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Spatial and temporal variability in stream dissolved organic carbon quantity and quality in an Adirondack forested catchment

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ABSTRACT

The dissolved organic carbon (DOC) quantity and quality in streams regulate many ecosystem processes at the watershed scale. There is, however, a dearth of information on the spatial variability of in-stream DOC quality in small catchments. Our study used direct DOC concentration measurements and fluorescence spectroscopy indices to determine how stream DOC quantity and quality changed over space and time in a forested catchment of the US Northeast, and provided insight into how these systems might respond to changes in land use and/or climate in the coming years. Land cover (e.g., wetlands, lakes) exerted a dominant role over changes in flow and/or air temperature at regulating DOC concentrations in the watershed. Wetland areas acted as large sources of humic-rich DOC, while lakes were DOC sinks, especially for humic-rich DOC. DOC quality indices were generally significantly ($p < 0.05$) correlated to DOC concentrations regardless of location and time of year, with high DOC concentrations (>7 mg C L^{-1}) primarily tied to the mobilization of terrestrial highly degraded humic rich DOC, likely to be less bioavailable (and less fresh) than the DOC exported at times when DOC concentrations are low (<7 mg C L^{-1}). Overall, results pointed to a two-phase DOC export whereby mobile and bioavailable fractions of DOC in surface water (protein-like DOC) are produced throughout the watershed (including the wetland), while recalcitrant humic-like DOC fractions are predominantly generated by the wetland, before preferentially sedimenting out in the lake. As the climate continues to change, we will likely find not only an increase in the amount of DOC exported at the watershed scale, but also a shift in the quality of this DOC toward less bioavailable DOC fractions rich in humic substances.

1. Introduction

The dynamics of organic carbon at the watershed scale is critically linked to many ecosystem services including plant growth, greenhouse gas emissions, soil biogeochemical transformations, and water quality (Rotkin-Ellman et al., 2004; Dosskey et al., 2010). In streams, the dynamics of dissolved organic carbon (DOC) has the potential to affect in-stream acidification processes, heterotrophic productivity, respiration, and ultimately rates of C cycling and short-term CO_2 outgasing (Wigington et al., 1996; Dalzell et al., 2005). Understanding how the concentrations and the forms of DOC change in streams over space and time is therefore extremely important to understand how ecosystems might respond to changes in land use and/or climate.

Many studies have shown that much of the DOC in streams under a variety of land uses is exported during high flow periods (Boyer et al., 1997; Inamdar et al., 2004; Vidon et al., 2008). In mountainous catchments of Colorado, Hornberger et al. (1994) showed that DOC concentrations were highest during the early stages of snowmelt. In the Adirondack Mountains, NY, Inamdar et al. (2004) showed drastic increases in DOC concentrations during storms. Several studies have also shown that as DOC concentrations change during high flow conditions, the proportion of aromatic substances exported in streams also increases (Hood et al., 2006; Vidon et al., 2008). On a seasonal basis, Waiser and Robarts (2004) showed for a series of wetlands across the Canadian Prairie Region that DOC concentrations increased twofold between Spring and Fall, while DOC specific UV absorption (SUVA), which is related to DOC aromaticity, decreased by approximately 30%. During the winter, in snow covered Adirondack mountainous

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catchments, stream DOC concentrations showed a direct positive response to rising temperatures and subsequent increase in runoff (Park et al., 2005). In south-central Ontario, Wilson and Xenopoulos (2008) suggested that seasonal changes in DOC export patterns in a series of forested to agricultural watersheds were primarily regulated by changes in flow paths and soil moisture conditions during the year.

Spatially, Bianchi et al. (2007) showed that autochthonous carbon production in headwater streams in the Mississippi River Basin had the potential to cause a shift in the chemical composition of organic carbon in streams. In a small forested watershed in Maryland, Inamdar et al. (2011) showed using a suite of optical indices (e.g., UV absorbance, DOC fluorescence properties) that surficial DOC sources to streams (e.g., wetlands) had a greater proportion of humic-like substances than groundwater DOC, while deeper DOC sources (e.g., groundwater) exhibited more protein-like fluorescence, therefore suggesting that groundwater DOC might be more bioavailable than wetland DOC. In Wisconsin and Michigan, Larson et al. (2007) showed that stream DOC concentrations and DOC UV absorbance were all significantly lower in streams with upstream lakes than in streams with no lakes.

However, although previous research has indicated that lakes and wetlands have the potential to affect DOC quantity and quality, and that autochthonous carbon production in headwater streams has the potential to cause a shift in the chemical composition of organic carbon in streams, there remains a critical lack of information on the spatial variability of in-stream DOC in small catchments (<1000 ha) from headwater locations, to areas influenced by large wetlands, or at the outlet of lakes. Most studies indeed tend to focus either on source characterization (e.g., Inamdar et al., 2011), large-scale variability (e.g., Bianchi et al., 2007), or temporal variability (e.g., Waiser and Robarts, 2004; Hood et al., 2006; Vidon et al., 2008). Determining to what extent the quantity (i.e., DOC concentration) and the quality (e.g., freshness, terrestrial vs. aquatic, humic-like fluorescence) of DOC vary from headwater locations to the watershed outlet can nevertheless provide key information on the importance of headwaters, lakes, and wetlands at regulating not only DOC quantity, but also DOC quality at the watershed scale. Understanding the importance of spatial variability in DOC quantity and quality relative to temporal variability can also provide insight into how forested watersheds of the US Northeast might respond to future changes in land use and climate.

