filters. Anderson and Stedmon (2007) compared results using both filter sizes and note <5% difference. Surface soils (5–10 cm depth) were collected in August 2014 near several lakes each in the Central ($n = 5$) and Ice margin ($n = 4$) regions and a known mass (12–25 g) of wet soil added to 50 mL ultrapure laboratory water and extracted in the dark for 24 h. Then, the soil extract solutions were filtered through GFF filters and treated as any other DOM sample.

2.3. Optical Properties

Prior to measurement for absorbance and fluorescence, samples were thawed to room temperature. Absorbance was measured between 240 and 750 nm on a Varian 300 UV spectrophotometer using 1, 5, or 10 cm quartz cells depending on the amount of CDOM present in the sample. Strongly absorbing samples having optical density >0.4 at 240 nm were diluted. Ultrapure Milli-Q laboratory water (18.2 MΩ resistivity) was used as a blank. Absorbance was converted to Napierian absorption coefficients (a , in m^{-1}) using the following equation:

$$a_{\lambda} = \frac{2.303A_{\lambda}}{L}, \quad (1)$$

where A is the blank-corrected absorbance from the spectrophotometer, λ is the wavelength in nm, and L is the path length of the quartz cell in meters. CDOM was quantified with the absorption coefficient at 254 nm, a_{254} . Several derived parameters from absorption were computed to assess CDOM quality. Specific ultraviolet absorption at 254 nm ($SUVA_{254}$) was computed as the decadal absorption at 254 nm divided by DOC concentration as an index of aromatic carbon content ($m^2 g^{-1} C$) (Weishaar et al., 2003). Likewise a_{375}^* was computed as the Napierian absorption at 375 nm divided by DOC concentration. The latter index was computed to compare our results with prior work (Anderson & Stedmon, 2007).

CDOM absorption decreases with increasing wavelength in an approximately exponential fashion. The rate of change in absorption with wavelength is quantified as the slope (S) of an exponential function fit to an absorption spectrum and is indicative of DOM quality. Absorption spectral slopes, S , were measured from 300 to 650 nm with the following equation:

$$a_{\lambda} = a_{\lambda_0} e^{-S(\lambda_0 - \lambda)} + K, \quad (2)$$

where λ_0 is 375 nm and K is a background constant. Spectral slopes also were measured from 275 to 295 nm ($S_{275-295}$) and from 350 to 400 nm ($S_{350-400}$) with the spectral slope ratio (S_R) being the ratio of the slopes computed over these two narrower wavebands (Helms et al., 2008).

CDOM fluorescence was measured on separate Varian Eclipse spectrofluorometers for the 2002–2003 data and the 2009–2014 data. For each instrument, standard corrections for lamp excitation and detector response were applied as well as corrections for inner filter effects. Fluorescence intensity was calibrated into Raman units (Cory et al., 2010; Lawaetz & Stedmon, 2009). Excitation wavelengths were sampled from 240 to 450 nm at 5 nm intervals. Emission wavelengths were sampled from 300 to 600 nm at 2 nm intervals. Milli-Q water was used as a blank. Emission spectra were concatenated into excitation-emission matrices (EEMs) and visualized as contour plots. Two parameters derived from EEM fluorescence, the biological index (BIX) and the humification index (HIX), were extracted from EEMs measured on each sample. BIX indicates recent autochthonous biological production, while HIX indicates the degree of complex, high molecular weight organic matter rich in aromatic moieties, resulting from the formation of humic substances (Birdwell & Engel, 2010).

2.4. Dissolved Organic Carbon (DOC)

After optical analyses, samples were acidified with 85% H_3PO_4 to pH 2 and sparged for 10 min with ultra-high purity argon to remove inorganic carbon (as CO_2). Sparged samples were then measured for DOC and $\delta^{13}\text{C}$ -DOC on an OI Analytical 1030D Aurora analyzer in wet oxidation mode coupled to a Thermo Delta V Plus isotope ratio mass spectrometer (Osburn & St-Jean, 2007). DOC concentrations were calibrated each analytical day with prepared solutions of caffeine, and $\delta^{13}\text{C}$ values were normalized to the Vienna Pee Dee belemnite (‰ versus PDB) scale with prepared solutions from IAEA sucrose ($\delta^{13}\text{C} = -10.8\text{‰}$) and caffeine ($\delta^{13}\text{C} = -27.77\text{‰}$). Error on DOC concentrations was $<3\%$, and reproducibility on $\delta^{13}\text{C}$ -DOC values was $\pm 0.19\text{‰}$ ($N = 23$).

2.5. Literature Data

Absorbance and DOC concentration data from 2002 and 2003 (exclusive of high conductivity oligosaline lakes) were acquired from Anderson and Stedmon (2007). Details of sampling and analysis protocols are contained therein. Briefly, CDOM absorbance was measured on a Shimadzu UV-2401PC spectrophotometer, while DOC concentrations were measured on a Shimadzu 5000 TOC analyzer. EEM fluorescence also was measured on those samples on a Varian Eclipse spectrofluorometer, but not included in that study; these data are included in the present study.

2.6. Parallel factor analysis Modeling

Parallel factor analysis (PARAFAC) was conducted on fluorescence EEMs from SW Greenland lakes sampled during 2002–2003 and during 2009–2014 (Stedmon et al., 2003). Each EEM was normalized to its integrated fluorescence, which allows highly fluorescent and weakly fluorescent samples to be modeled simultaneously without highly fluorescent samples exerting significant leverages on the PARAFAC model (Murphy, Bro, et al., 2014). A series of three to eight component models were fitted to the data, and a six-component model was validated. Model validation was achieved through splitting the data in half and modeling each half separately, fitting 10 models with random starts, and by inspection of residuals (Murphy, Bro, et al., 2014). The loadings in the excitation and emission mode for each component were matched to the OpenFluor database, a collection of PARAFAC models from a variety of natural and artificial systems (Murphy, Stedmon, et al., 2014). Matching at $>95\%$ similarity was used to determine if a component was identical to components from other models. MATLAB software and the toolbox DOMFluor were used for all PARAFAC models (Stedmon & Bro, 2008).

2.7. Statistical Tests

Most DOM concentration variables (e.g., a_{254} and DOC) had significantly different standard deviations as determined by Bartlett's test, so comparisons of DOM optical and chemical median values among lake regions were made using a Kruskal-Wallis nonparametric analysis of variance (ANOVA) with a Mann-Whitney posttest, or modeled with permutational multivariate analysis of variance (PERMANOVA) based on Euclidean distances (permutation $n = 9,999$ using a bootstrap approach) and conducted in PAST v.3.0. For correlation analysis, Pearson's coefficient (r) was computed for normally distributed data and Spearman's rho (ρ) was computed on ranks for nonnormally distributed data. Principal component analysis (PCA) was conducted on a subset of results using the PLS_Toolbox for MATLAB to explore DOM optical and chemical variables in relation to any separation of sample scores between the lakes, grouped by region. Data for PCA were mean-centered prior to modeling. A linear mixed effects regression model (lme) was fitted to

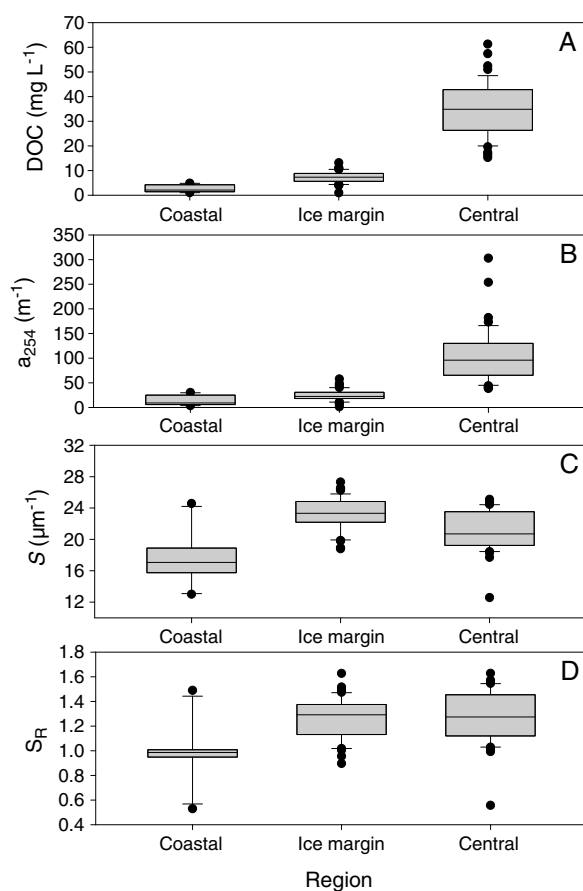


Figure 1. Boxplot of DOM properties in surface water samples collected from lakes in the cool-wet Coastal region, the warm-dry Central region, and the cool-dry Ice margin region of SW Greenland (see Table S1). (a) CDOM absorption coefficient, a_{254} ; (b) DOC concentration; (c) spectral slope value, S , from 300 to 600 nm; and (d) slope ratio, S_R . For Coastal lakes, $N = 10$; for Central lakes, $N = 46$; and for Ice margin lakes, $N = 40$.

seasonal $SUVA_{254}$ and DOC-specific fluorescence (SUVF) data from 2014 using the Statistics and Machine Learning Toolbox for MATLAB. These variables were included as fixed effects, which influenced the slope of the regression and random effects grouped by month, which influenced the intercept.

