Dissolved and particulate organic carbon fluxes from an agricultural watershed during consecutive tropical storms

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Received 9 August 2013; revised 18 September 2013; accepted 20 September 2013; published 7 October 2013.

[1] Low-frequency high-magnitude hydrologic events mobilize a disproportionate amount of dissolved organic carbon (DOC) from watersheds, but few studies measure the role of extreme storms in exporting organic carbon from croplands. We use high-resolution measurements of storm runoff to quantify DOC and particulate organic carbon (POC) fluxes from an agricultural field during consecutive tropical storms that delivered 41 cm of rainfall to the Virginia Coastal Plain. Over a 2 week period, we measured exports of 22 kg DOC ha^{-1} and 11.3 kg POC ha^{-1}. Ultraviolet absorbance measurements indicate that the aromatic DOC fraction systematically increased as plant-derived aliphatic carbon was depleted during the initial event. Croplands can have event-scale carbon losses that equal or exceed published estimates of annual export for perennial streams draining forested and mixed land use watersheds. We quantify aromatic DOC fractions approaching 50%, indicating that agricultural stormflow can produce a significant load of relatively photoreactive carbon. **Citation:** Caverly, E., J. M. Kaste, G. S. Hancock, and R. M. Chambers (2013), Dissolved and particulate organic carbon fluxes from an agricultural watershed during consecutive tropical storms, *Geophys. Res. Lett.*, *40*, 5147–5152, doi:10.1002/grl.50982.

1. Introduction

[2] Dissolved and particulate organic carbon (DOC and POC) inputs to waterways regulate nutrient availability and primary productivity [*Carpenter et al.*, 1998; *Sigleo and Macko*, 2002; *Wang et al.*, 2004], contaminant transport [*Kalbitz and Wennrich*, 1998], and the global carbon cycle [*Hedges et al.*, 1997]. Despite the paramount importance of organic carbon molecules to terrestrial, marine, and global biogeochemical processes, carbon export from watersheds remains poorly described. Terrestrial organic carbon export is controlled by soil and vegetation type [*Dittmar et al.*, 2006; *Wickland et al.*, 2007;*Wallace et al.*, 2008], microbial community composition [*Cragg and Bardgett*, 2001], and water residence times and hydrologic flow paths [*McDowell and Likens*, 1988; *Dalzell et al.*, 2005]. All of these factors are ultimately controlled by land use, topography, and climate. The wide spectrum of variables that control organic matter export and form thus need further study in order to predict how different landscapes regulate carbon cycling [*Cole et al.*, 2007; *Lu et al.*, 2013].

[3] Most of the work describing carbon fluxes from watersheds has focused on large perennial streams draining forested, grassland, or peatland catchments [*Cronan and Aiken*, 1985; *McDowell and Likens*, 1988; *Boyer et al.*, 1997; *Worrall et al.*, 2002; *Wickland et al.*, 2007]. It is well documented that large magnitude storms export a disproportionate amount of carbon from forested ecosystems [*McDowell and Likens*, 1988; *Yoon and Raymond*, 2012]. Recent measurements from a forested catchment draining the Maryland Piedmont showed that a single event (Hurricane Irene) was responsible for one fifth and over one half of the 2011 DOC and POC fluxes, respectively [*Dhillon and Inamdar*, 2013]. Moreover, in this climate, the ratio of POC to DOC can increase by nearly 1 order of magnitude with storm intensity. Given that human modifications to landscapes can significantly impact drainage patterns and organic matter characteristics, more measurements are needed that describe how storms mobilize carbon across a range of land uses.

[4] Croplands and pastures together account for 40% of the Earth's land surface [*Foley et al.*, 2005], but only in the last decade has the export of carbon from agricultural landscapes begun to receive attention. Agricultural runoff has relatively high carbon loads from the leaching of crop residues and soil organic matter by rain and irrigation waters [*Dalzell et al.*, 2005, 2007; *Vidon et al.*, 2008]. As with forested watersheds, agricultural DOC export is controlled by hydrology. For example, in the Midwestern U.S., watersheds dominated by agricultural land use export 71% to 85% of the DOC during flows that occur less than 20% of the time [*Dalzell et al.*, 2007]. Relative to watersheds vegetated with uncultivated plant species, agricultural watersheds export structurally complex DOC with larger aromatic fractions [*Graeber et al.*, 2012], although composition varies temporally as dominant flow paths change [*Hernes et al.*, 2008; *Vidon et al.*, 2008]. Highly aromatic DOC is typically derived from leaching of upper humus-rich soil horizons, and it can affect ecosystem functioning by decreasing primary production through shading [*Carpenter et al.*, 1998], influencing thermal stratification of water bodies [*Caplanne and Laurion*, 2008], and providing labile carbon compounds for microbial uptake [*Moran and Zepp*, 1997].

