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The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments

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Abstract. Dissolved organic carbon (DOC) concentrations and DOC export are studied during storms to examine the relationship between DOC concentration and stream discharge and to assess the importance of storms on DOC export. Storms were monitored in seven subcatchments within two small watersheds (Harp 4–21 and Harp 3A) on the Precambrian Shield in Central Ontario, Canada. Stream DOC concentrations increase during storms by as much as 100% and 410% in Harp 3A and Harp 4–21 respectively. The seasonal regression between DOC and stream discharge is significant in subcatchments without wetlands ($r^2 > 0.7$) but is not significant in the two subcatchments with small wetland areas ($r^2 < 0.06$). On average, regressions based on weekly data yield accurate estimates of DOC export but the variation in regressions among individual storms and the small number of high DOC samples result in uncertainties of more than 30% in DOC export. The period-weighted calculation of DOC export from weekly data underestimates export by 14% and 22% in Harp 3A and Harp 4–21 respectively. Storms were responsible for 57% to 68% of the DOC export in the autumn and 29% to 40% of the DOC export in the spring. A single large storm accounted for 31% of the autumn DOC export in Harp 3A. The importance of individual storms for DOC export and the variation in the relationship between DOC and stream discharge among storms make it difficult to predict the effects of climate change on DOC export and DOC concentrations.

Introduction

The transport of dissolved organic carbon (DOC) through the hydrological cycle affects processes such as carbon cycling (McDowell & Likens 1988), water acidification (Eshleman & Hemond 1985; Driscoll et al. 1989), soil formation (Dawson et al. 1978), and the sorption, transformation and transport of nutrients, toxic metals and organic compounds (e.g. McDowell 1985; Jardine et al. 1989). Accurate measurement of the mass of DOC transported in streams is necessary to calculate either the output from a catchment or the input to rivers or lakes. The DOC export in streams varies greatly due to the large spatial and temporal variability in both the availability of DOC within catchments and the water flowpaths that transport much of the DOC to the stream (Cronan 1990; Easthouse et al. 1992).

Export of DOC is often calculated using regressions of stream discharge and stream DOC concentrations (e.g. Moore, 1989). Stream DOC concentration can be directly (Meyer & Tate 1983) or inversely related (Hornberger et al. 1995) to stream discharge or even independent of stream discharge depending on the hydrologic, biological and geochemical processes operating within catchments. In upland catchments and humid climates, a direct relationship between DOC concentration and stream discharge is frequently observed at scales that vary from small seeps and streams to large continental rivers (Mulholland & Watts 1982; Thurman 1985). However, it is also apparent that DOC concentration is influenced by many factors that are poorly related or unrelated to stream discharge such as the availability of leachable organic carbon or adsorption of DOC to soil (e.g. Nelson et al. 1993). Consequently, stream discharge explains only a portion of the total variability in DOC (generally $0 < r^2 < 0.7$) and may be a poor predictor of DOC concentration. Therefore, it is important to consider the uncertainties resulting from the regression between DOC and stream discharge and the types of catchments in which regressions can be used most successfully.

Many studies examine DOC export over seasonal or annual periods; the significance of individual storms are only briefly, if ever, discussed (e.g. McDowell & Fisher 1976). However, studies reporting data for individual events frequently demonstrate short term increases in DOC concentrations (McDowell & Likens 1988). Since DOC increases with discharge in many streams (Meyer & Tate 1983; Moore 1989; Eckhardt & Moore 1990) and stormflow is often a large proportion of the total flow, storm periods may represent a significant proportion of total DOC export budgets. Knowledge of the processes affecting DOC during storms is therefore important for understanding both the short and long term dynamics of DOC cycling in catchments.

Substantial changes in precipitation and evapotranspiration are potential consequences of global warming and climatic change (IPCC 1990). Any climatic change that significantly influences runoff will also affect DOC export from catchments. Before predicting the effects of climate change on DOC export, it is necessary to consider what types of hydrologic changes may lead to altered DOC export and whether it is possible to predict these changes reasonably. For example, the relationship between DOC and stream discharge could be used to predict the possible influences of hydrological changes on DOC export, yet it would be necessary to understand how the relationship between DOC and discharge varies with different hydrologic conditions within different catchments.

This paper examines the changes in DOC concentration and DOC export during runoff events in two small catchments. The purposes are: 1) to examine the spatial and temporal changes in the relationship between DOC concentration and stream discharge and their effect on estimating DOC export; 2) to assess the relative importance of stormflow and baseflow conditions on DOC concentration and DOC export; and 3) to discuss the type of information required to predict the effects of climatic change on DOC export and whether reasonable predictions can be made given the present understanding of DOC dynamics and climate change. The hydrologic pathways governing DOC transport to the stream during runoff events are discussed in a companion paper (Hinton et al., submitted, 1997).

Site description

The two headwater streams under investigation are located in the Harp Lake catchment in Central Ontario, Canada. Harp 4–21 is a 3.7 ha catchment covered by a mixed forest of sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), poplar (*Populus spp.*), balsam fir (*Abies balsamea*) and hemlock (*Tsuga canadensis*) (Figure 1a). Groundwater flow through glacial tills up to 15 m thick maintains perennial stream discharge (Hinton et al. 1993). The stream channel is narrow (0.2–1.5 m) with no stagnant water. Soils in Harp 4–21 are podzolic with poorly developed or absent eluviation in the A horizon. The A horizon is approximately 3–10 cm thick along the hillslopes and becomes approximately 23 cm thick near the stream. The geology, hydrogeochemistry and hydrology of the catchment are described by Jeffries and Snyder (1983), Dankevy (1989), MacLean (1992), and Hinton et al. (1993; 1994).

Harp 3A is a 21.7 ha catchment with two small wetlands (0.4 ha and 0.2 ha) and several other small areas (<0.1 ha) where ponding occurs (Figure 1b). The hillslopes are covered predominantly by sugar maple; both cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*) are present in the conifer wetland (wetland 2). Wetland 3 has a partial canopy of yellow birch and black spruce. Wetland 2 is characterized by hummock-hollow topography with a *Sphagnum* ground layer and by water pools approximately 5 to 25 cm deep. Surface runoff through wetland 3 occurs both as slow flow across the ponded surface and as poorly channelized flow in the stream. Flow is also channelized through the ponded area downstream of W3. The podzolic soils in Harp 3A are very similar to those in Harp 4–21 except that the A horizon near the stream is not as thick and does not appear visually to be as humic-rich.

