

Storm event patterns of particulate organic carbon (POC) for large storms and differences with dissolved organic carbon (DOC)

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Received: 5 November 2012 / Accepted: 19 August 2013 / Published online: 3 September 2013
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Abstract This study compared the storm event patterns, sources, and flow paths for particulate (POC) and dissolved organic carbon (DOC <0.45 μm) with a special focus on responses during large storm events. The study was conducted in a 12 ha forested catchment in the mid-Atlantic, Piedmont region of USA. A total of 14 storm events were sampled over a 16-month period (September 2010 to December 2011) including large, intense storms (precipitation >150 mm) associated with two hurricanes—Nicole (2010) and Irene (2011). Storm-event concentrations for suspended sediment (SS), POC and DOC varied between 10–7589, 0.05–252, and 0.7–18.3 mg L^{-1} , respectively. Within-event POC concentrations continued to increase for the large hurricane storms whereas DOC displayed a dilution at peak streamflow discharge. Flow-weighted mean POC concentrations decreased for closely spaced, successive storm events whereas no such decrease was observed for DOC. These results suggest that there are

important differences in the supply and transport (leaching rates and kinetics) for POC and DOC which occur at different temporal scales. The % POC content of SS was highest for the summer events. Summer events also registered a sharper increase in DOC with stream discharge and then a decline for peak flow, suggesting critical seasonal controls on storm-event POC and DOC responses. End-member mixing analysis revealed POC is transported with surface runoff while DOC is transported by saturation overland flow and rising groundwater into the soil horizons. A mixing model for sediment sources failed to identify key end-members but event mixing patterns revealed near-stream sources for small events and more distal, upland sediment sources for large and intense storms. This study highlights the need to better understand POC and DOC responses in headwater catchments especially for the large, intense, storm events that are predicted to increase in intensity with climate change.

Keywords Climate change · Organic carbon · Watersheds · Storm events · Runoff · Water quality

Responsible Editor: Eran Hood

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Introduction

Organic carbon, which can be transported in both dissolved (DOC) and particulate forms (POC) plays a key role in many ecological processes and has major implications for environmental and human health.

DOC influences the acid–base chemistry of acid sensitive freshwater systems (Herczeg et al. 1985), affects the complexation, solubility and mobility of trace metals such as iron, aluminum, zinc and mercury (Buffle 1984; Driscoll et al. 1988; Hope et al. 1994), and attenuates light penetration into aquatic ecosystems (Cory et al. 2007; Brooks et al. 2005). POC acts as a carrier for the transport of organic chemicals (Ni et al. 2008) and is believed to be responsible for the export of hydrophobic contaminants (Luo et al. 2009). Both POC and DOC regulate aquatic metabolism (Cole 2013) and can influence drinking water quality when C reacts with chlorine to form carcinogenic disinfection byproducts (DBPs, Chow et al. 2008; Hrudey 2009). At regional to global scales, organic carbon transported through streams and rivers is a globally significant carbon flux that has recently received considerable attention (Battin et al. 2008; Butman and Raymond 2011; Cole et al. 2007). Thus, understanding how POC and DOC amounts vary in runoff and the mechanisms and flow paths responsible is important.

Exports of organic carbon from catchments are strongly influenced by storm events, especially the large ones (Fellman et al. 2009; Hood et al. 2006; Inamdar et al. 2006, 2011; Raymond and Saiers 2010; Townsend-Small et al. 2008). Previous studies (Bass et al. 2011; Crisp and Robson 1979; Oeurng et al. 2011; Wiegner et al. 2009) have reported that storm events that constituted only 10–20 % of the total study period contributed to >80 % of POC and >70 % of DOC exports. While the concentrations and exports of both POC and DOC have typically been known to increase with storm events, the relative response of these constituents is not always similar (Dhillon and Inamdar 2013; Pawson et al. 2008; Wiegner et al. 2009). Wiegner et al. (2009) reported a twofold increase in concentration of DOC, but an 11-fold increase in the concentration POC during storms. This difference can be even greater for storms of exceptional intensity and magnitude. Jeong et al. (2012) working in a 38 ha headwater catchment in South Korea, showed that one extreme event that contained 20 % of the annual precipitation was responsible for 62 and 23 % of the annual POC and DOC load, respectively. Our recent work in the catchment used for this study showed that extremely large storms associated with Atlantic hurricanes (precipitation in excess of 100 mm) resulted in POC exports that were

6–8 times the DOC values (Dhillon and Inamdar 2013). Future climate-change predictions suggest that the intensity of storm events is likely to increase for the northeast USA with a greater potential for stronger hurricanes and tropical storms (Bender et al. 2010; Karl et al. 2009). Understanding how POC and DOC responses would respond and differ for such climate-driven extreme events is important for assessing impacts on ecosystem processes and services.

Studies have also revealed that there are subtle, but important distinctions between storm-event responses of POC and DOC (Alvarez-Cobelas et al. 2012; Kim et al. 2010). While there is variation among events, POC concentrations typically tend to peak earlier than DOC on the discharge hydrograph (Coynel et al. 2005; Jeong et al. 2012). In addition, rate of change (increase and decrease) for POC is much quicker than that for DOC (Oeurng et al. 2011; Johnson et al. 2006; Pawson et al. 2012). Alexandrov et al. (2003), Coynel et al. (2005), Pawson et al. (2008), and Rovira and Batalla (2006) have also reported a gradual reduction in POC concentrations for close, successive storm events while the same was not known for DOC. These discrepancies suggest important differences in POC and DOC with respect to sources, hydrologic flow-paths, and the leaching kinetics of these constituents. Investigating these differences and understanding the mechanisms responsible is important for developing realistic and reliable mechanistic models for C transport and fate in catchments.

The primary goal of this study was to investigate the runoff patterns and sources of POC during storm events, and simultaneously, investigate how and why POC responses differed from DOC for the largest storm events. This study builds on our recent work in a 12 ha forested catchment in the mid-Atlantic Piedmont where we have already characterized the hydrologic flow paths and developed a conceptual runoff model (Inamdar et al. 2013); identified the sources of DOC in the catchment (Inamdar et al. 2012); and characterized the temporal patterns and flow paths for DOC during storm events (2011). Thus, this background on runoff flow paths and DOC provided us a strong footing for comparing against POC results. We have also (Dhillon and Inamdar 2013) compared POC and DOC mass exports for a wide range in storm magnitude—from small to large events associated with remnants of hurricanes. This comparison indicated that while POC exports were comparable to

DOC for small to moderate events, the POC exports outpaced DOC and increased exponentially for the largest storm events (Dhillon and Inamdar 2013). Here, we further examine these storm events to investigate the reason for these disparate responses in POC and DOC. In addition, we assess the relationship between POC and suspended sediment (SS). The data set includes SS, POC and DOC concentrations in stream runoff (12 ha outlet) for 14 storm events sampled from September 2010 through December 2011. Precipitation during this study period was greater than previous years (2008–2010) and contained three large storms (precipitation in excess of 100 mm), two of which were associated with remnants of Hurricanes Nicole (2010) and Irene (2011). To identify the sources of sediment and POC for storms, soil and sediment sources were sampled spatially at multiple catchment locations and a mixing model framework was used to determine potential sediment end-members. Specific questions that we address are:

- How do the responses of POC and DOC compare for storm events of varying magnitude, intensity and timing (seasonal occurrence as well as sequential storm events)?
- How do the POC concentrations relate to SS concentrations?
- How do the within-event temporal patterns of POC and DOC compare?
- What are the sources of SS and POC in the catchment?

While previous studies have investigated POC patterns and sources, the work presented here is novel in that we focus on differences in POC and DOC for storms of varying magnitude, intensity and seasonal occurrence and explain these patterns using mixing models for runoff flow paths and sediment sources.

Site description and methods

Site description

The monitored catchment (12 ha) (Fig. 1) is part of an ongoing study on C (Inamdar et al. 2011, 2012, 2013) and is located within the Fair Hill Natural Resources Management Area (39°42'N, 75°50'W) in Cecil County, Maryland. It is part of the Big Elk Creek drainage basin and lies within the Piedmont

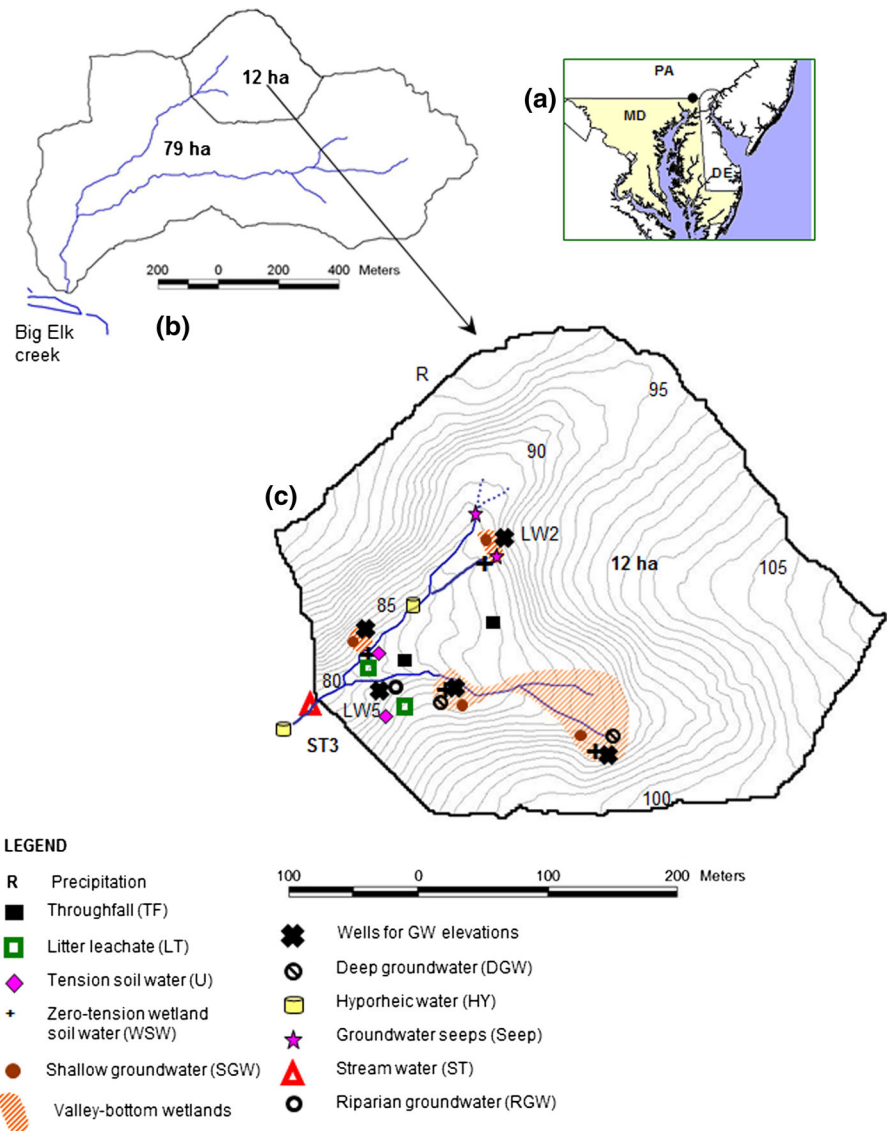
physiographic region and drains into the Chesapeake Bay. Cecil County has a humid, continental climate with well-defined seasons. The 30 year climate norm (1981–2010) for northeastern Maryland reveals a mean annual precipitation of 1,205 mm. Snowfall is ~450 mm and is concentrated in a few events with a quick melt of the snowpack. The highest mean monthly air temperature is 25.7 °C, occurring in July. The lowest mean monthly air temperature of –0.1 °C occurs in January (Maryland State Climatologist Office Data Page, <http://metosrv2.umd.edu/~climate/>, accessed June 21, 2013).