In our study, we therefore used a series of fluorescence indices to characterize the spatial and temporal variability of the nature of stream DOC (Coble, 1996; Fellman et al., 2008, 2009; Hood et al., 2005, 2006; McKnight et al., 2001) in a small Adirondack catchment (352 ha) in order to address the following two questions: (1) How do stream DOC quantity and quality change from headwater locations to the outlet of the watershed as the stream transits through a wetland and a lake and (2) Are those changes consistent over time? The implications of our finding for watershed management are also discussed.

2. Materials and methods

2.1. Site description

The Arbutus watershed (352 ha) is located in the Adirondack Mountains, NY within the Huntington Wildlife Forest (43°59′N, 74°14′W). The mean annual temperature and total annual precipitation averaged 4.8 °C and 1080 mm from 1981 to 2000, respectively (Park et al., 2005). Arbutus Lake occupies a surface area of 50 ha, and the Archer Creek sub-catchment (above the Inlet, Fig. 1) represents an area of 135 ha. Elevation ranges from 513 m to 748 m above sea level. Upland soils are generally <1 m in depth and are dominated by Becket–Mundal series sandy loams (coarse-loamy, isotic, frigid, oxyaquiz Haplorthods). These temperate forest spodosols typically have an O-horizon (5 cm thick), a Bs-horizon (~80 cm thick), and a C-horizon. There is no A horizon and an E horizon can be found occasionally. Soils in valley bottoms and hillslope hollows generally have deeper depths of ~2 m consisting of Greenwood Mucky peats in valley bottom wetlands. Similar soils are found throughout the Adirondack region and are characteristic of the US northeast (Sommers, 1986). A large palustrine wetland is located immediately upstream of the lake inlet (Fig. 1), while seep-fed headwater wetlands can be found in the headwaters (S14head and S15head; Fig. 1). Vegetation in the upper hillslopes of the watershed is primarily comprised of northern hardwoods consisting of American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), yellow birch (*Betula alleghaniensis*), and white pine (*Pinus strobus*). Low lying areas near the lake margin are often dominated by conifer stands composed of eastern hemlock (*Tsuga canadensis*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*).

2.2. Field and laboratory measurements

Air temperature and stream flow at the inlet of the lake were continuously monitored between January 1 and December 31, 2012 (study period) as part of routine hydrological measurements conducted in the study watershed since 1983 (Mitchell et al., 2009). Seven-day (7dQ) and 30-day (30dQ) antecedent discharge (Fig. 2) were determined by calculating the mean discharge (Q) for the seven and 30 days prior to each measurement point. Mean daily temperature (Temp) and seven-day antecedent temperature (7dTemp) were obtained from a long-term weather station located between sampling station S15weir and S14weir (Fig. 1) within Archer Creek.

During the snow-free season in 2012 (April to October), a series of water samples were collected throughout the watershed for a variety of flow conditions (Fig. 2). Stream sampling locations included two locations in the headwaters of Archer Creek watershed at the outlet of two seep-fed headwater wetlands (S14head, S15head; Fig. 1) and two other headwater locations routinely sampled for water quality as part of the long-term monitoring program of the watershed (S14weir, S15weir; Mitchell et al., 2009). Lower in the watershed, water samples were also collected immediately before the stream enters the large palustrine wetland described above (Merge site; Fig. 1), and immediately after the wetland at the inlet of the lake (Inlet site; Fig. 1). With its relatively flat topography and relatively organic rich soil relative to headwater locations, the Merge site constitutes a transition point from headwater locations (S14 and S15 locations) to areas influenced by wetlands (Inlet site). Water samples were also collected at the outlet of Arbutus Lake (Outlet site; Fig. 1).

Together, these sites represent the range of conditions existing in the watershed from headwater locations (S14head, S14weir, S15head, S15weir) to low-land areas (Merge), wetland-influenced areas (Inlet), and lake-influenced areas (Outlet). Although smaller tributaries and ground water draining into the lake were not sampled in this study, Archer Creek represents close to 50% of the contributing area to the lake. Land cover and landscape geomorphology are homogenous throughout Arbutus watershed. Archer Creek therefore represents typical inputs into the lake as indicated in previous studies (Mitchell et al., 2001, 2009; Park et al., 2005; Kang and Mitchell, 2013).

At each sampling location, water samples were collected (from date D1 to D12; Fig. 2) using standard methods (sterile gloves, acid washed containers, etc.; Vidon et al., 2013) and were kept on ice in the field until returned to the laboratory where they were filtered within 24 h of collection using 0.7 μm GF/F filters (Whatman, Inc.®).

