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Event controlled DOC export from forested watersheds

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Abstract We performed a meta-data analysis to investigate the importance of event based fluxes to DOC export from forested watersheds. A total of 30 small eastern United States forested watersheds with no wetland component, with a total of 5,176 DOC and accompanying discharge measurements were used in this analysis. There is a clear increase in DOC concentration during hydrologic events (storms and snow melt) that follows a power relationship. We estimate that 86% of DOC is exported during events. The majority (70%) of this event based DOC flux occurs during the rising hydrograph and during large events. Events with a discharge greater than 1.38 cm day^{-1} make up only 4.8% of the annual hydrograph, yet are responsible for 57% of annual DOC flux. The relationship between event discharge and both DOC concentration and flux is also regulated by temperature and antecedent conditions, with a larger response in both fluxes and concentrations to events during warmer periods and periods where the preceding discharge was low. The temperature relationship also shows seasonality indicating a potential link to the size or reactivity of watershed OM pools. The 86% of DOC lost during events represents a conservative estimate of the amount of allochthonous forested DOC transported laterally to streams. Future research on watershed cycling of DOC should take into account the importance of events in regulating the transport of DOC to downstream ecosystems, determine the relative importance of abiotic versus biotic processes for the temperature regulation of event-associated DOC fluxes, and elucidate the interactions between processes that respond to climate on event versus longer time scales.

Keywords Precipitation · Climate change · DOC · DOM

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Introduction

The question of how organic matter (OM) moves from terrestrial ecosystems to streams and impacts downstream aquatic ecosystems is of fundamental importance (Lindeman 1942; Teal 1962; Fisher and Likens 1972; McDowell and Likens 1988; Webster and Meyer 1997; Hedin et al. 1998; Grimm et al. 2003; Cole et al. 2007). Knowledge of the mechanisms that control the fluxes and transport pathways of dissolved organic matter (DOC) is requisite to managing aquatic food webs and sustaining or restoring ecosystem health (Bormann et al. 1969; Gomi et al. 2002; Rabalais et al. 2002; Bernhardt et al. 2005). With respect to metabolic budgets, the export of stream-water DOC represents a loss of reduced compounds and limiting nutrients from terrestrial ecosystems (Qualls and Haines 1991;

Hedin et al. 1995; Kalbitz et al. 2000; Neff et al. 2003). This land-derived DOC represents a source of allochthonous energy for heterotrophs in receiving lakes, rivers, reservoirs, and estuaries (Wetzel 1992; Smith and Hollibaugh 1993; Kemp et al. 1997; Raymond and Bauer 2000; Pace et al. 2004; Aller and Blair 2006), and the decomposition of DOC within these water bodies releases nutrients that fuel new primary and secondary production.

Watershed cycling of DOC has equally important implications for applied biogeochemistry and water quality (Kaplan et al. 2006). DOC affects the efficiency of drinking-water treatment efforts (Garvey and Tobiason 2003; Sharp et al. 2004), and its presence can lead to the formation of potentially harmful disinfection by-products (Singer 1994; Chow et al. 2008). Complexation reactions with DOC influence the fate and transport of a variety of hazardous pollutants, such as mercury (Haitzer et al. 2002; Aiken et al. 2005; Selvendiran et al. 2006; Shanley et al. 2006). DOC also regulates microbially-mediated reactions controlling contaminant toxicity (Watras et al. 2005), alters stream-water pH (Wigington et al. 1996), absorbs harmful UV-light (Morris et al. 1995), and influences the cycling of aluminum and iron oxides (McKnight et al. 1992).

Interactions between terrestrial biota, soil chemistry, microbiological processes, and hydrological phenomena affect DOC cycling within watersheds and the transfer of terrestrial DOC to streams (Likens and Bormann 1995; Qualls et al. 2002). The important contribution of precipitation and snowmelt events to total annual DOC export has been documented (Ciaio and McDiffett 1990; Brown et al. 1997; Hinton et al. 1998; Volk et al. 2002; Even et al. 2004; Wellington and Driscoll 2004; Inamdar et al. 2006; Saunders et al. 2006), and recent observations indicate that the chemical composition and reactivity of soil-water and stream-water DOC changes markedly during rainfall and snowmelt (Easthouse et al. 1992; Buffam et al. 2001; Kaushal and Lewis 2003; Dalzell et al. 2005, 2007; Volk et al. 2005; Hood et al. 2006; Vidon et al. 2008). Although it is evident that hydrologic events (i.e., rainfall, snowmelt) serve as "hot moments" for the loss of labile carbon, organic-bound nutrients, and DOC-associated pollutants from the terrestrial landscape (McClain et al. 2003), quantitative linkages between event-based DOC concentrations and stream discharge and other watershed characteristics have not been well elucidated.

In this paper, we derive quantitative relationships suitable for approximating USGS observations on DOC concentrations in stream waters that drain 30 forested watersheds that have no wetland component. The relationships that emerge reveal that DOC export is controlled by high-discharge events that comprise disproportionately small fractions of the watersheds' annual water yields. This meta-data analysis also illuminates a temperature and antecedent-discharge regulation of event-based DOC export.