[5] In this study, our objective was to characterize and quantify episodic carbon transport from croplands. Given that DOC concentrations and export vary in response to low-frequency hydrologic events and in-stream processing, landscape-scale carbon dynamics are best measured at high-resolution spatial and temporal scales [*Dalzell et al.*, 2007]. Topographic variability can cause runoff to converge in channels, creating concentrated flow that occurs only during

Additional supporting information may be found in the online version of this article.

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0094-8276/13/10.1002/grl.50982

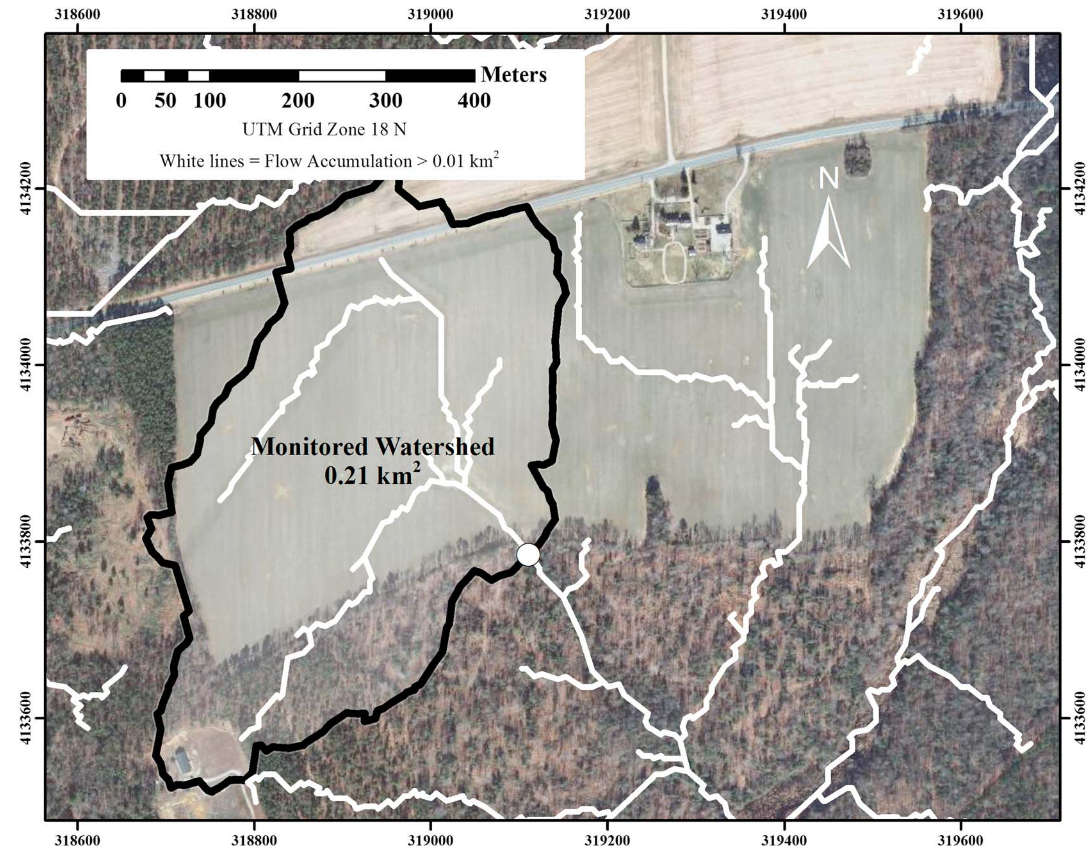

Figure 1. Air photo showing the boundary of the agricultural study watershed (black line), ephemeral channels (white lines), and the monitoring station location (white circle).

storm events [*Dosskey et al*., 2002]. These channels may be significant conduits for transport, but the dissolved and particulate-phase export of major elements in these systems has not been quantified. We hypothesize that ephemeral channels draining cropland fields deliver significant amounts of terrestrial carbon to perennial waterways during extreme hydrologic events. Because organic matter can be oxidized or degraded by bacterial action over short-length scales, both the quantity and quality of carbon fluxes need to be measured near the source rather than farther down gradient in the perennial segments of the channel, where traditional water quality monitoring efforts are focused.

