

# Comparisons of wetland and drainage lake influences on stream dissolved carbon concentrations and yields in a north temperate lake-rich region

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**Abstract** Processes occurring at various scales interact to influence the export of organic carbon from watersheds to freshwater ecosystems and eventually the ocean. The goal of this study was to determine if and how differences in wetland extent and presence of lakes influenced dissolved organic carbon (DOC) concentrations and yields in streams. We monitored stream flow, DOC and dissolved inorganic carbon concentrations periodically for 2 years at four sites with forested watersheds, four sites with wetland watersheds, and four sites with wetland watersheds that also contained in-network lakes. As expected, the presence of wetlands resulted in higher DOC concentrations and yields, but the impact of lakes was less clear on the magnitude of DOC concentrations and yields. With respect to temporal dynamics, we found positive relationships between stream flow and DOC concentration (median  $r^2 = 0.89$ ) in streams without upstream lakes. The relationships for forested sites are among the strongest reported in the literature, and suggest a clear shift in hydrologic flowpath from intersecting mineral soils at low flow, to

organic soils at high flow. In streams with upstream lakes, the relationship between flow and concentration was non-significant for three of four sites unless time lags with flow were applied to the concentration data, after which the relationship was similar to the non-lake streams (median  $r^2 = 0.95$ ). These findings suggest that lakes buffering temporal patterns in streams by hydrologically delaying pulses of carbon, but provide little support that in-line lakes have a net effect on carbon exports in this region.

**Keywords** DOC · Lake · Stream · Aquatic landscape · Carbon processing

## Introduction

Processes occurring at various scales interact to influence the export of organic carbon to downstream aquatic ecosystems and eventually the ocean. Because carbon plays a central role in a diverse range of ecosystem processes (Schlesinger 1997; Prairie 2008), examination of the factors that affect its transport and transformation to downstream aquatic systems and eventually the ocean is critical for understanding this rapidly changing cycle. This is particularly relevant given current large-scale changes in land-use, hydrology, and climate, all of which alter carbon cycling at local to global scales (Köhler et al. 2008; Butman and Raymond 2011; Stanley et al. 2012).

In north temperate and boreal latitudes, large amounts of dissolved organic carbon (DOC) are transported across and by aquatic ecosystems. Despite their limited spatial extent, these freshwater systems can have a disproportionately large role in carbon cycling from local (Elder et al. 2000) to regional (Jonsson et al. 2007; Christensen et al. 2007; Buffam et al. 2011) and even global scales (Cole et al.

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2007; Battin et al. 2009; Tranvik et al. 2009). In general terms, concentrations and fluxes of DOC in streams and rivers are a function of the magnitude of terrestrial loading, inputs from upstream aquatic ecosystems, storage within the system (e.g., sedimentation), and transformations between organic and inorganic carbon forms (e.g., microbial or photochemical oxidation, photosynthesis). In northern latitudes, peatlands are often important sources of DOC to surface waters, and the extent of wetlands in drainage basins is positively correlated with DOC concentrations and fluxes in streams (Rasmussen et al. 1989; Hope et al. 1994; Aitkenhead et al. 1999). However, wetland extent typically explains roughly only half of the observed carbon concentrations in fluvial systems (Mulholland 2003). Because of the large amount of variance still to be explained, recent studies have emphasized the need to additionally integrate system hydrology and aquatic processing into a unified model (Futter et al. 2007; Laudon et al. 2011; Hanson et al. 2011; Stanley et al. 2012).

While wetlands are recognized as major sources of allochthonous DOC to many aquatic ecosystems, hydrologic linkages dictate the delivery of this DOC to surface waters. For example, changes in flow paths resulting from variation in water table height can be critical for explaining temporal variation in stream water DOC (Hope et al. 1994; Hornberger et al. 1994; Hinton et al. 1997). DOC concentrations often increase in streams as discharge (Q) increases due to rising water tables intersecting organic rich surface soils and transporting that organic matter to streams (Pearce et al. 1986; Grieve 1990; Dawson et al. 2011), with riparian soils a particularly important source (Bishop et al. 1995; Seibert et al. 2009). However, in wetland-dominated areas, increases in discharge can result in decreases in DOC concentration and negative or non-significant DOC/Q relationships (Hinton et al. 1997; Gorham et al. 1998; Laudon et al. 2011). This contrasting pattern has been attributed to one of several hydrologic/hydrochemical mechanisms in wetlands: a flushing-out of DOC-rich peat porewaters during high flow, a rise of water table above the highest-DOC peat porewaters, or a higher proportion of overland/over-ice flow during spring snowmelt in northern wetlands, all resulting in dilution of DOC (Buffam et al. 2007; Laudon et al. 2007). Consequently, DOC/Q relationships have the potential to provide insights into the pathways of organic carbon transport to surface waters, and may be expected to show complex patterns in mixed forest-wetland landscapes.

Once carbon enters aquatic networks, lakes may be important sites regulating the movement of carbon to downstream ecosystems. There is a long-standing recognition that lakes have a significant influence on the magnitude and timing of hydrologic fluxes to downstream

reaches because of their water storage capacity. Lakes can delay the movement of water downstream (FitzGibbon and Dunne 1981) depending on storage deficits (Spence 2000), and this hydrologic storage and eventual release to downstream ecosystems (i.e., *hydrologic buffering*) have the potential for two effects on the export of carbon independent of any biogeochemical transformation. First, because the movement of water transports carbon, reductions in flow variability downstream of lakes may similarly reduce the temporal variability of carbon. Early examples have in fact demonstrated that lakes can reduce variation in nutrient fluxes during storms (Oliver and Grigoropoulos 1981). The same pattern has also been observed for DOC, with less variability in concentrations in streams exiting a lake relative to input stream concentrations (Goodman et al. 2011). The second way in which hydrological buffering by lakes can alter downstream fluxes is by modifying the timing of downstream solute fluxes. In situations in which little or no storage deficit exists in a lake, upstream inputs of 'new' event water to a lake displaces 'old' lake water to downstream ecosystem, followed by a delayed and potentially reduced downstream solute pulse as new event water is integrated into the lake (Goodman et al. 2011). Consequently, lakes have the capacity to disrupt stream concentration/Q relationships by dissociating solute pulses from hydrologic pulses due only to the hydrologic buffering capacity of these lentic systems.