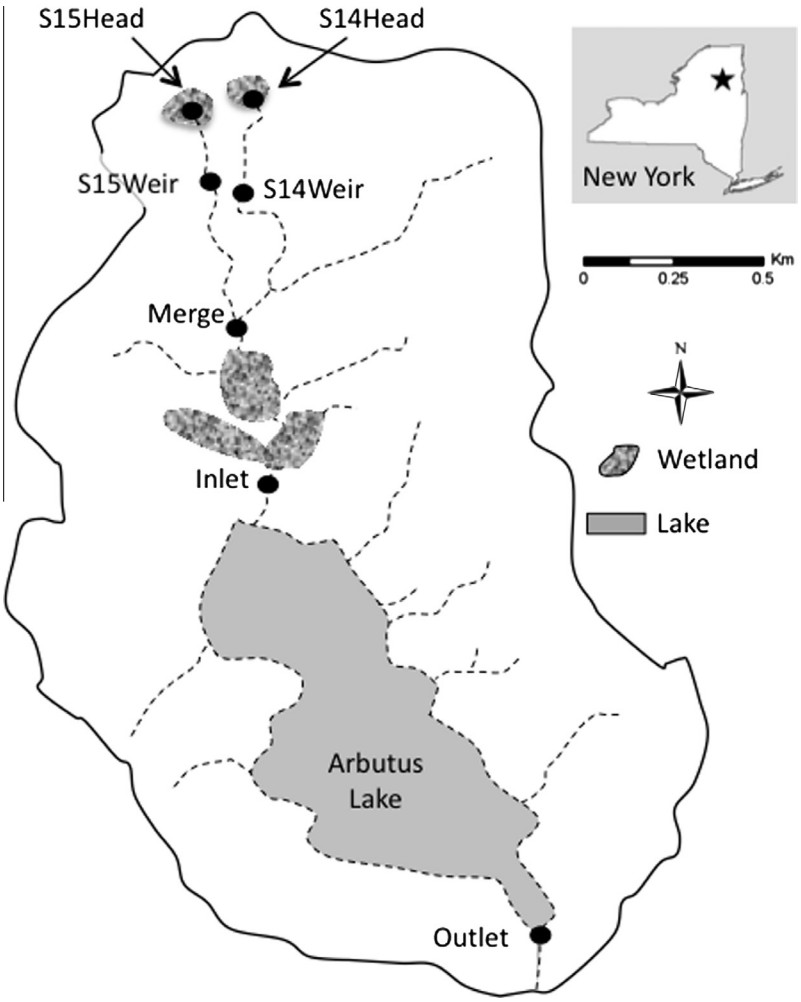

Fig. 1. Experimental site location in New York State, and water sampling locations (S14head, S15head, S14weir, S15weir, Merge, Inlet, Outlet) in Arbutus Watershed, NY.

An aliquot of each sample was acidified using 2 molar H_2SO_4 and refrigerated until analysis for dissolved organic carbon (DOC) using a Tekmar carbon analyzer (Phoenix8000®, Tekmar, Mason, OH). An external DOC standard (Organic carbon standard 1000 ppm, LabChem, Pittsburg, PA) was used for quality control purpose. Another aliquot (not acidified) of each sample was immediately (same day as filtration) analyzed for the fluorescence properties of DOC on a Fluoromax-4 spectrofluorometer ®(Horiba Jobin-Yvon Inc.) and corrected for instrument bias with manufacturer provided correction files. Following the procedure described in Cory and McKnight (2005), a daily lamp scan, cuvette check, and Raman water scan were run to assure instrument stability, and collect the area under the Raman curve so all data could be normalized by this area to correct for any instrument drift over time. Following daily checks, all scans were collected in S/R mode (ratio). For each of the samples, a series of 5 indices were determined. We calculated the fluorescence index (FI) as the ratio of the intensities at 470 and 520 nm for an excitation wavelength of 370 nm (McKnight et al., 2001). FI values between 1.2 and 1.5 indicate carbon of terrestrial origin (rich in lignin), while higher values (1.7–2.0) indicate microbial carbon sources (poor in lignin; McKnight et al., 2001; Hood et al., 2006). We calculated the tryptophan to tyrosine ratio (Trypto/Tyro) as the ratio of the intensities for the tryptophan peak (Excitation = 275 nm, Emission = 340 nm) and tyrosine peak (Excitation = 275 nm; emission = 340 nm) (Coble, 1996). These amino-acids are indicative of protein-like DOC and therefore of relatively bio-available DOC. Because Tryptophan is considered a less degraded peptide material than tyrosine, higher values of this ratio (range: 0.5–2) would indicate less degraded protein than lower values of this ratio (range: 0–0.5) (Inamdar et al., 2011; Fellman et al., 2009; Yamashita and Tanoue, 2004). We also calculated two indicators of the presence of humic substances in the samples defined as Humic A (HumA) (Excitation = 260 nm; Em = max (380,460), 5 nm emission intervals) and Humic C (Hum C) (Excitation = 350 nm; Em = max (420–480), 5 nm emission intervals) (Coble, 1996). Although the exact compounds associated with peaks A and C are unknown, they have been associated with the presence of melanoidins that are humic substances in water (Ertel and Hedges, 1983). Finally, we calculated the humification index (HIX) as the sum of the fluorescence intensities between 300 and 345 nm, and the sum of the intensities between 300–345 nm and 435–480 nm, for an excitation wavelength of 254 nm (Ohno, 2002). The HIX varies between 0 and 1 with high values indicating a high degree of humification. The presence of melanoidins (high Hum A and Hum C values) and/or the presence of highly humic DOC (high HIX values) would indicate highly humic and poorly bioavailable DOC fractions. For all analyses, triplicates were run in 10% of the samples for quality control purposes. The relative standard deviations for all triplicate analyses were <3%. When means for two groups were compared to establish significant differences between groups, unpaired *t*-test assuming equal variance with a 95% confidence interval were used. For all tests, significance was established at $p < 0.05$. All calculations were performed in PAST (Hammer et al., 2001).