2. Methods

[6] In March of 2011 we began to monitor an incised ephemeral channel draining a 21 ha catchment comprised entirely of croplands in the James River portion of the Chesapeake Bay watershed in Southeastern Virginia (37°20'3.97"N; 77°2'39.39"W). This agricultural field is managed in a way that is common on the Mid-Atlantic coastal plain, whereby corn, soy, and winter wheat are grown in rotation, with cover species planted between cycles. The field is on Quaternary-aged interbedded sand, silt, and clay, and soils are loam, with some clayey, silty, and sandy loams also present. We used a lidar-based digital elevation model with 3 m resolution in a geographic information system database to model flow direction and accumulation and define the watershed draining to the monitoring location (Figure 1). The field slopes between 2% and 6% and is surrounded by a >30 m forest buffer of second-growth mixed hardwoods. However, like many agricultural fields, field runoff concentrates in the ephemeral channel during intense storms and effectively bypasses the riparian buffer [*Dosskey et al*., 2002].

[7] Rainfall was recorded at the site using a tipping bucket rain gauge attached to a HOBO data logger. During storm events, runoff samples were collected from the incised channel approximately 30 m downstream from the field edge (Figure 1). The height of the water in the channel was monitored using a Campbell Scientific SR50A sonic range sensor controlled by a Campbell Scientific CR510 data logger. Distance to the water was recorded every 5 min, and detection of water depths greater than 6 cm triggered sample collection by an Isco 3700 automatic sampler. Discharge (Q) in the channel was measured directly during stormflow on four separate occasions by measuring the dilution of injected salt. We used the direct discharge measurements and a surveyed cross section of the channel to calibrate roughness in Manning's equation, allowing us to calculate discharge from our near-continuous water depth data.

[8] Runoff samples were processed by passing 100 mL through a Millipore 0.7 μm glass fiber filter. Oven-dried filters (105°C) were weighed prefiltration and postfiltration to determine suspended sediment concentrations. Filtrate for each sample was divided and stored frozen in glass or polycarbonate bottles, and nonpurgable carbon (DOC) concentrations were determined using a Shimadzu TOC-V-L. We measured specific ultraviolet light absorbance of the processed water samples at 254 nm ($SUVA_{254}$) to evaluate DOC aromaticity [*Weishaar et al*., 2003]. Sediment-laden filters were

Table 1. Precipitation, Flow, and Flux Data Collected During Hurricane Irene and Tropical Storm (TS) Lee

	Hurricane Irene	TS Lee	
	27–29 August	6–10 September	Combined
Precipitation (cm)	19.9	21.4	41.3
Duration of rainfall (h)	19.75	67.37	–
Flow volume (m^3)	16,000	12,700	28,700
Duration of flow (h)	44	65	109
DOC flux (kg ha^{-1})	12.7	9.3	22
POC flux (kg ha^{-1})	6	5.3	11.3
TOC flux (kg ha^{-1})	18.7	14.6	33.3

acidified with 2N HCl overnight at 60°C to remove inorganic carbon, and particulate organic carbon (POC) concentrations were determined using a PerkinElmer 2400 CHN Elemental Analyzer. Mass fluxes were calculated for DOC (<0.7 µm), POC (≥0.7 µm), and by addition, total organic carbon (TOC). To calculate mass fluxes, measured concentrations (mass L^{-1}) were multiplied by flow at the time of collection (L $second^{-1}$). We used these data to generate rating curves between mass/second and flow to calculate DOC, POC, and TOC fluxes (see the supporting information).

3. Results and Discussion

[9] In the late summer of 2011, the Mid-Atlantic U.S. was hit by two consecutive tropical systems: Hurricane Irene and Tropical Storm (TS) Lee. In the 6 weeks preceding Hurricane Irene, only 4.6 cm of rainfall was recorded, and the ephemeral channel was completely dry. Hurricane Irene then delivered 20 cm of rainfall that fell in <20 h. The storm generated channel flow for 44 h on 27–29 August 2011 (Table 1 and Figure 2), and we collected 19 runoff samples during this time period as approximately 16,000 m^3 of water passed through the channel. The hydrograph generated by Hurricane Irene can be described as a single sharp peak with a maximum discharge of 1.35 m^3 s^{-1} (Figure 2).