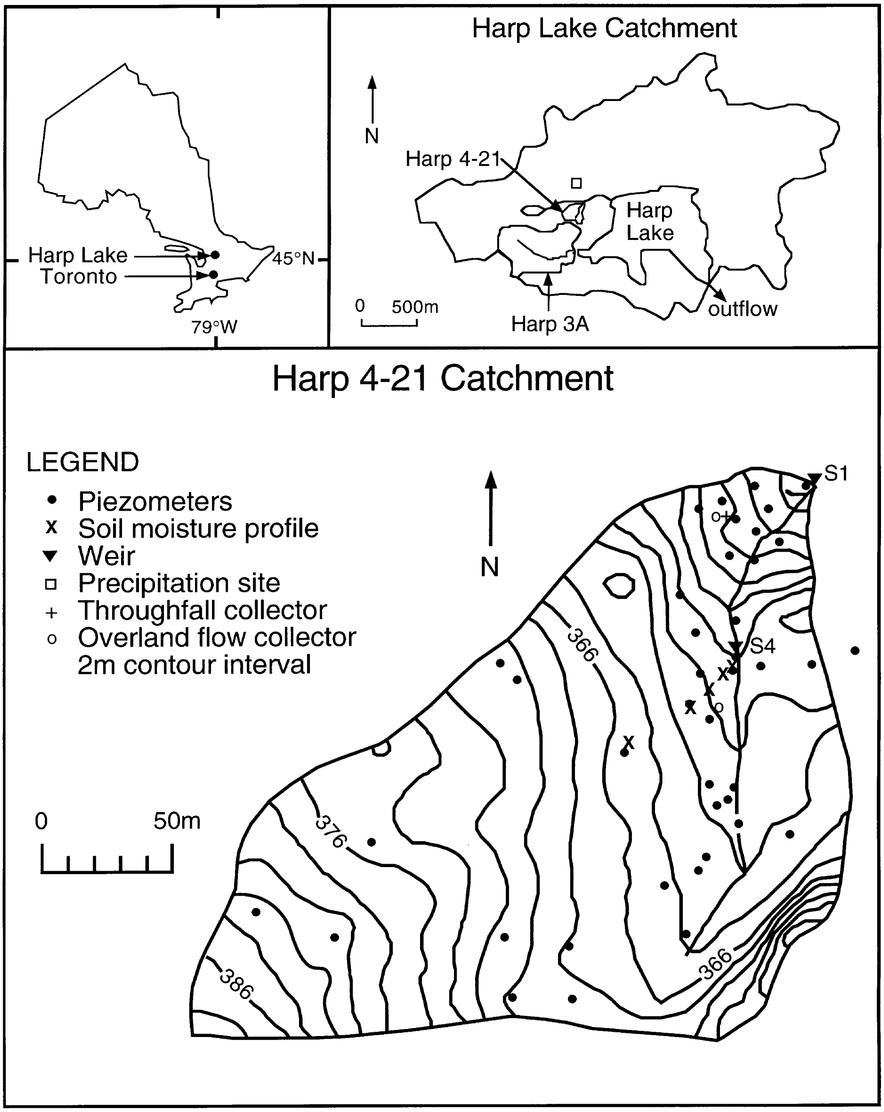

Figure 1a. Location and instrumentation of the a) Harp 4–21 and b) Harp 3A catchments.

Due to the thinner (<1.5 m) glacial sediments in Harp 3A, there is less water storage in the hillslopes and the water table is absent from most of the hillslopes during the summer. Consequently, all surface ponding disappears and the Harp 3A stream dries out upstream of P76 during the summer. Downstream of P76, groundwater flow through lacustrine silts and clays maintains very low summer baseflow (≈ 0.1 l/s).

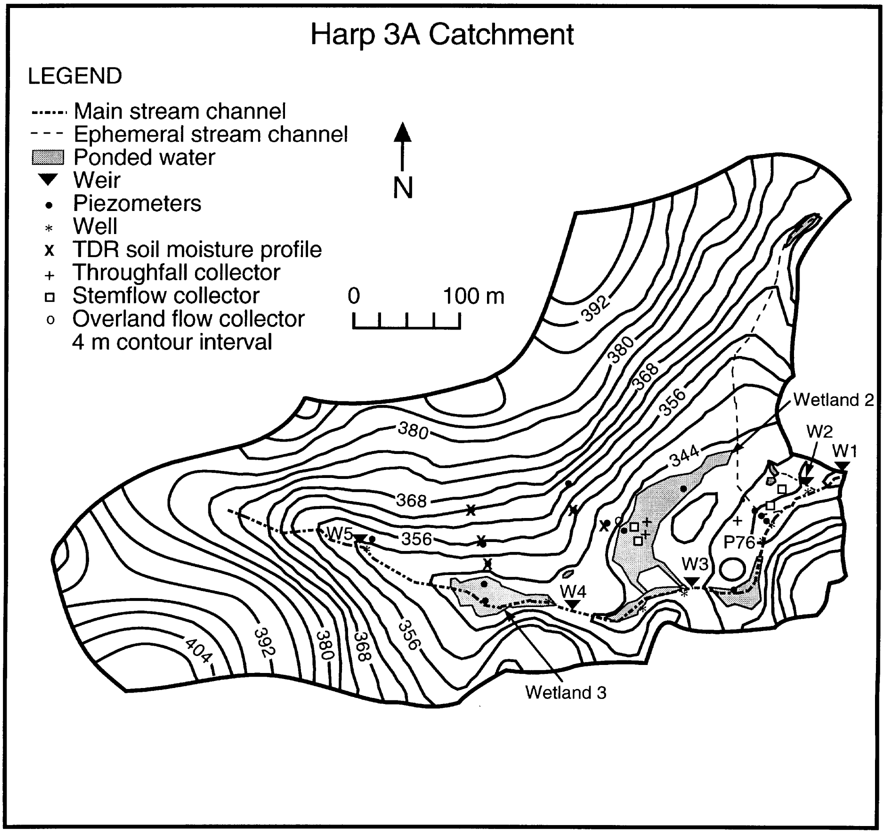

Figure 1b. Continued.