The study catchment is underlain by the Mt. Cuba Wissahickon formation and includes pelitic gneiss and schist with subordinate amphibolite and pegmatite. The soils belong to the Glenelg series which consists of deep, well-drained, soils on nearly level to moderately steep slopes. On hillslopes, soils are coarse loamy, mixed, mesic Lithic Dystrudepts while seasonal water saturation in the valley bottoms leads to the formation of Oxyaquic Dystrudepts. The catchment is covered with deciduous forest (61 % areal cover) with pasture along the edges. Dominant tree species are *Fagus grandifolia* (American beech), *Liriodendron tulipifera* (yellow poplar), and *Acer rubrum* (red maple) (Levia et al. 2010).

Hydrologic monitoring

Stream flow discharge was monitored at the outlet of the 12 ha catchment (ST3 in Fig. 1) using a 6-in. Parshall flume and the water flow depths were recorded every 15–20 min using a Global Water Instrumentation, Inc. logger and pressure transducer. Discharge was computed using measured water levels and standard flume equations. Depth to groundwater (from the soil surface) was available from two locations within the catchment—LW2 and LW5 (Fig. 1). Groundwater wells consisted of PVC pipes (5 cm diameter) extending ~2 m below the ground surface that were continuously slotted from a depth of 0.3 m below the soil surface. Water levels in these wells were recorded every 30 min using Global Water loggers. Precipitation and air temperature data were available at 5-min frequency from a Delaware Earth Observation System (DEOS) weather station located in the Fairhill NRMA, about 1,000 m from the outlet of the catchment (DEOS 2012).

Fig. 1 **a** Study location in Piedmont region of Maryland; **b** the 12 ha study catchment; and **c** instrumentation and sampling within the 12 ha study site



Runoff sampling and pre-processing

SS, POC and DOC data were available for 14 storm events collected over a 16 month period from September 2010 to December 2011 (Fig. 2). Baseflow sampling was performed once a month for stream water, however, since SS and POC concentrations were below detection for the initial set of samples, baseflow sampling was limited to DOC only. Storm event sampling for stream water was performed using an automated ISCO sampler installed at the outlet of the 12 ha catchment and triggered to sample when the rainfall amount exceeded 2.54 mm in a 1 h period (or

in some event manually triggered on the expected arrival of the storm). ISCO samples were collected in the “non-uniform time” program mode with a sampling frequency that ranged from as low as 15 min on the hydrograph rising limb to 3 h on the recession limb.

All stream water samples were collected in HDPE bottles and filtered through a 0.45 μm filter paper (Millipore, Inc.; Catalog #HAWP 04700) within 24 h of collection and stored at 4 °C. The weight of the particulate material was determined after drying the filters at 103–105 °C for 1 h and the weight of the sediment was divided by the sample volume to obtain

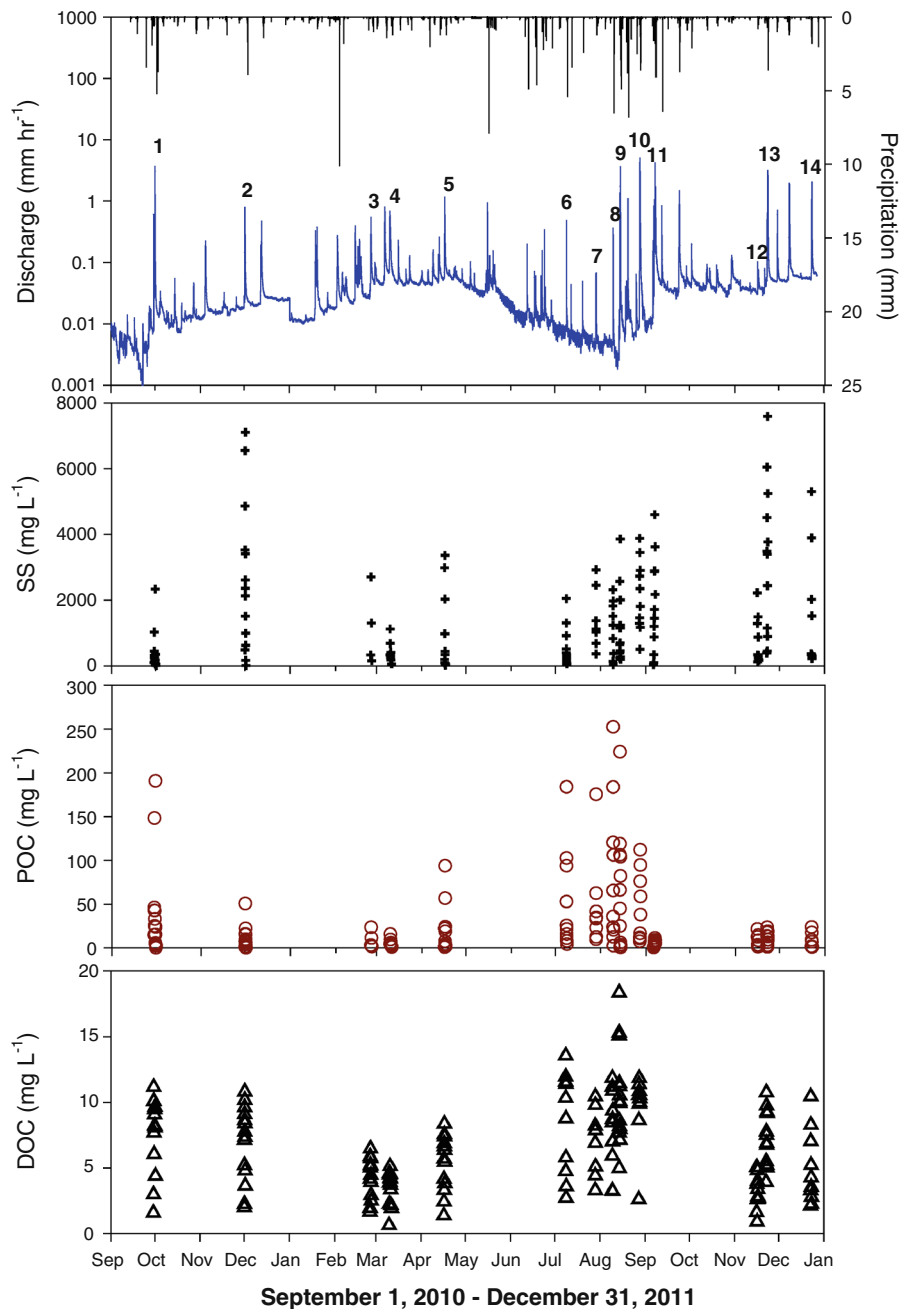
the concentration of SS in mg L^{-1} . The SS represented a size range of $0.45 \mu\text{m}$ to about 1 mm .

Chemical analyses of water and sediment samples

The dissolved ($<0.45 \mu\text{m}$) constituents were determined at the Biogeochemistry Laboratory at SUNY-

ESF, NY, which is a participant in the USGS QA/QC program (Inamdar and Mitchell 2007). The water samples were analyzed for: major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and silica (Si) using a Perkin-Elmer ICP-AEC Div 3300 instrument; and dissolved organic carbon (DOC) using the Tekmar–Dohrmann Phoenix 8000 TOC analyzer. The sediment collected on the

Fig. 2 Time-series plot for the study period (September 2010–December 2011) for precipitation (mm) and discharge (mm h^{-1}); SS (mg L^{-1}); POC and DOC concentrations (mg L^{-1}) for the sampled events. The numbers for the 14 sampled storm events are indicated in the figure



filters was analyzed at the University of Delaware (UD) soil testing laboratory. Total organic carbon (TOC) in the samples was determined using the Elemental TC and TN analyzer—Elementar VarioMax following Dumas method and reported as % C content of the sediments. The % C content (hereafter % POC) was multiplied with the concentration of SS (mg L^{-1}) to determine the concentration of particulate organic carbon (POC) in runoff (mg L^{-1}). Where sufficient sediment was available (e.g., the large events) the sediment was scraped off the filter and combusted. For samples where the sediment amount was small and could not be scraped, the filter along with the sediment was combusted. The % C content for these samples was corrected by subtracting the mean of % C content of blank filters. This procedure was replicated to check for consistent results. Major cations and trace elements (Mn, Al, Cu, Zn) in the sediment were determined by microwave digestion of sediment samples followed by analysis through inductively coupled plasma mass spectrometry (ICP-MS).