[10] Nine days later, soils in the field were still saturated, and presumably, the water table was generally elevated from Hurricane Irene. Beginning on 7 September, Tropical Storm Lee delivered an additional 21 cm of rainfall over the course of 67 h, and flow persisted in the monitored channel for 65 h (Table 1 and Figure 2). In that time, approximately 12,700 m^3 of water passed through the channel and 24 samples were collected. Three distinct periods of rainfall intensity are mirrored in the hydrograph as three distinct flow maxima of roughly the same magnitude (Figure 2). A cumulative rainfall plot is given in the supporting information.

3.1. Dissolved Organic Carbon Fluxes and Sources

[11] Even though channel base flow is absent and stormflows are rare, high fluxes and concentrations of organic carbon during storms indicate that this ephemeral channel is a conduit for substantial organic carbon export (Table 1 and Figures 2 and 3). Between March and October, seven minor hydrologic events generated measurable flow in the channel (depth of water >6 cm). The occurrence of two major consecutive hydrologic events provides a unique opportunity to assess the effects of antecedent field moisture conditions on organic carbon fluxes and sources from a single agricultural field. Because of the narrow time frame that we studied, seasonal factors including crop cover, fertilizer applications, and temperature did not vary dramatically between the storm events that we measured. At the sampling time, corn had been recently harvested from the fields, leaving stalk residues on the field.

[12] During both tropical storms, DOC concentrations were negatively correlated with discharge (Figures 3a and 3b). This dilution can be attributed to the large volume of meteoric water, which typically has DOC concentrations <3 mg/L [*McDowell and Likens*, 1988], and discharge clearly increased at a rate faster than DOC could be leached from the vegetation residues or soil. This contrasts with the response of a forested watershed in the Catskills to Hurricane Irene, which showed no DOC dilution as the storm reached its maximum intensity [*Yoon and Raymond*, 2012]. Despite the dilution effect that we measured, fluxes were magnified during peak flows because changes in DOC concentrations were trivial compared with changes in discharge (Figures 2, 3a, and 3b). In addition to the dilution process, DOC hysteresis indicated differing hydrologic flow paths during Hurricane Irene and TS Lee. The DOC hysteresis for Hurricane Irene has a clockwise shape (Figure 3a), which can be attributed to the initial flushing of soluble material from a landscape [*Evans and Davies*, 1998; *House and Warwick*, 1998]. $SUVA_{254}$ values during Hurricane Irene showed an increasing proportion of aromatic DOC over time, indicating either the introduction of a new source of aromatic DOC or the depletion of an aliphatic source (Figure 2). Hysteresis and $SUVA_{254}$ data together suggest that the primary source of DOC was more

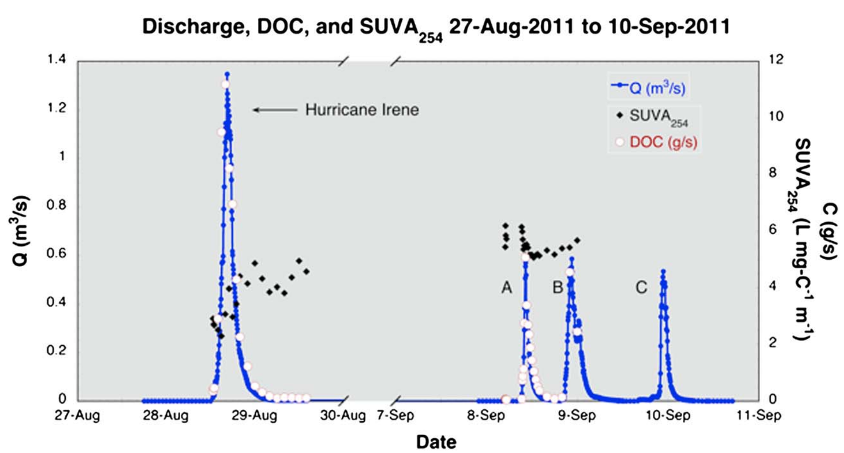

Figure 2. Channel flow, DOC, and SUVA measurements for the two consecutive tropical storms.

