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SYNTHESIS AND EMERGING IDEAS

Long-term trends in dissolved organic carbon concentration: a cautionary note

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Abstract Dissolved organic carbon (DOC) plays an important role in surface water chemistry and ecology and trends in DOC concentration have been also associated with shifts in terrestrial carbon pools. Numerous studies have reported long-term trends in DOC concentration; however, some studies consider changes in average measured DOC whereas other compute discharge weighted concentrations. Because of differences in reporting methods and variable record lengths it is difficult to compare results among studies and make regional generalizations. Furthermore, changes in stream discharge may impact long-term trends in DOC concentration and the potentially subtle effect of shifts in stream flow may be missed if only measured DOC concentrations are considered. In this study we compare trends in volume-weighted vs. average measured DOC concentration between 1980 and 2001 at seven headwater streams in south-central Ontario, Canada that vary in wetland coverage and DOC (22-year mean vol. wt.) from 3.4 to 10.6 mg l^{-1}. On average, annual measured DOC concentrations were 13–34% higher than volume-weighted values, but differences of up to 290% occurred in certain years. Estimates of DOC flux were correspondingly higher using measured concentration values. Both measured and volume-weighted DOC concentrations increased significantly between 1980 and 2001, but slopes were larger in measured data (0.04–0.35 mg l^{-1} $year^{-1}$ compared with 0.05–0.15 mg l^{-1} $year^{-1}$) and proportional increases at the most wetland-influenced sites ranged from 32 to 43% in volume-weighted DOC and from 52 to 75% in measured DOC. In contrast, DOC flux did not change with time when estimated using either method, because of the predominant influence of stream flow on DOC export. Our results indicate that changes in stream flow have an important impact on trends in DOC concentration, and extrapolation of trend results from one region to another should be made cautiously and consider methodological and reporting differences among sites.

Keywords Dissolved organic carbon · Hydrology · Streams · Wetlands · Long-term trends

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Introduction

Dissolved organic carbon (DOC) plays an important role in aquatic systems by influencing light regime and nutrient supply, acidity, trace metal transport and bioavailability, and water treatment and potability. There is considerable interest in determining trends in surface water DOC concentrations because of

potential linkages with recovery from acidification and climate warming, and positive, negative and stationary trends have each been reported (Forsius et al. 2003; Jeffries et al. 2003; Evans et al. 2005; Skjelkvåle et al. 2005; Burns et al. 2006). Reports of positive trends in DOC at sites in northern Europe and northeastern North America are the subject of much debate (e.g., Tranvik and Jansson 2002; Roulet and Moore 2006), and several studies have suggested that regional-scale drivers may be involved, including increasing CO_2 (Freeman et al. 2004), climate warming (Freeman et al. 2001), continued nitrogen (N) deposition (Pregitzer et al. 2004; Findlay 2005), and decreased sulphate (SO_4) deposition (Evans et al. 2006).

Comparisons among sites and identification of potential regional-scale drivers, however, are hampered by differences in record length and methods of reporting, both of which influence trend detection and magnitude (Table 1). In almost all cases, trends in DOC concentration are assessed on monthly blocks of data using the non-parametric Mann–Kendall test; however, in some cases trends are computed on arithmetic means of measured concentrations (e.g., Worrall et al. 2004), whereas other studies account for changes in stream flow by calculating volume-weighted or flow-corrected DOC concentrations (Burns et al. 2006; Eimers et al. 2007a, b; Table 1). Variations in stream flow may have a large influence on concentrations of chemicals like DOC, which exhibit strong hydrologic control (e.g., Boyer et al. 1997; Schiff et al. 1998; Pastor et al. 2003); as a consequence, trends in measured DOC concentrations may simply result from changes in hydrology (Tranvik and Jansson 2002; Pastor et al. 2003). It is important to determine whether trends in DOC concentration reflect changes in DOC flux, because increases in DOC concentration have been interpreted as evidence of shifts in soil carbon pools (Freeman et al. 2001).

In this paper we compared changes in average measured DOC concentration with volume-weighted DOC at seven intensively monitored study catchments that vary in wetland coverage, and where detailed measurements of DOC concentration and stream flow were available for a 22-year period (1980–2001). Our objective was to evaluate the impact of differences in reporting methods on DOC concentrations and trends, and to determine whether trends in measured and volume-weighted DOC concentration reflect changes in DOC flux.