Methods

Our study focuses on 30 small, USGS gauged watersheds that are dominated by forest land cover (Table 1) and distributed across eight states in the eastern Unites States (Table 1) within the U.S. Geological Survey (USGS) Hydrologic Units 1, 2, and 5 (Fig. 1). The selected watersheds average 55.8 km^2 in area and are homogeneous with respect to land cover (Table 1). We limited our analysis to watersheds with low wetland coverage because of the known role of wetlands in elevating stream-water DOC concentrations (Raymond and Hopkinson 2003). The percent forest coverage in all watersheds exceeds 80% and averages 96%, and the percent wetland coverage in each watershed is less than 1.2%.

Our analysis uses data published by USGS and includes 5,176 DOC measurements (USGS parameter code 00681) and daily measurements of stream discharge (USGS parameter code 00060). Collectively, the measurements were made between 1977 and 2008, although most records do not span the entire period (Table 1). Because we used daily stream-flow measurements, sub-daily DOC observations were averaged over the entire day, which yielded a total of 4,078 days with DOC measurements. Measurements of volumetric discharge were normalized by watershed area to facilitate comparisons between watersheds of different size.

To identify hydrologic events from the time-series data on stream discharge, we separated the discharge hydrographs into their quickflow and baseflow components, such that

Table 1 30 USGS forested watersheds used in this analysis and their average flow and DOC flux

USGS site ID	Name	Start year	End year	n	Avg DOC (mg l^{-1})	Area (km^2)	Flow (cm $year^{-1}$)	DOC flux (g m^{-2} $year^{-1}$)
01054200	Wild River at Gilead, ME	1981	2006	51	4.3	180.2	108.1	4.8
01137500	Ammonoosuc River, NH	1993	1995	34	2.6	226.8	67.0	2.0
01170100	Green River, MA	1993	2004	66	1.5	107.2	71.9	1.3
01174565	W. B. Swift River, MA	1983	1985	69	2.9	32.6	78.4	2.7
01349711	West Kill, NY	1997	1999	61	1.5	12.9	108.6	1.9
01349840	Batavia Kill, NY	1997	2001	54	2.4	5.3	125.6	4.6
01362200	Esopus Cr., NY	1996	1995	25	1.2	164.9	81.3	1.0
01364959	Rondout Cr., NY	1984	2002	307	2.0	13.9	109.3	2.6
01434006 80	E.B. Neversink, N.E. of Denning, NY	1991	2006	416	2.6	23.1	113.7	4.0
01434013	E. B. Neversink, E of Ladelton, NY	1991	1994	84	1.5	48.2	99.6	1.8
01434017	E. B. Neversink, NR Claryville, NY	1991	2006	110	1.4	59.3	95.0	3.1
01434021	W. B. Neversink, NR Frost Valley, NY	1986	2006	497	2.1	2.0	172.1	5.7
01434022 65	W. B. Neversink, at B. NR Frost Valley, NY	1991	1993	69	0.9	20.4	94.6	1.9
01434025	Biscuit Brook, Frost Valley, NY	1983	2006	1043	1.9	9.6	97.5	2.5
01434105	High Falls Brook, Frost Valley, NY	1983	1999	127	2.1	7.1	85.5	1.1
01434176	W. B. Neversink, NR Claryville, NY	1991	1995	64	0.9	65.5	82.2	1.7
01434498	W. B. Neversink, at Claryville, NY	1991	2006	95	1.2	87.5	95.6	2.4
01435000	Neversink River, NR Claryville, NY	1986	2006	310	1.9	172.4	97.0	2.1
01545600	Young Womans Cr., NR Renovo, PA	1981	2007	81	2.3	119.6	57.1	1.2
01559795	Bobs Cr., NR Pavia, PA	1993	1997	18	3.6	43.0	72.7	0.8
01571827	Swatara Cr., below Ravine, PA	1985	1986	20	1.3	119.9	50.6	0.5
01610400	Waites Run, NR Warden., WV	2001	2004	28	1.4	32.6	n.d	n.d.
03015795	East Hickory Cr., NR Queen, PA	1996	1998	27	2.1	52.6	73.0	1.4
03039925	North Fork Bens Cr., at North Fork Reservoir, PA	1983	1993	110	1.1	8.9	76.6	0.8
03039930	S. Fork Bens Cr., NR Thomasdale, PA	1983	1985	26	1.2	8.5	91.0	1.3
03201600	Big 4 Hollow Cr., NR Lake Hope OH	1978	1981	56	2.7	2.5	123.1	4.9
03201660	Big 4 Hollow Cr., bl E. F. nr. Lake Hope, OH	1979	1983	35	3.2	1.9	141.6	4.4
03201700	Big Four Hollow Cr. nr. Lake Hope OH	1978	1979	62	3.2	2.6	125.1	3.0
03207965	Grapevine Cr., NR Phyllis, KY	1976	1989	22	4.3	16.1	66.7	2.3
03282100	Furnace Fork, NR Crystal, KY	1987	2008	21	2.8	25.7	64.7	2.6
Average		1988	1997	131	2.2	55.8	94.0	2.4

Annual flow is the average annual flow from the gauging stations and DOC flux is average annual output from LOADrunner

$$Q = Q_q + Q_b \quad (1)$$

where Q is measured total stream discharge (cm day^{-1}), Q_q is quickflow, which is the ephemeral component of stream discharge that begins shortly after the onset of precipitation or snowmelt, and Q_b is baseflow, which is the comparatively steady component of stream discharge that continues well after the cessation of a hydrologic event. We used the local minimum HYSEP method (Sloto and Crouse 1996) to separate the stream-discharge hydrographs and to compute Q_q and Q_b from time-series measurements of Q. We identified