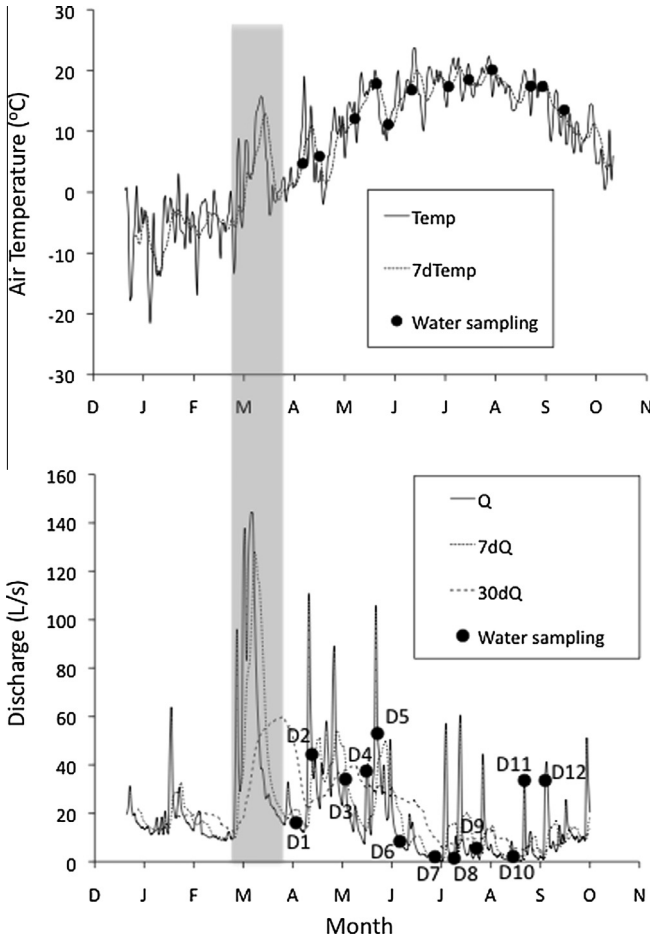

Fig. 2. Average daily air temperature (Temp), seven-day antecedent daily air temperature (7dTemp), daily discharge (Q), seven-day antecedent daily discharge (7dQ), and 30-day antecedent daily discharge (30dQ) in Arbutus watershed for year 2012. Black dots indicate water-sampling dates (D1–D12). The gray-shaded area indicates the spring snowmelt period (March 7 to April 8).

3. Results

3.1. Temperature and hydrology

Average daily temperature during the 2012 study year was 6.4 °C or 1.6 °C above average, with highest temperatures observed in June, July and August (3 month-mean = 17.1 °C), and coldest temperatures in December, January, and February (3 month-mean = −5.3 °C) (Fig. 2). Following the snowmelt period (March 7 to April 8) during which discharges >140 L/s were observed, discharge (Q) progressively declined during the sampling period from April 16 (D1) to October 19 (D12), except during or immediately after precipitation events. Six of the sampling dates (D1, D6, D7, D8, D9, D10) occurred when discharge was below the annual mean flow of 22 L/s, while others occurred during peak flow (D3, D4, D11, D12) or at high flow immediately following peak flow (D2, D5) (Fig. 2).

3.2. Spatial variability in Bulk DOC concentration

Regardless of the time of year (see temporal discussion below), DOC concentrations strongly varied depending on location throughout the watershed (Fig. 3). With the exception of one outlier date discussed below (D1, April 16, 2012), DOC concentrations at headwater locations (S14head, S14weir, S15head, S15weir) over the study period remained below 2.7 mg/L with an average DOC concentration of 1.6 mg/L for these four locations (without D1). DOC concentrations were significantly higher ($\alpha = 0.05$, $p < 0.05$) at the Merge site (mean DOC = 4.4 mg/L without D1), and even higher at the Inlet site (mean DOC = 7.7 mg/L without D1) after passage through the wetland. The lake acted as a sink for DOC and reduced DOC concentration to levels similar to those observed at the Merge site (Outlet mean DOC = 5.1 mg/L without D1).

3.3. Spatial variability in DOC quality

DOC quality also exhibited strong spatial patterns regardless of date with headwater sites (S14head, S14weir, S15head, S15weir), the Merge site, the Inlet site, and the Outlet site exhibiting strong spatial differences between one another. FI values were highest at headwater locations (mean FI = 1.61) and lowest at the Inlet and Outlet site (Inlet mean FI = 1.36; Outlet mean FI = 1.37). The Merge site presented intermediate FI values (mean FI = 1.49). Trypto/Tyro values, Hum A values, and Hum C values were also significantly lower ($\alpha = 0.05$, $p < 0.05$) at headwater locations (S14head, S14weir, S15head, S15weir) than at other sampling sites. All three indices (i.e. Trypto/Tyro, Hum A, Hum C) progressively increased in the lower reaches of the watershed before entering the lake (Merge site to Inlet site). Although the Humic A and Humic C values were significantly lower at the Outlet site than at the Inlet site ($\alpha = 0.05$, $p < 0.05$), the mean Trypto/Tyro ratio at the Outlet and Inlet sites were not statistically different ($\alpha = 0.05$, $p > 0.05$). Although the HIX value at S14head was significantly higher than at S15head, the HIX values at all the headwater sites were significantly lower than at the Merge and Inlet sites (Fig. 3). After passage through the lake, the HIX values dropped back to levels similar to those observed at the headwater locations. Outlet HIX values were significantly ($\alpha = 0.05$, $p < 0.05$) lower than at the inlet of the lake. When all the data were lumped together, the DOC quality indices were all significantly correlated to one another over time ($p < 0.05$), with the exception of the Trypto/Tyro ratio and the HIX index, which were not ($p > 0.05$; Table 1). Indices Hum A, Hum C and HIX were all significantly positively correlated to DOC, while FI and the Trypto/Tyro ratio were negatively correlated to DOC (Table 1).