In addition to the strictly physical effects of hydrologic buffering on downstream fluxes, slowing the movement of water can also provide critical time for carbon processing within lakes (Hanson et al. 2011). Early observations that a majority of lakes are supersaturated with carbon dioxide (CO<sub>2</sub>) and a significant conduit of carbon to the atmosphere (Cole et al. 1994) have evolved into a growing consensus that lakes have the potential to be biogeochemical hotspots of carbon processing (i.e., *chemical reactors*) that may regulate the movement of carbon across the landscape by reducing exports to downstream ecosystems (Algesten et al. 2003; Cole et al. 2007; Tranvik et al. 2009). At watershed scales, the role of lakes as chemical reactors has been suggested not only by widespread CO<sub>2</sub> supersaturation, but also by observations that both organic carbon concentrations (Larson et al. 2007) and fluxes (Mattsson et al. 2005) are lower in streams draining watersheds with upstream lakes than in sites without upstream lakes. However, all else being equal, lower carbon concentrations in drainages with upstream lakes are not always observed (Lottig et al. 2012). While globally it is estimated that aquatic ecosystems, particularly lakes, reduce carbon exports to the ocean by 50 % (Cole et al. 2007; Tranvik et al. 2009), failure to detect this lake effect has been reported in several studies. In some cases, high flushing rates through lakes offer little opportunity for biogeochemical transformations

**Table 1** Summary of watershed characteristics for three stream type categories based on land cover and drainage characteristics: sites with watersheds dominated by forest cover (+F), sites in watershed with

mixed forest and wetland cover (+WF), and sites with mixed forest and wetland cover, plus a lake embedded in the drainage network (+LWF)

	+F	+WF	+LWF
Number of sites	4	4	4
Watershed area (km <sup>2</sup> )	6.59 <sup>a</sup> (3.01–11.21)	24.58 <sup>b</sup> (12.68–32.73)	21.81 <sup>b</sup> (14.00–34.72)
Forest (%)	91.33 <sup>a</sup> (87.88–95.81)	52.02 <sup>b</sup> (42.45–61.97)	46.07 <sup>b</sup> (36.03–58.48)
Wetland (%)	1.74 <sup>a</sup> (0.10–3.43)	44.17 <sup>b</sup> (33.66–56.72)	45.68 <sup>b</sup> (34.85–50.35)
Open water (%)	0.34 <sup>a</sup> (0–1.16)	1.41 <sup>a</sup> (0–3.62)	5.44 <sup>b</sup> (2.78–9.58)
Drainage lake (%)	0 <sup>a</sup> (0–0)	0 <sup>a</sup> (0–0)	4.43 <sup>b</sup> (2.38–8.41)
Seepage lake (%)	0.34 <sup>a</sup> (0–1.16)	1.41 <sup>a</sup> (0–3.62)	1.02 <sup>a</sup> (0.07–2.42)

Values are means (range). Superscripts indicated categorical groupings based on Tukey's range test ( $p < 0.05$ )

(Canham et al. 2004; Stets et al. 2010), resulting in little or no effect on downstream carbon. Lakes can also shift from sources to sinks of carbon between seasons (Goodman et al. 2011) or between wet and dry years (Einola et al. 2011), which could also confound the 'chemical reactor' effect across seasons and discharge regimes. Overall, the emergence of inconsistent and variable lake effects on carbon dynamics suggests that a major challenge is identifying how lakes alter carbon dynamics at a variety of spatial scales (Lottig et al. 2012).

The goal of this study was to determine if and how landscape (i.e., differences in wetland extent) and drainage network characteristics (presence of lakes) influenced DOC concentrations and yields in streams within a hydrologically complex landscape. Examination of differences in *magnitude*, *variability*, and *timing* of concentrations and yields among streams that vary in both landscape characteristics and drainage network composition also allowed us to assess the role of lakes as possible hydrologic buffers or chemical reactors with respect to stream DOC, and more broadly, the role of lakes in modulating DOC export from this lake-rich landscape.

## Methods

### Study area

Wisconsin's Northern Highlands Lake District (NHLD; ca. 5,000 km<sup>2</sup>) contains more than 7,500 lakes and 1,500 streams. The region is situated along the northern extent of the temperate zone in northern Wisconsin, and Upper Peninsula Michigan, USA. The NHLD was strongly affected by the retreat of glaciers between 10,000 and 12,000 years ago (Magnuson et al. 1997). Land cover is predominantly a mix of deciduous and coniferous forest (52 %), lakes (13 %), and wetlands (28 %) (Homer et al. 2004), and over 70 % of wetlands in the region are peat

forming (Buffam et al. 2010). Lakes range from small dystrophic lakes less than 1 ha in area to systems >2,500 ha, while streams range from small intermittent channels to large order systems such as the Wisconsin, Chippewa, and Wolf Rivers. A more detailed description of the region, including physical and biogeochemical characteristics of lakes and streams is provided by Hanson et al. (2007) and Lottig et al. (2011). Drainages within the NHLD flow either into the Mississippi River or the Laurentian Great Lakes.