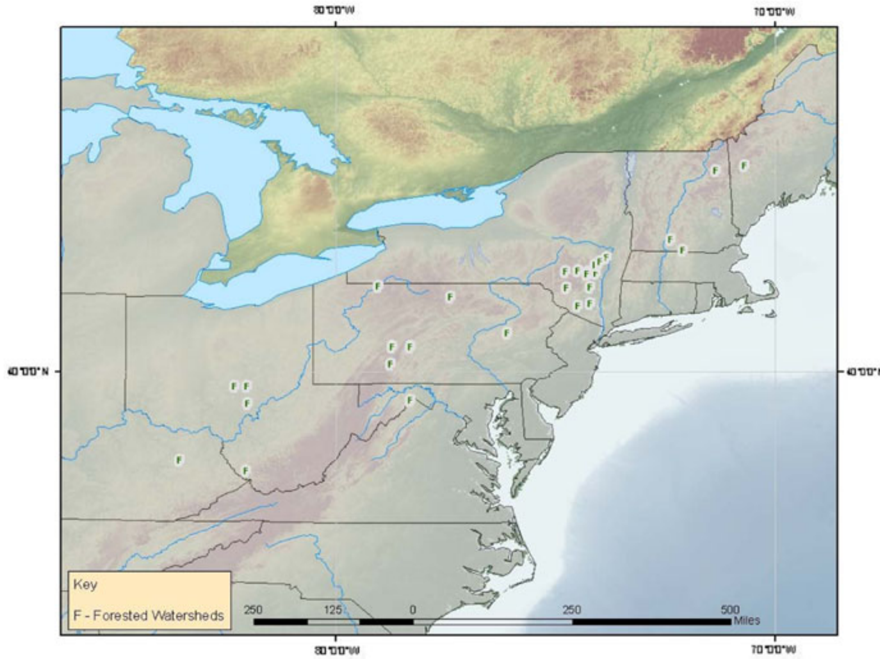

Fig. 1 Locations of 30 watersheds used in our analyses of DOC export

hydrologic events as those days for which $Q > Q_b$ and non-events as days for which $Q = Q_b$. The events were further separated into rising-hydrograph days, designated as those event days associated with the ascending limb and peak of a rising hydrograph, and falling-hydrograph days, designated as those event days on the descending limb of the hydrograph.

The data on DOC concentration from all 30 study sites were combined and regrouped according to their occurrence during non-events, rising-hydrograph events, and falling-hydrograph events. Each group of DOC measurements was then binned by stream discharge (Q). The highest-Q bin contained measurements of DOC concentration made under conditions in which $Q > Q_L^1 = 5$ cm day^{-1}, where Q_L^1 is the value of stream discharge associated with the lower bound of discharge bin 1. The upper and lower bounds for the remaining discharge bins were computed by

$$Q_L^i = \frac{Q_L^{i-1}}{2} + 0.1\, Q_L^{i-1} \quad \text{for} \quad i = 1 \text{ to } N_b \tag{2a}$$

and

$$Q_U^i = Q_L^{i-1} \quad \text{for} \quad i = 1 \text{ to } N_b \tag{2b}$$

where the superscript i denotes the bin number, N_b is the total number of bins, and the subscripts L and U refer to a bin's lower and upper discharge bounds, respectively.

Discharge-concentration relationships are often described using power-law equations (Vogel et al. 2003; Wheatcroft et al. 2010). We tested the assumption that the bin-averaged measurements of DOC concentration could be described as power-law functions of stream discharge, such that

$$\overline{C}^i = \alpha\left(\overline{Q^i}\right)^n + \beta \tag{3}$$

where $\overline{C}^i$ is the bin-averaged DOC concentration and $\overline{Q}^i$ is a mean discharge computed by averaging daily discharges within the ith bin for those days in which measurements of DOC concentration were made. The parameters α, n, β quantify the relationship between $\overline{C}$ and $\overline{Q}$. Separate sets of these regression parameters were estimated for non-events, rising-hydrograph days, and falling-hydrograph days.

We estimated the annual export of water associated with the ith discharge bin, Q_A^i (cm year^{-1}), by

$$Q_A^i = 365\overline{\overline{Q^i}}f^i \tag{4}$$

where $\overline{\overline{Q^i}}$ is the grand-average daily discharge for the ith bin (cm day^{-1}) and f^i is the fraction of days in which $Q_L^i < Q \leq Q_U^i$. Whereas $\overline{Q}$ in Eq. 3 was computed with daily discharges from the subset of days in which DOC measurements were available, $\overline{\overline{Q}}$ in Eq. 4 was calculated from complete records of daily discharge. In particular, estimates of $\overline{\overline{Q}}$ were calculated from 171 annually complete records of daily discharge collected from the study watersheds at times that overlapped the periods of DOC measurement.

The annual export (flux) of DOC associated with the ith discharge bin, F^i (g m^{-2} year^{-1}), was computed on the basis of stream discharge and relationships between stream discharge and DOC concentration:

$$F^i = \frac{365\overline{\overline{Q^i}} f^i \overline{\overline{C^i}}}{100} \quad (5)$$

where $\overline{\overline{C^i}}$ is an average daily stream-water DOC concentration (mg l^{-1}) computed by using the $\overline{\overline{Q}}^i$ in power-law functions (i.e., Eq. 3) parameterized from the regressions of $\overline{C}$ versus $\overline{Q}$.