3.4. Seasonal variability in DOC quantity and quality

All of the "headwater" sites were grouped together (S14head, S14weir, S15head, S15weir) because of the consistent lack of statistical differences between these sites in terms of DOC quantity and quality (Fig. 3). This grouping resulted in one group and three distinct sites within the catchment: the headwater group (see above), the Merge site, the Inlet site, and the outlet site. Extremely high DOC concentration (range = 13–20 mg/L) were observed on April 16, 2012 (D1) on the descending limb of the hydrograph during snowmelt (March 7 to April 8)(Fig. 4). Following this initial flush of DOC, stream DOC concentrations showed little variation at headwater locations and at the Outlet site. Peaks in DOC concentrations nevertheless occurred at the Inlet site, and to some extent at the Merge site, during peak flow (D4, D5, D11; Fig. 2) but also at baseflow during warm summer days following intense high flow events (D8, D9; Fig. 2). At the inlet site, stream DOC concentrations ($n = 11$) were not correlated to flow over the study period ($R = 0.07$, $p > 0.05$).

More complex seasonal patterns were observed at the sites with respect to DOC quality. At the headwater sites, a progressive decline in FI was observed with high values >1.6 from April to July, and lower values <1.6 for the rest of the year. Low FI values (<1.4) at the Outlet showed little seasonal variability. However, at the Inlet site, clear decreases in FI values were observed on D4 (peak flow), D8 (post-storm baseflow), D9 (post-storm baseflow), D11

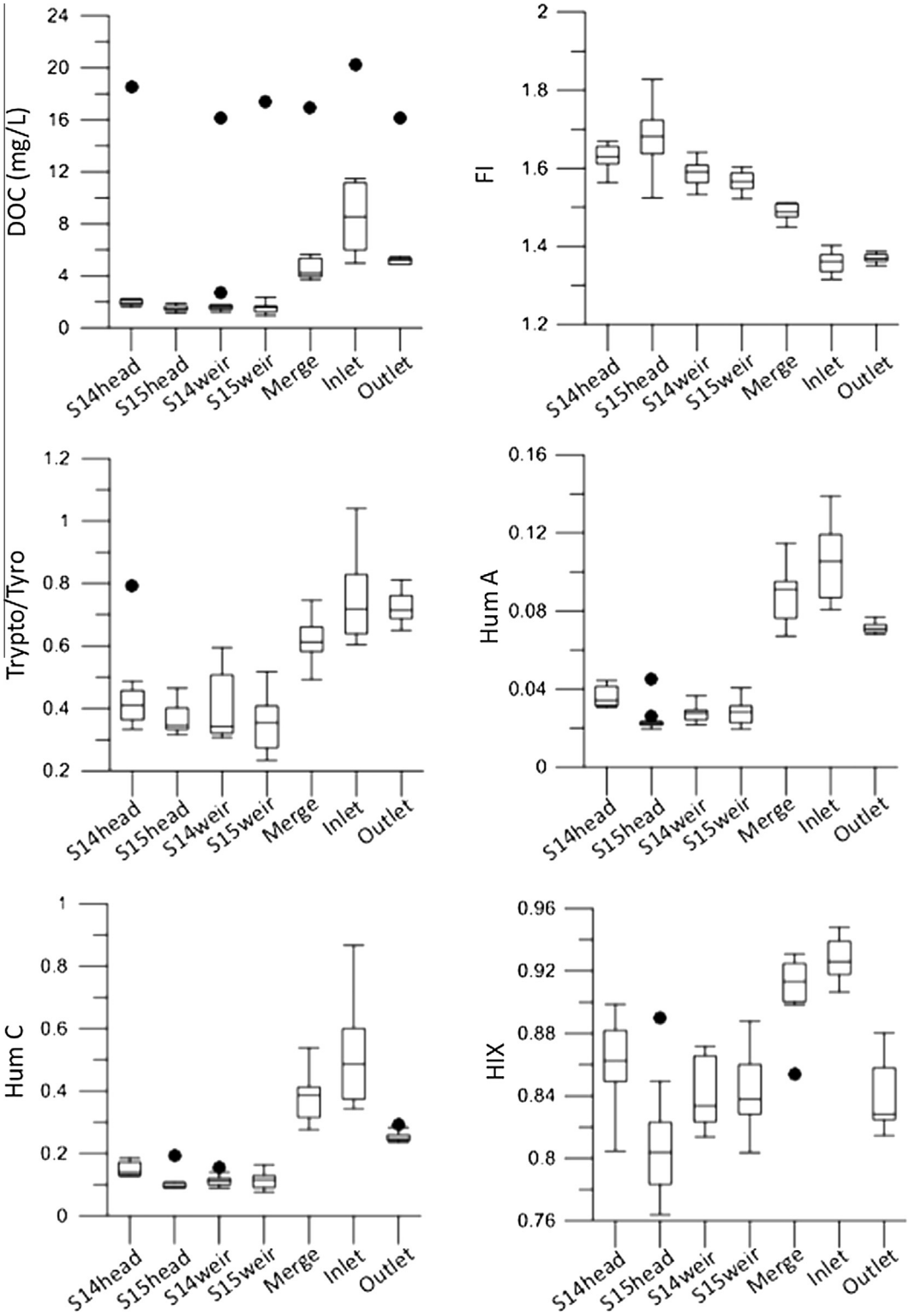

Fig. 3. Box plots (median, 5th, 25th, 75th, 95th percentiles) showing the concentration of dissolved organic carbon (DOC) and DOC quality indices (unitless) at each of the water sampling locations (see Fig. 1 for sampling location description) between April and October 2012. Black dots, when present, indicate outliers. (Acronyms: FI = fluorescence index, Trypto/Tyro = tryptophan to tyrosine ratio, Hum A = humic A index; Hum C = humic C index; HIX = humification index).