### Site selection and data collection

In order to better understand how landscape composition interacts with in-line lakes (i.e., drainage lakes embedded in the surface water network) to influence watershed DOC dynamics, streams were selected based on the amount of wetlands in their watersheds and the presence or absence of upstream lakes in the drainage network. Watershed boundaries were determined for each sampling location from a ~30 m digital elevation model and ArcGIS version 9.1 (Environmental Systems Research Institute, Inc., Redlands, CA, USA). Percentages of forest, wetland, and open water (hereafter referred to as lakes) in each watershed were calculated from the 2001 National Land Cover Dataset (Homer et al. 2004). Our approach was to select four sites within each of three categories that represented progressive increases in land cover complexity. In the first and simplest category, watershed land cover was dominated by a single cover type of forests (mean = 91 %; Table 1; hereafter +F sites). Sites in the second category were defined by presence of both forests and wetlands in the upstream watershed (mean = 44 %; Table 1; hereafter +WF sites). The final grouping of sites further increased the complexity of the watershed by including sites that contained drainage lakes within the upstream drainage network (hereafter +LWF sites). This final grouping of sites were selected to mimic the +WF sites with respect to

watershed size and wetland extent (mean wetland cover = 46 %; Table 1), but with the added interaction of in-line lakes embedded in the drainage network. Thus, each grouping represents an increase in watershed complexity; first, dominated by single land cover variable, second, dramatic shift and increase in the extent of wetland land cover, and finally, addition of in-line lakes in the drainage network.

Multiple analysis of variance (MANOVA) was used to compare all watershed properties among the stream categories. Watershed area was log transformed to approximate normality and landscape characteristics were arcsin-square root transformed. Because the MANOVA was significant ( $F = 4.58$ ,  $df_{1,2} = 10,20$ ,  $p = 0.002$ ), we assessed differences in watershed characteristics among the three stream categories using analysis of variance (ANOVA). When an ANOVA indicated significant differences, pairwise comparisons were conducted using Tukey's range test. No significant differences in wetland extent were observed between +WF and the +LWF sites ( $p > 0.05$ , Table 1). Significant differences were observed in the size of watersheds between +F versus the +WF and +LWF watersheds (Table 1). This is a consequence of landscape characteristics of the region where large watersheds almost always have substantial amounts of wetland present (regional average 28 %) and we were unable to locate +F watersheds of comparable size to the +WF sites. In a similar fashion, we were also unable to locate +LWF watersheds in the region that were primarily forested due simply to regional landscape characteristics, and thus the lack of a +F-lake category. The +F sites contained no in-line drainage lakes within the surface drainage network and the amount of open water identified by the 2001 NLCD was significantly less ( $p < 0.05$ ) between +F sites (~1 %) versus the +WF and +LWF sites (9 %). Across all sites, forest landcover was negatively correlated with wetlands ( $\rho = -0.95$ ;  $p < 0.01$ ) and watershed area ( $\rho = -0.78$ ;  $p < 0.01$ ). All other potential landscape correlations were insignificant ( $p > 0.18$ ).

All sites were sampled approximately every 8 weeks from July 2007 through October 2008 for a total of eight sampling periods. In +LWF watersheds, samples were collected at the nearest access point (typically of a road crossing) downstream of the drainage lake. In three of the four sites, this was within 0.7 km of the lake outlet. In the other site, access to the stream within this same distance was prohibited by a landowner, so the stream was sampled at a point 1.5 km downstream from the lake. During open water periods, Q was measured using cross sectional area and water velocity (Marsh-McBirney Model 2000 Portable Flowmeter). Discharge was not estimated during winter months when sampling was done through the ice. Because

the sites were ungauged, daily discharges were infilled using six United States Geological Survey (USGS) permanently gauged streams in the region. Daily Q was determined for summer and fall (June–November) periods only as ice cover and spring snowmelt prevented collection of accurate measurements. Analysis of aforementioned USGS discharge records indicated that on average 33 % of annual runoff occurred during this time period (min = 17 %, max = 50 %). Infilling of daily Q in the 12 study streams was accomplished by comparing measured Q in the study streams to gauged Q in the USGS streams using linear regression and selecting the USGS gauged stream with the strongest relationship (linear regression  $r^2$ ) to predict daily Q in the ungauged site (Hirsch 1979; Harvey et al. 2010; Buffam et al. 2011). The resultant models used to infill daily Q values between sampling events were generally very significant (mean  $r^2 = 0.92$ ; Table 2). Further, no significant difference was observed between the summer and fall runoff in USGS streams (mean = 0.06 mm/year) and the study streams (mean = 0.05 mm/year;  $t = 0.56$ ,  $p = 0.59$ ).

Water chemistry samples were collected from the middle of the channel. Filtering was done in the field using an in-line 0.45  $\mu\text{m}$  membrane filter. Samples were stored on ice and returned to the laboratory where they were preserved and analyzed according to North Temperate Long Term Ecological Research (NTL-LTER) protocols (<http://lter.limnology.wisc.edu>). Although the focus of this work is on DOC, we also use dissolved inorganic carbon (DIC) results to support DOC patterns when appropriate. DOC and DIC were measured on a Shimadzu TOC-V carbon analyzer. Collectively, we refer to DOC and DIC concentrations and yields as carbon when not specifically addressing a single variate. We estimated seasonal (June–November) carbon yields ( $\text{mg}/\text{m}^2$ ) using daily discharge record (see above) and daily carbon concentrations estimated using concentration-discharge relationships (CQ; see below for more detail). When non-significant CQ relationships existed, we linearly interpolated carbon concentrations between sampling events.

#### Data analysis

A variety of statistical approaches were used to analyze data collected in this study (Table 3). Relationships between landscape characteristics and carbon concentrations and yields were identified using Pearson's  $\rho$ . Watershed land cover characteristics are often correlated and thus can confound interpretation of statistical results. To address this issue of non-independence, we used a partial correlation test (Johnson and Wichern 2007; Zar 2009) to determine if significant correlations existed in the other

**Table 2** Regression results for discharge relationships and concentration-discharge (CQ) relationships for all stream sites in the forested (+F), mixed forest-wetland (+WF) and mixed forest-wetland plus lake (+LWF) categories