Methods

The seven headwater catchments (HP3, HP3A, HP4, HP5, HP6, HP6A, PC1) are located in the district of Muskoka (Harp Lake; HP) and County of Haliburton (Plastic Lake; PC) on a southern extension of the Precambrian Shield at the southern limit of the Boreal ecozone. Bedrock in the region is primarily granitized biotite and hornblende gneiss, with amphibolite and schist (HP3A, HP4) and diorite (HP6) present in some catchments. Surficial geology is variable and ranges from thin till (<1 m) with exposed bedrock (PC1, HP6A) to minor till plains (>1 m thick) and rock ridges (HP3, HP3A) or mixtures of the above (HP4, HP5, HP6). The area is part of the Great Lakes-St Lawrence forest region and is dominated by semi-natural, mixed hardwood forests. The upland portion of PC1 is dominated by white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*) and red maple (*Acer rubrum*) whereas sugar maple (*A. saccharum*), American beech (*Fagus grandifolia*) and yellow birch (*Betula allegheniensis*) typify forests at the HP subcatchments. Conifer (white cedar, *Thuja occidentalis*; black spruce, *Picea mariana*) *Sphagnum* peatlands are common in low lying areas.

Dissolved organic carbon concentrations in surface waters in this region vary as a function of wetland influence, and wetland coverage (%) at the seven study catchments was related to average stream DOC (1980–2001; vol. wt. concentration) through the relationship: $[DOC] = 0.7\,[\%wetland] + 1.2$; $r^2 = 0.71$; $p < 0.05$ (Eimers et al. 2007a); although the location of wetlands relative to the catchment outflow (where stream chemistry and flow are monitored) is also important. At PC1, for example, a 2.2 ha conifer-*Sphagnum* swamp occupies less than 10% of the total catchment area, but by virtue of its location near the catchment outflow, more than 85% of the runoff draining the catchment passes through the wetland before entering the lake and as a consequence the wetland has a strong influence on stream water chemistry (Eimers et al. 2004a, b).

The seven headwater catchments have been monitored by the Ontario Ministry of Environment Dorset Environmental Science Centre (DESC) for stream

Table 1 List of recent studies reporting long-term changes in surface water DOC concentration: magnitude of change; proportion of sites reporting significant changes; time period of trend calculation; sampling frequency and method of reporting; location and reference

Increase (+) or decrease (−) as % change or mg l^{-1} a^{-1}	# Of sites; % showing significant trends (if available)	Time period	Method; sampling frequency[a]	Location	Reference
Mean +0.056 mg l^{-1} a^{-1}	5, 80%	1992–2001	Flow-corrected, monthly	Streams, Catskills NY USA	Burns et al. (2006)
Mean +0.091 mg l^{-1} a^{-1}	12, 75%	1992–2001	Measured; monthly	Lakes, Adirondacks, NY USA	Burns et al. (2006)
Mean +0.079 mg l^{-1} a^{-1}	17, 41%	1982–2001	Measured; monthly	Lakes, Adirondacks, NY USA	Driscoll et al. (2003)
+30% to +80%	4	1970–1990	Measured; weekly	Streams, Experimental Lakes Area ON Canada	Schindler et al. (1997)
−15% to −25%	3	1972–1990	Measured; monthly	Lakes, Experimental Lakes Area, ON Canada	Schindler et al. (1997)
Mean +0.092 mg l^{-1} a^{-1}	51; 33% increase	1985–1993	Measured; 1–6 samples per year	Lakes, QC, Canada	Bouchard (1997)
Mean +0.11 mg l^{-1} a^{-1}	7; 86%	1980–2001	Volume-weighted; weekly	Streams, ON, Canada	Eimers et al. (2007a, b)
	43; 14% increase; 10% decrease; 76% no trend	1990–1997	Measured; variable sampling frequencies	Lakes, ON and QC, Canada	Jeffries et al. (2003)
	8; 12% increasing; 88% no trend	1988–2001	Measured; once annually	Lakes, Killarney Park, ON Canada	Keller et al. (2003)
Median −0.11 mg l^{-1} a^{-1}	161; 3% increasing; 5% decreasing; 92% no trend	1983–1995	Measured; once annually	Lakes, Sudbury region, ON Canada	Mallory et al. (1988)
Mean +0.17 mg l^{-1} a^{-1}	198; 77% increasing; 23% no trend	8–40 years (1961–2000)	Measured; monthly to quarterly	Streams, lakes and reservoirs, UK	Worrall et al. (2004)
+0.06 to +0.51 mg l^{-1} a^{-1}	22, 100% increasing	1988–2003	Measured; monthly (streams) to quarterly (lakes)	Lakes and streams, UK	Evans et al. (2005)
+9%	1	1983–2000	Inferred from COD[b] measurements; weekly	River, Czech Republic	Hejzlar et al. (2003)
	344; 12% increasing	1990–1999	Measured; once annually	Lakes in Norway, Sweden and Finland	Skjelkvale et al. (2001)