Harp 4–21 and Harp 3A are subdivided into two (S1 and S4) and five (W1–W5) subcatchments respectively. Subcatchments S1, S4, W2 and W5 drain hillslopes with little ponded water and small stream surface areas. Hillslopes also comprise most of the area within subcatchments W3 and W4, however, wetlands 2 and 3 reside in the flat valley bottoms of W3 and W4 (Figure 1b). Although subcatchment W1 also drains hillslopes and only has small areas of ponded water, it is influenced by wetland runoff from W3 and W4. Most catchments in the region are influenced by wetlands.

Methods

Sampling methods

Sampling was conducted from September 27 to November 20, 1992 (autumn season) and from May 2 to June 4, 1993 (spring season) in Harp 3A and from September 27 to November 10, 1992 and from May 2 to May 30, 1993 in Harp 4–21. The autumn season included storms both during and following the leaf fall period (≈ September 27 to October 13). Snowmelt was complete prior to the start of the spring season and spring storms followed leaf-out. The entire length of the Harp 3A stream as well as the secondary channels were flowing during both sampling periods. Each sampling period was further subdivided into stormflow and baseflow periods. Stream water samples were collected from five weirs in Harp 3A (W1–W5) and two weirs in Harp 4–21 (S1, S4). Previous sampling in Harp 4–21 during spring (May 1 to June 30) and autumn (October 4 to November 11) 1989 storms are used for comparison with the 1992–93 data.

DOC analysis

Stream and groundwater samples were filtered in the field through 80 μm and 44 μm polyester screening into site-designated, opaque polyethylene bottles. All 1992 and 1993 samples were subsequently filtered through 0.45 μm cellulose nitrate filters into glass scintillation vials, acidified with HNO_3 to a pH near 2 to prevent microbial degradation of the DOC and kept refrigerated and in darkness until analysis. DOC concentration was measured using a Dohrmann DC-190 total carbon analyzer at the University of Waterloo (UW). Dissolved inorganic carbon was stripped from the sample, DOC was combusted to CO_2 in a 800 °C oven, CO_2 was then dehumidified, passed through a Cu scrubber and measured by an infrared detector. The instrument blank measured 0.1 mg/l.

DOC concentrations reported from 1989 were analyzed by the Ontario Ministry of the Environment (MOE) using the persulfate oxidation method (MOE 1983). Comparison of 33 split samples analyzed using both methods demonstrated that MOE results were lower by an average of 0.8 $\pm$ 0.4 mg/l in the range of 2–12 mg/l. All 1989 MOE results have been adjusted by 0.8 mg/l to correspond to UW values.

Methods of calculating DOC export

Several methods are available for calculating the nutrient fluxes from catchments based on measurements of stream discharge and stream water chemistry including the period-weighted method and several regression-based procedures (Dann et al. 1986; Johnson 1979). The method employed becomes important when the concentration is flow dependent. In the period-weighted method, the average concentration of successive samples is multiplied by the volume of water leaving the catchment during the interval. The total export is obtained by summing the export during individual sampling intervals. In the regression-based methods, a regression between concentration and stream discharge combined with continuous measurements of discharge with time is used to calculate concentration with time. Export can then be calculated easily by multiplying concentration with discharge and summing to obtain the total export. The period-weighted method accounts for changes in flow volume but does not consider changes in concentration with stream discharge. In contrast, the regression-based methods explicitly take into consideration the changes in concentration with discharge. However, since the concentrations are calculated from the regression, this method does not use the measured concentration data to calculate export and errors in the regressions lead to uncertainty in the estimate of DOC export.

This study uses an alternative calculation method that retains the measured concentration data and considers both the changes in concentration with discharge and the volumes of flow associated with successive samples. The method combines both procedures by assuming that DOC concentration varies linearly with discharge between successive samples and will be referred to as the sample-interpolation method. The DOC export is calculated in three steps. Firstly, stream discharge is determined at 20-minute intervals from the continuous measurements of stage as determined from stream charts (Figure 2a). Secondly, a linear equation between DOC and stream discharge is calculated for every two successive stream samples (Figure 2b). DOC is interpolated at 20-minute intervals to obtain a continuous record of DOC (Figure 2c). The interpolated DOC is calculated using the measured stream discharge (from step 1) and the linear equation between DOC and discharge (Figure 2b). When a local minimum or maximum in stream discharge exists between two samples (between samples B-C, D-E and H-I), the linear equation between DOC and discharge on the receding limb of the hydrograph is extrapolated to the measured streamflow minimum or maximum (extrapolations 1 and 3). If there are no high-discharge data on the receding limb and better data are available on the rising limb, the equation is extrapolated to the time of peak flow from the rising limb of the hydrograph to avoid large extrapolations (extrapolation 2). Thirdly, DOC exports for each time interval are the products of the calculated DOC and the volumes of discharge that are summed to yield the total export. The average DOC concentration equals the total DOC export divided by the total runoff during the period of interest. This sample-interpolation procedure is only appropriate when many samples have been collected, particularly near each minimum and maximum in stream discharge, to define all the changes in DOC concentration with discharge. This procedure could also be used for the calculation of export of other solutes given sufficient sample collection and a relationship between solute concentration and stream discharge. For the small storm on October 24 during which no samples were collected but discharge was measured, the DOC was calculated using the slope of DOC versus discharge between baseflow and peak discharge from the previous storm on October 16 storm.

Uncertainties in using data collected on a regular sampling interval are quantified for the autumn 1992 data in the Harp 4–21 and Harp 3A catchments at S1 and W1. The interpolated DOC data was subdivided at weekly intervals to simulate weekly sampling. DOC exports were calculated from the weekly data using both the period-weighted and regression methods. The accuracy and precision of the DOC exports were estimated from averages and standard deviations of seven arbitrarily chosen weekly data sets, each offset by an increment of one day. The results are reported as a percentage of the DOC export estimated by the sample-interpolation method used in this study. DOC exports were also calculated using only the measured data to examine the accuracy of the period-weighted and regression methods for intensively sampled storms.