Drainage type	Site	Infill Q ( $r^2$ )	Unlagged CQ <sup>a</sup>		Lagged CQ <sup>b</sup>		
			DOC ( $r^2$ /slope)	DIC ( $r^2$ /slope)	CQ lag (days)	DOC ( $r^2$ /slope)	DIC ( $r^2$ /slope)
+F	A1	0.94	0.90/2.5	0.93/−2.6			
	A2	0.89	0.98/0.15 <sup>c</sup>	0.87/−0.14 <sup>c</sup>			
	A3	0.96	0.88/2.4	1.00/−6.0			
	A4	0.87	0.99/3.9	0.88/−4.3			
+WF	B1	0.72	0.69/7.8	0.69/−2.4			
	B2	0.89	0.97/0.11 <sup>c</sup>	0.80/−0.03 <sup>c</sup>	−3	0.99/0.07 <sup>c</sup>	0.85/−0.02 <sup>c</sup>
	B3	0.92	0.82/3.4	0.89/−3.3			
	B4	0.94	0.89/15.2	0.69/−3.7			
+LWF	C1	1.00	0.24/−	0.66/−	20	1.00/4.5	0.79/−
	C2	0.99	0.01/−	0.12/−	38	0.99/9.3	0.63/−4.9 <sup>d</sup>
	C3	0.94	0.85/2.7	0.71/−2.2	5	0.90/3.2	0.54/−2.2 <sup>d</sup>
	C4	0.93	0.57/−	0.00/−	9	0.80/4.8	0.24/−

Infill Q refers to the relationship between field-measured discharge (Q) at a site and Q at an adjacent USGS gauge. Regression strength ( $r^2$ ) and direction (slope) for relationships between concentration and discharge include results for regressions using unlagged Q (Q for the date of DOC and DIC sampling) and lagged Q. No results are reported if no significant relationship existed between C and Q at any lag length

<sup>a</sup> CQ relationship estimated from log-linear regression at lag = 0

<sup>b</sup> CQ relationship estimated from log-linear regression at lag = identified significant lag

<sup>c</sup> CQ relationship estimated from linear regression relationship instead of log-linear

<sup>d</sup> Moderately significant (between 0.05 and 0.1)

**Table 3** Summary of statistical approaches used in this study

Analysis	Statistical test	Rationale
Correlation among landscape variables and stream carbon dynamics	Partial autocorrelation test	Accounts for correlated landscape variables when assessing potential relationships with stream carbon
Differences in carbon concentrations and yields among watershed types	Repeated measures analysis of variance (RM-ANOVA)	Accounts for repeatedly sampling the same locations through time when assessing carbon differences among watershed types
	Repeated measures analysis of covariance (RM-ANCOVA)	Accounts for variation in continuous landscape variables between watersheds and repeated sampling when assessing differences in carbon among watershed types
Relationship between discharge and carbon concentrations	Simple linear regression	Determines strength of relationship between discharge and carbon concentrations in streams
	Cross-correlation analysis	Identifies when (time lag) discharge and carbon concentrations are most correlated

variates after removing variation associated with the strongest correlate.  $p$ -values for all multiple comparisons were Bonferroni adjusted and DOC and DIC concentrations and yields were log transformed to meet normality requirements. Values reported in the text were estimated from non-transformed data for ease of interpretation.

Differences in *magnitudes* of DOC and DIC concentrations and yields in the three stream types were assessed using repeated measures analysis of variance (RM-ANOVA). While our study design controlled for forest, wetland, and lake extent among the stream types, minor variations in these landscape characteristics and other

watershed attributes occurred within each of the three stream groups (Table 1). When RM-ANOVA identified significant differences between stream types, we used a repeated measures analysis of covariance (RM-ANCOVA) to determine if differences in the strongest landscape correlate identified above were driving categorical differences, or if the categorical differences were influenced by some other factor. Covariates were mean-centered in order to eliminate adjustments that can make the main effect weaker in repeated measure models when covariates are introduced (Delaney and Maxwell 1981). Differences in *variability* of DOC concentrations and yields were assessed

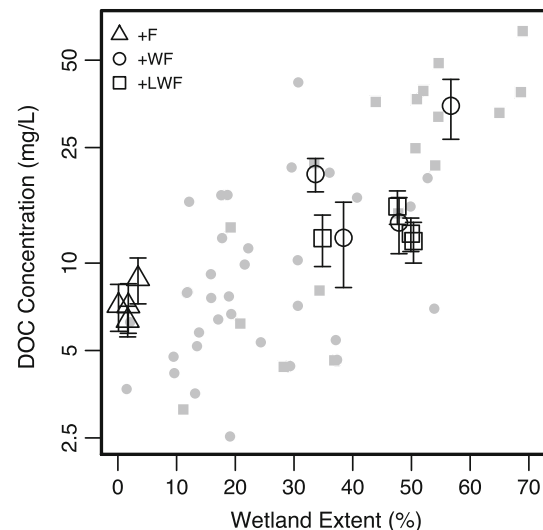
by comparing coefficient of variation (CV) across the three site categories using ANOVA. Tukey's Range Test was used for any pairwise comparisons.

To quantify the potential effect of wetlands and inline lakes on the *timing* of carbon yields, we quantified how changes in flow influenced temporal patterns in organic and inorganic carbon concentrations using CQ relationships. The degree to which carbon concentrations were influenced by changes in discharge was quantified as the linear regression coefficient of determination ( $r^2$ ). The dynamic range (order of magnitude difference between the highest and lowest flows) of measured  $Q$  in each stream (min = 0.8, median = 1.78, max = 3.36) with associated DOC/DIC samples used to develop CQ relationships was similar to annual dynamic ranges observed in gauged USGS streams (min = 0.8, median = 1.69, max = 3.06 orders of magnitude). In addition to assessing CQ relationships with un-lagged data, we also examined a second set of relationships using lagged  $Q$  data to identify any significant lags in the solute concentration and discharge time series (i.e., changes in the timing of carbon yields due to the disassociation of the hydrologic pulse from the solute pulse in an upstream lake). We identified time lags (max lag = 6 weeks; time between sampling events) in DOC concentration and daily discharge time series using cross-correlation function for all streams in this study. If significant lags existed, we identified the most significant lag for DOC (our focal variate) and estimated CQ relationships at this lag in addition to assessing the relationship for non-lagged data.

Finally,  $r^2$  values were compared among stream types using ANOVA to assess how differences in land cover and drainage network composition influenced relationships between DOC, DIC and stream flow. When significant differences were detected, pairwise comparisons were conducted using Tukey's range test.