Table 1 continued

Increase (+) or decrease (−) as % change or mg l^{-1} a^{-1}	# Of sites; % showing significant trends (if available)	Time period	Method; sampling frequency[a]	Location	Reference
+0.05 to +0.08 mg l^{-1} a^{-1}	12 geographic regions; 50% increasing, 8% decreasing	1990–2001	Measured; variable sampling frequencies	Lakes in Europe and eastern North America (189 sites in total)	Skjelkvale et al. (2005)
No consistent trends	10% increasing; <5% decreasing	1990–1999	Measured; once annually	Lakes, Finland	Forsius et al. (2003)
+0.03 to +0.22 mg l^{-1} a^{-1}	13, 77% increasing	1987–2003	Measured; 6–12 samples per year	Lakes, Finland	Vuorenmaa et al. (2006)

[a] Frequency of sample measurements used in calculations of mean values

[b] Chemical oxygen demand

flow and chemistry using consistent methods since 1980. Streams were typically sampled weekly or fortnightly, with increased sampling frequency (sometimes daily) during spring melt. In total, between 1,530 (PC1) and 2,200 (HP4) stream water samples were analyzed for DOC between 1980 and 2001, which translates to an average sampling frequency of 1.3–1.9 samples/week. On average, 20, 25, 20 and 35% of the total annual sampling effort occurred in the summer, fall, winter and spring, respectively, whereas the majority of annual stream flow occurs in the spring (51–57%; 0.26–0.31 m) followed by the fall (19–23%; 0.10–0.14 m), winter (17–19%; 0.09–0.11 m) and summer (5–9%; 0.03–0.05 m). DOC in stream water was analyzed using standard methods (Dillon and Molot 2005).

To assess the role of reporting method in determining DOC trends, both measured and volume-weighted average DOC concentrations were compared. Measured averages were simply the un-weighted averages of raw, measured DOC concentrations, whereas volume-weighted DOC concentrations first required the calculation of DOC export (or flux). DOC export (g m^{-2}) in stream water was calculated using the 'mid-point method', in which integrated daily flow is multiplied by the DOC concentration at the mid-point of the sampling interval (Scheider et al. 1979; Jeffries et al. 1988). For example, if a DOC concentration of x mg l^{-1} was measured in stream water on Day 1, and y mg l^{-1} was measured on Day 7, then x mg l^{-1} was applied to days 2–3 inclusive, and y mg l^{-1} was applied to days 5–6 inclusive, and the DOC concentration on Day 4 was $(x + y)/2$. The measured or estimated DOC concentration for each day was then multiplied by the total volume of stream flow on that day to estimate daily DOC flux. This method is similar to the period-weighted method, which is commonly used to estimate chemical export when weekly concentration data are available (Likens et al. 1977; Dann et al. 1986). Daily estimates of DOC flux were summed for each year (hydrologic year: June 1–May 31) or season (summer: June–July–August; fall: September–October–November; winter: December–January–February and spring: March–April–May), and volume-weighted concentrations were subsequently calculated by dividing the flux during a particular interval of time by the total volume of stream discharge for the same period. Annual and seasonal 'measured' DOC fluxes were calculated for comparison by simply multiplying the

average of measured DOC concentrations in a year or season by the total annual or seasonal volume of stream flow.