Each sampling season was subdivided into stormflow and baseflow periods. The criterion used to distinguish between these periods is the hydrograph separation method proposed by Hewlett and Hibbert (1967). The start of the stormflow period is defined by an increase in stream discharge; the end of the period is defined by adding 0.0055 L/s to the stream baseflow for each hectare of catchment area for each hour (0.05 $ft^3/s/mi^2/hr$) following the start of stormflow until the receding limb of the hydrograph is intersected (Figure 3). Although these criteria are entirely arbitrary, they provide a consistent method to define stormflow periods. Based on these criteria, stormflow generally ends prior to the return to baseflow DOC concentration so that the baseflow period may also include a portion of the receding limb of the storm hydrograph. The term stormflow used in this paper is distinct from Hewlett and Hibbert’s (1967) definition of quickflow in that it includes all runoff during storm periods. Stormflow and baseflow periods were determined at W1 in Harp 3A and applied to the other catchments so that DOC exports from the different catchments can be compared for the same storm duration.

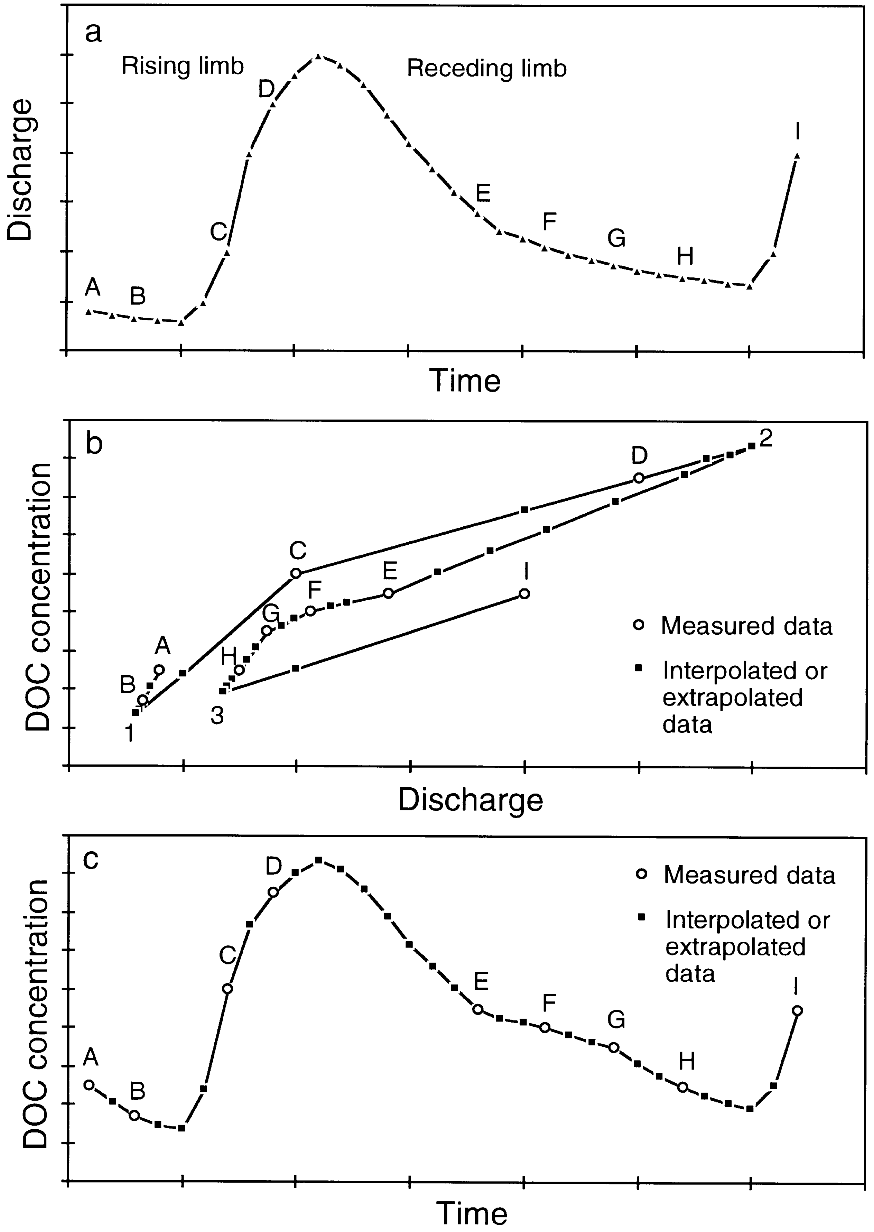

Figure 2. Schematic example of the sample-interpolation method of calculating DOC concentrations. Panel a shows the continuous measurement of stream discharge divided into discrete time intervals. Panel b shows measured DOC (open circles with letters) plotted against measured stream discharge. DOC is interpolated or extrapolated (squares) between pairs of samples using measured stream discharge. Numbers 1 and 3 indicate data extrapolated from the receding limbs and number 2 is extrapolated from the rising limb of the hydrograph. The resulting DOC concentrations are plotted in panel c. The method is discussed further in the text.

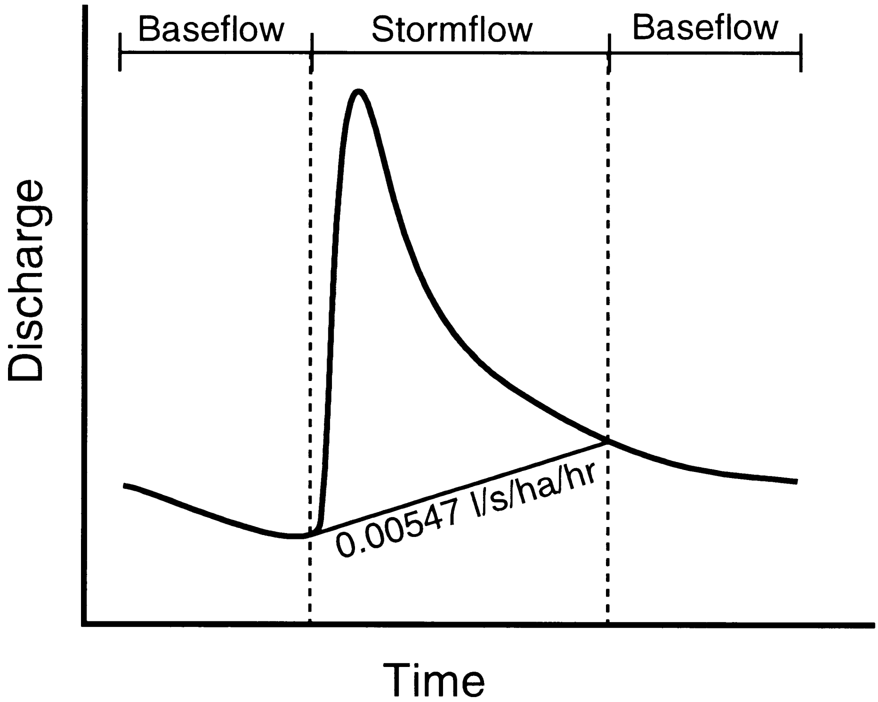

Figure 3. Criteria for graphical hydrograph separation to define periods of stormflow and baseflow.