3. Results

3.1. DOC and CDOM Concentrations in Lakes Along Kangerlussuaq

DOC and CDOM concentrations varied both seasonally and spatially in lakes across SW Greenland (Figure 1), but in general were highly related ($\log \text{DOC} = -0.415 \pm 0.061 + 0.955 \pm 0.037 \times \log a_{254}$; adjusted $R^2 = 0.88$; $p < 0.0001$; $n = 96$). Summary statistics were based on ranks because most variables did not pass Bartlett's test of equal standard deviations. In general, the central lake group had much higher median concentrations of DOC (34.92 mg L^{-1}) than the Coastal lake group (2.14 mg L^{-1}) or the Ice margin lake group (7.33 mg L^{-1}) (Table 1). The Central lake group had the lake with the overall highest DOC concentration (61.30 mg L^{-1}), while the Ice margin lake group had the lowest DOC concentration (0.98 mg L^{-1}), which was very similar to the minimum DOC concentration of the Coastal lake group (1.02 mg L^{-1}). The Central lake group also had the largest amount of CDOM quantified as the absorption coefficient at 254 nm (a_{254} ; Table 1) and exemplified in absorption spectra from 250 to 550 nm (Figure S1 in the supporting information). Median a_{254} value for the Central lake group (96.10 m^{-1}) was over fourfold higher than the median for the Ice margin lake group (22.47 m^{-1}) and nearly tenfold higher than the Coastal lake group (9.36 m^{-1}). When considered together, these differences in median DOC concentrations and median a_{254} values were significantly different among the lake groups (PERMANOVA: $F = 59.43$; $P = 0.0001$). Further, both DOC and a_{254} were negatively correlated with m.a.p. (Pearson's $r = -0.891$ and -0.770 , respectively; $P < 0.0001$ for both variates).

3.2. CDOM Absorption and Fluorescence

CDOM quality, as determined by spectral slope values (S and S_R), also varied among the lake groups. Median S value for the Coastal lake group was $17.07 \mu\text{m}^{-1}$ and increased for the Ice margin lake group ($20.71 \mu\text{m}^{-1}$) to the highest median value for the Central lake group ($23.33 \mu\text{m}^{-1}$). Significant differences were found between medians of all lake groups, indicating that the Central lakes had higher CDOM absorption than the Ice margin and Coastal lakes ($P < 0.0001$; Figure S1). A similar result was found for differences among S_R values for each lake group. Median S_R values were lowest for the Coastal lakes (0.99) and higher for the Central (1.29) and Ice margin (1.28) lakes. The Coastal lake S_R values were significantly different from both the Central lakes and the Ice margin lakes ($P < 0.001$ in each case), though the Central and Ice margin lakes were not significantly different from one another ($P = 0.562$).

Despite the Central lake group being markedly different from the Coastal and Ice margin lakes with respect to DOC concentration and CDOM absorbance, excitation-emission matrix (EEM) spectra of examples of lakes from each lake group exhibited both common and distinct patterns (Figure S2). The DOM fluorescence intensity varied widely as across lake groups and was greatest for the Central lakes. For example, Coastal lake AT10 had fluorescence values approaching four QSU and centered on excitation/emission (Ex/Em) of 240/430 (nm/nm), squarely in the region of typical freshwater CDOM fluorescence (Figure S2a). Notable secondary Ex/Em occurred in the protein-like fluorescence region (275/340). Central lake SS2 had fluorescence values approaching nearly 60 QSU (Figure S2b), whereas Ice margin lake SS906 had maximum fluorescence

Table 1
Summary Statistics for Surface Water (0.5 m Depth) DOM Properties in the SW Greenland Lakes

Variable		Lake group		
		Coastal (<i>n</i> = 10)	Central (<i>n</i> = 46)	Ice margin (<i>n</i> = 40)
DOC (mg C L ⁻¹)	Median	2.14	34.92	7.33
	Min.	1.02	15.31	0.98
	Max.	4.90	61.30	13.17
<i>a</i> ₂₅₄ (m ⁻¹)	Median	9.36	96.10	22.47
	Min.	3.71	38.75	1.58
	Max.	30.41	302.89	57.86
<i>S</i> (μm ⁻¹)	Median	17.07	23.33	20.71
	Min.	13.00	18.79	12.57
	Max.	24.57	27.32	25.10
<i>S_R</i>	Median	0.99	1.29	1.28
	Min.	0.53	0.90	0.56
	Max.	1.49	1.63	1.63
SUVA ₂₅₄ (L mg C ⁻¹ m ⁻¹)	Median	2.23	1.18	1.40
	Min.	1.18	0.57	0.64
	Max.	3.21	2.96	2.30
<i>a</i> ₃₇₅ [*] (L mg C ⁻¹ m ⁻¹)	Median	0.73	0.17	0.23
	Min.	0.19	0.06	0.07
	Max.	0.93	0.65	0.72
δ ¹³ C-DOC (‰ versus VPDB) ^a	Median	-26.20	-24.53	-24.71
	Min.	-27.39	-25.49	-32.85
	Max.	-25.79	-23.05	-22.08
BIX	Median	0.52	0.68	0.68
	Min.	0.45	0.49	0.50
	Max.	0.62	0.87	1.38
HIX	Median	4.63	4.81	3.13
	Min.	2.56	2.16	1.17
	Max.	6.41	11.13	8.37

^aNo δ¹³C-DOC values available for the lakes sampled during 2002 and 2003, in which case number of observations for the Coastal, Central, and Ice margin lake groups were *n* = 7, *n* = 30, and *n* = 24, respectively.

values approaching 10 QSU (Figure S2c). Central lake SS2 lacked the strong fluorescence signal that was observed in the Coastal lake AT10 EEM.

Indices of biological production (BIX) and humification (HIX) also varied among lake groups (Table 1) (Birdwell & Engel, 2010). The Coastal lakes had lower BIX values than the Central or Ice margin lakes, and in each case, the differences were significant ($P < 0.001$ for each). Median BIX values for the Central and Ice margin were not significantly different ($P > 0.05$). Median HIX values showed very similar degrees of humification among the three lake groups (Table 1). The Coastal lakes had the narrowest range of HIX values, while the Central lakes had the highest. Only the Central and Ice Margin lake groups were significantly different from one another with respect to HIX ($P = 0.002$).

DOM quality in the lakes could also be described by a six-component PARAFAC model of DOM fluorescence (Figure S3). The spectral characteristics of the six components were matched to 50 models in the OpenFluor database (accessed 17 December 2016) and assignments of each component are discussed in more detail in the supporting information (Table S3) (Gonçalves-Araujo et al., 2015; Kothawala et al., 2012; Lapierre & Del Giorgio, 2014; Osburn et al., 2015; Stedmon et al., 2007; Williams et al., 2013; Yamashita et al., 2010). The first three components of the PARAFAC model exhibited spectral features consistent with largely allochthonous sources of DOM to lakes (Aiken, 2014; Fellman et al., 2010; Senesi, 1990; Wünsch et al., 2015). By contrast, the last three components of the PARAFAC model exhibited spectral features suggesting autochthonous and/or microbially modified sources of DOM (Klapper et al., 2002; Murphy et al., 2011; Nimptsch et al., 2015; Shutova et al., 2014; Yang et al., 2014). Maximum fluorescence intensity (FMax) of each PARAFAC component varied for each lake group and showed a clear contrast between lakes and soil extracts (Figure 2). Similar to CDOM absorption, the

Central lakes had the highest fluorescence intensities for all components of the three lake groups (Figure 2a). Lakes were most dominated by C2 and C1 but showed a distinct difference in the relative amount of C3. Highest to lowest mean FMax values were ranked differently among the lake groups. For the Coastal lakes, mean FMax values for C3 were lowest: C2 > C1 > C4 > C6 > C5 > C3. For the Central lakes, C3 was dominant: C3 > C2 > C1 > C4 > C5 = C6. For the Ice margin lakes, C3 and microbial humic-like C4 were of equal intensity, while these lakes contained much less C6 fluorescence: C2 > C1 > C3 = C4 > C5 > C6. The components were ranked similarly for the soil DOM extracts: C1 = C2 > C4 > C5 > C3 = C6 (Figure 2b). C3 was notably lacking in the soil DOM extracts from the Central and Ice margin regions compared to those regions' lakes, suggesting that C3 very likely was indicative of transformation and degradation of DOM within the lakes. Median C3 values were significantly greater in the Central lakes compared to other lake groups ($P < 0.001$). Thus, the Central lakes appeared to have the most transformed or degraded DOM compared to DOM in the Ice margin or the Coastal lakes, exhibiting the least similarity to the soil DOM extracts.