The nonparametric seasonal Mann–Kendall (MK) test was used to detect monotonic trends in DOC concentration and flux with time (Hirsch et al. 1982). A p value of 0.05 was used to indicate a statistically significant trend. Slopes (rates of increase or decrease) of significant trends were determined by Sen's method. Slopes of volume-weighted and measured DOC were compared through analysis of covariance, and differences between volume-weighted and measured averages for individual streams were assessed using the Student's t-test (paired two-sample for means) after first testing for equal variances (F-test). Differences were considered significant at $p < 0.05$ (two-tail). Pearson correlation coefficients (r) were used to examine relationships between DOC concentration, flux and export.

Results

Differences between measured and volume-weighted DOC

Average volume-weighted DOC concentrations ranged from a low of 3.4 ± 0.3 mg l^{-1} at predominantly upland-draining HP3A to a maximum of 10.6 ± 2.6 mg l^{-1} at HP5, which had the largest wetland component of the seven study catchments (Table 2). With the exception of HP3A, measured DOC concentrations were higher than volume-weighted averages, and differences were statistically significant at HP3, HP5, HP6A and PC1, each of which had a long-term (22-year vol. wt.) average DOC concentration greater than 7 mg l^{-1}. Long-term average measured DOC concentrations were 23–34% higher than volume-weighted values at the four highest DOC streams, although measured concentrations were close to double volume-weighted values in certain years (e.g., HP5 1987/1988 measured DOC = 16 mg l^{-1}; volume-weighted DOC = 8.6 mg l^{-1}; Fig. 1). Because DOC export is a product of concentration and stream discharge, annual DOC export at the four highest DOC sites was similarly 23–34% greater when estimated using measured concentrations compared with the mid-point method. Average 'measured DOC export' ranged from 1.7 g m^{-2} a^{-1} (HP3A) to 8.0 g m^{-2} a^{-1} (HP5) compared with mid-point estimates of 1.9 g m^{-2} a^{-1} (HP3A) to 6.2 g m^{-2} a^{-1} (HP5).

Inter-seasonal differences in DOC concentration were greatest at the four highest DOC streams (i.e., >10 mg l^{-1}: HP3, HP5, HP6A, PC1), where summer maxima exceeded winter or spring minima by at least 2-fold (Table 3). In contrast, low DOC, upland-dominated HP3A exhibited the least intra- or inter-seasonal variation in DOC concentration (Table 3). Measured DOC concentrations were significantly greater (15–26%) than volume-weighted values at the four highest DOC streams in the spring only, except at HP6A where differences were significant in the summer and fall (Table 3). DOC export in the spring was similarly 15–26% higher when estimated using measured DOC concentrations at the most wetland-influenced sites. Measured and

Table 2 Long-term average measured and volume-weighted DOC concentrations (mg l^{-1}) at the seven study sites; their rates of increase between 1980 and 2001 (Sen slopes: mg l^{-1} a^{-1}); statistical significance (*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$) and percentage change during the 22-year period relative to the 1980–1984 average

	% Wetland	Measured			Volume-weighted		
		Avg. conc.	Slope; p	% Increase	Avg. conc.	Slope; p	% Increase
HP3	9	**10.3 ± 1.6**	0.20; ***	52	**8.4 ± 1.3**	0.12; **	38
HP3A	3	**3.0 ± 0.2**	n.s	–	**3.4 ± 0.3**	n.s	–
HP4	8	6.0 ± 0.5	0.036; *	14	5.9 ± 0.6	0.046; *	18
HP5	13	**13.6 ± 2.6**	0.27; **	56	**10.6 ± 2.6**	0.15; **	38
HP6	10	7.0 ± 1.5	0.18; ***	69	6.2 ± 1.1	0.10; **	43
HP6A	9	**10.0 ± 1.9**	**0.24**; ***	68	**7.4 ± 1.1**	**0.094**; *	32
PC1	9	**12.9 ± 2.8**	**0.35**; ***	75	**9.8 ± 1.5**	**0.12**; **	32

Bold values are significantly different at $p < 0.05$ (two-tailed Student's t-test); n.s. is not significant