In addition to exploring an average export behavior with Eqs. 3–5, we examined how the relationship between annual fluxes of water and DOC varied among the study watersheds using more conventional means. In particular, DOC export from each watershed was calculated with Loadrunner, a pre- and post-processing program developed at Yale that links to the LOADest computer program written by the USGS (Runkel et al. 2004). The equation that governs Loadrunner is

$$F_{LR} = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi t) + a_4 \cos(2\pi t) \quad (6)$$

where F_{LR} is the Loadrunner computed stream-water flux of DOC (g m^{-2} day^{-1}), t is time centered Julian days, and a_0, a_1, a_2, and a_3, and a_4 are constants. The constants were estimated through non-linear regression by using the available measurements of DOC flux and corresponding measurements of stream discharge (Q) as the response and predictor variables, respectively. Once the constants were estimated through regression, F_{LR} was computed with (6) for those days in which DOC measurements were unavailable, and the total annual DOC flux (F_A) for each watershed was computed through summation of the daily F_{LR}.

Results

Concentrations

The arithmetic and flow-weighted average concentrations of DOC equaled 2.1 and 1.8 mg l^{-1}, respectively. These low concentrations reflect, in part, the small percentage of wetland coverage within the forested watersheds selected for this study.

Concentrations of DOC tend to increase with stream discharge (Fig. 2), and the relationships between bin-averaged DOC concentration and the corresponding average stream discharge for non-event days,

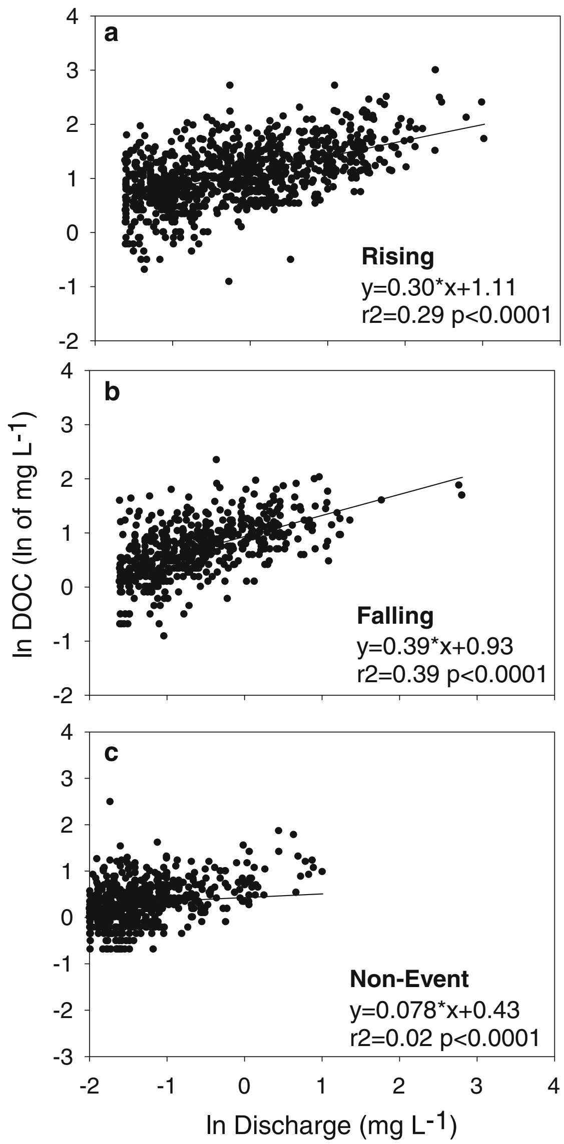

Fig. 2 Relationships between the natural logarithm of stream discharge and the natural logarithm of stream-water DOC concentration for rising, falling, and non-event periods of the hydrograph. Only data from hydrologic events with discharges greater than 0.2 cm day^{-1} were used in the top two linear regressions. The standard errors for the slope and y intercept of the rising hydrograph data are 0.0155 and 0.0157, respectively, and 0.0235 and 0.0247 for the falling hydrograph

rising-hydrograph days, and falling-hydrograph days could be expressed with power-law equations (Fig. 3), such that

$$\text{Rising-hydrograph days}: \overline{C} = 1.83 + 1.40\overline{Q}^{0.60}; \quad r^2 = 0.99,\ P < 0.0001 \tag{7}$$

$$\text{Falling-hydrograph days}: \overline{C} = 0.84 + 1.84\overline{Q}^{0.41}; \quad r^2 = 0.93, P = 0.0024 \tag{8}$$

$$\text{Non-event days}: \overline{C} = 1.24 + 1.00\overline{Q}^{0.89}; \quad r^2 = 0.99, P = 0.0009 \tag{9}$$

Comparison of these expressions reveals that the relationship between DOC concentration and discharge differs between rising hydrograph days and falling hydrograph days. That is, DOC concentrations associated with the rising hydrograph are greater than those measured at equal discharges on the falling hydrograph (Fig. 3). Calculations based on (7)–(9) demonstrate that falling-hydrograph DOC concentrations are 76% of rising-hydrograph concentrations at low discharge (i.e., $Q = 0.2$ cm day^{-1}) and 81% of rising-hydrograph concentrations at moderate discharge ($Q = 0.6$ cm day^{-1}). Similar percent differences of DOC concentrations between rising and falling periods of the hydrograph are found when applying the regression results from the raw (unbinned) data (Fig. 2). We note that there is a slight increase in DOC concentrations at very low flows (i.e., $Q < 0.05$ cm day^{-1}) on the falling hydrograph and during nonevents (Fig. 3), presumably due to autotrophic in-stream production.