3.3. δ¹³C-DOC Values

Stable carbon isotope values of DOC (δ¹³C-DOC) were generally consistent across lake groups. The median δ¹³C-DOC value for the Coastal lakes was (-26.20‰), which was isotopically depleted compared to the Central lake group (-24.53‰) and the Ice margin lake group (-24.71‰), the latter of which has the widest range of values, including a highly depleted δ¹³C-DOC value of -32.85‰ for lake SS911. A Kruskal-Wallis test revealed that median δ¹³C-DOC values for the Coastal lakes were significantly depleted relative the Central lakes ($P < 0.001$) and the Ice margin lakes ($P < 0.01$), whereas the median δ¹³C-DOC values for the Central and Ice margin lakes were not significantly different.

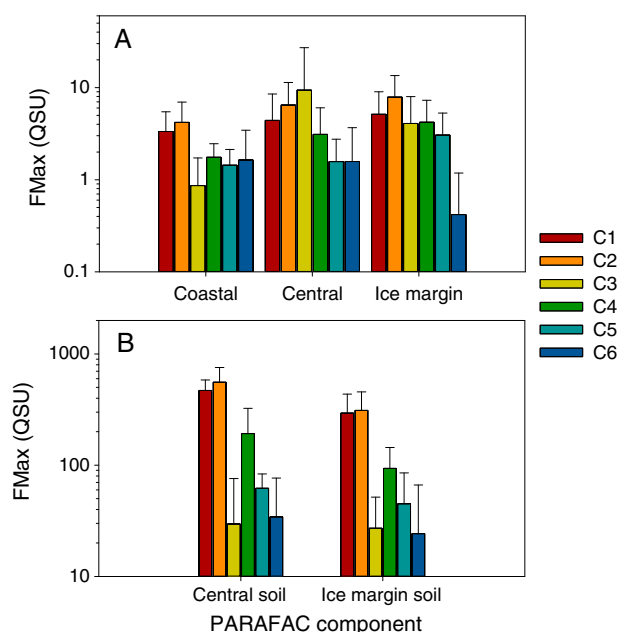


Figure 2. Distribution of maximum fluorescence (FMax, in quinine sulfate units, QSU) for PARAFAC components C1–C6 in (a) the 3 lake regions and (b) associated extracts from soil samples. See Table S3 for component assignments. Mean values are shown along with error bars representing the standard deviation. Note difference in scales between lake samples and soil extracts.

3.4. Controls on Greenland Lake DOM Quantity and Quality

Ordination by PCA of DOC-normalized absorbance and fluorescence results (SUVA and SUVF, respectively) along with qualitative indicators (S , S_R , BIX, and HIX) allowed us to view hydrological connectivity, internal DOM production, and photodegradation as the key processes describing the quality of DOM in these lakes (Figure 3). The first three components explained 79% of the variability in the data; we then correlated the PC axis values against CDOM variables (Table 2) and against conductivity data for the lakes (2013 data only; Table S4).

Principal component 1 (PC1) accounted about 40% of the variability in the CDOM lake data and was also positively correlated with m.a.p. (Pearson's $r = 0.874$, $P < 0.001$, $n = 14$) and negatively correlated to conductivity (2013 samples only, Pearson's $r = -0.595$, $P = 0.025$; $n = 14$; Table S4). Thus, PC1 represented increasing hydrological connectivity between lakes and their catchments. Values for $SUVF_{C1}$, $SUVF_{C2}$, $SUVA_{254}$, and a_{375}^* had very high Spearman's rho (ρ) correlation values to PC1, which supported our hypothesis that hydrological connectivity mobilized allochthonous aromatic-rich DOM into the lakes (Table 2 and Figures 3a and 3c). Moreover, S_R was negatively correlated with PC1 ($\rho = -0.586$; Table 2), which indicated that samples having high scores on PC1 also had comparatively higher molecular weight. These effects on the linkage of hydrological connectivity and soil-derived DOM were strongest for the Coastal lakes which also had the highest m.a.p.

PC2 (~26% variation explained) had the highest significant and positive ρ values found for BIX, $SUVF_{C4}$, and $SUVF_{C5}$, all indicators of recent biological sources of DOM (Table 2) (Birdwell & Engel, 2010). These substances are enriched in lakes having moderate to high amounts of primary and secondary production, including macrophytes (Lapierre & Frenette, 2009; Tank et al., 2011; Zhang et al., 2013). PC2 was negatively correlated to m.a.p. ($r = -0.866$; $P < 0.0001$; $n = 14$) and positively correlated with conductivity ($r = 0.574$, $P = 0.032$, $n = 14$; Table S4), which suggested accrual of internally produced DOM in the lakes with evapoconcentration. This result is consistent with a decline in hydrological connectivity, and hence in the influence of soil-derived DOM.

Scores on PC3 (~13% variation explained) had the highest negative correlation with m.a.p. ($r = 0.923$; $P < 0.0001$; $n = 14$) and positive correlation with conductivity ($r = 0.743$, $P = 0.002$, $n = 14$) (Table S4). Further, the scores on PC3 had positive correlations with the humification index (HIX) and $SUVF_{C3}$, and a significant negative correlation with S_R (Table 2). These correlations combined indicate that this PC axis reflected a combination of microbial and photochemical processing of lake DOM.

Scores for samples coded by lake group showed clear separation among the three climatic regions when PC1 was plotted against PC2 or PC3 (Figures 3b and 3b). Scores from the cool-wet Coastal region cluster in the bottom right of each scatterplot and reflect the higher degree of hydrological connectivity as postulated by Anderson and Stedmon (2007). In Figure 3b, scores from both the cool-dry Ice margin region and warm-dry Central region dominate the top part of the PC1-PC2 biplot, which suggests that internally produced DOM is important in those lakes. Scores from the warm-dry Central lake region dominate the top part of the PC1-PC3 biplot (Figure 3d); most scores are negative on PC1 but also positive on PC3. Loadings for S , S_R , and BIX all plot negatively on PC1, but notably S and S_R plot positively on PC3 and nearly directly opposite the indicators for soil DOM (e.g., $SUVA_{254}$, a_{375}^* , and $SUVF_{C2}$). Further, $SUVF_{C3}$, $SUVF_{C6}$, and HIX all cluster in the top-right region of the loadings biplot, positive on both PC1 and PC3. HIX is higher in environments with more humified DOM, but HIX values also decrease with photodegradation (Birdwell & Engel, 2010; Catalán et al., 2013). Moreover, lakes from the warm-dry Central region had higher scores on PC3 for these variables than did lakes from the cool-dry Ice margin region. These results indicate that substantial microbial and photochemical degradation, both of which can be enhanced by retention time, exert a major secondary control of DOM in these lakes as a consequence of drier conditions and loss of hydrological connectivity.