Results and discussion

DOC concentrations as a function of stream discharge

In contrast to stream water concentrations of major ions that are generally diluted during storms (Likens et al. 1977), DOC increases during runoff events at all locations (Figure 4). The magnitude of the increase in DOC during individual runoff events ranges from 0.7 to 4.1 mg/l (15% to 100% of baseflow DOC) at W1 and from 3.9 to 11.4 mg/l (120% to 410% of baseflow DOC) at S1.

Regressions between DOC and stream discharge for individual runoff events at W1 and S1 are significant ($p < 0.05$) with r^2 values ranging from 0.56 to 0.98 (except Nov. 10 storm at W1, $r^2 = 0.26$). The positive relationship between DOC and stream discharge during storms suggests the inflow of water with high DOC to the stream and/or increased leaching of organic carbon within the stream. The good correlations also justify the use of the sample-interpolation method for calculating DOC concentration and DOC export. Weaker correlations at wetland sites W3 and W4 ($0.12 < r^2 < 0.93$)

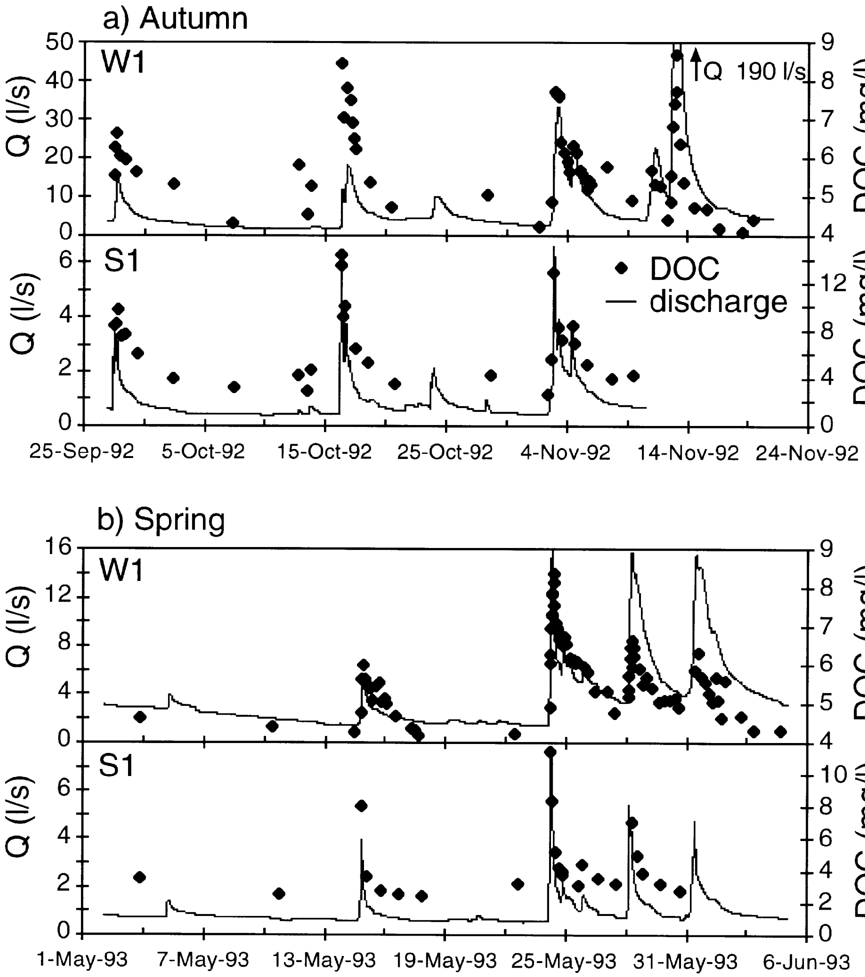

Figure 4. Stream discharge (lines) and DOC concentrations (diamonds) during the a) autumn and b) spring sampling seasons at W1 and S1. Note the different vertical scales.

may result from the influence of flushing DOC from stagnant portions of the wetlands (Hinton et al. 1997).

The seasonal regressions between DOC and stream discharge show the highest correlations at S1, S4, W2 and W5 (autumn), lower correlations at W1, and no significant relationship at W3 and W4 (Table 1). The lower correlations of the seasonal regressions reflect the variability in the regressions among individual storms (Figure 5).

One of the most prominent factor affecting the correlation in the seasonal regressions appears to be the presence or absence of wetlands. Despite

Table 1. Regressions between DOC concentrations and stream discharge during the autumn and spring sampling seasons. DOC concentrations are expressed in mg/l and stream discharges are expressed in l/s.

Site	Autumn 1992[1]	r^2	Spring 1993[2]	r^2
W1	[DOC] = 0.021 Q + 5.46	0.32*	[DOC] = 0.145 Q + 4.70	0.43*
W2	[DOC] = 0.403 Q + 3.50	0.83*	–	–
W3	[DOC] = 0.006 Q + 7.33	0.005	[DOC] = 0.137 Q + 7.99	0.06
W4	[DOC] = 0.027 Q + 5.76	0.03	[DOC] = 0.112 Q + 5.56	0.01
W5	[DOC] = 0.102 Q + 3.81	0.71*	[DOC] = –0.076 Q + 3.21	0.01
S1	[DOC] = 1.828 Q + 3.38	0.88*	[DOC] = 1.290 Q + 2.03	0.96*
S4	[DOC] = 3.094 Q + 2.87	0.83*	[DOC] = 1.693 Q + 2.48	0.68*
	Autumn 1989[3]		Spring 1989[4]	
S1	[DOC] = 4.540 Q + 2.83	0.83*	[DOC] = 1.048 Q + 4.81	0.81*

Sampling seasons:
[1] September 27–November 20, 1992 at W1 to W5 and September 27–November 10, 1992 at S1 and S4.
[2] May 2–June 4, 1993, at W1; May 2–May 30, 1993, at W3-W5 and S1.
[3] October 4–November 11, 1989.
[4] May 1–June 30, 1989.
* Significant at $P<0.01$.