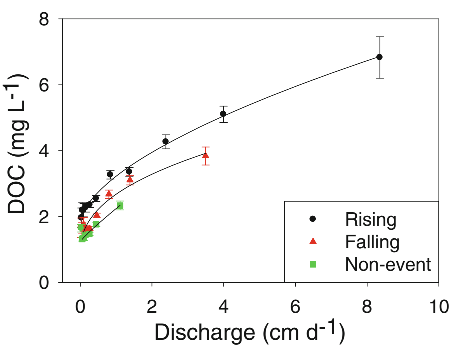

Fig. 3 Relationship between stream discharge and stream-water DOC concentrations for forested watersheds of the eastern United States. DOC concentrations are bin-averaged by stream discharge (see "Methods"). The *error bars* are standard errors

Fluxes

Application of Eq. 4 yielded a total average annual water flux $\left(= \sum_{i=1}^{N_b} Q_A^i\right)$ of 103 cm year^{-1}. Non-event days occurred 53% of the time and were characterized by daily stream discharges that ranged from 0 to 2.7 cm day^{-1} and averaged 0.18 cm day^{-1}. Although non-event days occurred more frequently than the sum of the rising-hydrograph and falling-hydrograph days (Fig. 4a), event days accounted for 74% of the annual water export (Fig. 4b; Table 2). The average daily discharge associated with rising-hydrograph days equaled 1.1 cm day^{-1} and exceeded the average discharge of the falling-hydrograph and non-event days by 0.53 and 0.92 cm day^{-1}, respectively.

The total annual DOC flux $\left(= \sum_{i=1}^{N_b} F^i\right)$ equaled 3.05 g DOC m^{-2} year^{-1}. Only 14% of annual DOC export occurred during the low-flow non-events periods (Fig. 4c), which contributed 26% of the annual stream discharge. The remaining 86% of the annual DOC flux occurs in association with either the rising or falling stream-water hydrograph (Fig. 4c; Table 2). Because DOC concentration increases with stream discharge (see Eqs. 7–9), larger discharge events, which occur infrequently, contribute disproportionately to the annual DOC flux (Fig. 4c). For example, events with discharges greater than 1.38 cm day^{-1} comprise only 4.8% of the annual hydrograph, but are responsible for 57% of annual DOC flux.

Results of the LOADrunner analysis, which involved evaluation of 171 annual records of stream discharge and DOC concentration from the study watersheds, revealed that annual DOC flux ranged from 0.3 to 9.2 g m^{-2} year^{-1} while annual stream discharge varied from 29 to 223 cm year^{-1} (Fig. 5). The annual fluxes of DOC increased in a nonlinear fashion with annual stream discharge, and 67% of the variation in this relationship could be described by a second-order polynomial function (Fig. 5):

$$F_A = 0.00010 Q_A^2 + 0.018 Q_A - 0.27 \tag{10}$$

where F_A is the annual DOC flux (g m^{-2} year^{-1}) and Q_A is the annual stream-water discharge (cm year^{-1}).

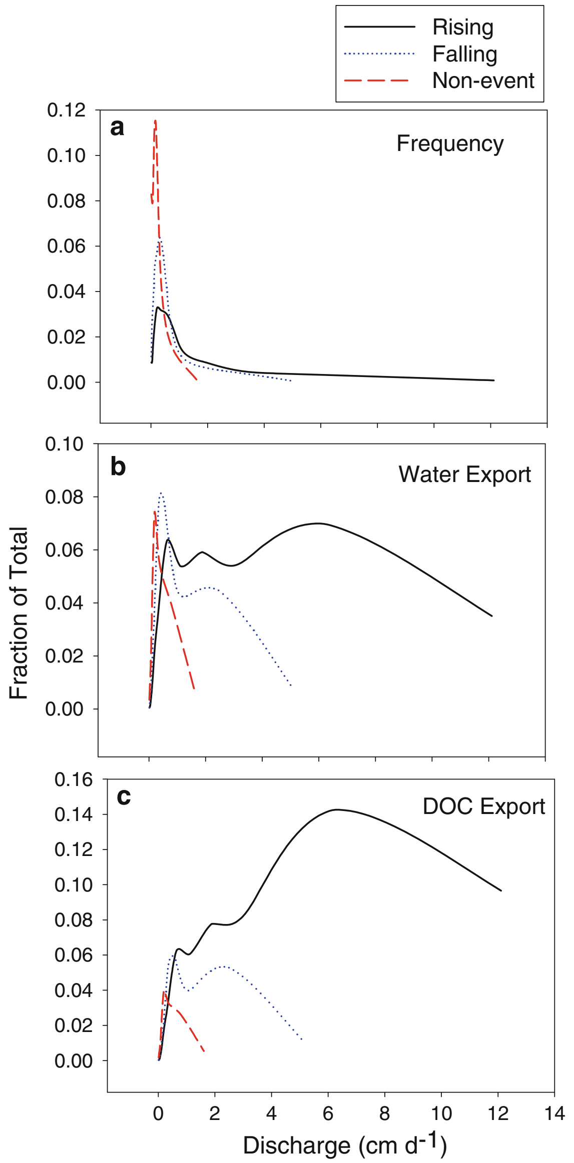

Fig. 4 Frequency of stream-discharge measurements (**a**), fraction of annual stream-water export (**b**), and fraction of DOC export (**c**) as a function of stream discharge