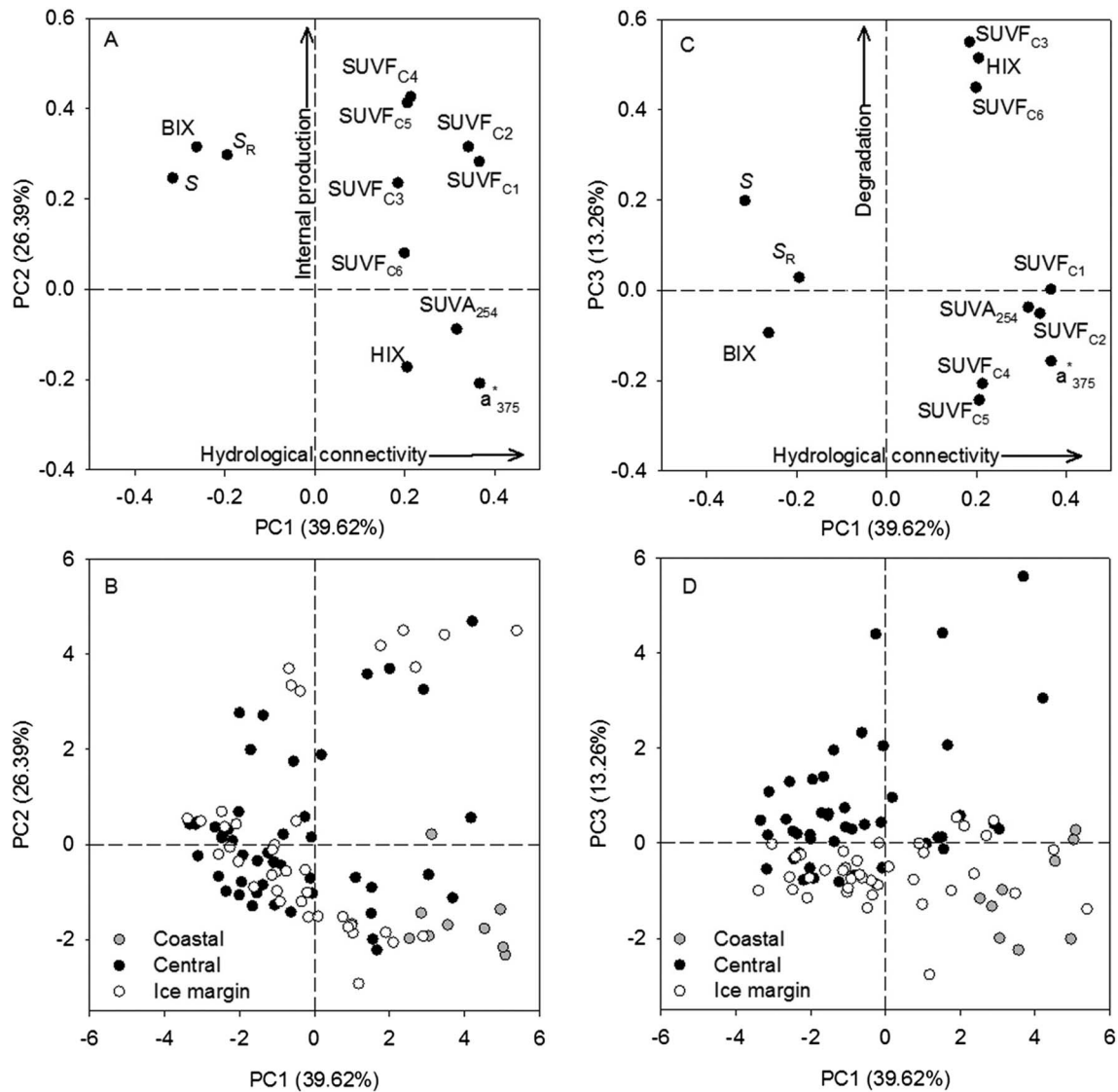


Figure 3. (a and c) Loadings and (b and d) scores plots of lake CDOM properties from PCA. PC1 represented hydrologic connectivity, PC2 represented internal production of DOM, and PC3 represented degradation. Refer to Table 1 for variable definitions.

It is important to note that several lakes from different lake groups overlap with respect to where their scores plot in this analytic space. We interpret this overlap to represent the gradient of temperature and precipitation that distinguishes the cool-wet from the warm-dry and cool-dry lake regions. This climatic gradient is reflected in conductivity values of the lakes (Anderson et al., 2001; Ryves et al., 2006).

3.5. Seasonal Effects of DOM Quality

Seasonal variability of DOM quality in the lakes was revealed the $SUVF_{C1}$ and $SUVA_{254}$ data from the Central and Ice margin lakes in 2014, and the soil extract data, also from 2014 (Figure S4). A linear mixed effects (lme) regression model fit to these data, with $\log SUVA_{254}$ as the predictor variable and with a random intercept that varied by month, revealed two groups of samples: those in June and August, which trend along a slope with the soil extracts, and those largely from April, which have a similar slope but a different intercept (Table S5). The model was substantially improved by inclusion of the soil extract data ($r^2 = 0.95$; $P < 0.001$; $n = 34$), compared to their exclusion ($r^2 = 0.87$; $P < 0.0002$; $n = 25$), yet no significant difference in slope value was found with or without the soil extract data (unpaired t test with Welch correction: $P = 0.8858$).

Table 2
Correlation Matrix of CDOM Variables With Scores of Three Components From PCA

Spearman's rho	PC1 (39.62%)	PC2 (26.39%)	PC3 (13.26%)
SUVA ₂₅₄	0.781	0.047	-0.032
S	- 0.748	0.295*	0.275*
S _R	- 0.586	0.147	0.077
S ₂₇₅	0.819	-0.210**	-0.296*
a* ₃₇₅	0.884	-0.166	-0.176
BIX	- 0.633	0.391	0.016
HIX	0.561	-0.154	0.465
SUVF _{C1}	0.909	0.326	-0.058
SUVF _{C2}	0.838	0.319	-0.172
SUVF _{C3}	0.255	0.165	0.531
SUVF _{C4}	0.579	0.593	-0.315*
SUVF _{C5}	0.561	0.554	- 0.495
SUVF _{C6}	0.239**	0.170	0.570

Note: **Boldface** values indicate *P* values <0.001.
P* < 0.01. *P* < 0.05.

4. Discussion

4.1. Hydrological Connectivity Drives Soil-Derived DOM Inputs Into SW Greenland Lakes

Our results suggested that DOM quality in lakes across SW Greenland exhibits shifts in both sources and processing along decreasing precipitation gradients that weaken hydrological connectivity between lakes and the soils in their watersheds. The results complement the Sobek et al. (2007) paradigm of hierarchical regulation of DOC concentration in lakes by showing that at higher m.a.p., there is a greater influence of catchment soils on DOM quality, even at low DOC concentrations. This explanation is consistent with our observations from the Coastal lakes, situated in a region with higher m.a.p., which indicated a stronger hydrological connectivity between the Coastal lakes and their watersheds, despite lower median DOC concentrations. Coastal lakes had lower $\delta^{13}\text{C}$ -DOC values, larger SUVA₂₅₄ values, and a larger relative amount of C1 and C2 fluorescence relative to C3 fluor-

escence (Table 1). Further, the distribution pattern of PARAFAC components for the Coastal lakes more closely resembled the soil extracts, which were dominated by C1 and C2 fluorescence, indicating DOM of very similar quality (Figure 2).

The low median DOC concentration in the Coastal lakes (2.14 mg L⁻¹) was likely due to the wetter climatic regime in the Coastal lake region but also perhaps to the soil properties of each lake's catchment (Table 1) (Nielsen, 2010; cf. Mulholland, 2003). Flushing of soil OM into streams and catchments varies considerably with rainfall dynamics and soil properties, and higher rainfall does not always equate to higher DOC concentrations (Raymond & Saiers, 2010; Sobek et al., 2007) despite evidence that high DOC concentrations in lakes resulted from higher connectivity (Martin & Soranno, 2006). Flushing implies short retention time; thus, we expect younger DOM in the Coastal lakes (Anderson & Stedmon, 2007).

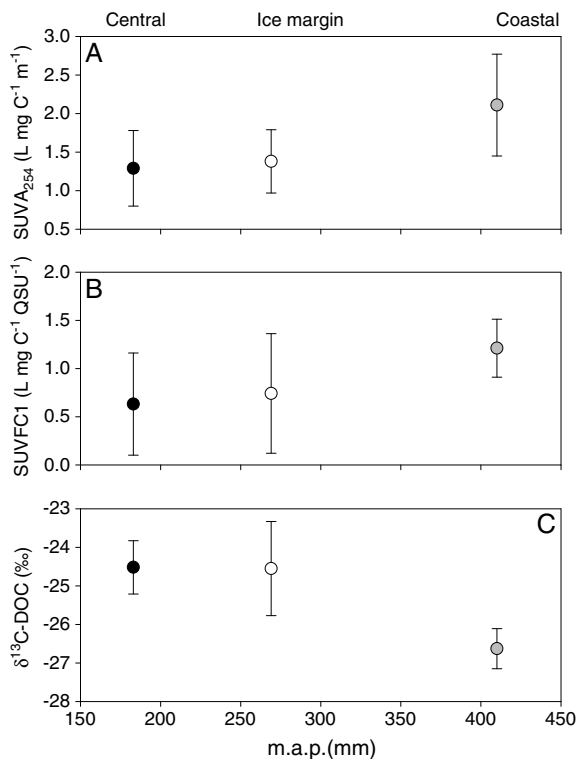


Figure 4. DOM qualitative properties plotted as a function of mean annual precipitation (m.a.p.) for each lake group (indicated above top figure). Values for (a) SUVA₂₅₄, (b) SUVF for PARAFAC component C1, and (c) $\delta^{13}\text{C}$ -DOC.