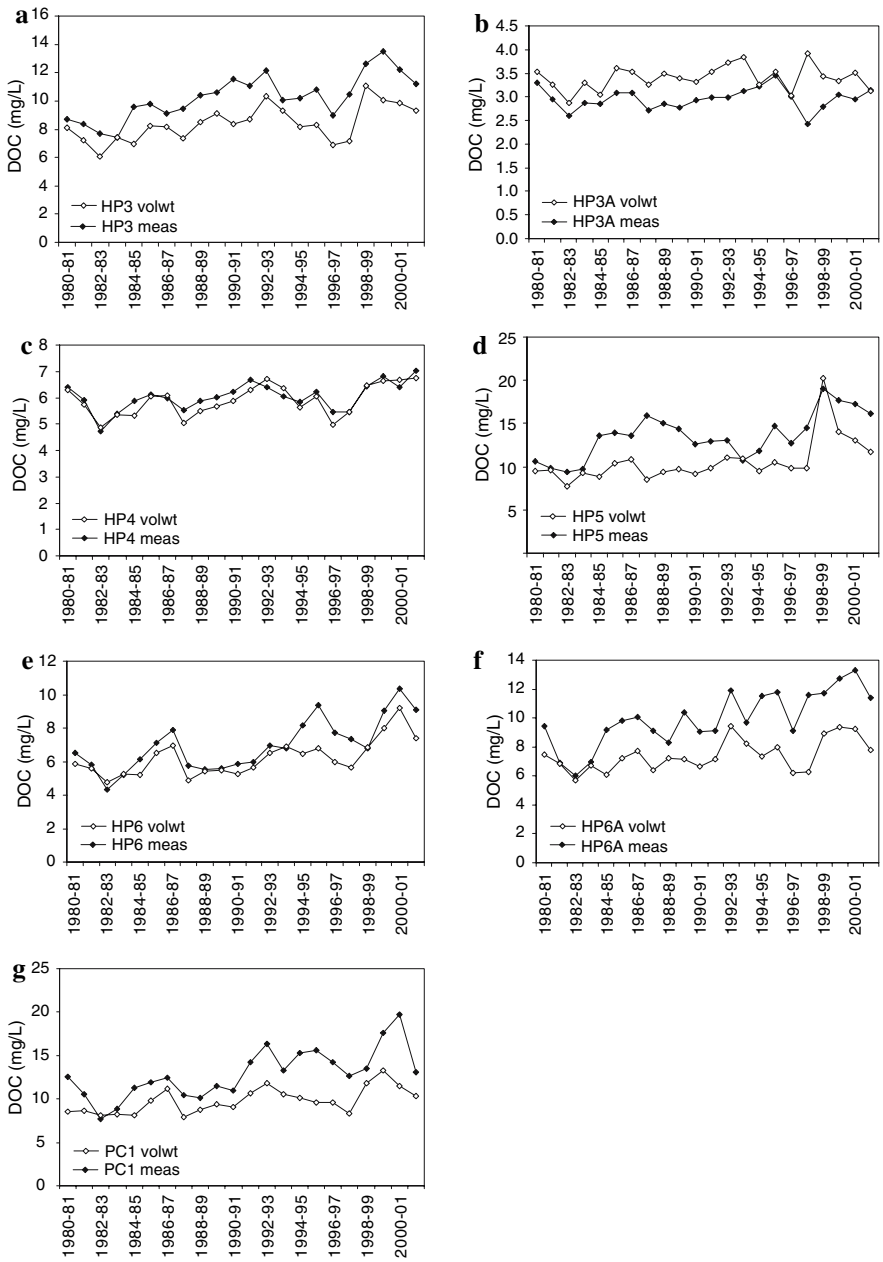

Fig. 1 Annual average measured (*solid diamond*) and volume-weighted (*open diamond*) dissolved organic carbon concentrations in HP3 (**a**), HP3A (**b**), HP4 (**c**), HP5 (**d**), HP6 (**e**), HP6A (**f**) and PC1 (**g**): 1980–2001

volume-weighted DOC concentrations were most similar at HP4 (<5%) (Table 3).