(peak flow), and D12 (peak flow). Opposite of FI, the Trypto/Tyro ratio at the headwater and Merge sites progressively increased over the course of the snow-free season, with lowest values observed on D1, on the tail end of the spring flush following snowmelt (March 7 to April 8). At the Inlet and Outlet sites, Trypto/Tyro values remained below 0.3 during the study period. Trypto/Tyro values were especially stable at the outlet site (mean Trypto/Tyro ratio = 0.25), except on the tail end of the snow melt hydrograph (D1) when a low value of 0.07 was recorded.

Beside clear differences in absolute values (see above and Fig. 3), Hum A and Hum C showed little temporal variability at the headwater sites and at the outlet of the watershed. At the

Table 1
Correlation coefficient (R) between dissolved organic carbon (DOC) and DOC quality indices throughout the watershed for the duration of the study period. (Acronyms: FI = fluorescence index, Trypto/Tyro = tryptophan to tyrosine ratio, Hum A = humic A index; Hum C = humic C index; HIX = humification index). Bold characters indicate significant correlations at $p < 0.05$).

All sites	DOC	FI	Trypto/Tyro	Hum A	Hum C	HIX
DOC	1					
FI	**−0.44**	1				
Trypto/Tyro	**−0.61**	**0.88**	1			
Hum A	**0.44**	**−0.78**	**−0.58**	1		
Hum C	**0.44**	**−0.66**	**−0.49**	**0.96**	1	
HIX	**0.41**	**−0.37**	−0.23	**0.77**	**0.82**	1

Merge and Inlet sites, Hum A and Hum C values progressively increased over the course of the snow-free season, with highest values observed on D4 (peak flow), D8 (post-storm baseflow), D11 (peak flow), and D12 (peak flow). HIX values were more variable, except maybe at the Inlet site where less variability was observed. For the headwater sites, the Merge site, and the outlet site, lowest HIX values all occurred during peak flow on D5 (June 5, 2012). However, highest HIX values at the outlet site were observed at the beginning of the sampling season (D1–D3), while highest values occurred in late summer – early fall at headwater sites (D10–D12).

4. Discussion

Over the duration of our study, DOC concentrations and DOC quality indices (Fig. 3) throughout our watershed for the 2012 snow-free season were consistent with DOC concentrations and DOC chemical and isotopic composition previously reported for the Arbutus watershed (Inamdar et al., 2004; Dittman et al., 2009; Kang and Mitchell, 2013), and DOC quality indices (FI, HIX, Trypto/Tyro) reported for a forested watershed in Maryland (Inamdar et al., 2011).

4.1. Spatial and temporal variability of bulk DOC quantity

On a date-by-date basis (Fig. 4), DOC concentration patterns exhibited some level of temporal variability consistent with previous studies in Arbutus watershed (Inamdar et al., 2004; Kang and Mitchell, 2013) and elsewhere (Hornberger et al., 1994; Hood et al., 2006; Wagner et al., 2008). For instance, highest DOC concentrations were observed at high flow (e.g., dates D4 and D11,