Storm event attributes and catchment hydrologic conditions

The start of a storm event was defined with the rise in streamflow discharge following precipitation. The end of the event was defined when the streamflow discharge returned to within 10 % of the pre-event values. Catchment hydrologic conditions during and prior to the storm events were characterized using a number of metrics (Table 1): total amount of precipitation for the storm event (mm), maximum 5-min rainfall intensity (mm), total specific discharge for the event (mm per unit catchment area), peak specific discharge (mm h^{-1}), and ratio of total specific discharge to total precipitation for the event (runoff ratio). Antecedent soil moisture conditions prior to the storm events were characterized with: (a) 7-day sum of precipitation (API7, mm); (b) 24-h average of stream runoff (AR24, mm); and (c) 7-day average of groundwater depths (m, groundwater index) for wells LW2 and LW5.

Flow-weighted means and correlation analyses

The flow-weighted mean concentration (C_m) for SS, POC and DOC for individual storm events was calculated using the formula :

$$C_m = \frac{\sum_{i=1}^{i=n} C_i \cdot Q_i}{\sum_{i=1}^{i=n} Q_i}$$

where C_i was the measured concentration of SS, POC or DOC and Q_i was the corresponding discharge value at time i during the storm event. To investigate how SS, POC and DOC concentrations varied with storm event attributes and catchment antecedent moisture conditions (Table 1), a Pearson correlation analysis was performed between flow-weighted mean event concentrations of SS, POC and DOC and the hydrologic metrics.

End-member mixing model analysis (EMMA) and storm-event DOC patterns

EMMA for hydrologic flow paths and runoff sources has already been implemented for the study catchment (Inamdar et al. 2011, 2013). The potential runoff sources were—rainfall, throughfall, litter leachate, tension soil water, wetland soil water, shallow groundwater, riparian groundwater and deep groundwater (sampling locations in Fig. 1 here and Fig. 5 in Inamdar et al. 2013). EMMA was performed following the procedures of Hooper (2003) and Inamdar (2011). Selected tracers included Na^+ , Ca^{2+} , Al, Si, and DOC. EMMA space was defined by streamflow chemistry and individual watershed runoff sources (mean concentrations) were projected in this space to determine which runoff end-member influenced runoff chemistry.

As described previously in Inamdar et al. (2013), surficial and groundwater end-members were clearly differentiated in EMMA space with the surficial sources (rainfall, throughfall, and litter leachate) on the right-hand side of the mixing space and the soil water and groundwater sources being clustered together on the left-hand side (Fig. 5 in Inamdar et al. 2013). While there were differences among individual events, overall, all storm events displayed a consistent temporal pattern in runoff source or end-member sequencing (Fig. 8 in Inamdar et al. 2013). Stream water was composed of groundwater sources (e.g., seeps) at the start of event; contributions from throughfall and litter leachate composed the rising limb of the discharge hydrograph, and soil water and shallow groundwater sources contributed to the recession limb of the hydrograph. Using the procedures of Inamdar et al. (2013) temporal patterns for

Table 1 Hydrologic attributes of the 14 sampled storm events during for the study period September 2010 through December 2011

Event no.	Date	Season	Duration (h)	Precipitation			Streamflow discharge				7-day GW depth ^a	
				Amount (mm)	Intensity (mm)	API7 (mm)	Amount (mm)	Peak (mm h ⁻¹)	RR	AR24 (mm)	LW2 (m)	LW5 (m)
High POC concentration events ^a												
1	9/30/2010 ^b	Su	61:15	151	5.2	20.3	13.5	3.7	0.09	0.2	0.3	0.8
8	8/9/2011	Su	14:30	21	6.5	7.2	0.5	0.4	0.02	0.6	0.2	0.7
9	8/14/2011	Su	30:45	104	4.9	31.3	9.3	3.6	0.09	0.1	0.2	0.7
10	8/27/2011 ^c	Su	59:00	155	3.6	20.5	32.7	5.0	0.21	22.3	0.2	0.6
Medium POC concentration events ^a												
5	4/16/2011	Sp	30:00	37.7	1.2	23.7	7.1	1.2	0.19	1.3	0.1	0.4
6	7/8/2011	Su	19:45	23.4	5.4	3.7	0.8	0.5	0.03	0.2	0.1	0.7
7	7/28/2011	Su	7:00	11.0	1.2	0.7	0.1	0.1	0.01	0.1	0.2	0.7
Low POC concentration events ^a												
2	12/1/2010	W	56:30	34.7	3.9	4.8	3.8	0.8	0.11	0.4	0.3	0.5
3	2/25/2011	W	62:16	21.2	1.0	10.1	6.3	0.5	0.30	0.7	0.1	N/A
4	3/10/2011	Sp	48:30	45.9	1.2	45.4	11.1	0.7	0.24	1.7	0.1	N/A
11	9/6/2011 ^d	Su	44:00	102	4.1	0.9	16.5	4.2	0.16	0.3	0.2	0.4
12	11/16/2011	F	40:15	17.1	0.8	2.6	2.0	0.1	0.12	1.6	0.0	0.5
13	11/22/2011	F	84:15	52.8	3.6	26.1	16.1	3.2	0.31	1.1	0.0	0.5
14	12/23/2011	W	48:00	35.0	1.8	1.6	9.5	2.0	0.27	1.3	0.0	0.4

Seasons: *Su* summer (June–September), *F* autumn (October–November), *W* winter (December–February), *Sp* spring (March–May)

^a The storm events have been grouped based on their flow-weighted mean POC concentration (POC_m) (High—POC_m >60 mg L⁻¹; Medium—POC_m 10–60 mg L⁻¹; Low—POC_m <10 mg L⁻¹); API7 is the sum of precipitation for 7 days preceding the event; AR24 is average antecedent stream discharge for 24 h; RR is the runoff ratio (ratio of discharge amount and total precipitation for event); 7-day GW depth is the average of groundwater depth for 7 days preceding the event at wells LW2 and LW5

^b Storm associated with remnants of hurricane Nicole

^c Storm associated with remnants of hurricane Irene

^d Storm associated with remnants of Tropical depression Lee

selected storms used in this study along with the runoff end-members are reported in EMMA space in Fig. 3.

The within-event temporal patterns for DOC were described in Inamdar et al. (2011). In general, storm-event DOC concentrations increased with the increase in discharge, peaked at or after the discharge peak, and receded slowly on the hydrograph recession limb. Primary sources of DOC in the catchment were identified as throughfall, litter leachate, and surficial soil water and were assumed to occur in that order.

Sediment sources and mixing model

Soil and sediment samples to characterize the potential sources of runoff sediment were sampled from multiple locations spatially distributed within the 12 ha

watershed during July 2010 (Dhillon 2012). Eleven different locations were sampled which accounted for four potential sediment sources—riparian wetlands (eight samples from two sites), upland soils (sixteen samples from four upland sites at varying elevations and distance from stream), stream bed (six samples from three sites in the stream bed) and stream bank (eight samples from two sites). At each sampling location, samples were collected from the A and B soil horizons and each sample had one replicate. Prior to the analysis, the samples were homogenized using pestle and mortar and sieved through a 2 mm sieve. Similar to SS, these soil samples were analyzed for the full suite of major cations and trace elements.

Using procedures similar to those for EMMA for hydrologic flow paths (Inamdar 2011), an EMMA

analyses was also performed to identify the sources or end-members for runoff sediment (or POC). Runoff sediment chemistry replaced stream water chemistry and watershed runoff sources were replaced with sediment and soil chemistry sampled at various locations in the catchment. Sediment tracers selected included—Al, Cu, Zn, Mn, Ca^{2+} , Mg^{2+} , Fe, and K^{+} based on linear mixing trends in bivariate plot analysis (Inamdar 2011). The sediment sources were then projected into the EMMA mixing space defined by the runoff sediment chemistry. Sources that enclose the runoff sediment indicate potential end members. The intent here was primarily to identify the potential sediment sources and not to determine the specific amounts or proportions of sediment contributed by these individual sources.

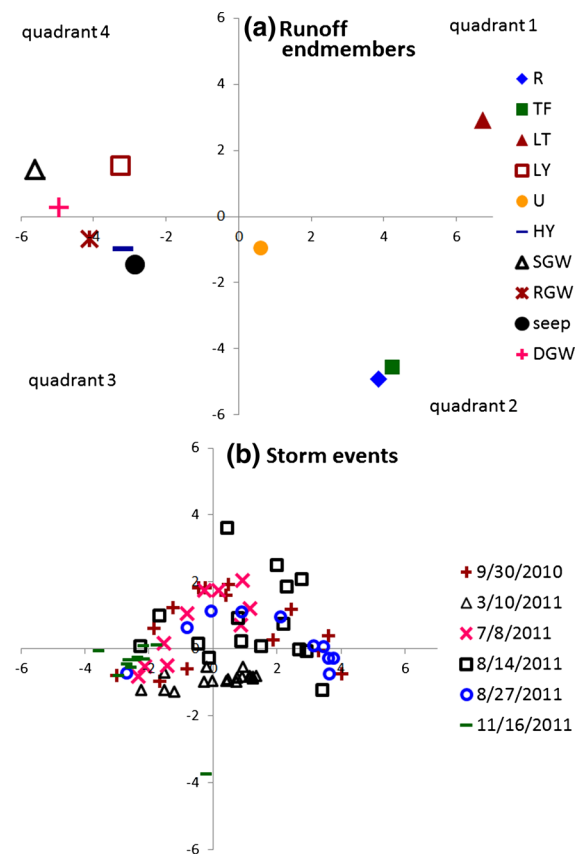


Fig. 3 Runoff end-members (a) and selected storm events (b) in EMMA space to determine the influence of runoff end-members on stream water chemistry. Runoff end-members include: *R* rainfall, *TF* throughfall, *LT* litter leachate, *LY* zero-tension soil water, *U* tension soil water, *HY* hyporheic water, *SGW* shallow groundwater, *RGW* riparian groundwater, *seep* hillslope seeps, and *DGW* deep groundwater

Results

Hydrologic attributes of sampled storm events

A total of 14 storm events were sampled over the study period of 16 months from September, 2010 to December, 2011 (Fig. 2; Table 1). The total precipitation for the 16-month study period was 1,842 mm. Of this, 1,462 mm of precipitation was observed in year 2011 (January through December). The annual precipitation for 2011 was higher than the previous years—2008 (1,052 mm), 2009 (1,238 mm) and 2010 (972 mm). Total stream discharge measured at the 12 ha outlet (ST3) for the 16 month study period was 497 mm, resulting in an annual runoff ratio of 0.27.