Trends in measured and volume-weighted DOC

Both volume-weighted and measured DOC concentrations increased significantly between 1980 and 2001 at six of the seven streams (HP3, HP4, HP5, HP6, HP6A, PC1) (Fig. 1). However, rates of increase in measured DOC concentrations (0.04–0.35 mg l^{-1} a^{-1}) were up to 2.9-times larger (PC1) than trends in volume-weighted DOC (0.05–0.15 mg l^{-1} a^{-1}) (Table 2). The rate of DOC increase was more rapid at higher stream DOC concentrations (e.g., rate of increase in vol. wt. DOC (in mg l^{-1} a^{-1}) = 0.016 × DOC (long-term mean in mg l^{-1}) − 0.024; $r^2 = 0.73$). As a consequence, proportional increases in DOC concentration

Table 3 Seasonal average measured and volume-weighted DOC concentrations (±SD, mg l^{-1}), respectively

	Summer		Fall		Winter		Spring	
	Meas.	Vol. wt.	Meas.	Vol. wt.	Meas.	Vol. wt.	Meas.	Vol. wt.
HP3	16.0 ± 3.7	15.7 ± 3.4	11.4 ± 2.0	11.1 ± 1.8	6.9 ± 2.0	7.0 ± 2.0	**7.6 ± 1.6**	**6.6 ± 1.2**
HP3A	**2.9 ± 0.6**	**3.6 ± 0.8**	**3.3 ± 0.5**	**3.8 ± 0.6**	**2.6 ± 0.3**	**2.9 ± 0.4**	3.0 ± 0.2	3.1 ± 0.3
HP4	6.7 ± 0.7	7.0 ± 1.0	7.2 ± 0.9	7.5 ± 0.8	5.6 ± 0.6	5.9 ± 0.6	4.9 ± 0.7	4.8 ± 0.7
HP5	21.3 ± 9.4	21.6 ± 11.2	17.5 ± 2.8	16.7 ± 3.3	9.0 ± 2.4	9.0 ± 2.1	**8.7 ± 2.1**	**7.3 ± 1.5**
HP6	10.9 ± 2.6	10.7 ± 2.5	8.1 ± 2.1	7.9 ± 1.6	4.7 ± 0.9	5.0 ± 1.0	5.3 ± 1.1	5.0 ± 0.8
HP6A	**18.7 ± 2.7**	**15.7 ± 3.6**	**13.9 ± 2.6**	**11.8 ± 2.3**	6.9 ± 2.0	6.6 ± 1.5	**6.9 ± 1.7**	**5.6 ± 0.9**
PC1	19.7 ± 4.1	18.2 ± 3.7	14.9 ± 2.9	13.9 ± 2.0	9.4 ± 1.7	8.9 ± 1.6	**9.3 ± 1.7**	**7.4 ± 0.2**

Bold values are significantly different at $p < 0.05$

during the 22-year period (i.e., mg l^{-1} increase calculated from trend slopes divided by the 1980–1984 average DOC concentration) were relatively similar at the most wetland-influenced sites, ranging from 32 to 43% in volume-weighted concentrations (average 36 ± 5%), and from 52 to 75% in measured DOC (average 64 ± 10%; Table 2).

Trends in DOC flux and stream flow

Annual stream flow did not change significantly between 1980 and 2001 at any of the stations, and flow varied greatly between years (up to 300%; data not shown). There were similarly no statistically significant trends in seasonal stream flow, although spring flow tended to decline ($p < 0.1$) at PC1 and HP6A over the 22-year period (data not shown).

Pearson correlation coefficients (r) between DOC export and annual stream flow ranged from 0.64 (HP5) to 0.94 (HP3A) when DOC export was estimated using the mid-point method, and from 0.66 (PC1) to 0.97 (HP3A) when DOC export was estimated using measured DOC concentrations. In contrast, correlations between DOC export and concentration ranged from 0.096 (HP3A) to 0.48 (HP6) in volume-weighted data and from 0.21 (HP3) to 0.74 (HP3A) in measured data. As a consequence of the relatively strong correlation between flow and DOC export and lack of trends in stream flow, increases in DOC concentration between 1980 and 2001 were not translated into positive trends in DOC export.