Key terrestrial DOM quality parameters for each lake group, such as SUVA₂₅₄, specific UV fluorescence for C1 (SUVF_{C1}), and $\delta^{13}\text{C}$ -DOC values, illustrated the first-order control on lake DOM properties exerted by hydrological connectivity, using m.a.p. as a proxy (Figures 4a–4c). Each parameter changed with decreasing m.a.p. in a way which indicated that loss of hydrological connectivity of a lake to its watershed diminished the influence of soil-derived DOM sources in the lakes. For example, SUVA₂₅₄ values indicated less aromatic DOM as m.a.p. decreased ($r^2 = 0.17$; $P < 0.001$; $n = 96$), while SUVF_{C1} (normalized to DOC as for a_{254}) indicated a loss of soil humic fluorescence across this environmental gradient ($r^2 = 0.08$; $P = 0.005$; $n = 96$) (Figures 4a and 4b). These weaker correlation coefficients reflect the fact that mean values were significantly different between Coastal lakes and Inland and Ice margin lakes, but not significantly different between Ice margin and Central lakes. This result can be explained by the larger difference in m.a.p. between Coastal lake group and the Ice margin or Central groups (141 and 227 mm, respectively) than between the Central and Ice margin groups (86 mm). Moreover, as m.a.p. decreases from the coast inland, $\delta^{13}\text{C}$ values of lake DOM increased from approximately -26‰ to approximately -24.5‰ ($P < 0.001$; Table 1); which reflected a shift from soil-derived terrestrial DOM, which is rapidly transferred to the lakes, as at the coast, to processed DOM in the Central and Ice margin lakes (Figure 4c). Typical $\delta^{13}\text{C}$ -DOC values for terrestrial DOM fall between -25 and -29‰ (Bauer, 2002). Thus, the Coastal lakes exhibited the strongest hydrological connectivity, reflected in the largely soil-like quality of their DOM (Figure 3).

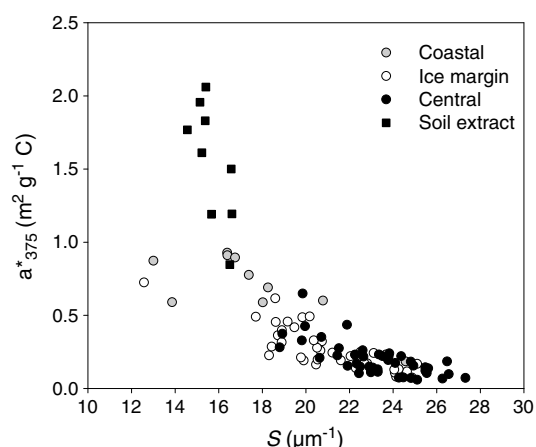


Figure 5. DOC-specific absorption at 375 nm (a_{375}^*) plotted as a function of spectral slope, S , value and grouped by lake region; soil extracts are included. Also included in this plot are data from Anderson and Stedmon (2007).

The gradient of hydrological connectivity demonstrated on the quality of DOM in the SW Greenland lakes follows earlier work that proposed a model based on a_{375}^* values plotted against S values, which showed regional separation between Coastal lakes (which had high values of a_{375}^* and low values of S) and Central and Ice margin lakes (which had low a_{375}^* values and high S values) (Anderson & Stedmon, 2007). We combined the Anderson and Stedmon (2007) data from 2002 to 2003 with the 2009–2014 data from the present study and included the soil extracts as a model of a purely terrestrial end-member source of DOM in the lakes (Figure 5). The regional differences are clear in that the Coastal lakes have a_{375}^* values of 0.5 to 1.0 $\text{L mg C}^{-1} \text{m}^{-1}$ and S values between 14 and 20 μm^{-1} . The soil extracts have higher a_{375}^* values than the cluster of Coastal lakes, as would be expected from the humic substances recently extracted from soil organic matter (Jaffé et al., 2008). However, the S values of the soil extracts fall within the range observed for the Coastal lakes. Therefore, our results support the hypothesis of Anderson and Stedmon (2007) that this separation was caused by the degree of the hydrological connectivity whereby lakes

that are better connected to their watersheds in the cool, wet Coastal region has “fresher” CDOM than lakes that are disconnected in the drier Central and Ice margin regions.

By contrast, Central and Ice margin lakes are markedly different from the soil extracts with a_{375}^* values between 0.06 and 0.75 $\text{L mg C}^{-1} \text{m}^{-1}$ and S values generally above 18 μm^{-1} . High values for S and low a_{375}^* suggest CDOM, which has since been photodegraded and is comparable to prairie lakes also influenced by evapoconcentration and extensive solar photodegradation (Osburn et al., 2001, 2011; Waiser & Robarts, 2004). The significant differences in these CDOM qualitative parameters between the low m.a.p., arid Central and Ice margin lakes, and the high m.a.p. Coastal lakes indicate that alternative processes beyond simple dilution of soil-sourced DOM exert a major second-order control on DOM quality and quantity in these Arctic lakes. The largest changes occur in the Central lakes, which are the most disconnected from their watersheds and have the longest retention times under conditions of decreasing m.a.p. and increasing evapoconcentration. Thus, drier climates of the Central and Ice margin lake groups also result in higher stocks of refractory DOC than the wetter Coastal lake group, due to decreasing m.a.p., and, as a result, a longer retention time allowing for a greater influence of internal processes within those lake groups.

4.2. Internal Processes in SW Greenland Lakes Modify and Amend Inputs of Soil-Derived DOM

The negative relationship between PC2 and m.a.p. supported our hypothesis that the deviation of DOM quality in the SW Greenland lakes away from characteristics consistent with soil sources was mainly caused by processes resulting from a lack of hydrological connectivity. This reduces the supply of terrestrial, soil-derived DOM and enhances evapoconcentration, promoting accumulation of both allochthonous and autochthonous DOM (Osburn et al., 2011). As a result of declining m.a.p., both internal DOM production and photodegradation appear to modulate the soil-derived DOM signature in Ice margin and Central lake groups.

Internal DOM production may be dominated by lateral inputs from littoral submerged and emergent vegetation. The SW Greenland lakes in this study are oligotrophic: chlorophyll a concentration is $<1 \mu\text{g L}^{-1}$, total N ranges from 0.1 to 1.5 mg L^{-1} , and total phosphorus ranges from 5 to 10 $\mu\text{g L}^{-1}$ (Anderson et al., 2001; Saros et al., 2015; Whiteford et al., 2016). It is thus unlikely that annual water column primary production alone could support the DOC concentrations in these lakes, e.g., roughly 35 mg L^{-1} for the Central lakes. However, considering that the Central lake group exhibited the driest conditions (lowest m.a.p.), we hypothesize that macrophytes and/or aquatic mosses or benthic microalgae growing along the littoral zone supplement the autochthonous input.

In macrophyte-rich temperate lakes, strong protein- and C2-like fluorescence has been observed similar to the macrophyte-rich waters of the Florida Everglades, in which a PARAFAC component was found to be a statistical match to C2 in the SW Greenland lakes model (Lapierre & Frenette, 2009; Yamashita et al., 2010; Zhang et al., 2013). Although we had no measurements of macrophyte exudates, we suspect, based on field

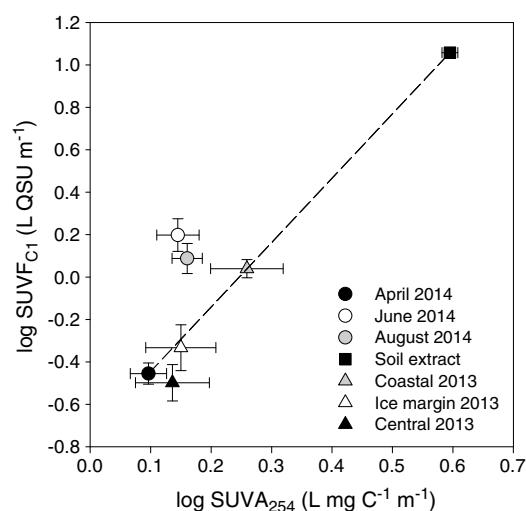


Figure 6. Comparison of mean DOC-normalized fluorescence of PARAFAC component 1 ($SUVF_{C1}$) and absorbance ($SUVA_{254}$) properties in SW Greenland lakes grouped by month (circles, 2014 only) and by region (triangles, 2013 only). The Coastal lakes were not sampled in 2014. DOM leached from soils in both the inland and ice margin lakes is included (black square) as a terrestrial end-member. April is taken to represent the under-ice period. The error bars are the standard error of the mean. The regression equation between April 2014 and Soil extract represented by the dotted line is $\log SUVF_{C1} = -0.748 + 3.035 \times \log SUVA_{254}$.

values $>3.0 \text{ L mg C}^{-1} \text{ m}^{-1}$ (Kothawala et al., 2014). Photodegradation results in much lower $SUVA_{254}$ values approximating $1.0 \text{ L mg C}^{-1} \text{ m}^{-1}$ (Catalán et al., 2013; Spencer et al., 2009). Median S_R value for the Central lake group was >1.0 (Figure 2); typical values of S_R for terrestrially dominated CDOM in lakes are 0.6 to 0.8 and increase with photodegradation, while median HIX values were ~ 5 , roughly half the value for lake DOM prior to photodegradation (Catalán et al., 2013; Osburn et al., 2011). Further, $SUVF_{C3}$ was highly correlated to PC3, and this component was matched with a variety of PARAFAC models, as a fluorescence signal that remained in DOM after extensive photodegradation (Kothawala et al., 2014; Osburn et al., 2014).