Of the 14 storm events, seven events were sampled in summer (June–September), two in autumn (October–November), three in winter (December–February) and two in spring (March–May). The maximum 5-min rainfall intensity for the events varied from 0.8 to 6.5 mm (Table 1). Peak streamflow discharge during storm events varied from 0.07 to 5.0 mm h^{-1} (Fig. 2). The largest amount of precipitation (155 mm) was recorded for the event of August 27, 2011 (event 10, Table 1), which was associated with remnants of hurricane Irene (NOAA, 2012) and had a precipitation return period of 25 years (Appendix C, Ward and Trimble 2004). This event also produced the highest peak discharge (5.0 mm h^{-1}) and highest total amount of streamflow discharge (32.7 mm) for the study period. Similarly, the event of September 30, 2010 (event 1) was associated with remnants of Hurricane Nicole (NOAA, 2012) and yielded a rainfall amount of 151 mm and had a precipitation return period of 25 years (Appendix C, Ward and Trimble 2004). In contrast, storm events of July 28, 2011 (event 7) and November 16, 2011 (event 12) produced the lowest discharge peaks. Event 7 (July 28, 2011) produced the lowest amount of streamflow runoff during the study period. Among all events, the summer events of September 30, 2010, August 9, 2011, August 14, 2011 and August 27, 2011 had the highest rainfall intensity (Table 1) while the events of February 25, 2011 and November 16, 2011 had the lowest rainfall intensity. The events of February 25, 2011, November 22, 2011 and December 23, 2011 had the highest runoff ratios while the summer events of July 8, 2011, July 28, 2011 and August 9, 2011 had the lowest runoff ratios.

Low values of API7 and AR24 and high values of 7-day GW depth (Table 1) indicated drier catchment conditions. Based on a combination of these indices, the catchment was at its driest preceding the event of September 30, 2010. Catchment conditions were also very dry during the summer events of July 28, 2011, August 9, 2011 and August 14, 2011. The catchment was at its wettest prior to the event of December 23, 2011 when water levels for well LW2 were at the soil surface (zero values in Table 1). Similarly, the catchment was also very wet during the events of November 16, 2011 and November 22, 2011. In general, soil moisture conditions were driest during later summer (August–September).

The events with the largest precipitation inputs (e.g., September 30, 2010 and August 14 and 27, 2011; Table 1) produced the strongest shifts of stream water composition towards surficial end-members (Fig. 3). In contrast, the smallest event in terms of precipitation amount and intensity (e.g., November 16, 2011, Table 1), barely produced any shift away from the region of groundwater end-members, suggesting minimal contributions from surficial runoff sources. Other events with intermediate precipitation amounts (March 10 and July 8, 2011) produced mixing loops and shifts that were between the two extremes described above.

Storm event concentrations of SS, POC and DOC

SS, POC and DOC concentrations increased rapidly with the increase in stream flow (Fig. 2), however, the increase in POC concentrations outpaced the increase in DOC concentration such that the peak concentration of POC was 2–20 times higher than that of DOC for individual storm events. DOC concentrations ranged from 0.7 to 18.3 mg L⁻¹ while POC and SS concentrations ranged from 0.05–252 to 10–7,589 mg L⁻¹, respectively. SS concentrations were especially influenced by streamflow discharge. The top three events with the highest streamflow discharges (August 27, September 6 and November 22, 2011; Table 1) also had the highest flow-weighted mean SS concentrations (Table 2), but not in the order of the discharge amounts. In addition, the late fall and winter events of November 22, 2011 and December 1, 2010 which occurred under wet antecedent conditions and had high stream discharge produced the highest peak SS concentrations of 7,589 and 7,102 mg L⁻¹,

respectively. The influence of runoff amount on SS is further supported by the Pearson correlation values (Table 3). Correlation was highest for total and peak streamflow discharge with the relationship being significant ($p < 0.05$) for peak discharge.

In contrast to SS, storm event POC concentrations revealed a slightly different trend. Flow-weighted mean POC concentrations were highest for the high-flow summer events (e.g., September 30, and August 9, 14, and 27, Fig. 2 and Table 2) but fairly low for the other high-flow events that occurred in fall and winter (e.g., November 22 and December 23, 2011). POC concentrations were also very low for the high-flow summer event of September 9, 2011. Mean POC concentration was highest for the summer event of August 9, 2011 despite having relatively low precipitation and discharge amounts. However, this event did have the highest precipitation intensity of 6.5 mm h⁻¹ among all the recorded events (Table 1). The influence of precipitation intensity is supported by the significant correlation between POC concentrations and precipitation intensity ($p < 0.01$; Table 3).

It should be noted that POC concentrations were determined by multiplying the % POC content of sediment with the SS amounts; and % POC contents for the summer events were highest whereas the winter and late fall events had the lowest % POC (Table 2). This seasonal trend is obvious when SS and POC are plotted against each other (Fig. 4). This plot displays a triangular region extending from the origin with summer events falling along the lower edge with high POC concentration per unit SS (mild slope of the SS–POC relationship) and the winter and late fall events forming the upper edge with low POC content per unit SS mass (steep slope). Events from spring (e.g., April 16) occupied a region between these two extremes (Fig. 4). Very large summer events with some depletion of POC (e.g., August 27, 2011) were shifted to the left and in a region in the middle whereas summer events where considerable depletion of POC occurred (e.g., September 9, 2011, further details below) were completed shifted towards the edge containing the winter events.

A comparison of POC versus DOC for the storm events also revealed important similarities as well as differences. The top five events with flow-weighted mean POC concentrations (September 30, August 9, 14, 27 and July 8) also had the highest DOC values. However, DOC concentrations were also elevated for

Table 2 Flow-weighted mean and peak concentrations (mg L^{-1}) of SS, POC and DOC for sampled storm events in runoff at the outlet of the 12 ha catchment

Events		SSC (mg L^{-1})		POC (mg L^{-1})		DOC (mg L^{-1})		% POC
No.	Date	FW mean	Maximum	FW mean	Maximum	FW mean	Maximum	FW mean
High POC concentration events ^a								
1	9/30/2010 ^b (Su)	801	2,330	67.8	190	8.2	11.2	7.8
8	8/9/2011 (Su)	1,366	2,310	112	252	9.0	11.9	8.9
9	8/14/2011 (Su)	1,905	3,854	70.3	223	10.0	18.3	5.4
10	8/27/2011 ^c (Su)	2,169	3,874	66.4	112	10.0	11.9	3.1
Medium POC concentration events								
5	4/16/2011 (Sp)	560	3,356	14.5	93.7	5.4	8.4	4.6
6	7/8/2011 (Su)	653	2,042	58.4	183	9.5	13.6	8.7
7	7/28/2011 (Su)	1,458	2,917	33.3	175	7.3	10.4	2.9
Low POC concentration events								
2	12/1/2010 (W)	1,824	7,102	8.3	50.5	6.1	10.8	0.5
3	2/25/2011 (W)	1,038	2,702	9.0	23.4	3.9	6.5	0.9
4	3/10/2011 (Sp)	421	1,113	5.9	15.5	3.3	5.1	1.4
11	9/6/2011 ^d (Su)	2,883	4,599	7.1	11.3	N/A ^e	N/A	0.3
12	11/16/2011 (F)	546	2,266	5.3	21.8	3.3	5.1	1.0
13	11/22/2011 (F)	3,032	7,589	8.2	23.4	7.5	10.8	0.3
14	12/23/2011 (W)	2,007	5,298	9.0	23.7	5.3	10.5	0.5

^a The storm events have been grouped based on their flow-weighted mean POC concentration (POC_m) (High—POC_m is more than 60 mg L^{-1} ; Medium—POC_m is between 10 and 60 mg L^{-1} ; Low—POC_m is less than 10 mg L^{-1}). The storm events within the groups have been listed in the chronological order

^b Storm associated with remnants of hurricane Nicole

^c Storm associated with remnants of hurricane Irene

^d Storm associated with remnants of Tropical depression Lee

^e DOC was not measured

the high-flow winter and late fall events of December 1, 2010, and November 22 and December 23, 2011, whereas POC values for these events were among the lowest (Table 2). Not surprisingly then, correlation analyses (Table 3) indicated that while both POC and DOC were significantly correlated with precipitation intensity ($p < 0.01$), only DOC was strongly correlated with peak streamflow discharge ($p < 0.05$). When pooled by seasons, *t*-tests indicated that POC and DOC concentrations for summer were significantly greater ($p < 0.05$) than the other seasons but there was no significant difference among the spring, fall, and winter events.