## Results

Dissolved organic carbon concentrations were negatively correlated with forest cover ( $\rho = -0.47$ ;  $p < 0.01$ ), and positively correlated with wetland extent ( $\rho = 0.51$ ;  $p < 0.01$ ; Fig. 1) and watershed area ( $\rho = 0.42$ ;  $p < 0.01$ ). However, a partial autocorrelation test indicated that no significant correlation existed with forest or watershed area after accounting for variation in wetland extent ( $p = 1.00$ ; the strongest correlated). No significant correlation with DOC concentration was observed with open water ( $p = 0.18$ ). Furthermore, splitting the open water classification between seepage and drainage water bodies within each watershed also did not result in any significant correlation ( $p > 0.14$ ). Finally, DIC concentrations were



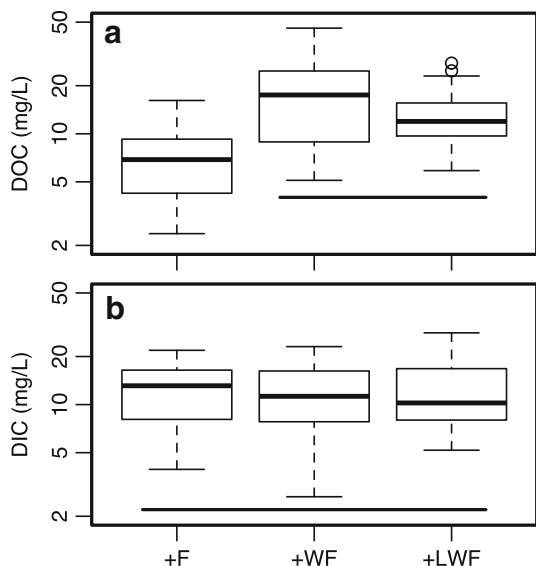
**Fig. 1** Relationship between average DOC concentration (mg/L) and wetland extent (%) for forest (+F), wetland-forest (+WF), and lake-wetland-forest (+LWF) streams. Error bars represent  $\pm 1$  standard error. Grey filled points represent the regional baseflow DOC/wetland relationship from Lottig et al. (2012) for context

not significantly correlated with any landscape feature ( $p > 0.57$ ).

On average, DOC concentrations were significantly lower ( $p < 0.02$ ) in +F streams (median = 7.00 mg/L) relative to +LWF (median = 11.95 mg/L) and +WF streams (median = 17.49 mg/L) (Fig. 2a). Including wetlands as a covariate in the repeated measures ANOVA did not change the overall results with respect to the +WF and +LWF comparison, but did indicate that, after accounting for differences in wetland extent between watersheds, DOC concentrations at +F sites were not significantly different from the other two groups ( $p > 0.77$ ). DIC concentrations were similar across all three stream types (RM-ANOVA,  $F = 0.33$ ,  $p = 0.73$ ) and median concentrations differed among all three categories by less than 3 mg/L (+LWF = 10.24 mg/L, +WF = 11.27 mg/L, +F = 13.12 mg/L; Fig. 2b).

In contrast to concentrations, DOC yields (Table 4) from June through November in +F streams (mean = 0.6 g/m<sup>2</sup>) were significantly lower than +WF streams (mean = 1.1 g/m<sup>2</sup>;  $p = 0.03$ ), but not statistically different from +LWF streams (mean = 0.7 g/m<sup>2</sup>). DOC yields in +LWF streams were lower, but not statistically different from +WF streams ( $p = 0.19$ ). The pattern for seasonal DIC yield was slightly different (Table 4), with the highest DIC yields observed in +LWF sites (0.6 g/m<sup>2</sup>), lowest in +WF sites (0.3 g/m<sup>2</sup>) and +F (0.3 g/m<sup>2</sup>); Table 2).

The variability of DOC and DIC concentrations, measured as CVs, were not significantly different among the three stream categories (ANOVA,  $F < 1.46$ ,  $p > 0.28$ ). However, we did observe clear differences in the influence



**Fig. 2** DOC (a) and DIC (b) concentrations for the three stream categories. *Box plots* show median values and inter-quartile (IRQ) ranges. *Whiskers* extend  $\pm 1.5 \times$  the IRQ range and the *points* beyond the *whiskers* indicate outliers. *Solid horizontal line* denotes results of pairwise comparison

of discharge on the un-lagged DOC and DIC concentrations (i.e., CQ relationships) between categories. CQ relationships for both DOC and DIC were always significant in all eight sites without upstream lakes (+F and +WF), while only significant in one of the four +LWF sites (Fig. 3). In all the +F and +WF sites and the single +LWF site with significant DOC CQ relationships, DOC

increased with increases in discharge (Table 2; Fig. 3), while DIC declined (Table 2; Fig. 3). Average  $r^2$  values for the unlagged DOC CQ relationships were strongest in +F (mean = 0.93) and +WF (mean = 0.84) sites and weakest in +LWF sites (mean = 0.41; Fig. 4a; Table 2). A similar pattern in CQ relationship strengths was observed for DIC concentrations but the relationships were generally not as strong as for DOC. CQ relationships for +F and +WF sites were always significantly different from +LWF sites regardless the amount of wetland in the watersheds for both DOC ( $p < 0.04$ ) and DIC ( $p < 0.04$ ) concentrations.