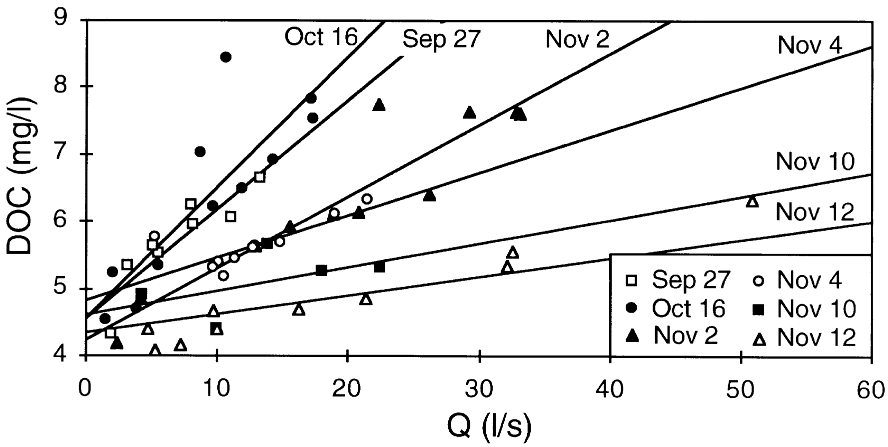

Figure 5. Regressions between DOC concentration and stream discharge for individual autumn storm events at W1. r^2 values: Sep. 27 = 0.80, Oct. 16 = 0.70, Nov. 2 = 0.86, Nov. 4 = 0.65, Nov. 10 = 0.26, Nov. 12 = 0.94.

increases in DOC during individual storms at W3 and W4, there is no significant correlation when all the data are combined into one seasonal regression. At W3 and W4 the variability in the regressions among storms is large. High

DOC is not restricted to periods of high stream discharge. Ponded water with high DOC may be flushed from the wetland at relatively low discharge during smaller storms. Furthermore, other factors such as the input of fresh litter to the wetland surface during the autumn and variable contact time between water and organic matter can lead to additional variability in the seasonal regressions. Similar results are reported in southern Quebec where four catchments containing wetlands show no significant (logarithmic) relationships between DOC and stream discharge and four catchments without wetlands show significant direct correlations (Eckhardt & Moore 1990).

The variability in the regressions among storms is smallest at S1 and S4, two catchments that lack wetlands. In addition, comparison of soil moisture and groundwater levels in Harp 4–21 and Harp 3A suggest that differences in groundwater flow are a possible explanation for better correlations in Harp 4–21. Groundwater flow through thicker glacial till in the Harp 4–21 catchment (S1 and S4) maintains elevated groundwater levels adjacent to the stream throughout the year and perennial stream baseflow (Hinton et al. 1993). Since the soils adjacent to the stream are close to saturation prior to each storm (MacLean 1992), changes in water flowpaths during individual storms are similar and slopes of the regressions for individual storm events show less variation than in Harp 3A. Thin or absent till in the Harp 3A catchment is not able to store sufficient water to sustain groundwater flow within the hillslopes throughout the summer. Consequently, soil moisture and groundwater levels decline and baseflow ceases. During the autumn, soil moisture and groundwater levels vary among storms as infiltration replenishes the depleted soil moisture. Water flowpaths in autumn also change from one storm to the next. The resulting slopes of the regressions between DOC and stream discharge change among storms and the combined seasonal regressions are weaker at W2 and W5 than at S1 and S4. The lack of correlation at W5 in the spring is due, in part, to dry conditions experienced in early May and the small hydrologic response to subsequent storms. At W1, the seasonal regressions are significant but weak (Table 1), indicating the mixed influence of variable hillslope flowpaths and flow from wetlands 2 and 3.

The variability in hydrological conditions among years can result in larger errors in calculated DOC than the variability among storms. In Harp 4–21, the seasonal regressions at S1 changed drastically from the dry conditions of autumn 1989 to the wet conditions of autumn 1992 (Table 1). The average absolute difference between actual DOC measured at S1 in 1989 and those calculated using the discharges from 1989 with the seasonal regressions from autumn 1992 and spring 1993 are 1.4 mg/l and 2.4 mg/l (22% to 36% of actual DOC respectively) with errors in individual samples of up to 4.9 mg/l

(120% of actual DOC). Therefore, data sets spanning several years are not recommended for seasonal regression calculations.

Where individual runoff events have not been sampled intensively, seasonal or annual regressions between DOC and discharge are frequently used to calculate DOC from stream discharge records (Meyer & Tate 1983; Moore 1989). Even where seasonal regressions are relatively good, estimates of individual DOC concentrations using seasonal or annual regressions may have large uncertainties for two important reasons. Firstly, because slopes of the regressions vary among storms at every site, there is a resultant loss of precision in DOC which has been calculated from seasonal regressions that average results from several individual storms. The absolute differences between the actual and calculated DOC averages between 0.3 mg/l and 1.3 mg/l (10% and 22% of actual DOC) for the different subcatchments with errors for individual samples of up to 6.5 mg/l (60% of actual DOC). Because the regressions for individual events diverge with increasing discharge (Figure 5), the precision in calculated DOC decreases at high flows when DOC export is greatest.

Secondly, DOC concentrations estimated from seasonal regressions are imprecise because they are often determined from data in which there are few measurements of DOC at high discharges. Samples collected at regular intervals often miss high discharge conditions because of their short duration. Using the interpolated data from the autumn of 1992 as the entire population of samples, the probability of randomly collecting a sample in the upper third of the DOC concentration range was 5% and 0.8% at sites W1 and S1 respectively. Consequently, regressions must either be extrapolated to discharges beyond the sampled range or are biased by the few samples collected at high discharge since the data at high discharge reflect unique conditions of short duration for each storm. High discharge can occur from a variety of weather conditions such as spring snowmelt, rain-on-snow storms, intense thunderstorms or prolonged rainstorms so that different storms are likely to produce different DOC at high discharge.

The problems with annual regressions are demonstrated in Figures 5a in Schiff et al. (1997) which shows all the DOC data collected during two years of routine sampling (n = 392) in Harp 4–21 (S1). The regression is poor (r^2 = 0.17) because samples were collected over a wide range of hydrological conditions during different storms and seasons. The samples with the highest DOC (above 6 mg/l) were all collected during the autumn whereas the samples with the highest flows (above 2.5 l/s) were all collected during spring snowmelt. This bias in the regression would tend to overestimate spring DOC export and underestimate autumn DOC export.