Table 2 Percentage of the number of days in a year, water flux and DOC flux exported during different stages of the hydrograph

	Frequency	% water flux	% DOC flux
Rising	18	42	60
Falling	29	32	26
Non-event	53	26	14

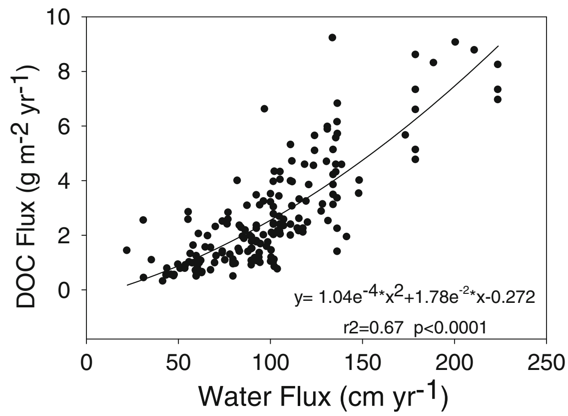

Fig. 5 The relationship between annual stream-water water flux and DOC flux computed through the application of Loadrunner

Substitution of the average annual discharge ($Q_A = 103$ cm year^{-1}) into (10) yields a corresponding annual DOC flux of 2.6 g m^{-2} year^{-1}, which is in reasonably close agreement with the calculation made on the basis of Eq. 5 (i.e., $\sum_{i=1}^{N_b} F^i = 3.05\,\mathrm{g\,m^{-2}}$ year^{-1}).

Discussion

Our results show stream-water DOC concentrations increase with stream discharge (Fig. 2), and bin averaging shows a power-law relationship between discharge and concentration (Fig. 3). The lower DOC concentrations during the falling hydrograph indicate that the DOC storm response is hysteretic (Butturini et al. 2006) and may, for example, reflect temporary depletion of the terrestrial DOC supply due to soil-water flushing (Hornberger et al. 1994; Boyer et al. 2000) or, perhaps, changes in the timing of runoff contributions from the riparian zone and hill slope during the course of a rainfall event (Hinton et al. 1998; McGlynn and McDonnell 2003). DOC that appears in small streams during hydrologic events is derived primarily from allochthonous terrestrial sources (Royer and David 2005). The percentage of DOC exported during events from the forested watershed studied here was 86%, which can thus be viewed as a conservative estimate of the allochthonous/terrestrial contribution to stream DOC export from small (<100 km^2) forested watersheds without wetlands.

Although the importance of hydrologic events to DOC flux has been demonstrated before (Ciaio and McDiffett 1990; Denning et al. 1991; Murdoch and Stoddard 1993; Brown et al. 1997; Hinton et al. 1998; Volk et al. 2002; Even et al. 2004; Wellington and Driscoll 2004; Inamdar et al. 2006; Saunders et al. 2006), this study shows that events dominate DOC flux from forested end-member watersheds on a regional scale. Calculations based on Eq. 5 indicate that 86% of DOC is exported during events (rising and falling hydrograph), with 60% of this being exported during the rising hydrograph. Loadrunner predicts that 76% of DOC is exported during the rising and falling hydrograph (data not shown). The discrepancy (~10%) in the percent predicted to be exported during events arises because Loadrunner does not separate DOC export by the period of the hydrograph, which causes the model to provide low values of DOC during events and high values during non-events. For this study, Loadrunner provided DOC concentrations during events that were on average 0.18 mg l^{-1} lower than the actual measurements, and a non-event concentrations that were on average 0.03 mg l^{-1} too high (data not shown). Studies that do not attempt to sample the rising hydrograph and account for differences between the periods of the hydrograph will also introduce some error to their flux measurements and thus future studies should take care to target hydrologic events for sampling DOC, particularly the rising hydrograph. The importance of events and event-based sampling will be amplified if forecasts that predict an increase in the frequency of extreme precipitation events prove reliable (Palmer and Ralsanen 2002).

Despite combining data from multiple sites, a broad relationship exists between stream discharge and DOC concentrations for the rising and falling periods of the hydrograph (Figs. 2, 3). With respect to the event fluxes, it has been noted that antecedent soil moisture can be important to DOC levels in soil solution and streams (Schiff et al. 1998; Wilson and Xenopoulos 2008; van Verseveld et al. 2009). Although we do not have event-by-event data on soil moisture, we did find that accounting for antecedent discharge (as an index of pre-event watershed wetness) improves our ability to predict event-based DOC concentrations. In particular, the residuals of the linear relationship (converted to concentration) between the ln(Q) and ln(C) (Fig. 2a)