Potential changes in timing of DOC and DIC transport relative to hydrologic transport through drainage networks were identified in several drainage networks by incorporating time lags into the assessment of CQ relationship strength. Using lagged discharge records had the greatest effect on two of four CQ relationships in +LWF sites (C1 and C2) where discharge explained less than 24 % of the DOC variance at a zero time lag versus >90 % when incorporating 20–38 day time lags (Table 2). After accounting for the significant time lags, relationships between DOC (+), DIC (–), and discharge were similar to other sites with zero lag significant relationships (Table 2). Time lags were also identified in two sites (B2 and C3) with significant CQ relationships at a zero time lag. However, the most significant time lags identified in these three sites were relatively short ( $\leq 5$  days) in relation to time lags in other +LWF sites and did not substantially alter the amount of temporal variation in DOC concentrations explained by changes in discharge (Table 2). Overall,

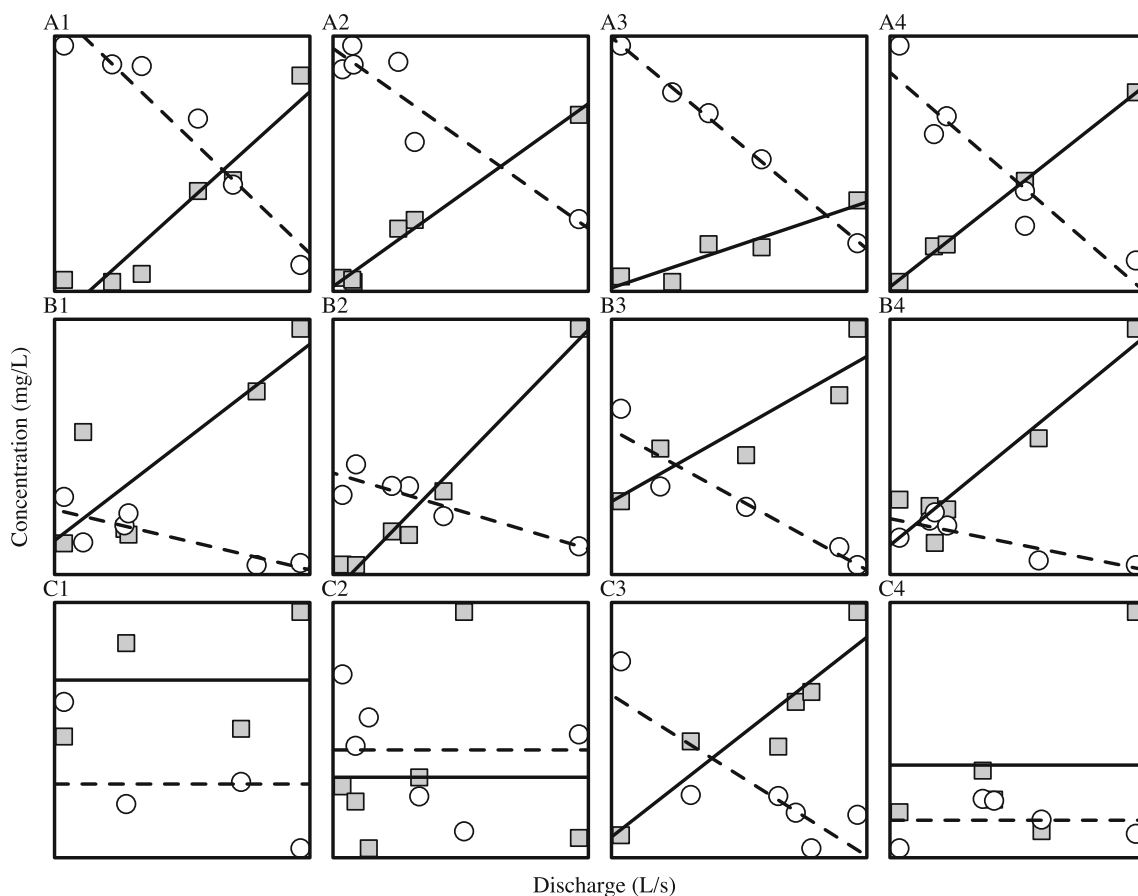
**Table 4** Average DOC and DIC fluxes from June through November (2007 and 2008) for all stream sites in the forested (+F), mixed forest-wetland (+WF) and mixed forest-wetland plus lake (+LWF) categories

Drainage type	Site	Unlagged		Lagged	
		DOC flux (g/m <sup>2</sup> )	DIC flux (g/m <sup>2</sup> )	DOC flux (g/m <sup>2</sup> )	DIC flux (g/m <sup>2</sup> )
+F	A1	0.6	0.3		
	A2	0.7	0.5		
	A3	0.4	0.4		
	A4	0.6	0.2		
+WF	B1	0.6	0.1		
	B2	1.5	0.8	1.1	0.9
	B3	1.3	0.3		
	B4	1.8	0.1		
+LWF	C1	0.6 <sup>a</sup>	0.4 <sup>a</sup>	0.6	0.4 <sup>a</sup>
	C2	1.3 <sup>a</sup>	1.2	1.1	1.3 <sup>b</sup>
	C3	0.9	0.3 <sup>a</sup>	0.8	0.3 <sup>b</sup>
	C4	0.4 <sup>a</sup>	0.2 <sup>a</sup>	0.4	0.2 <sup>a</sup>

Fluxes calculated for unlagged and lagged data (see Table 2)

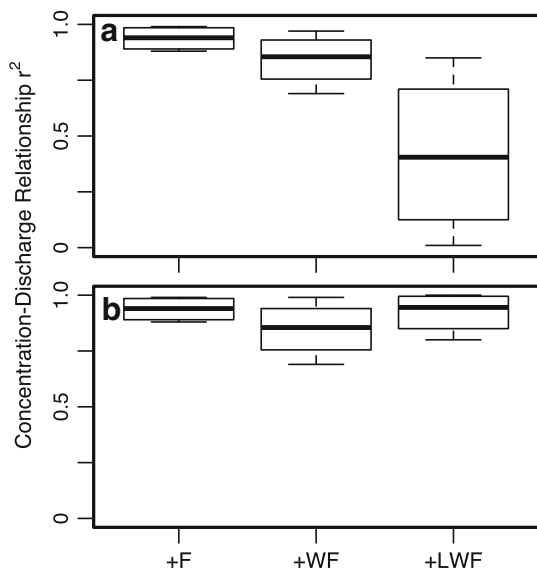
<sup>a</sup> No significant CQ relationship, fluxes were calculated using discharge and linearly interpolated carbon concentrations between sampling events

<sup>b</sup> Fluxes estimated using CQ relationship, but CQ relationships were significant at the  $p = 0.05$ – $0.10$  level



**Fig. 3** Concentration discharge relationships for +F (a1–a4), +WF (b1–b4), and +LWF sites (c1–c4). DOC—solid trend lines and filled squares, DIC—long dashed trend lines and open circles. Horizontal

regression lines indicate no significant relationship between discharge and concentration for associated variates and the trend line is plotted as the mean value for the variable (i.e., intercept = mean, slope = 0)



**Fig. 4** Concentration discharge (CQ) relationship strengths for unlagged dissolved organic carbon (DOC; a) and lagged DOC (b) for the three stream categories. Boxplots show median values and interquartile (IRQ) ranges. Whiskers extend  $\pm 1.5 \times$  the IRQ range and the points beyond the whiskers indicate outliers

including time lags resulted in discharge explaining a similar amount of variation (ANOVA,  $F < 3.4$ ,  $p > 0.08$ ) in +LWF sites as +WF sites (Fig. 4; Table 2).