The $\delta^{13}\text{C}$ -DOC values for the lakes were negatively correlated to corresponding scores on PC1 ($r = 0.61$; $P < 0.0001$; $N = 60$), meaning that more depleted values occurred in lakes with stronger hydrological connectivity. The roughly 2‰ depletion of $\delta^{13}\text{C}$ -DOC values for the Coastal lakes relative to the Central lakes matches those typical for terrestrial DOM in lakes (e.g., Osburn et al., 2001). Given that freshwater $\delta^{13}\text{C}$ -DOC values increase as photodegradation proceeds due to a loss of aromatic-rich molecules such as lignin, this process is a reasonable explanation for the variation of carbon stable isotope values of the DOM in the SW Greenland lakes (Osburn et al., 2001, 2011; Spencer et al., 2009). Thus, while decreasing hydrological connectivity shifts DOM sources toward internal inputs, longer retention time in the Central lakes allows for accumulation of high concentrations of less-colored DOC resulting from substantial photochemical degradation.

4.3. Variability in Greenland Lake DOM Across Seasonal and Climatic Gradients

Large intra-annual variability in the DOM quality of the SW Greenland lakes in 2014 was described by the lme regression model (Table S5 and Figure S4). Indeed, this seasonal variability in SW Greenland lake DOM properties suggested a “pulse-process” dynamic as the arctic summer creates a complex environment in which hydrology, climate, and sunlight modulate DOM sources and cycling in these lakes. Mean values (\pm standard error as error bars) of $SUVA_{254}$ and $SUVF_{C1}$ illustrate this dynamic (Figure 6). Mean values of monthly data (April, June, and August) for 2014 from the lme model were combined with mean values of the three lake groups for 2013 to represent the climatic gradient of decreasing m.a.p. The mean soil extract values also are presented to represent strong hydrological connectivity to the landscape, as for Figure 5.

April samples were taken under ice, representing conditions prior to the open water period and the lowest influence of soil DOM in the lakes, hence the lowest mean values of both $SUVA_{254}$ and $SUVF_{C1}$. We

observations, that macrophytic DOMs, or even perhaps the multicellular green alga, *Chara*, are important additional sources of DOM in these lakes (Tank et al., 2011). In the western Canadian Arctic, lakes of the Mackenzie River Delta that have high macrophyte productivity also had $SUVA_{254}$ values $>2.0 \text{ L mg C}^{-1} \text{ m}^{-1}$, strong protein-like fluorescence matching our C5 and $\delta^{13}\text{C}$ -DOC values, which overlap with $\delta^{13}\text{C}$ -DOC values from the Greenland lakes (range: -26 to -28%) (Tank et al., 2011). Thus, macrophytes and/or aquatic mosses/macroalgae and associated epiphytic and benthic microalgae also could be of key importance as additional DOM sources, especially in the Central lakes.

However, the drier climates (lower m.a.p. and higher evaporation) of the Central and Ice margin lake regions are also conducive to photochemical degradation of DOM because low hydrological connectivity reduces the supply of “fresh” soil humic DOM in runoff from the landscape but also increases water residence within each lake. Coupled with the near-continual sunlight exposure during the Arctic summer, longer water residence time creates optimal conditions for extensive photodegradation with effects consistent with the optical and chemical properties of DOM we have measured for the SW Greenland lakes.

CDOM evidence from the Central lakes provided the strongest support that photodegradation is a dominant process at these sites. For example, median $SUVA_{254}$ values for the Central lake group were $<1.5 \text{ L mg C}^{-1} \text{ m}^{-1}$, whereas humic rivers and lakes typically have

interpret these results to represent the annual accrual of processed DOM in the lakes, in other words, the DOM “state” of the lakes after the end of the arctic summer and during the period of under-ice microbial processing over the winter (Bertilsson et al., 2013). Mean soil extract values and April under-ice values thus represented end-points of fresh “pulsed” DOM and degraded “processed” DOM, respectively, defined by the dotted regression line in Figure 6. June and August mean values deviate from this line. April was significantly lower than both June (MANOVA: $P < 0.001$) and August ($P < 0.0001$); August was significantly different than June ($P = 0.02$). While both months shared characteristics with soil DOM (a similar intercept in the lme model), their deviations toward higher log $SUVF_{C1}$ are consistent with an increase in structurally complex humic DOM, such that might arise not only from soil sources seeping into the lakes after ice melt but also from internal inputs of macrophytes or *Chara* (Tank et al., 2011). We have no observations of these lakes between August and early autumn during ice-formation, but such observations might clarify the seasonal patterns described here. Along with extensive and parallel processing of autochthonous and allochthonous DOM, via photochemical and/or microbial degradation as seen in other studies, we hypothesize that June and August DOM properties return to values similar to April DOM by autumn during ice-formation (Guillemette et al., 2013; Osburn et al., 2011).

The seasonal “pulse-process” dynamic described here is similar to DOM dynamics observed in the Green Lakes Valley catchment in the Colorado Rocky Mountains, USA (Miller & McKnight, 2010). Under-ice DOM in alpine and subalpine lakes exhibited C3-like fluorescence and was notably lacking in C1-like fluorescence. However, the summer snowmelt, which dominates the lakes’ hydrologic cycles, shifts DOM quality to more complex humic material with C1-like fluorescence. Later in the season, the fluorescence signal shifted back to C3-like fluorescence, while $SUVA_{254}$ values declined from ~ 4.0 to $1.5 \text{ L mg C}^{-1} \text{ m}^{-1}$ (Miller & McKnight, 2010). The consistency between seasonal patterns in these two regions is supported by the pulse of snowmelt driving the hydrologic cycles in these two very different environments.

The mean values for the Coastal lakes fell along the “pulse-process” line, indicating the pulses of soil DOM from surface soil horizon thaw and subsequent seepage into the lakes due to strong hydrological connectivity in these lakes but also its subsequent degradation after the initial pulse. Across the climatic gradient of decreasing m.a.p., the Coastal lakes were significantly different from Ice margin (MANOVA: $P = 0.018$) and from Central lakes (MANOVA: $P = 0.0033$); Ice margin and Central lake groups were not significantly different. This indicated that internal processes ongoing in those lakes during the open water period were more similar to one another than to the Coastal lakes. Thus, despite relatively low input fluxes of soil DOM after ice melt, evapoconcentration in these arid regions can both concentrate DOM but also facilitate its photochemical degradation (Mulholland, 2003). Based on the $SUVA_{254}$ and $SUVF_{C1}$ results in Figure 6, the lowest m.a.p., highest DOC Central lakes exhibit the strongest effects of these parallel processes, especially photodegradation.

4.4. Implications for Carbon Cycling in Arctic Lakes

Results of our study have important implications for lake C cycling in the Arctic. First, the climatic gradient under which the SW Greenland lakes currently exist provides a means of predicting future Arctic lake C cycling scenarios with respect to DOM. Recent work on the Arctic hydrological cycle has revealed that while many Arctic regions currently are in a water surplus in fluvial systems driven by permafrost melt, other regions may become drier (Bring et al., 2016). This means that circumpolar lakes situated in cool wetter climatic regimes with strong hydrological connectivity (e.g., Toolik) could have reduced connectivity under a drier future climate and evolve toward an end-point along the hydrological connectivity-C processing gradient represented by the Central lakes in the present study. Moreover, Šmejkalová et al. (2016) used Moderate Resolution Imaging Spectroradiometer satellite observations from 2000 to 2013 to suggest that ice-out is occurring sooner in Arctic lakes. Early ice-out would result in longer periods of open water while altered precipitation patterns might cause longer residence times in Arctic lakes. Earlier ice-out and longer residence times create opportunities for photochemical and biological degradation in lakes (Curtis & Schindler, 1997; Osburn et al., 2011; Waiser & Robarts, 2004) but also cause lakes to accumulate recalcitrant DOM reaching the high mean concentrations ($>30 \text{ mg L}^{-1}$) we have observed in the Central lake group in SW Greenland.

Second, strong evidence from this and prior work indicates that sunlight plays a key role in shaping lake DOM properties (Anderson & Stedmon, 2007). It is well known that Arctic freshwater DOM is highly reactive to both sunlight and bacteria (Cory et al., 2014; Mann et al., 2012; Osburn et al., 2009). Despite the clear evidence for the importance of photochemistry in carbon cycling via the production of CO_2 from DOM (e.g., Cory et al.,

2014; Osburn et al., 2001; Spencer et al., 2009), macrophyte-dominated lakes may in fact act as CO₂ sinks (Tank et al., 2011). Thus, further work is required to elucidate for the SW Greenland lakes, their ultimate role in CO₂ evasion or sequestration.