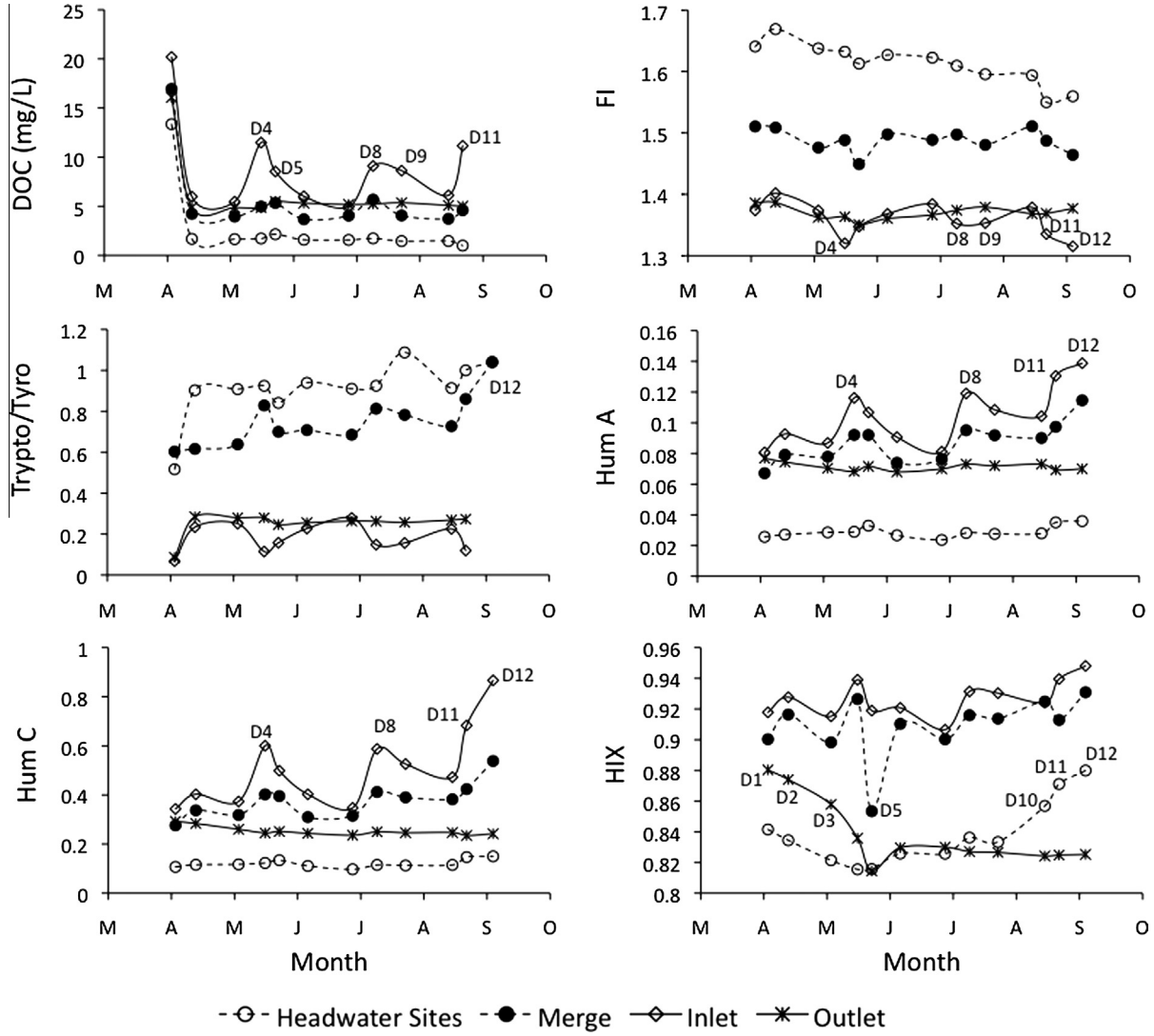

Fig. 4. Variations in dissolved organic carbon (DOC) and DOC quality indices (unitless) over time for headwater sites (S14head, S15head, S14weir, S15weir) and the Merge site, the Inlet site, and the Outlet site. Labels D1–D12, when noted, refer to specific sampling dates (see Fig. 2) and are used to facilitate the description and/or discussion of the results (Acronyms: FI = fluorescence index, Trypto/Tyro = tryptophan to tyrosine ratio, Hum A = humic A index; Hum C = humic C index; HIX = humification index).

Figs. 2 and 4) and immediately following the snowmelt period (e.g., D1, April 16, 2012; Fig. 4). Relatively high DOC values also occurred during summer baseflow (D8, D9; Fig. 2), especially at the Inlet (Fig. 4). Although technically observed during baseflow conditions, these relatively high DOC concentrations for sampling dates D8 and D9 at the Merge and Inlet sites correspond to the two sampling dates with the highest daily and 7-day antecedent temperatures, and are on the tail-end of two high flow events that generated discharges >60 L/s. This suggests that these high DOC concentrations were likely tied to precipitation events in the days preceding sampling (Fig. 2). Increases in soil and sediment mineralization rates in the lower section of the watershed and the wetland (and ultimately DOC release) as temperatures increase during the summer may also help explain the relatively high DOC concentration for these two dates at the Inlet site (and to some extent at the Merge site) in spite of low flow conditions on these dates (Fig. 2) (Inamdar et al., 2004; Mitchell et al., 2006).

Nevertheless, although DOC concentrations changed over time, the range of variability of DOC concentrations at each location over time was much less than spatial differences between headwater locations, the Inlet site (wetland influenced), and the outlet of the lake (Fig. 3). This stresses the dominant role of land cover (e.g., wetlands, lake, upland) in affecting DOC concentrations in the watershed on an annual basis.

4.2. Spatial and temporal variability of DOC quality

Fluorescence indices are only qualitative estimates of the chemical composition of DOC, and ultimately of the bioavailability of DOC (McKnight et al., 2001; Inamdar et al., 2011). However, the use of multiple indices together can provide a clear picture of progressive changes in DOC quality over space and time, and this, independently of DOC concentration. Although FI, HIX, HumA, Hum C, and Trypto/Tyro provide different information on DOC quality (see materials and methods), the significance of the correlation between all these indices (Table 1) allows for the identification of clear changes in DOC quality over both space and time in our study watershed.

FI values <1.5 tend to indicate DOC of terrestrial origin (allochthonous), while FI values >1.7 suggest DOC of aquatic origin (autochthonous) (McKnight et al., 2001). High FI values between 1.6 and 1.7 at headwater locations suggest that stream DOC at these locations was a mixture of terrestrial and aquatic sources. This is consistent with the presence of well-oxygenated streams in the headwater of Arbutus watershed where terrestrial DOC is quickly mobilized and processed by within-stream organisms, which subsequently release lignin-poor aquatic DOC in the stream. This observation is consistent with several studies that have shown that autochthonous (aquatic) DOC can represent a significant portion of DOC in headwater streams (Minshall, 1978; Schaller et al., 2004; Royer and David, 2005). Lower in the watershed where the stream enters the wetland area, a large input of terrestrial DOC leads to both an increase in DOC concentrations at the Inlet site, and a clear decrease of FI values in the 1.3–1.5 range, which is typical of terrestrial DOC (McKnight et al., 2001). Clear increases in Hum A, Hum C, and HIX values in the stream at the Inlet site (after the wetland) are consistent with an increase in the proportion of terrestrial DOC (rich in humic substances) as the stream transited through the wetland. This suggests that in addition to changing DOC concentrations in the stream, the wetland also reset the chemistry of stream DOC. Supporting this interpretation of these results, Kang and Mitchell (2013) found that as surface waters move through this watershed there was an overall increase in refractory DOC (from 1.5 to 4.5 mg C L^{-1}). Highest DOC concentrations were found in a wetland site (4.7 mg C L^{-1}), and at the lake inlet, immediately after passage through the wetland (4.8 mg C L^{-1}).