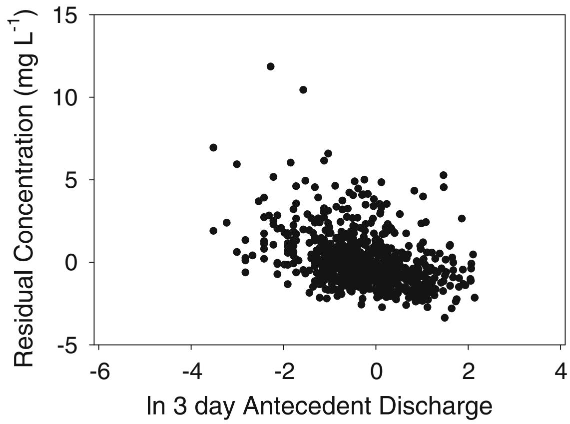

Fig. 6 The concentration residuals of Fig. 2a in as a function of $Q_{3\text{-day}}$, the sum of stream discharge for the 3 days prior to the day of DOC sampling

vary inversely with the sum of the preceding 1, 3, 7, and 12 days discharge, with r^2 values of 0.106, 0.123, 0.100, and 0.0703, respectively (Fig. 6). Thus, events that occur after drier conditions (characterized by lower antecedent discharge) correlate with higher stream-water DOC concentrations due to greater accumulation of flushable soil-water DOC or DOC precursors between events. The relationship between antecedent discharge and DOC concentrations could also be due to changes in hydrologic flow paths as different landscape units are linked to the stream during flow events (e.g., Ocampo et al. 2006).

There is also a relationship between stream water temperature and DOC concentration for the rising- and falling-hydrograph periods (Fig. 7). At higher water temperatures the concentrations of DOC during the rising and falling hydrograph are greater (Fig. 7). Similarly to a recent study conducted within a Vermont watershed (Sebestyen et al. 2009), we could have expressed this as a seasonal relationship. Researchers have also found a relationship between 60 day antecedent air temperature and DOC concentration for a watershed in Norway (Futter and de Wit 2006), and the number of growing degree days and DOC export from watersheds in Canada (Creed et al. 2008). A multiple linear regression that uses daily water temperature (T), daily discharge (Q), and 3-day antecedent discharged ($Q_{3\text{-day}}$) as the predictor variables yields the following relationships for our study watersheds:

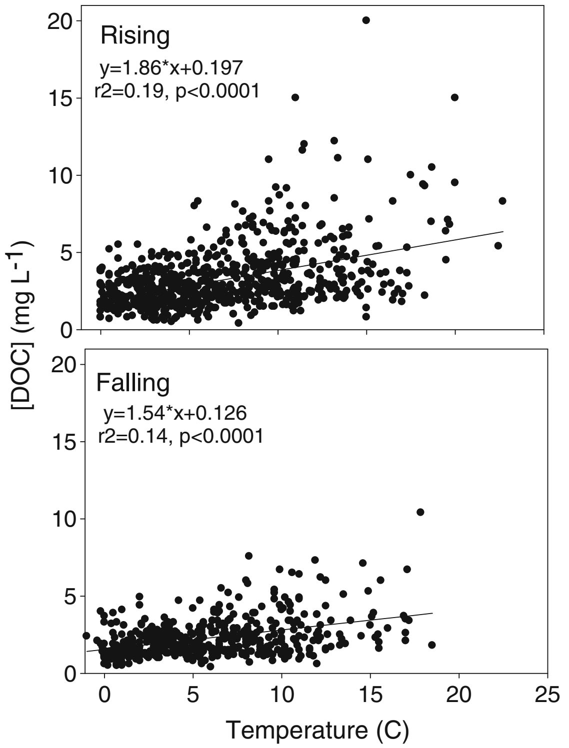

Fig. 7 The relationship between DOC concentrations associated with the rising and falling hydrograph and temperature. No relationship was found for the non-event data. Similarly to Fig. 2, only events with discharge greater than 0.2 cm day^{-1} are used in the regressions

Rising hydrograph:

$$C = 1.48 \ln(Q) - 0.64 \ln(Q_{3-\text{day}}) + 0.17T + 2.17; \quad r^2 = 0.59 \tag{8}$$

$$F = 1.40 \ln(Q) - 0.14 \ln(Q_{3-\text{day}}) + 0.05T - 3.88; \quad r^2 = 0.92 \tag{9}$$

Falling hydrograph:

$$C = 1.16 \ln(Q) - 0.27 \ln(Q_{3-\text{day}}) + 0.11T + 2.17; \quad r^2 = 0.45 \tag{10}$$

$$F = 1.40 \ln(Q) - 0.016 \ln(Q_{3-\text{day}}) + 0.04T - 3.90; \quad r^2 = 0.88 \tag{11}$$

where C is daily DOC concentration in mg l^{-1} and F is the daily DOC flux in g m^{-2} day^{-1}. According to Eq. 9, a one degree increase in water temperature during an event will increase DOC fluxes by 5.5%. Despite grouping a large number of watersheds across a range of latitude and longitude, an r^2 of 0.92 for event fluxes approximates r^2 values for multiple regressions of DOC export from the Sleepers watershed in Vermont (Sebestyen et al. 2009, $r^2 = 0.91$) and a study of 33 catchments in Canada ($r^2 = 0.89$), where the percentage of wetlands coverage the explained variance (Creed et al. 2008). Thus, although it "is impossible to predict the entire pattern of solutes during storms with satisfactory precision" in even a single watershed (Butturini et al. 2008), it appears that the response of DOC export to hydrologic events across a range of forest types and climate is controlled by similar processes.