Discussion

Differences between measured and volume-weighted DOC

Measured DOC concentrations (and therefore fluxes) were up to 34% greater than volume-weighted values and differences were largest for the high DOC, most wetland-influenced streams. Furthermore, divergences between measured and volume-weighted DOC at wetland-influenced sites were largest in the spring (March–April–May), when stream flow is highest (~55% of annual). These observations are consistent with strong hydrologic control of DOC in wetland outflows, particularly during the spring months. Previous work at these sites has shown that there is a significant negative correlation between daily stream flow and DOC concentration at wetland-influenced streams in annual and spring data series (Schiff et al. 1998; Eimers et al. 2007a), which has been also noted at other mid-to-high latitude sites (e.g., Laudon et al. 2004). In contrast, relationships between daily discharge and DOC concentration in the summer, fall and winter were not observed (Eimers et al. 2007b). Relatively low biological activity and rapid flow rates during the spring snow melt season likely maximize the potential for hydrologic control of DOC export in this season, whereas biotic factors play a larger role in determining DOC concentrations in the summer and fall, and both low hydrologic and biological activity in winter limit DOC variability in this season (Mulholland and Hill 1997; Turmel et al. 2005; Dittman et al. 2007).

The observation that measured DOC > volume-weighted DOC concentration in spring suggests a sampling bias in this season toward lower flow/higher concentration conditions. Two factors may contribute to this bias. First, sampling effort during the spring (~35% of annual) is lower than the proportion of stream flow in this season, which means that samples may not have been collected across the full spectrum of flow conditions. Second, data records for years in which daily sampling occurred in the spring (1983/1984–1986/1987) indicate that DOC concentrations reach an annual minimum when discharge peaks at the height of spring melt, and the duration of this 'minimum DOC/maximum flow' condition is relatively short (i.e., <10 days), yet as much as 50% of total spring flow may occur during this period (Eimers et al. 2007a). A stream sampling strategy that misses this window would therefore produce a very different estimate of volume-weighted DOC concentration and period-weighted flux. Obviously the most accurate estimates of DOC fluxes and concentrations in wetland-outflows during the spring will be achieved through frequent, flow-proportional sampling, and because DOC export in the spring accounts for 36–50% of annual export, improved estimates of spring export would have a proportional impact on the accuracy of annual DOC flux estimates in wetland-influenced systems.

Relatively small differences between measured and volume-weighted DOC concentrations at predominantly upland-draining streams with low DOC indicate a weaker influence of stream flow on DOC patterns in these systems and therefore a smaller impact of sampling frequency on DOC flux estimates. The two most upland-influenced catchments considered in this study (HP3A and HP4) also differ from the other streams due to the presence of thick glacial till (HP4) or lacustrine silt and clay deposits (HP3A) near their outflows, which sustain base flow even during particularly dry summers (Hinton et al. 1997). Relatively low and invariable DOC concentrations in HP3A and HP4 compared with the more wetland-influenced systems are consistent with predominantly subsurface flow paths in upland soils that maximize the potential for DOC adsorption to mineral surfaces (Qualls 2000). Indeed, previous hydrologic studies in this region have shown that subsurface flow paths through mineral soil deliver the majority of storm runoff in upland catchments (Renzetti et al. 1992; Hinton et al. 1998), and DOC concentrations in soil percolate decline rapidly with depth through the soil profile from more than 20 mg l^{-1} in the forest floor to 1–4 mg l^{-1} in B-horizon mineral soil (LaZerte and Scott 1996).

Trends in average measured, and volume-weighted DOC

Both measured and volume-weighted DOC concentrations increased significantly between 1980 and 2001 at all of the wetland-influenced streams; however, the mean rate of increase in measured DOC (0.21 mg l^{-1} a^{-1}) was double the rate of increase in volume-weighted DOC (0.11 mg l^{-1} a^{-1}). Rates of increase in measured DOC calculated for these sites are similar to trends in average measured DOC reported by Worrall et al. (2004) for surface waters in the UK (see Table 1). However, the duration of data record has a strong impact on trend detection and magnitude, and when we recalculate Sen slopes for measured DOC between 1988–1989 and 2000–2001 to match the records for 101 UK streams studied by Worrall et al. (2004), we do not observe significant trends in DOC at any of our sites, whereas 84/101 UK streams exhibited significant increases in DOC concentration ranging from 0.05 to 0.50 mg l^{-1} a^{-1} during that time period. Similarly, when we recalculate trends in volume-weighted DOC for 1992–2001 to compare with flow-corrected rates reported by Burns et al. (2006) for primarily upland-draining streams in the northeastern USA (average 0.06 mg l^{-1} a^{-1}, $n = 5$, 80% significant), we find non-significant trends. The interval for which trends are calculated, therefore, strongly influences the detection and magnitude of trends and should be considered when comparing among sites and making regional generalizations.