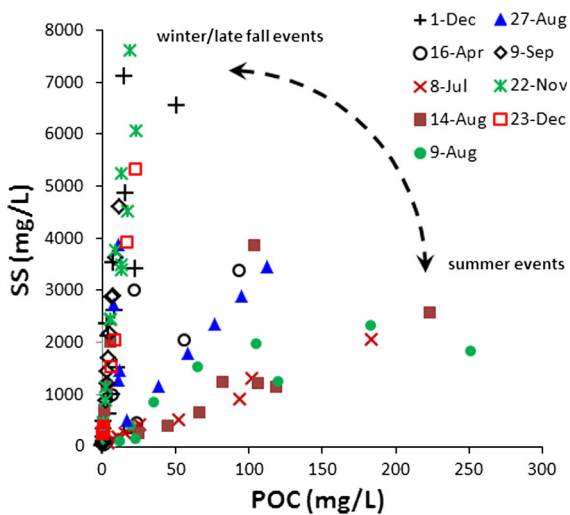
An important distinction between POC and DOC responses occurred for a sequence of successive storm events that occurred within a period of 1 month (August 9, 2011–September 8, 2011; Events 8–10 in

Fig. 5). Event 8 (August 9, 2011) had a high flow-weighted mean POC concentration of 112 mg L^{-1} and peak POC concentration of 252 mg L^{-1} (Table 2) despite a low discharge value (Table 1). Following this high, flow-weighted POC concentrations displayed a gradual decline for events 9–11 (Fig. 5) despite elevated streamflow discharge for events 10 and 11 (Table 2). These storm events also revealed a gradual impoverishment in the % POC. Event 8 had a % POC value of 8.9 % which decreased to 5.4 % in event 9, 3.1 % in event 10 and 0.26 % in event 11. Although DOC was not measured for Event 11, DOC concentrations clearly did not follow the decline indicated by POC values. It should be noted though that despite the declining trend, the magnitude of flow-weighted POC concentrations was still much greater than DOC.

Table 3 Pearson correlation matrix among the hydrologic variables and flow-weighted mean POC (POC_m) and DOC (DOC_m) concentrations

Parameter	SS_m	POC_m	DOC_m
Q_t	0.50	0.01	0.28
Q_{max}	0.63*	0.18	0.56*
AR24	0.21	0.22	0.32
P_t	0.32	0.33	0.52
PI_{max}	0.28	0.76**	0.82**
AP7d	-0.14	0.04	-0.01
AP24	0.30	0.27	0.47
RR	0.28	-0.61*	-0.48
LW2	0.02	0.59*	0.55*
LW5	-0.07	0.82**	0.67*

Correlation is significant at $p < 0.05$ level for * and $p < 0.01$ for **; Q_t —total discharge; Q_{max} —peak discharge; AR24—average antecedent stream discharge for 24 h; P_t —total precipitation; PI_{max} —peak 5-min precipitation intensity; AP7d—7-day antecedent precipitation preceding the event; AP24—24-h antecedent precipitation preceding the event; RR—runoff ratio—ratio of discharge amount and total precipitation for event; LW2 and LW5—average of groundwater depth for 7 days preceding the event at wells LW2 and LW5 respectively

**Fig. 4** Relationship between SS and particulate organic carbon (POC) concentration for selected events highlighting the change in slopes of the relationship between summer and winter events

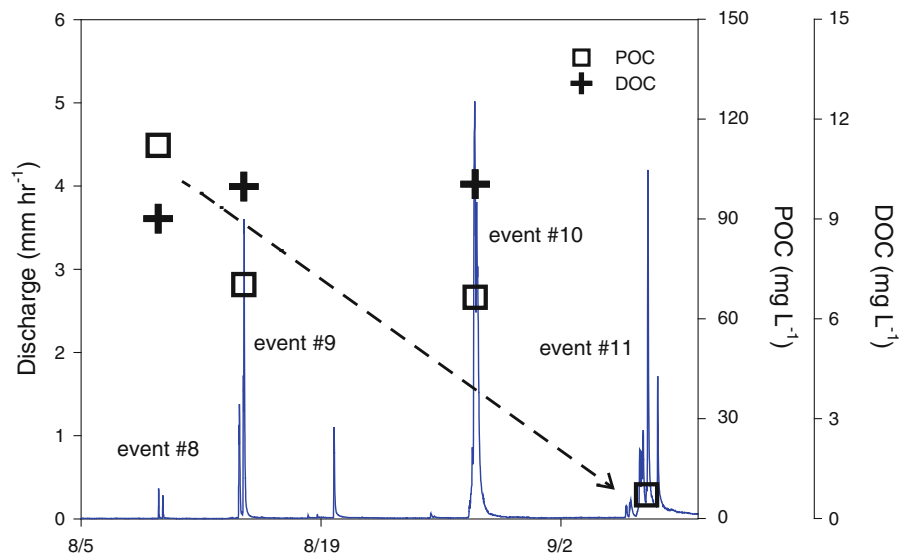
Within-event temporal patterns of SS, POC and DOC

Within-event temporal patterns of SS, POC, and DOC for four events of different magnitude—September 30,

2010, July 8, 2011, August 14, 2011, and August 27, 2011 are presented in Figs. 6, 7, 8 and 9. Except for the Hurricane Irene event of August 27, SS and POC followed similar temporal patterns with a peak in concentrations on the rising limb of the streamflow hydrograph and decline in concentrations thereafter. SS concentrations for the event of August 27 displayed two separate peaks while the POC concentrations occurred as a single delayed peak. In terms of magnitude, however, there were notable differences in the responses of SS and POC, especially for large storms consisting of two sub events (Figs. 6, 8). Concentrations of SS increased with streamflow discharge for the event of September 30 and the POC peak was higher for the second subevent which also had higher discharge. This pattern was also repeated for the event of April 16, 2011 (figure not included). Conversely, for the event of August 14, 2011 (and all other events with two sub-events), peak POC concentrations for the second subevent were lower than the first subevent even though the discharge values were higher for the second subevent (Fig. 8). The low POC concentrations for the second sub-events were due to the lower % POC content of the soil sediments. For e.g., for the event of August 14, 2011, the % POC dropped from 8.7 % during the first discharge peak to 2.7 % during the second discharge peak. This indicates that POC values may not always closely follow the trend in SS concentrations.

DOC concentrations also generally increased with streamflow discharge, but there was greater temporal variability in DOC patterns than those observed for POC (Figs. 6, 7, 8, 9). Typically, the peak in DOC concentrations followed the POC peaks. Unlike POC, DOC concentrations however, decreased much more gradually through hydrograph recession and did not drop back to the pre-event values for most of the events. While most storms revealed an increase in DOC with discharge and a peak in concentration in the vicinity of the discharge peak (e.g., Fig. 7 and Inamdar et al. 2011), the largest storm events—September 30, 2010 (event 1), August 14, 2011 (event 9), and August 27, 2011 (event 10)—revealed a slight decrease in DOC concentrations at or near the peak discharge (Figs. 6, 8, 9). POC did not follow this pattern. All three of these events had rainfall amounts in excess of 100 mm, with events 1 and 10 exceeding 150 mm of rainfall. For events 1 and 9 (Figs. 6, 8), DOC concentrations did indeed peak with discharge for

Fig. 5 Streamflow discharge and flow-weighted mean POC and DOC concentrations for four successive storm events in summer, 2011 at the outlet of the 12 ha catchment. Storm events included—August 9 (event 8), August 14 (event 9), August 27 (event 10), and September 6 (event 11). DOC concentrations for event 11 were not available. Flow-weighted POC concentrations decreased systematically for the four sequential events but the same response was not reproduced for DOC



the first subevent, but for the second subevent which had a larger discharge peak, a slight dilution of DOC is observed. Similarly, for the event of August 27, 2011, DOC concentrations increased quickly on the rising limb of the hydrograph (Fig. 9) but then dipped slightly when discharge was at its maximum. The same pattern however did not extend to within-event export of POC.

The difference in responses for POC and DOC with streamflow discharge is further illustrated by the concentration-discharge plots of POC and DOC for all the 14 events (Fig. 10). These CQ plots for DOC also provide additional insights into the influence of event magnitude and seasonality on DOC. The increase in DOC concentrations with discharge for the summer events (e.g., July 8 and 28, August 14 and 27 and September 30) was much more rapid (steeper slope) than the non-summer events (e.g., April 16, March 10, December 23) which displayed a more gradual increase (Fig. 10 inset). Furthermore, the CQ pattern for the summer events also displayed a leveling-off in DOC concentrations with increasing discharge and a subsequent decline for very high discharge values (Fig. 10). This response was not apparent for the non-summer events. From Fig. 10 (inset), it appears that, in general, for our study site, DOC concentrations increased sharply until about a discharge of 0.2 mm h^{-1} ; then leveled off until a discharge rate of 1.0 mm h^{-1} , followed by a decline in concentrations thereafter. However, no such behavior is replicated by POC.

Sources for runoff sediment from the mixing model

EMMA plot including potential sediment sources and runoff sediment for storm events are included in Fig. 11. Nearly all of the sediment sources were located in quadrant 3 of the EMMA plot (Fig. 11a). The wetland and stream bed sources were closer to the origins of the axis while the upland and stream bank sources were located further away from the origin and in the lower portion of the quadrant 3. When compared against runoff sediment chemistry (Fig. 11b) it is clear that the sampled sources did not enclose the runoff sediment chemistry and that there were likely additional sources of sediments which were not sampled. The large shifts of runoff events towards quadrant 4 suggest that there was another unknown source in this quadrant which was not identified in this study. Despite our inability to capture all sediment sources the storm sediment patterns reveal some interesting trends. High rainfall intensity ($>3.5 \text{ mm h}^{-1}$; red symbols in Fig. 11b) summer events such as September 30, 2010 (event 1), July 28, 2011 (event 7), August 9, 2011 (event 8), August 14, 2011 (event 9) and August 27, 2011 (event 10) were spread out in the third and fourth quadrants of the EMMA space. On the other hand, most of the low intensity ($<3.5 \text{ mm h}^{-1}$; green symbols in Fig. 11b) winter and spring storm events such as events of December 1, 2010 (event 2), February 25, 2011 (event 3) and March 10, 2011 (event 4) were clustered on the right-hand side of the EMMA space in the vicinity of the stream bed end-member.