Third, the role of microbial activity in degrading DOM in SW Greenland lakes is virtually unknown. Our results clearly show dynamic changes in the quality of DOM on a seasonal basis (Figure 6). The trend in these changes appears to be driven by environmental factors such as seasonal evapoconcentration and photodegradation, but perhaps modulated by biological processing. The arid environment of SW Greenland makes runoff less important than littoral or pelagic processes mediated by aquatic microbes. The oligotrophic nature of these lakes (Chl *a* < 1 μg L⁻¹; Whiteford et al., 2016) suggests that planktonic production of DOM is low. Knowledge of bacterial community composition, enzyme activities, rates of bacterial production, and rates of respiration are key important biogeochemical information sorely needed for these lakes.

In summary, we have examined the DOM concentration and quality for lakes in SW Greenland over a climatic gradient of cool, wet coastal conditions to a warm, dry inland interior, to cool, dry climate close to the present margin of the Greenland ice sheet. We found large variability that results in rapid changes to DOC and CDOM concentration and quality, which appears to result from changing source inputs (phytoplankton and macrophytes) and rapid microbial and photochemical cycling (Cory et al., 2014). DOC-specific absorbance (SUVA₂₅₄) and fluorescence (SUVC₁) elucidated distinctions among soil inputs of DOM, internal DOM production, and photochemical (and possibly microbial) degradation, insightful metrics to evaluate lake ecosystems with respect to DOM quality along gradients of hydrological connectivity and climate. The age of the organic matter, the relative abundance of terrestrial biomarkers such as lignin, bacterial activity, and the importance of benthic production in these lakes are knowledge gaps that could provide further insight into the rate of DOM input, cycling and, by extension, CO₂ sequestration or evasion. Given the large number of lakes across the de-glaciated landscape of SW Greenland, our results support prior findings that Greenland's inland waters could be an important regulator of its regional carbon cycling (e.g., Anderson et al., 2009; Cole et al., 2007; Saros et al., 2015; Tranvik et al., 2009).

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References

- Aiken, G. (2014). Fluorescence and dissolved organic matter: a chemist's perspective. In P. G. Coble, et al. (Eds.), *Aquatic organic matter fluorescence* (pp. 35–74). Cambridge: Cambridge University Press.
- Anderson, N. J., Harriman, R., Ryves, D. B., & Patrick, S. T. (2001). Dominant factors controlling variability in the ionic composition of West Greenland lakes. *Arctic, Antarctic, and Alpine Research*, 418–425.
- Anderson, N. J., Saros, J. E., Bullard, J. E., Cahoon, S. M., McGowan, S., Bagshaw, E. A., ... Yde, J. C. (2017). The Arctic in the twenty-first century: Changing biogeochemical linkages across a paraglacial landscape of Greenland. *BioScience*, 67(2), 118–133.
- Anderson, N. J., & Stedmon, C. A. (2007). The effect of evapoconcentration on dissolved organic carbon concentration and quality in lakes of SW Greenland. *Freshwater Biology*, 52(2), 280–289.
- Anderson, N. J., D'andrea, W., & Fritz, S. C. (2009). Holocene carbon burial by lakes in SW Greenland. *Global Change Biology*, 15(11), 2590–2598.
- Bauer, J. E. (2002). Carbon isotopic composition of DOM. In D. A. Hansell & C. A. Carlson (Eds.), *Biogeochemistry of marine dissolved organic matter* (pp. 405–453). San Diego, CA: Academic Press.
- Bennike, O., & Björck, S. (2002). Chronology of the last recession of the Greenland Ice Sheet. *Journal of Quaternary Science*, 17(3), 211–219.
- Bertilsson, S., Burgin, A., Carey, C. C., Fey, S. B., Grossart, H. P., Grubisic, L. M., ... Smyth, R. L. (2013). The under-ice microbiome of seasonally frozen lakes. *Limnology and Oceanography*, 58(6), 1998–2012.
- Birdwell, J. E., & Engel, A. S. (2010). Characterization of dissolved organic matter in cave and spring waters using UV-Vis absorbance and fluorescence spectroscopy. *Organic Geochemistry*, 41(3), 270–280.
- Bring, A., Fedorova, I., Dibike, Y., Hinzman, L., Mård, J., Mermild, S. H., ... Woo, M. K. (2016). Arctic terrestrial hydrology: A synthesis of processes, regional effects and research challenges. *Journal of Geophysical Research: Biogeosciences*, 121, 621–649. <https://doi.org/10.1002/2015JG003131>
- Catalán, N., Obrador, B., Felip, M., & Pretus, J. L. (2013). Higher reactivity of allochthonous vs. autochthonous DOC sources in a shallow lake. *Aquatic Sciences*, 75(4), 581–593.
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., ... Melack, J. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10(1), 172–185.
- Cory, R. M., Crump, B. C., Dobkowski, J. A., & Kling, G. W. (2013). Surface exposure to sunlight stimulates CO₂ release from permafrost soil carbon in the Arctic. *Proceedings of the National Academy of Sciences of the United States of America*, 110(9), 3429–3434.
- Cory, R. M., Miller, M. P., McKnight, D. M., Guerard, J. J., & Miller, P. L. (2010). Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra. *Limnology and Oceanography: Methods*, 8(2), 67–78.
- Cory, R. M., Ward, C. P., Crump, B. C., & Kling, G. W. (2014). Sunlight controls water column processing of carbon in arctic fresh waters. *Science*, 345(6199), 925–928.
- Curtis, P. J., & Schindler, D. W. (1997). Hydrologic control of dissolved organic matter in low-order Precambrian Shield lakes. *Biogeochemistry*, 36(1), 125–138.
- Fellman, J. B., Hood, E., & Spencer, R. G. (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnology and Oceanography*, 55(6), 2452–2462.