We have previously reported a strong negative correlation (r: −0.62 to −0.69) between the magnitude of spring (March–April–May) stream flow and annual volume-weighted DOC; such that DOC concentrations were higher in years with lower spring flow (Eimers et al. 2007a). These years also had lower-than-average winter snow accumulation and spring rain (Eimers unpublished). In contrast, there was no correlation between annual stream flow and annual DOC concentration (measured or volume-

weighted), despite the large contribution of spring discharge to annual hydrologic budgets (Eimers et al. 2007a). Furthermore, positive trends in annual volume-weighted DOC at wetland-influenced streams between 1980 and 2001 were driven by relatively high concentrations in the latter years of record (particularly 1998 and 2000), consistent with low spring flow in these years (Eimers et al. 2007a). Because relatively high DOC concentrations in the latter years of record were associated with lower spring discharge, positive trends in DOC concentration between 1980 and 2001 were not translated into increased DOC export. This is important, because rising DOC concentrations are often interpreted in the absence of flow data as indicative of shifts in soil carbon pools (e.g., Freeman et al. 2001). In this region, the average trend in measured DOC concentration was double the rate estimated using volume-weighted values, and if rates of increase in measured concentrations are assumed to represent trends in DOC flux, this would result in a substantial overestimation of DOC loss from catchments.

Driscoll et al. (2003) and other authors (e.g., Evans et al. 2005) have noted a positive correlation between the magnitude of trend in DOC and mean DOC concentration, such that rates of increase are greater for higher DOC, more wetland-influenced lakes and streams. We similarly observed a strong correlation between DOC trend and concentration and proportional increases in volume-weighted DOC were fairly comparable across sites, particularly at the higher DOC systems. Similar proportional increases in DOC across wetland-dominated sites argue for a consistent driving mechanism. Certainly, the number of sites in the Northern Hemisphere that have reported rising trends in DOC concentration has led to considerable debate in the literature, and a variety of possible regional-scale drivers have been proposed, including CO_2 enrichment (Freeman et al. 2004), nitrogen deposition (Pregitzer et al. 2004; Findlay 2005), decreased SO_4 deposition (and anticipated declines in soil acidity and ionic strength; Evans et al. 2006), and climate warming (Freeman et al. 2001). While shifts in hydrology may occur synchronously across relatively large spatial scales, changes in stream flow or precipitation patterns have been generally discounted as a potential cause of rising DOC (e.g., Evans et al. 2006, Worrall and Burt 2005). Certainly, some sites reporting positive trends in DOC concentration have also observed increases in DOC flux, which suggests that factors other than hydrology are involved (Worrall et al. 2003). However, our results indicate that changes in stream flow during the period of maximum DOC export (i.e., spring) have a substantial impact on annual average DOC concentrations. Furthermore, positive trends in DOC concentration at these sites were not matched by increases in DOC export because of the overarching influence of stream flow on DOC flux and negligible trends in annual stream discharge.

We conclude that long-term trends in DOC concentration should be evaluated only after accounting for the impact of stream flow-either through a volume weighting calculation as used here, or through the analysis of discharge–concentration relationships as in Burns et al. (2006). In this study, relationships between DOC and flow were only apparent in the spring, but because of the dominance of spring flow in the annual water budget, shifts in hydrology during this period had a proportionately large impact on annual DOC trends. Spring melt is the primary hydrologic event in seasonally snow-covered catchments, which characterize high elevation and northern locations, and where wetlands are also common (e.g. Agren et al. 2007). Our results therefore may be applicable over a larger region, and we strongly suggest that shifts in seasonal hydrology be considered when analyzing trends in DOC.

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