Many of the processes that govern DOC production, transport, and export from watersheds are sensitive to temperature and watershed wetness. For instance, seasonal and weekly rates of primary production (Aber et al. 1995; Kindermann et al. 1995) and potentially root exudation are affected by temperature and rainfall. The production of leaf litter is controlled, in part, by these seasonal rates of primary production (Bray and Gorham 1964). Soil respiration responds to precipitation events (Lee et al. 2004), and dissolution of leaf litter and soil organic matter and desorption of adsorbed DOC are regulated by temperature and soil-moisture levels (Christ and David 1996). Our findings provide further evidence that temperature and watershed wetness (as qualified by antecedent stream discharge) influence DOC export on event time scales (hours) and highlight the importance of increasing our understanding of how interactions between temperature and wetness affect the biogeochemical processes that govern DOC fluxes through forested watersheds.

Temperature and antecedent discharge can impact DOC export through both short-term processes (e.g., dissolution, desorption, and microbial activity) and long-term processes (e.g., primary production, leaf-litter accumulation, and soil OM pools). Our results suggest that event based DOC export increases with temperature, presumably because rates of processes important at short time scales, such as desorption, dissolution, and decomposition, increase with temperature. Increased temperature, however, also increases evapotranspiration and decreases water storage in soils, and on time scales of days to weeks can dry soils causing a decrease in discharge and DOC export (Raymond and Oh 2007). Thus, although this study illuminates a dependence of DOC export on watershed wetness and temperature that applies for event time scales, climatic feedbacks that occur at longer time scales will likely introduce additional complexity to descriptions of DOC export.

The general conclusion that the DOC-export response to climate change will depend on interactions between multiple processes that operate on different time scales is supported by two recent studies. Sebestyen et al. (2009) focused on hydrologic controls of DOC export from a forested watershed in Vermont and predicted that changes in precipitation patterns associated with projected climate change would lead to an increase in DOC export. A second study, which emphasized processes that control DOC pool size and involved application of a terrestrial ecosystem model to a watershed in nearby New Hampshire, concluded that decreases in litterfall and soil OC mineralization would lead to lower DOC export under future climate (Campbell et al. 2009). Despite different conclusions, both of these studies are valuable in elucidating mechanisms that could dictate how forested watersheds will respond to future climate scenarios. Additional attention should be devoted to understanding how coupled hydrological and biochemical processes that occur across different temporal scales regulate DOC concentrations and fluxes. The newly developed INCA-C model takes step in this direction through coupling of a hydrologic model with a process-based ecosystem model (Futter et al. 2007). Currently, this model predicts annual DOC concentrations well and is suited for studying long-term trends in DOC concentration, yet it currently underestimates DOC concentrations during events (Futter et al. 2009a, b) due to a lack of understanding of the mechanisms that control DOC production and consumption in soils (Futter et al. 2007), particularly at event scales.

We can extend our analysis to explore the potential for feedbacks between ecosystem processes and DOC fluxes that operate on different time scales. One can see the seasonal influences of ecosystem processes on DOC flux when this flux is normalized to discharge across the calendar year (Fig. 8). The flux of DOC normalized to discharge roughly tracks the seasonal trend in stream temperature (Fig. 8). The fluxes in the fall, however, are higher at the same temperature

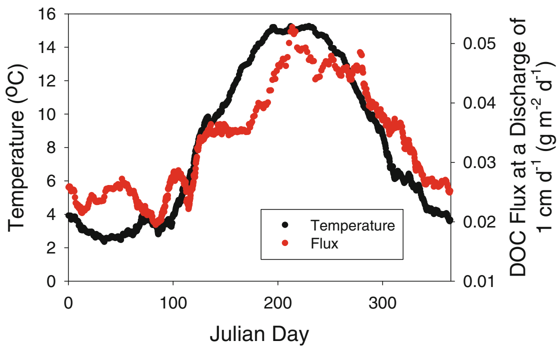

Fig. 8 Seasonal variation of temperature (*black circles*) and DOC flux normalized to a flow of 1 cm day^{-1} (*red circles*). This graph was created by sorting the rising hydrograph data by year day (the same data used in Fig. 7), determining the *y*-intercept and slow of flow versus flux step-wise for 40 data points, and plotting it against the average year day for the 40 data points. Data was wrapped to get an annual year-day cycle

compared to the spring (Fig. 8). One might attribute the general linkage to temperature to be driven by processes that occur on short, event-based temporal scales, which, in turn, are influenced by seasonal feedbacks to climate that increase the size and reactivity of OM pools, leading to a shift in the observed temperature/export relationship in the fall. Currently, there is insufficient knowledge of the controls and feedbacks between processes that operate on different time scales to predict with confidence how watershed DOC export will respond under future climatic scenarios.

Finally, new research demonstrates that the chemical composition of DOC changes during events with observations showing event DOC is more labile (Buffam et al. 2001), with a high aromaticity (Vidon et al. 2008), and from a different source (Dalzell et al. 2007) than non-event DOC. Thus, there is probably a much larger flux of labile DOC to streams and rivers than previously thought. Furthermore, because this labile material is coming out during events it is likely transported downstream to higher order systems before it is utilized. A critical area of future research is to further document how the composition of DOC shifts during events because the composition of DOC is as important as quantity in affecting the impact of DOC export on the biogeochemistry of forests and downstream ecosystems.

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