Aside from the changes in FI, HIX, Hum A, and Hum C values discussed above, the trypto/Tyro ratio also clearly increased in the lower portion of the watershed (Merge site) and through the wetland (Inlet site). This indicates fresher, less degraded protein-like DOC in the lower section of the watershed and after the wetland, than in the headwaters. Although the wetland provided the stream with a large amount of DOC (high DOC concentrations) rich in humic substances (high Hum A, Hum C and HIX), our results suggest that protein-like DOC fractions continued to be generated in the stream as it transited through the lower section of the watershed and the wetland. In other words, although the proportion of humic substances in DOC increased after passage through the wetland, the fraction of the DOC that was most bioavailable (protein-like DOC) continued to be produced in the stream as water moved through the lower section of the watershed and the wetland. It is important to note that as DOC quantity (see above) and quality change from the headwater sites to the inlet, the Merge site represented a transition point between headwater locations (S14 and S15 locations) and wetland influenced areas (Inlet), which is consistent with its location in an area of the watershed with relatively flat topography and relatively organic rich soil relative to headwater locations.

4.3. Lake DOC quality dynamics

Fluorescence indices also indicate that the lake primarily acts as a sink for humic-like DOC. Indeed, as the DOC concentration decreases from the inlet to the outlet of the lake, a clear decrease in the humic content of DOC (i.e. Hum A, Hum C, HIX) is observed, indicating that the proportion of humic substances in the DOC exiting the lake is less than at the inlet. At the same time, the DOC maintains its terrestrial signature (low FI) and does not increase in freshness or bioavailability since it maintains its Trypto/Tyro ratio, suggesting that in-lake processes did not significantly affect DOC composition at the outlet of the lake. We hypothesize that the decrease in the proportion of humic substances (i.e. Hum A, Hum C, HIX) along with the decrease in overall DOC concentration between the Inlet and Outlet sites was due to some DOC being removed in the lake and that the DOC that was " preferentially removed" was predominantly humic-like DOC. Indeed, although a decrease in bulk DOC concentration could have been due to dilution by other sources of water (e.g., groundwater seepage, DOC inputs from un-sampled areas), fluorescence indices are independent from DOC concentration. Consequently, any change in FI, HIX, Hum A, or Hum C represents a change in the chemical composition of DOC, as opposed to any dilution effect. Because the proportion of humic rich DOC decreases as water transits through the lake (regardless of any change in bulk DOC concentration), we hypothesize that the lake reduced the amount of "humic-like" DOC in total DOC and therefore acted as a preferential sink for humic rich DOC fractions. These results are consistent with those reported by Kang and Mitchell (2013) showing that within lake processes in this watershed result in the lake acting as a sink for refractory DOC fractions. It is likely that the DOC that is removed in the lake is deposited at the bottom of the lake, as suggested by the work of Owen et al. (1999) showing the presence of allochthonous dissolved organic matter in Arbutus Lake sediments. From a temporal perspective, with an average hydrological retention time of 0.6 years (Driscoll and VanDreason, 1993; Mitchell et al., 2001), the within-lake processes help attenuate temporal variations in DOC quantity and quality observed at the Outlet (Fig. 4).

4.4. Relationships between DOC quality and DOC quantity

Consistent with other studies (Hood et al., 2006; Wagner et al., 2008; Kang and Mitchell, 2013), our results also indicated that DOC

quality was generally significantly ($p < 0.05$) correlated to DOC concentration regardless of location and time of year (Table 1). As DOC concentration increased, the proportion of humic substances in the DOC increased (see positive correlation with Hum A, Hum C, and HIX), the proportion of terrestrial DOC in stream DOC increased (see negative correlation with FI), and the freshness of the DOC decreased (see negative correlation with Trypto/Tyto values). These correlations suggests that high DOC concentrations were likely primarily tied to the mobilization of terrestrial, highly degraded humic rich DOC, that would be less bioavailable (and less fresh) than the DOC exported at times when DOC concentrations were low.

Considering that many climate change models suggest that the frequency and intensity of large storm events will increase in the near future in the US Northeast (Karl and Knight, 1998; Milly et al., 2005), and that many studies show an increase in bulk DOC concentration with flow (Hornberger et al., 1994; Inamdar et al., 2004; Hood et al., 2006; Wagner et al., 2008; Kang and Mitchell, 2013), we should see not only an increase in the amount of DOC exported at the watershed scale, but also a shift in the quality of this DOC toward less bioavailable DOC fractions, rich in humic substances in years to come. Although the exact consequences of this potential shift in the quantity and quality of DOC exported at the watershed scale on ecosystems in poorly understood at this point, it is likely to negatively affect stream primary productivity, and ultimately the health of downstream ecosystems as stream DOC quantity and quality affect in-stream acidification processes, heterotrophic productivity, respiration, and ultimately rates of C cycling and short term CO_2 outgasing (Wigington et al., 1996; Dalzell et al., 2005).

5. Conclusion

Overall, our results stress the dominant role of land cover/landscape position in regulating both stream DOC quantity and quality over the duration of the study, primarily because the range of variability of DOC concentrations at each location over time (in spite of changes in DOC concentration with flow) was much less than spatial differences between headwater locations, the Merge site, the Inlet site (wetland influenced), and the outlet of the lake. In particular, our results stress the importance of wetlands as being a large sources of humic-rich DOC, and the potential role of lakes as DOC sinks, especially for humic-rich DOC. Our results also indicate that although some of the highest DOC concentrations occur at high flow, discharge alone is a poor predictor of DOC concentration at the watershed scale during the snow-free season as high DOC concentrations occur during both high and low flow. Finally, our results point to a two-phase DOC export whereby a mobile and bioavailable fraction of DOC (protein-like DOC) is being produced throughout the watershed, while the production of a more recalcitrant humic-like DOC fraction is primarily associated with the wetlands of the watershed. From a management perspective, the dominant role of land cover/landscape position in regulating stream DOC quantity and quality suggests that land cover changes in the coming years (e.g., changes in the amount and connectivity of wetlands), if any, may play a more important role than climate change in regulating DOC exports in forested watersheds of the Northeast US.

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