## Discussion

The goal of this study was to determine if and how landscape (i.e., differences in wetland extent) and drainage network (presence of lakes) characteristics influence DOC concentrations and yields in streams within a hydrologically complex region. The NHLD is an ideal setting for addressing this goal because it is a carbon-rich region in which lakes, streams, and wetlands are dominant features of the landscape (Cardille et al. 2007; Buffam et al. 2011), similar to other formerly glaciated north-temperate and boreal regions. As has been widely reported in other studies (Aitkenhead et al. 1999; Mulholland 2003) including a wider one-time survey in the NHLD (Lottig et al. 2011), presence of wetlands in the watershed was associated with high stream DOC concentrations and yields. However, we failed to detect any significant differences in DOC



magnitude and variability among streams with and without upstream lakes. Instead, our results indicated that the major effect of drainage lakes on carbon dynamics was to decouple discharge and concentrations downstream of lakes.

The coupling of concentration and stream flow has long been recognized as an important factor influencing the temporal variability of DOC in drainage networks (Hope et al. 1994; Hornberger et al. 1994; Hinton et al. 1997). Concentration often increases as Q increases due to the rising water tables intersecting organic-rich surface soils (Pearce et al. 1986; Grieve 1990; Dawson et al. 2011). We saw this positive relationship in both +F and +WF streams where, on average, 85 % and up to 100 % of the temporal variation in DOC concentrations could be explained by differences in Q. Concurrent and often equal decreases in DIC concentrations provide further evidence of flow paths shifting from groundwater sources at baseflow to surficial sources at higher flow, as groundwater in the NHLD is typically DOC-poor and DIC-rich (Schindler and Krabbenhoft 1998; Elder et al. 2000). The slight decreases in CQ relationship strength for DIC and DOC in the +WF sites relative to their forested (+F) counterparts are consistent with hydrologic attenuation in larger catchments (Dawson et al. 2011) and more consistent flow path interactions with organic rich soils, regardless of flow regime (Hinton et al. 1997).

While correlations between C and Q were strong for streams without upstream lakes, most of these relationships were weak or non-existent in +Lake sites. The decoupling of concentration and flow downstream of lakes combined with a lack of overall differences in concentration among stream categories are consistent with the hypothesis of lakes acting as hydrologic buffers on downstream ecosystems. If lakes slow the movement of water, we would expect high inflows from upstream to displace lake water downstream. Consequently, hydrologic pulses may not be delayed unless a storage deficit exists in the lake (Spence 2000), but the chemistry of water initially pushed out of the lake may be very different from the pulses entering the lake. While the temporal frequency of our sampling regime was limited, strong and very significant CQ relationships in most of the +LWF sites after incorporating a time lag for discharge is consistent with this hydrologic buffering explanation. Patterns such as this have been observed in alpine lakes where lakes do not buffer hydrologic pulses but do delay the transmission of the associated carbon pulse by several days, in turn altering the downstream CQ relationship (Goodman et al. 2011). Notably, we did not observe any differences in variability (as CVs) among stream types even though hydrologic buffering by lakes might be expected to reduce variability in +LWF sites relative to the other stream types. Similarities in CV among

these three categories may reflect strong groundwater dominance in the region that is associated with low variability in stream discharge (Watters and Stanley 2007). We also did not specifically focus on sampling high-variability flood pulses, but instead attempted to capture temporal dynamics at seasonal scales, which may have limited the opportunity to document low variability in +LWF sites relative to +F and +WF streams.

The presence of a significant CQ relationship in un-lagged data at a single +LWF site suggest that lakes do not always alter solute and hydrologic coupling, or that CQ relationships may reestablish quickly downstream of lakes. In this study, the three +LWF streams that were sampled within 0.7 km of the lake outlet exhibited no relationship with either DIC or DOC concentration and stream flow using un-lagged data. However, the one +LWF site with a significant DOC-Q relationship was sampled approximately 1.5 km downstream of the lake outlet. Thus, we are unable to determine if the significant CQ relationship reflects a persistent lake effect or re-establishment of this relationship within the longer stream reach. If lakes do influence downstream biogeochemical conditions, this result highlights the next questions of how far this influence persists and what determines the strength of such a lake effect on recipient streams.

While the results of these analyses clearly suggest that lakes have the potential to delay the movement of carbon downstream, caution needs to be taken when extrapolating these results to time periods and scales not captured by this study design. One of the limitations of this study is the lack of data to adequately assess the downstream movement of carbon during snowmelt periods. Due in large part to the low-relief, peatland-rich landscape and strong groundwater influence, variation in annual flow is minimal (Watters and Stanley 2007) suggesting that flushing during snowmelt periods may not be as important in this region as in other northern regions. This suggestion is supported in part by the fact that the dynamic range of summer/fall stream Q was similar to annual values- including snowmelt- during this study. Nonetheless, snowmelt can be an important period of carbon fluxes through surface water networks in the region in some years but not others (Kerr et al. 2008) and was not captured in this study. A second consideration is that the relationships between flow and discharge during a single hydrologic pulse are likely to be very different than the patterns observed in this study at seasonal scales. At the time scale of a single event, relationships between solutes and discharge often display hysteresis (Bond 1979; Andrea et al. 2006) that relate to the sources and pathways of water to streams, whereas the patterns in this study reflect the general relationship of varied discharge regimes on stream carbon concentrations. Undoubtedly, further study at higher frequencies and during potentially important time

periods such as snowmelt would provide additional valuable information for understanding the patterns suggested here.