Fig. 6 Precipitation (mm), streamflow discharge (mm h^{-1}), and SS, POC and DOC concentrations (mg L^{-1}) for the event of September 30, 2010 (remnants of hurricane Nicole) at the outlet of the 12 ha catchment. A slight dilution in DOC concentrations can be seen with the second discharge peak but no such response was seen for POC

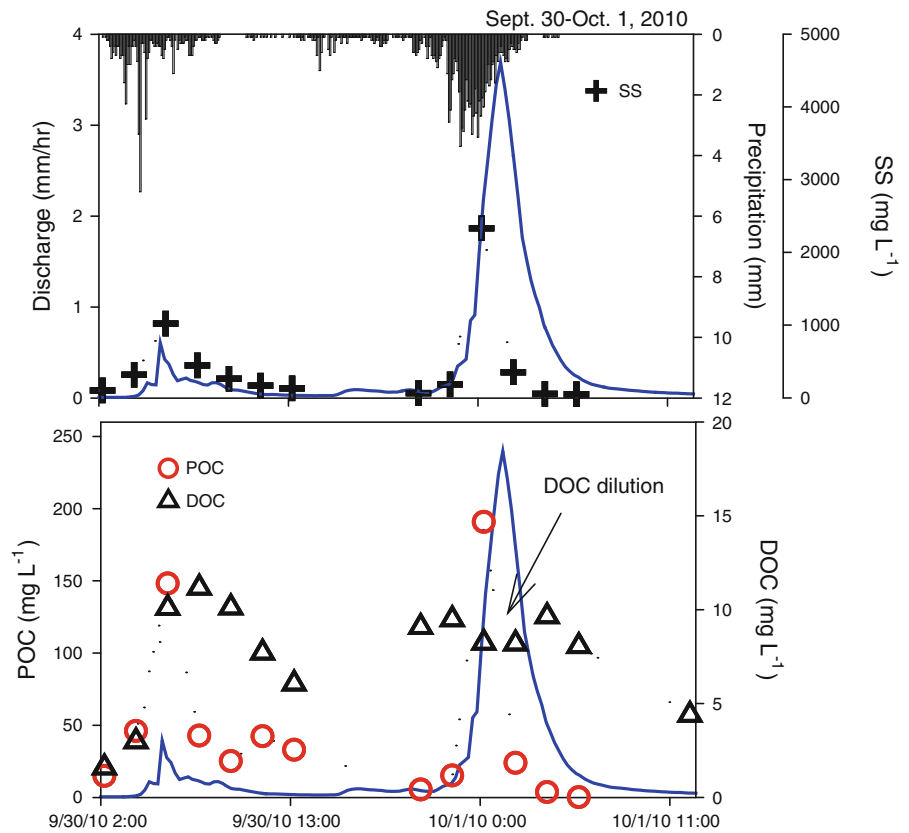


Fig. 7 Precipitation (mm), streamflow discharge (mm h^{-1}), and SS, POC and DOC concentrations (mg L^{-1}) for the event of July 8, 2011 at the outlet of the 12 ha catchment

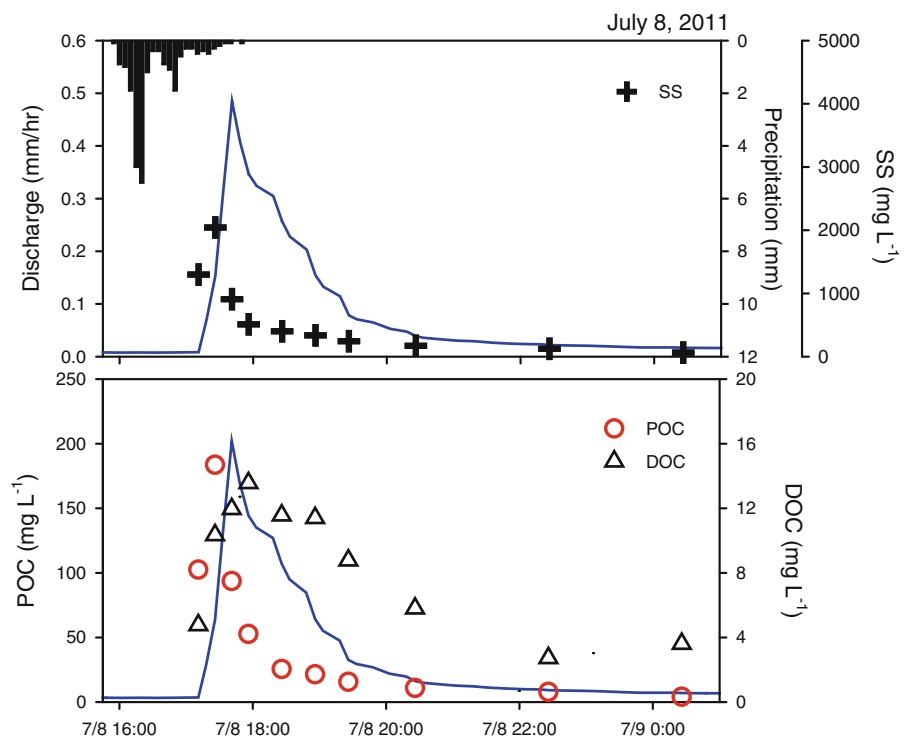


Fig. 8 Precipitation (mm), streamflow discharge (mm h^{-1}), and SS, POC and DOC concentrations (mg L^{-1}) for the event of August 14, 2011 at the outlet of the 12 ha catchment

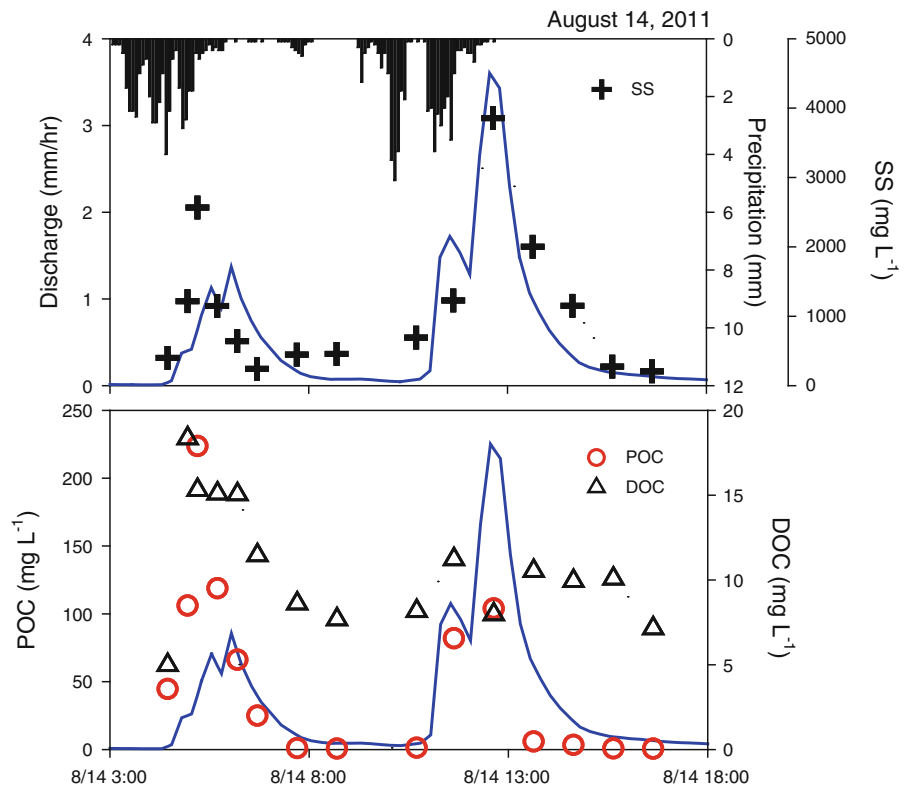
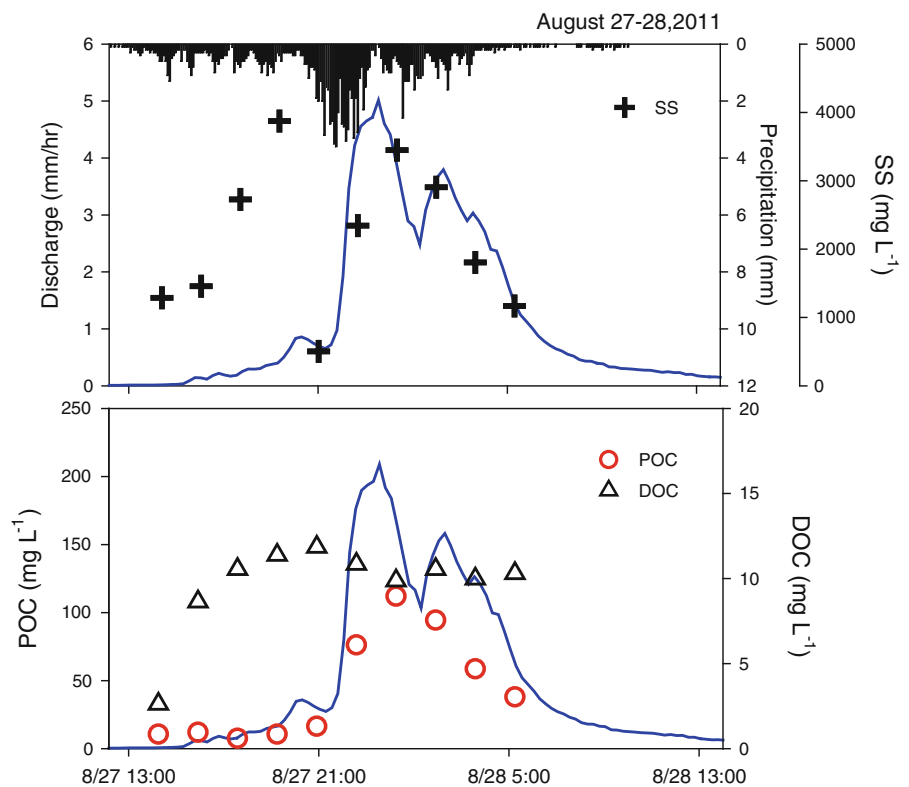


Fig. 9 Precipitation (mm), streamflow discharge (mm h^{-1}), and SS, POC and DOC concentrations (mg L^{-1}) for the event of August 27, 2011 (remnants of hurricane Irene) at the outlet of the 12 ha catchment