Table 2. Comparison of autumn DOC export at W1 and S1 calculated using period-weighted and seasonal regression methods from all measured data and weekly interval data. Results are expressed as a percentage of DOC export obtained using the sample-interpolation method. Uncertainties are expressed as the 90% confidence interval.

	Sampling interval			
	W1		S1	
Calculation method	All data	Weekly interval	All data	Weekly interval
Period-weighted	100	86 ± 9	103	78 ± 18
Seasonal regression	88	98 ± 32	88	93 ± 33

Uncertainty in estimating DOC export

Discrete sampling and the method used to calculate DOC export from DOC concentrations and stream discharge generate the largest uncertainties in the estimation of DOC export. Although increased sampling frequency during storms is recommended, the time and expense required for collection and analysis of many samples from individual storms are often prohibitive for long term studies of DOC export. Therefore, it is necessary to consider the uncertainties in DOC exports calculated from less data.

Seasonal regressions based on weekly data yield accurate results (98% and 93% of true export at W1 and S1 respectively) but the uncertainties in any single calculation of the DOC export at the 90% confidence interval are 32% and 33% respectively (Table 2). In contrast, the period-weighted results significantly ($p < 0.01$) underestimate DOC export by 14% at W1 and 22% at S1 because high DOC is not adequately represented by weekly sampling. However, when all the measured data were used, the period-weighted method provided accurate estimates of DOC export at both W1 and S1 (100% and 103% respectively). The DOC exports calculated from seasonal regressions using all the measured data underestimate DOC export by 12% but are within the range of uncertainty calculated from weekly data.

Underestimating DOC export in streams could influence DOC budgets for lakes since stream inflows are underestimated whereas the lake outflow is less likely to be underestimated because large and rapid changes in DOC concentrations are not observed. Consequently, the net CO_2 evasion rates calculated from DOC and dissolved inorganic carbon budgets for lakes in this area and the magnitude of the in-lake DOC sink may be larger than reported (Dillon & Molot 1997).

Table 3. Summary of DOC export from W1 and S1 during a) autumn 1992 and b) spring 1993. Numbers in parentheses are percentages of total values.

	W1			S1		
a) Autumn 1992	Stormflow	Baseflow	Total	Stormflow	Baseflow	Total
DOC export (kg)	129 (63.7)	73.3 (36.3)	202	10.6 (56.7)	8.1 (43.3)	18.7
Flow volume (1000 m^3)	19.9 (56.9)	15.1 (43.1)	35.0	1.32 (40.1)	1.97 (59.9)	3.29
Average [DOC] (mg/l)	6.5	4.8	5.8	8.0	4.1	5.7
Duration (days)	11.3 (20.5)	43.7 (79.5)	55.0	7.3 (16.4)	37.2 (83.6)	44.5
b) Spring 1993						
DOC export (kg)	21.5 (39.7)	32.7 (60.3)	54.2	3.3 (39.7)	4.9 (60.3)	8.2
Flow volume (1000 m^3)	3.6 (34.3)	6.9 (65.7)	10.5	0.56 (25.8)	1.61 (74.2)	2.17
Average [DOC] (mg/l)	6.0	4.7	5.2	5.8	3.1	3.8
Duration (days)	4.8 (14.1)	29.2 (85.9)	34.0	3.2 (11.0)	25.8 (89.0)	29.0

DOC export during runoff events

Contribution of DOC export by stormflow exceeds that by baseflow in autumn. Although stormflow occurs only 21% of the time, storms produced 57% of the flow volume and 64% of the DOC export at W1 during the autumn (Table 3). Stormflow DOC export is more important at terrestrial sites W2 and W5 (68% and 65% respectively) than at wetland-influenced sites W3 and W4 (57% and 59% respectively). In the spring, stormflow DOC export was slightly lower at W1 (40%) since the stormflow was a smaller proportion of total runoff (34%) and time (14%) (Table 3). Similar results are also observed at S1 (Table 3).

Periods of high discharge are responsible for the majority of DOC export (Figure 6). For example, autumn stream discharge at W1 exceeds 14.3 l/s only 10% of the time, yet the proportions of flow and DOC export occurring above this discharge are 43% and 50% respectively. Similar results are observed at all the stream sites where between 41% and 57% of the total autumn export of DOC are associated with the upper 10% of discharge values. The November 12 event accounted for 31% of the total autumn DOC export. The export during that single storm (63.4 kg) exceeds the total DOC export during the entire spring sampling period (54.2 kg).

Although much of the DOC export occurs during storms because of high runoff, increased DOC concentration during storms also increases DOC export. Average stormflow DOC is up to 3.9 mg/l greater than average baseflow DOC (Table 4). Consequently, the percentage of DOC exported during storms exceeds the percentage of stormflow runoffs by 5% to 7% at W1 and

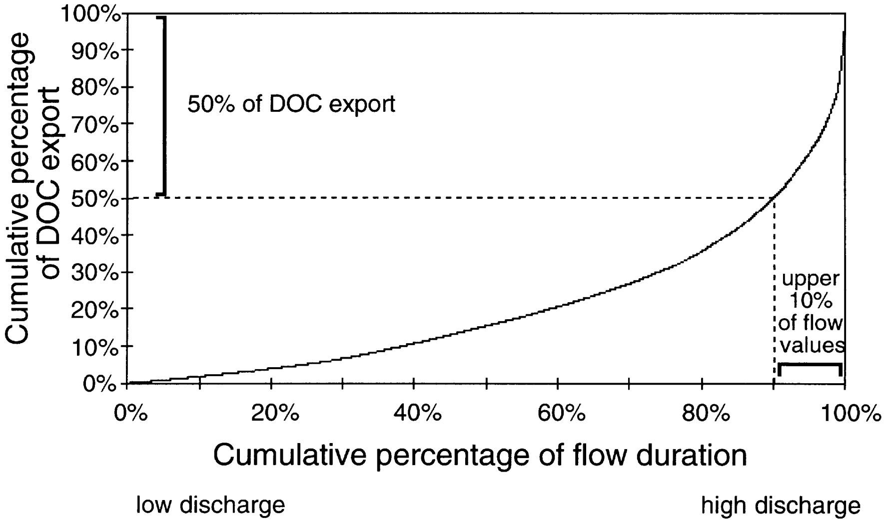

Figure 6. Cumulative percentage of DOC export as a function of cumulative percentage of flow duration at W1 during the autumn sampling period. 50% of the total DOC export is associated with the highest 10% of discharge values.