- Gonçalves-Araujo, R., Stedmon, C. A., Heim, B., Dubinenkov, I., Kraberg, A., Moiseev, D., & Bracher, A. (2015). From fresh to marine waters: Characterization and fate of dissolved organic matter in the Lena River Delta region, Siberia. *Frontiers in Marine Science*, 2, 108. <https://doi.org/10.3389/fmars.2015.00108>
- Guillemette, F., McCallister, S. L., & del Giorgio, P. A. (2013). Differentiating the degradation dynamics of algal and terrestrial carbon within complex natural dissolved organic carbon in temperate lakes. *Journal of Geophysical Research: Biogeosciences*, 118, 963–973. <https://doi.org/10.1002/jgrg.20077>
- 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.
- Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W. H., & Campbell, J. L. (2008). Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. *Journal of Geophysical Research*, 113, G04032. <https://doi.org/10.1029/2008JG000683>
- Klapper, L., McKnight, D. M., Fulton, J. R., Blunt-Harris, E. L., Nevin, K. P., Lovley, D. R., & Hatcher, P. G. (2002). Fulvic acid oxidation state detection using fluorescence spectroscopy. *Environmental Science and Technology*, 36(14), 3170–3175.
- Kothawala, D. N., Stedmon, C. A., Müller, R. A., Weyhenmeyer, G. A., Köhler, S. J., & Tranvik, L. J. (2014). Controls of dissolved organic matter quality: evidence from a large-scale boreal lake survey. *Global Change Biology*, 20(4), 1101–1114.
- Kothawala, D. N., von Wachenfeldt, E., Koehler, B., & Tranvik, L. J. (2012). Selective loss and preservation of lake water dissolved organic matter fluorescence during long-term dark incubations. *Science of the Total Environment*, 433, 238–246.
- Lapierre, J. F., & Del Giorgio, P. A. (2014). Partial coupling and differential regulation of biologically and photochemically labile dissolved organic carbon across boreal aquatic networks. *Biogeosciences*, 11(20), 5969–5985.
- Lapierre, J. F., & Frenette, J. J. (2009). Effects of macrophytes and terrestrial inputs on fluorescent dissolved organic matter in a large river system. *Aquatic Sciences-Research Across Boundaries*, 71(1), 15–24.
- Lawaetz, A. J., & Stedmon, C. A. (2009). Fluorescence intensity calibration using the Raman scatter peak of water. *Applied Spectroscopy*, 63(8), 936–940.
- Mann, P. J., Davydova, A., Zimov, N., Spencer, R. G. M., Davydov, S., Bulygina, E., ... Holmes, R. M. (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>
- Martin, S. L., & Soranno, P. A. (2006). Lake landscape position: Relationships to hydrologic connectivity and landscape features. *Limnology and Oceanography*, 51(2), 801–814.
- Miller, M. P., & McKnight, D. M. (2010). Comparison of seasonal changes in fluorescent dissolved organic matter among aquatic lake and stream sites in the Green Lakes Valley. *Journal of Geophysical Research*, 115, G00F12. <https://doi.org/10.1029/2009JG000985>
- Mulholland, P. J. (2003). Large-scale patterns in dissolved organic carbon concentration, flux, and sources. In S. E. G. Findlay & R. L. Sinsabaugh (Eds.), *Aquatic ecosystems: Interactivity of dissolved organic matter* (pp. 139–159). New York: Academic Press.
- Murphy, K. R., Bro, R., & Stedmon, C. A. (2014). Chemometric analysis of organic matter fluorescence. In P. Coble, et al. (Eds.), *Aquatic organic matter fluorescence* (pp. 339–375). New York: Cambridge University Press.
- Murphy, K. R., Hambly, A., Singh, S., Henderson, R. K., Baker, A., Stuetz, R., & Khan, S. J. (2011). Organic matter fluorescence in municipal water recycling schemes: toward a unified PARAFAC model. *Environmental Science & Technology*, 45(7), 2909–2916.
- Murphy, K. R., Stedmon, C. A., Wenig, P., & Bro, R. (2014). OpenFluor—an online spectral library of auto-fluorescence by organic compounds in the environment. *Analytical Methods*, 6(3), 658–661.
- Nielsen, A. B. (2010). Present conditions in Greenland and the Kangerlussuaq area. Working Report, Geological Survey of Denmark and Greenland. Retrieved from http://www.posiva.fi/files/1244/WR_2010-07web.pdf
- Nimptsch, J., Woelfl, S., Osorio, S., Valenzuela, J., Ebersbach, P., von Tuempling, W., ... Graeber, D. (2015). Tracing dissolved organic matter (DOM) from land-based aquaculture systems in North Patagonian streams. *Science of the Total Environment*, 537, 129–138.
- Osburn, C. L., Del Vecchio, R., & Boyd, T. J. (2014). Physicochemical effects on dissolved organic matter fluorescence in natural waters. In P. G. Coble, et al. (Eds.), *Aquatic organic matter fluorescence* (pp. 233–277). New York: Cambridge University Press.
- Osburn, C. L., Morris, D. P., Thorn, K. A., & Moeller, R. E. (2001). Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation. *Biogeochemistry*, 54(3), 251–278.
- Osburn, C. L., Retamal, L., & Vincent, W. F. (2009). Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea. *Marine Chemistry*, 115(1), 10–20.
- Osburn, C. L., & St-Jean, G. (2007). The use of wet chemical oxidation with high-amplification isotope ratio mass spectrometry (WCO-IRMS) to measure stable isotope values of dissolved organic carbon in seawater. *Limnology and Oceanography: Methods*, 5(10), 296–308.
- Osburn, C. L., Wigdahl, C. R., Fritz, S. C., & Saros, J. E. (2011). Dissolved organic matter composition and photoreactivity in prairie lakes of the US Great Plains. *Limnology and Oceanography*, 56(6), 2371–2390.
- Osburn, C. L., Mikan, M. P., Etheridge, J. R., Burchell, M. R., & Birgand, F. (2015). Seasonal variation in the quality of dissolved and particulate organic matter exchanged between a salt marsh and its adjacent estuary. *Journal of Geophysical Research: Biogeosciences*, 120, 1430–1449. <https://doi.org/10.1002/2014JG002897>
- Raymond, P. A., & Saiers, J. E. (2010). Event controlled DOC export from forested watersheds. *Biogeochemistry*, 100(1–3), 197–209.
- Ryves, D. B., Battarbee, R. W., Juggins, S., Fritz, S. C., & Anderson, N. J. (2006). Physical and chemical predictors of diatom dissolution in freshwater and saline lake sediments in North America and West Greenland. *Limnology and Oceanography*, 51(3), 1355–1368.
- Saros, J. E., Osburn, C. L., Northington, R. M., Birkel, S. D., Auger, J. D., Stedmon, C. A., & Anderson, N. J. (2015). Recent decrease in DOC concentrations in arctic lakes of southwest Greenland. *Geophysical Research Letters*, 42, 6703–6709. <https://doi.org/10.1002/2015GL065075>
- Senesi, N. (1990). Molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals. 2. The fluorescence spectroscopy approach. *Analytica Chimica Acta*, 232(1), 77–106.
- Shutova, Y., Baker, A., Bridgeman, J., & Henderson, R. K. (2014). Spectroscopic characterization of dissolved organic matter changes in drinking water treatment: from PARAFAC analysis to online monitoring wavelengths. *Water Research*, 54, 159–169.
- Šmejkalová, T., Edwards, M. E., & Dash, J. (2016). Arctic lakes show strong decadal trend in earlier spring ice-out. *Scientific Reports*, 6, 38449. <https://doi.org/10.1038/srep38449>
- Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., & Cole, J. J. (2007). Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography*, 52(3), 1208–1219.
- Spencer, R. G., Stubbins, A., Hernes, P. J., Baker, A., Mopper, K., Aufdenkampe, A. K., ... Six, J. (2009). Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. *Journal of Geophysical Research*, 114, G03010. <https://doi.org/10.1029/2009JG000968>

- Stedmon, C. A., & Bro, R. (2008). Characterizing dissolved organic matter fluorescence with parallel factor analysis: A tutorial. *Limnology and Oceanography: Methods*, 6(11), 572–579.
- Stedmon, C. A., Markager, S., & Bro, R. (2003). Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry*, 82(3), 239–254.
- Stedmon, C. A., Thomas, D. N., Granskog, M., Kaartokallio, H., Papadimitriou, S., & Kuosa, H. (2007). Characteristics of dissolved organic matter in Baltic coastal sea ice: allochthonous or autochthonous origins? *Environmental Science & Technology*, 41(21), 7273–7279.
- Tank, S. E., Frey, K. E., Striegl, R. G., Raymond, P. A., Holmes, R. M., McClelland, J. W., & Peterson, B. J. (2012). Landscape-level controls on dissolved carbon flux from diverse catchments of the circumboreal. *Global Biogeochemical Cycles*, 26, GB0E02. <https://doi.org/10.1029/2012GB004299>
- Tank, S. E., Lesack, L. F., Gareis, J. A., Osburn, C. L., & Hesslein, R. H. (2011). Multiple tracers demonstrate distinct sources of dissolved organic matter to lakes of the Mackenzie Delta, western Canadian Arctic. *Limnology and Oceanography*, 56(4), 1297–1309.
- 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>
- Tetzlaff, D., Soulsby, C., Bacon, P. J., Youngson, A. F., Gibbins, C., & Malcolm, I. A. (2007). Connectivity between landscapes and riverscapes—a unifying theme in integrating hydrology and ecology in catchment science? *Hydrological Processes*, 21(10), 1385–1389.
- Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., . . . Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54, 2298–2314.
- Vincent, W. F., Hobbie, J. E., & Laybourn-Parry, J. (2008). Introduction to the limnology of high-latitude lake and river ecosystems. In W. F. Vincent & J. Laybourn-Parry (Eds.), *Polar lakes and rivers, limnology of Arctic and Antarctic aquatic ecosystems* (pp. 1–23). Oxford: Oxford University Press.
- Waiser, M. J., & Robarts, R. D. (2004). Photodegradation of DOC in a shallow prairie wetland: evidence from seasonal changes in DOC optical properties and chemical characteristics. *Biogeochemistry*, 69(2), 263–284.
- 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 and Technology*, 37(20), 4702–4708.
- Whiteford, E. J., McGowan, S., Barry, C. D., & Anderson, N. J. (2016). Seasonal and regional controls of phytoplankton production along a climate gradient in South-West Greenland during ice-cover and ice-free conditions. *Arctic, Antarctic, and Alpine Research*, 48(1), 139–159.
- Williams, C. J., Frost, P. C., & Xenopoulos, M. A. (2013). Beyond best management practices: pelagic biogeochemical dynamics in urban stormwater ponds. *Ecological Applications*, 23(6), 1384–1395.
- Wünsch, U. J., Murphy, K. R., & Stedmon, C. A. (2015). Fluorescence quantum yields of natural organic matter and organic compounds: Implications for the fluorescence-based interpretation of organic matter composition. *Frontiers in Marine Science*, 2, 98. <https://doi.org/10.3389/fmars.2015.00098>
- Yamashita, Y., Maie, N., Briceño, H., & Jaffé, R. (2010). Optical characterization of dissolved organic matter in tropical rivers of the Guayana Shield, Venezuela. *Journal of Geophysical Research*, 115, G00F10. <https://doi.org/10.1029/2009JG000987>
- Yang, L., Choi, J. H., & Hur, J. (2014). Benthic flux of dissolved organic matter from lake sediment at different redox conditions and the possible effects of biogeochemical processes. *Water Research*, 61, 97–107.
- Zhang, Y., Liu, X., Osburn, C. L., Wang, M., Qin, B., & Zhou, Y. (2013). Photobleaching response of different sources of chromophoric dissolved organic matter exposed to natural solar radiation using absorption and excitation–emission matrix spectra. *PLoS One*, 8(10), e77515.