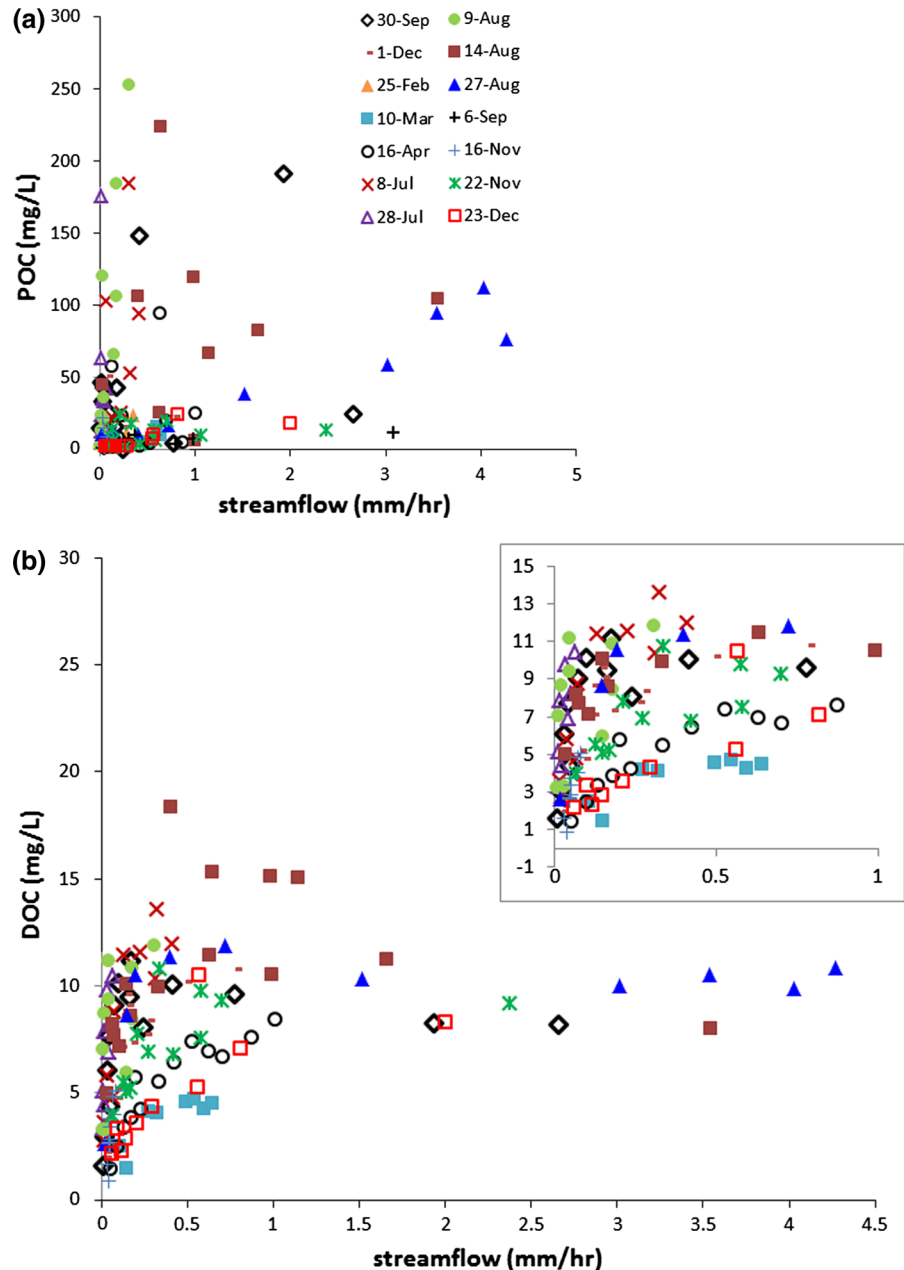
Discussion

Temporal patterns, flowpaths, and sources of POC and DOC

We performed EMMA analyses for both—the dissolved as well as the sediment phases of storm runoff. The dissolved phase EMMA characterized the hydrologic flow paths whereas the sediment EMMA enabled

us to identify the potential sources of sediment (e.g., stream bed, stream bank erosion, and uplands). Our previous work on DOC for this study site (Inamdar et al. 2011) has already shown that storm event DOC peaks, with the exception of few events, typically occurred at or after the discharge peaks producing an anticlockwise concentration-discharge (CQ; Evans and Davies 1998) hysteresis loop. Using EMMA analyses, we attributed this DOC leaching pattern

Fig. 10 POC and DOC concentrations versus streamflow discharge (CQ plots) for the 14 storm events. Summer storms compared to winter and spring events (note *inset*) displayed a sharper increase in DOC with discharge and then a decline for the largest flows. No such response was seen for POC



(e.g., Inamdar et al. 2011) to throughfall and litter leachate contributions followed by soil water contributions from surficial soils. Using the same model and rationale, the earlier expression of POC on the rising limb of the discharge hydrograph (and therefore clockwise CQ hysteresis) suggests that POC moved with saturation overland flow associated with event water (precipitation, throughfall and litter leachate end-members). The match in timing and magnitude of elevated event POC concentrations and the large shifts in EMMA space towards surficial runoff sources (Fig. 3) further supports this argument.

Unlike our EMMA for hydrologic flow paths, the EMMA for sediment sources did not yield definitive results since some of the key end-members could not be identified (Fig. 11). We did, however, find that the high-intensity summer events displayed greater diversity of sediment sources compared to the low-intensity storm events (Fig. 11). The low-intensity events were clustered between the near-stream sources such as wetlands, stream beds and another unidentified source. While the high-intensity summer events also showed a major contribution from the near-stream sources, they were more spread out on the EMMA plots and indicated an increased contribution of distal upland sources as well as the stream bank. This is possibly due to the increased erosive ability of runoff associated with high precipitation-intensity events. This is in agreement with previous studies such as Walling and He (1999) who have observed that the contribution of sediment from stream banks is substantially greater during high versus low flows. Using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes of SS, Jung et al. (2012) found that POC derived from eroded mineral soil fractions increased with increasing rainfall intensity and peak discharges. In our case, however, a more comprehensive sampling may be required to capture the complete spectrum of sediment sources as well as their evolution during the storm events.

Most previous studies have typically employed CQ hysteresis loop analyses to identify the origins of runoff sediment. Jeong et al. (2012) reported clockwise hysteresis patterns for both POC and DOC and attributed shallow hydrologic flowpaths and steep slope gradients for the quick mobilization of C in stream runoff. Coynel et al. (2005) and Oeurng et al. (2011) found a combination of both clockwise as well as anticlockwise loops for POC; with anticlockwise loops being associated with larger storm events or

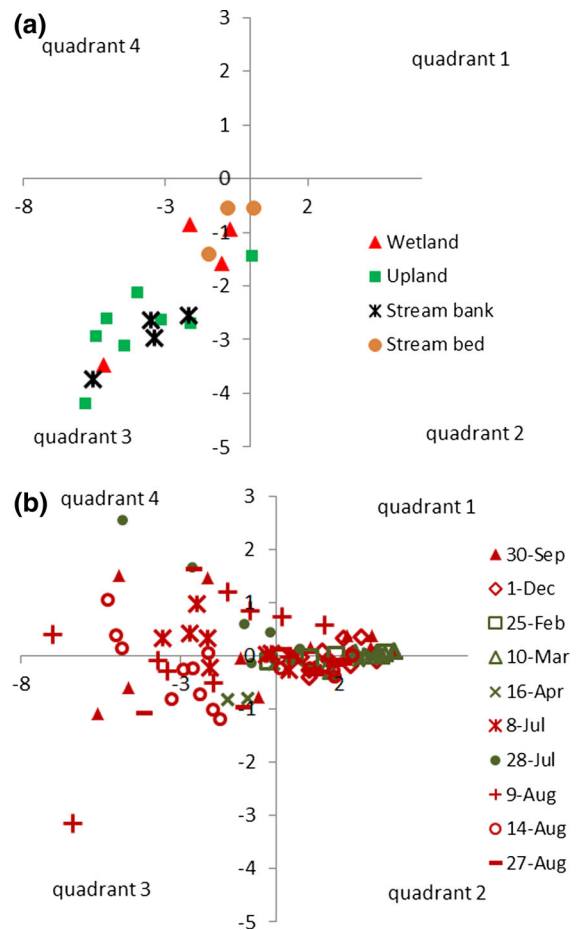


Fig. 11 **a** Distribution of sediment end-members in the mixing model space; **b** comparison of selected storm events in mixing space to evaluate the relative changes in sediment chemistry. In **b** events with precipitation intensity $>3.5 \text{ mm h}^{-1}$ are indicated in red symbols whereas events with low intensity ($<3.5 \text{ mm h}^{-1}$) are indicated in green symbols. Events with precipitation intensity $>3.5 \text{ mm h}^{-1}$ display a larger spread in mixing space indicating greater changes in sediment chemistry and more diverse sediment end-members. (Color figure online)

events occurring under wet catchment conditions. Oeurng et al. (2011) attributed the clockwise loops to POC originating from near-stream sources whereas the anticlockwise loops were associated with POC from more distal sources as erosive forces associated with larger storm events mobilized POC from hillslopes and upper reaches of the catchments. Similarly, Coynel et al. (2005) attributed the clockwise loops to POC-rich riparian sources while the anticlockwise patterns were credited to distal, less-erodible, and POC-poor sources. Extending the rationale of these studies, we hypothesize that the clockwise POC loops

for most storm events in our study indicate the dominance of near and within-stream POC sources in the catchment (as alluded by the sediment EMMA). Conversely, the anticlockwise POC loops for the large runoff events of August 27, 2011 (event 10) and September 6, 2011 (event 11) were likely due to the exhaustion of easily-erodible near and within stream sediment sources and the enhanced contribution of more compact, erosion-resistant soils and/or distal upland sources of sediment (as also suggested by EMMA). Both of these events had high precipitation amounts (Table 1) and were the last of four successive storm events within a month (events 8–11).