Table 4. Average DOC concentrations for periods of stormflow, baseflow and total flow during the autumn and spring sampling periods.

	Average DOC concentration (mg/l)					
	Autumn 1992			Spring 1993		
Site	Stormflow	Baseflow	Total flow	Stormflow	Baseflow	Total flow
W1	6.5	4.8	5.8	6.0	4.7	5.2
W2	5.5	3.4	4.6	–	–	–
W3	7.4	6.4	6.9	8.5	7.6	7.8
W4	6.4	5.0	5.7	5.8	5.1	5.3
W5	5.0	3.6	4.4	3.2	3.2	3.2
S1	8.0	4.1	5.7	5.8	3.1	3.8
S4	7.1	3.9	5.2	–	–	–

14% to 17% at S1 (Table 3). Increased DOC during storms has the largest influence on DOC export at S1 and S4 because baseflow DOC is low and relative increases in DOC from baseflow to stormflow are largest (Table 4). In contrast, baseflow DOC is highest at W3 and W4 because wetlands contribute additional DOC to the stream and relative increases in DOC during storms are smaller. Therefore, increased stormflow DOC is less important in catchments with wetlands.

Assessing the potential effects of climate change on DOC concentration and DOC export

Predictions of the hydrological consequences of climate change are necessary to predict changes in DOC export. Such predictions are needed at the catchment scale since changes in runoff resulting from altered precipitation and evapotranspiration will vary among catchments. For example, an increase in summer evapotranspiration would have a small effect on stream runoff and DOC export from Harp 3A (W1) since summer stream runoff is already extremely low (< 2% of summer precipitation). However, increased evapotranspiration could reduce groundwater discharge, stream runoff and DOC export during the summer in Harp 4–21 (S1).

Changes in the seasonal distribution of precipitation will also influence total runoff and DOC export since the runoff response to precipitation, expressed as the effective runoff (the ratio of precipitation to storm runoff), varies seasonally as a function of antecedent soil moisture conditions (MacLean 1992). Therefore, an increase in precipitation during the wet season would produce a greater increase in runoff and DOC export than a similar increase in precipitation during the dry season. The effect of changes in the seasonal distribution of precipitation would differ among catchments since runoff response to precipitation also varies differently among catchments. Seasonal changes in effective runoffs are larger in Harp 3A than in Harp 4–21; during the November 12, 1992 storm, the effective runoffs were 0.63 at W1 and 0.38 at S1 whereas during the May 24, 1993 storm they were 0.10 and 0.20 at W1 and S1 respectively.

Two potential consequences of climate change are an increase in the size and frequency of extreme events (IPCC, 1990; Gates et al., 1992). Considering the importance of storms and particularly large storms (e.g. November 12, 1992) on DOC export, changes in the frequency and size of large storms could have a large effect on DOC export. Therefore, it is not only important to recognize changes in the averages of climatic variables but also to consider variability in weather patterns leading to large storms.

Even given accurate estimates of the effects of climate change on stream discharge and stream runoff, estimates of the changes in DOC concentration and DOC export would be unreliable because the relationship between DOC and discharge varies substantially among storms (Figure 5), seasons and years (Table 1). Since the factors influencing these variations are not yet understood, it is not clear how the regression between DOC and discharge may vary under different climatic conditions. Furthermore, other factors such as changes in organic matter production, dissolution, decomposition and biologic activity which alter the availability of soluble organic carbon for leaching will also affect the regression. Therefore, it is difficult to predict the relative importance of changes in stream runoff and changes in regressions on DOC concentration and DOC export. Longer term studies examining DOC concentrations and DOC export during storms over a range of wet and dry seasons should provide additional insight into the important factors affecting stormflow DOC export and the relationship between DOC and discharge.

Conclusions

The relationships between stream DOC and discharge and the comparison of DOC export in the Harp 4–21 and Harp 3A catchments have provided some insight into both the uncertainties of calculating DOC concentration and DOC export and the role of storms on DOC concentration and DOC export. Unless the stream is sampled intensively enough to define the changes in stream discharge and DOC, the period-weighted method is not recommended for the calculation of DOC export because it does not take into consideration changes in DOC with discharge and DOC export is systematically underestimated. The calculation of DOC export using regressions is preferred, particularly if the storms are shorter than the sampling interval. Uncertainties in the calculation of DOC export using regressions are substantial and arise principally from two sources: variability in the regression between DOC and discharge and lack of samples with high DOC. Provided that sufficient samples have been collected, shorter time periods can be chosen for the regressions to reduce the variability arising from differences among individual storms. High DOC can be sampled by adopting flow-related sampling protocols or by augmenting regular sampling with high discharge samples using automated samplers. Alternatively, proportional samplers have been found to provide representative samples of the volume-weighted average DOC during storms (Meyer & Tate 1983).

DOC export during storms accounts for a substantial proportion of the total DOC export (Table 3), yet few studies specifically examine the processes affecting DOC export during runoff events (Easthouse et al. 1992; Hinton et al. 1997). Stream DOC increased during almost every storm at all sites, including wetlands. Consequently, the average stormflow DOC was greater than baseflow DOC (Table 4), indicating that the dominant processes controlling DOC concentration and export may differ substantially between baseflow and stormflow periods. Although the consequences of these changes in DOC were not studied, storms may also have substantial effects on the chemical nature of DOC and the abiotic and biotic utilization of DOC in the stream (Kramer et al. 1990; Meyer 1990). Greater emphasis on understanding DOC dynamics during storms is required.

The significant role of storms on DOC concentration and DOC export makes predictions of the effects of climate change difficult. Predictions would require considerable meteorological and hydrologic information such as changes in the frequency and size of storm events and changes in the seasonal distribution of precipitation and runoff. Predictions are further complicated by large variations in regressions between DOC and stream discharge among storms, seasons and years. Until these variations in regressions are related to hydrologic, biologic and geochemical characteristics of the catchments, the regressions will not be useful for assessing the possible effects of climate change.

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