In addition to the capacity to hydrologically buffer the movement of carbon in downstream ecosystems, lakes have also been highlighted as carbon processing hotspots at a variety of spatial scales (Algesten et al. 2003; Tranvik et al. 2009). Within the NHLD, a linked hydrologic-biogeochemical model suggests that lakes in the region, on average, process (i.e., mineralization, sedimentation) 50 % of organic carbon inputs (Cardille et al. 2007), and studies of individual lakes indicate net heterotrophy and retention or mineralization of allochthonous organic matter (Hanson et al. 2003; Hanson et al. 2004; Duarte and Prairie 2005). Yet observations from streams provide a mixed picture with respect to lake influence on DOC. Lower DOC concentrations have been observed in streams draining watersheds with upstream lakes relative to those lacking upstream lakes (Larson et al. 2007), consistent with the conclusion that lakes decrease downstream DOC. However, the same pattern is not evident at the regional scale where DOC concentrations and yields do not differ among streams with and without upstream lakes (Lottig et al. 2012). Reflective of these ambiguous findings, estimates from an integrated regional C budget (Buffam et al. 2011) suggest that riverine fluxes of carbon out of the NHLD are approximately 71 % of all allochthonous inputs to surface waters (i.e., 29 % retention), but concurrent estimates of C storage and net CO<sub>2</sub> emissions in surface waters (primarily lakes) are ca. 8 % greater than total allochthonous inputs (108 % retention). The apparent discrepancy highlighted above in the regional C budget can be explained by high uncertainty remaining in some of the regional C fluxes as noted by Buffam et al. (2011). For this region, revised estimates of any of the following annual fluxes in the noted direction would reduce the discrepancy: carbon inputs from watershed to surface waters (higher), lake net CO<sub>2</sub> emissions (lower), lake C sedimentation (lower), or regional riverine C export (lower). Emerging from this growing body of research is a clear need to better constrain regional estimates of C retention in lakes, and more generally, an increasingly complex picture of carbon cycling in hydrologically rich landscapes.

Results from this study suggest a limited role of drainage lakes in altering stream DOC concentrations and yields relative to streams/streams without such upstream lakes, and what influence there is appears hydrological rather than biogeochemical in nature. While there is growing evidence that lakes can reduce fluxes of DOC to downstream ecosystems and eventually the ocean (Mattsson et al. 2005; Tranvik et al. 2009; Weyhenmeyer et al. 2012), the observation that drainage lakes do not necessarily reduce downstream organic carbon fluxes is not novel (Canham

et al. 2004; Stets et al. 2010; Goodman et al. 2011). These apparently conflicting results regarding lake influences on fluvial DOC highlight two points. First, there is no reason to expect lakes to consistently reduce (or not reduce) downstream DOC dynamics from place to place, or even over time (Einola et al. 2011). Variation in lake morphology, residence time, and temperature, or the quality of DOC inputs to lakes can translate into large differences in allochthonous OC retention (Hanson et al. 2011), and residence time in particular appears to be emerging as a key constraint on the capacity of a lake to reduce downstream DOC fluxes (Stets et al. 2010; Weyhenmeyer et al. 2012). Second, caution is needed when extrapolating results such as ours to larger spatial scales or other regional settings. Our goal was to determine if we could detect a difference among streams with and without lakes using data from distinct stream types and not to assess the annual sink/source status of lakes. Lakes may be net C sinks, but also have no measurable effect on downstream C fluxes if C loading to lakes is greater than to streams upstream of the targeted study sites, and/or if any lake effect is rapidly overwhelmed by in-stream processes below the lake output. Further, our study focused specifically on lakes embedded within drainage networks (drainage lakes). While this type of lake accounts for approximately 75 % of lake surface area within the NHLD, seepage lakes (i.e., lakes lacking surface connections to a drainage network) are more numerous in the region, representing roughly 75 % of all lakes (United States National Hydrography Dataset). On the other hand, using information from seepage lakes studies to infer how lakes may affect fluvial DOC concentrations and fluxes may lead to erroneous conclusions, as would also be the case if stream DOC patterns were used to infer the OC source/sink status of lakes.

Our study assessed the extent to which known effects of wetlands and lakes on carbon dynamics translate into visible, predictable patterns of organic and inorganic carbon concentrations and yields in hydrologically complex landscapes. Overall, we observed that wetlands exerted predictable patterns on DOC concentrations/yields and relationships between DOC concentrations and stream flow. More significantly, our results illustrate that lakes embedded in surface water drainage networks appear to have little influence on average DOC concentrations and exports, but appear to have substantial influences on relationship between streamflow and DOC/DIC concentrations relative to drainage networks that do not contain embedded lakes. These findings are consistent with lakes buffering temporal patterns in streams (Goodman et al. 2011) but provide little support that in-line lakes have a net effect on carbon exports. Consequently, although drainage lakes may have the ability to alter the timing of carbon exports,

drainage networks in the NHLD containing lakes with the capacity to intercept and decrease fluvial OC exports do not appear to alter baseline patterns of watershed carbon exports.

Results from this study provide insight into future opportunities to better understand the role upstream lakes play in influencing the timing and magnitudes of downstream carbon yields across a range of spatial scales. One of the limiting aspects of this work is the frequency with which chemical sampling occurred (i.e., seasonal time scales). While our data suggest that lakes delay the movement of carbon to downstream ecosystems, higher-frequency sampling associated with changing discharge regimes or events is needed to more clearly identify this pattern in stream/river networks. In addition to collecting data at higher frequencies, capturing fluxes during hydrologically important periods such as snowmelt will be critical for understanding these patterns at annual time scales. Finally, we suggest that studies such as this are critical for understanding how hydrologically linked landscape elements interact to influence the timing, character and total magnitude of solute fluxes to downstream environments.

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