Storm event patterns of SS and POC

SS concentrations are often used as a surrogate for POC (Alvarez-Cobelas et al. 2012; Hope et al. 1994), and while our data reveal strong correlations between SS and POC there were key changes in the slopes of these relationships with events (Fig. 4). The four back-to-back events of August (Fig. 5) clearly showed that the % POC content of SS could change with sequential events and that this could be because of POC depletion of sediment sources due to hydrologic flushing; and/or mobilization of distal or upland sources of sediment with increasing hydrologic intensity which may be lower in their % POC contents. This phenomenon of exhaustion of POC for successive closely-spaced events has also been reported in previous studies (Alexandrov et al. 2003; Coynel et al. 2005; Oeurng et al. 2011; Rovira and Batalla 2006; Veysy et al. 1999). Veysy et al. (1999) explained this phenomenon through a conceptual model which proposes that the carbon-rich litter fraction is depleted in the earlier storm events resulting in the export of mineral-rich SS in the later events.

The slopes of the SS–POC relationships in Fig. 4 and the mean % POC content for storm events in Table 2, however, also suggest a strong seasonal pattern driven by hydrology and biotic processes. The summer events in general were much higher in % POC content than the winter and late fall events. Two potential explanations (among others) could be the hydrologic nature of the summer events and/or biogeochemical conditions that may enhance the production/supply of POC. Summer storms are generally associated with convective weather systems that generate high-intensity, short-duration precipitation

with a greater potential for forest floor disturbance and soil/sediment erosion as opposed to frontal systems in autumn and spring that generate long-duration, low-intensity precipitation. Our POC data already indicates a strong correlation with precipitation intensity and these events likely facilitated greater surface runoff and erosion and thus delivered larger amounts of carbon-rich sediment to the stream. Jeong et al. (2012) have also reported that rainfall intensity was a critical factor in influencing the storm event concentrations of POC. The summer events were also likely influenced by the repeated cycles of drying and rewetting of the soil surface and forest floor. Repeated cycles of drying and wetting of soils have been shown to enhance mineralization rates and therefore the production and release of carbon from the soil (Borken and Matzner 2009; Lundquist et al. 1999). It is likely that elevated summer temperatures along with drying and wetting cycles enhanced the breakdown of organic matter on the forest floor which was then flushed out with runoff associated with high-intensity summer events. These observations clearly suggest that we need to be extremely careful while using SS–POC relationships for predictions since the form (slope) of such relationships could change with season as well as for closely spaced back-to-back storm events.

POC and DOC exports patterns for storm events of varying magnitude and timing

The sharper rise in POC versus DOC has been reported for other studies (Johnson et al. 2006; Pawson et al. 2012). Johnson et al. (2006) found that the storm-event POC concentrations were 150 times their baseflow values while the DOC concentrations increased four times. The range in POC and DOC concentrations from this study is similar to the values reported for other studies (Oeurng et al. 2011; Johnson et al. 2006; Pawson et al. 2012). Concentrations in an 1,110 km² agricultural catchment in France (Oeurng et al. 2011) ranged between 0.1–173.2 mg L⁻¹ for POC and 1.5–7.9 mg L⁻¹ for DOC, which is slightly less than our values. In contrast, our POC concentrations were considerably less than those reported for an eroding peatland catchment in UK that yielded an average of 1.5–1,220 mg L⁻¹ for POC and 13.58–27.52 mg L⁻¹ for DOC (Pawson et al. 2012). It should be noted that in our study, the peak and flow-weighted mean concentrations for POC (Table 2) were always greater

than the corresponding DOC values across all events. This is unlike observations by Jeong et al. (2012) where POC concentrations were less than DOC for small discharge events, but exceeded the DOC values for events with higher discharge values.

Our previous observations on C mass exports (Fig. 3 in Dhillon and Inamdar 2013) indicated that the differences in POC and DOC were largest for the hurricane-associated storms (September 30, 2010 and August 27, 2011) and while POC mass export increased exponentially DOC was constrained to a linear increase. A thorough examination of within-event patterns and among-event differences in POC and DOC presented here help explain these differences. Within-event patterns of POC and DOC for the large hurricane events (Figs. 6, 9) showed that not only was the increase in DOC concentrations less than POC, but that DOC also displayed a dilution trend at peak stream flow discharges. This response for our study catchment suggests that while new POC stocks continued to be mobilized by erosive forces associated with increasing storm runoff the DOC supply could not keep up with the rate of runoff increase. Thus, for extremely large events (>100 mm precipitation) the DOC response in our catchment was supply-limited while the same phenomenon did not extend to POC. We believe this is one reason that explains the large disparity in POC and DOC mass exports observed in Fig. 3 in Dhillon and Inamdar (2013). In contrast to the within-event patterns, POC depletion was observed for consecutive storm events (Fig. 5) but the same pattern was not reproduced for DOC. The depletion of POC for the event of September 6, 2011 (last of the four sequential events), is also reflected in the mass exports in Fig. 3 of Dhillon and Inamdar (2013) with POC amounts for this event being much lower and even comparable to the DOC values. These observations suggest that POC and DOC could both become supply-limited for storm events but the time scale and thresholds at which this occurs differs for the two constituents. It appears that catchment supplies of DOC cannot keep up with very high runoff rates which occur at the time scale of hours/minutes but these supplies recover quickly between storms (days). On the other hand, POC supplies tend to run out with continuous hydrologic flushing by closely-spaced, (days) multiple, events. Future climate-change predictions (Karl et al. 2009) indicate increasing storm

intensity/magnitude with longer intervening dry periods. Based on our observations, such future events will increase the disparity in DOC and POC exports from catchments with DOC dilution occurring at peak flows.

The CQ plots in Fig. 10 also provided key insights into the differential nature of POC and DOC flushing with stream discharge. DOC displayed a more consistent pattern while the same was not seen for POC. DOC was rapidly mobilized with runoff during high-intensity summer events (indicated by the steep increase), but at the same time, this intensity resulted in DOC supply being outpaced by event water input. This is seen in the leveling off and decline of DOC concentrations. A similar response was however not observed for the long duration and low intensity spring and winter storms which revealed a more gradual increase in DOC with discharge (Fig. 10). We hypothesize that such DOC responses are likely occurring for other catchments similar to ours but with a different set of thresholds and slopes for the DOC response curves. The shapes of these curves would be dictated by the DOC pools in the catchment (supply) and the runoff sources and rate of runoff increase (transport). Understanding and quantifying the slopes of the DOC curves and the discharge thresholds would significantly advance our understanding of C response to storm events.

Overall, the seasonal occurrence of storms and associated attributes (e.g., precipitation intensity) was a critical factor that influenced the disparity between POC and DOC responses. We speculate that the occurrence of high-intensity hurricane events towards the tail end of the summer further enhanced the disparity between POC and DOC responses and exports. Events of similar magnitude in winter or spring (e.g., with lower intensity) may not have produced the same level of differences between POC and DOC. We also recognize that the differences in POC and DOC responses were especially apparent at the small 12 ha scale of our headwater catchment. It is well recognized that POC concentrations are elevated for small, headwater catchments (Alvarez-Cobelas et al. 2012; Pawson et al. 2012; Townsend-Small et al. 2008) and that POC concentrations decrease with increasing catchment scale as POC and sediment settle out as they are transported through the fluvial network (Battin et al. 2008; Hope et al. 1994).

Conclusions

High-frequency sampling of particulate and dissolved organic C in stream runoff from a headwater catchment during a large, intense, storm events, a few associated with remnants of hurricanes, provided rare and critical insights into storm-event C patterns. Key conclusions that that can be derived from this study are:

- The responses of POC and DOC differed substantially within large storm events as well as for closely spaced, sequential storm events. During large storms, DOC yielded a dilution trajectory at peak discharge, while POC concentration continued to rise. Flow-weighted mean POC concentrations decreased for closely-spaced sequential storms, suggesting an exhaustion of the POC pool, whereas the same pattern was not replicated by DOC. These observations suggest that there are important distinctions in the supply and transport of these two C constituents which may be apparent at different time scales and hydrologic thresholds.
- Seasonal hydrologic and biochemical conditions of storms had important implications for both POC and DOC. The % POC content of SS for summer storm was much greater than corresponding values for winter events. This suggests caution should be used if SS is used as a surrogate for POC. Similarly, DOC concentrations increased much sharply with discharge for summer versus non-summer events, but then also leveled off and displayed a dilution pattern at high flows. Thus, seasonal hydrologic and biogeochemical conditions may have an important role in shaping POC and DOC responses.
- The differences in the temporal patterns of POC and DOC during storm events as well as the nature and direction of C–Q hysteresis loops of POC and DOC alluded to different sources and flow paths of POC and DOC within the catchments. EMMA analysis revealed that while surficial flowpaths are important for both POC and DOC, POC is quickly mobilized with surface runoff while DOC expression in runoff is delayed and occurs in concert with surface runoff and leaching of surficial soil horizons. Near-stream, C-rich sediment sources contribute to POC during small to moderate storms but distal, mineral-rich sediment sources could become more important for the larger events.

- The sharp increases and changes in POC and DOC concentrations during storm events underscore the need to perform high-frequency sampling during storm events for accurate and thorough understanding of C response patterns and thresholds. Daily, weekly, or monthly sampling regimes will be unable to identify key responses that are critical to advancing our mechanistic understanding of C.

This work underscores the importance of POC in headwater catchments and for large events and the need to develop more realistic and robust models of POC and DOC supply and transport from headwater catchments. Considering future climate-change predictions of increasing intensity of the largest storms for the northeastern USA (Bender et al. 2010) such information is particularly urgent.

Acknowledgments The authors would like to acknowledge the support of Delaware Water Resources Center (DWRC) for providing a research assistantship to Gurbir Singh Dhillon for his master's thesis research. Instrumentation and sampling in the study catchments was funded through an existing grant from the National Science Foundation (NSF, Hydrologic Sciences Program, EAR-0809205). We also thank Dr. Myron Mitchell's Biogeochemistry Laboratory at Syracuse for the analyses on water samples and Karen Gartley and the UD Soils Laboratory for the POC analyses. We would like to thank Captain Wayne Suydam and the Fair Hill NRMA staff for providing access to the study site. We also thanks Drs. Tom Sims and Yan Jin for their suggestions and insights during Gurbir's MS thesis research. We would also like to recognize the support of graduate student colleagues including Shatrughan Singh, Sudarshan Dutta, Rachael Vaicunas and Zhixuan Qin for sample collection and analyses.

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