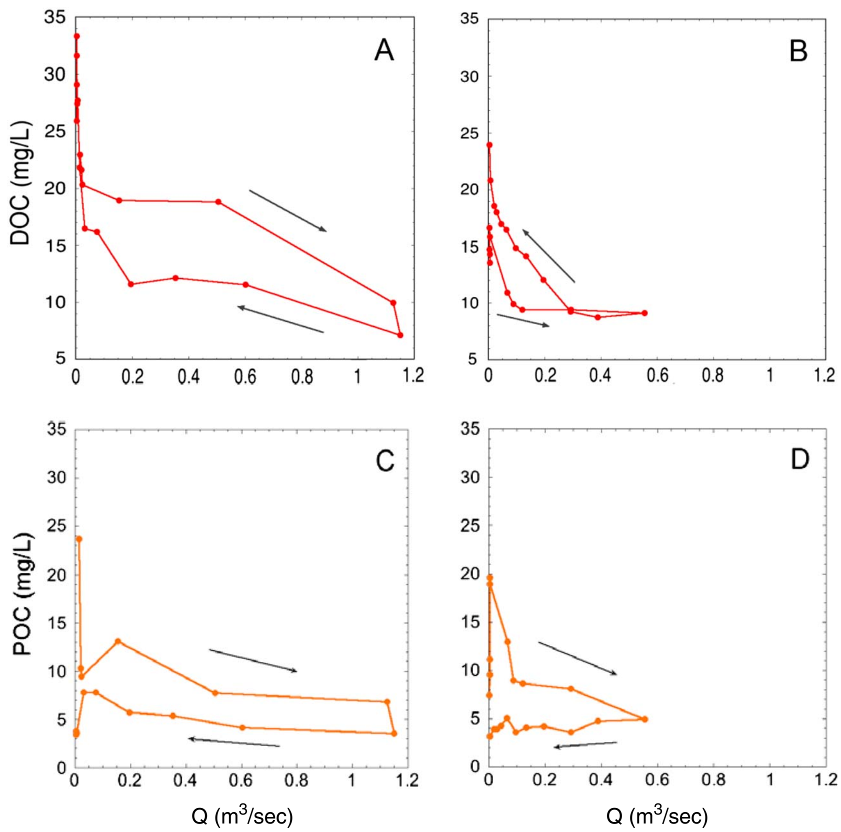

Figure 3. Hysteresis plots for DOC and POC concentrations with discharge (Q) during (a and c) Hurricane Irene and (b and d) Tropical Storm Lee.

aromatic and remained relatively constant. In contrast, $SUVA_{254}$ values remained relatively constant for TS Lee (Figure 2), and the DOC hysteresis shows a counterclockwise trend (Figure 3b). Counterclockwise solute-discharge hysteresis is usually associated with an initial influx of dilute surface runoff followed by the introduction of more concentrated soil water [*Evans and Davies*, 1998; *House and Warwick*, 1998]. In this case, the contribution of more dilute surface runoff was significant for the entire duration of the flow event, and the more concentrated falling limb represented the mixing of surface runoff with subsurface soil water.

[13] We measured relatively high $SUVA_{254}$ values over the 2 week period, especially in runoff from TS Lee which had an average $SUVA_{254}$ of 5.5 L mg C^{-1} m^{-1}. Typically, $SUVA_{254}$ has been reported to vary from 2 to 5 L mg C^{-1} m^{-1}, depending on the ecosystem [*Jaffé et al.*, 2008], but others have shown that agricultural runoff tends to have higher $SUVA_{254}$ compared with other land uses [*Vidon et al.*, 2008]. The increasingly aromatic nature (18 to 44%) of DOC exported from these croplands indicates a significant contribution from humic and fulvic soil acids as the storms progressed. While aromatic DOC typically generates less bacterial activity than aliphatic DOC [*Amon and Benner*, 1996], humic substances are highly susceptible to degradation and mineralization by photochemical reactions [*Allard et al.*, 1994]. Shading by photoreactive DOC can influence rates of primary production and impact thermal stratification in water bodies [*Caplanne and Laurion*, 2008]. Our study shows that agricultural fields can contribute disproportionately large amounts of DOC to watershed runoff during stormflow, with a significant labile and photoreactive fraction that can be ecologically significant downstream.

3.2. Particulate Organic Carbon Fluxes and Sources

[14] Hurricane Irene and Tropical Storm Lee exported similar quantities of POC (Table 1), and the values are statistically indistinguishable (within 10%) when POC export is normalized by total flow volume. Unlike DOC, POC concentration changed by over 1 order of magnitude throughout the two storms. The POC concentration was highest early on the rising limb of the hydrograph for Hurricane Irene and on the first two flow peaks for TS Lee (Figures 3c and 3d). Not surprisingly, periods of intense flow generated high concentrations of particulate organic matter. POC behavior was strongly controlled by erosion, as power law relationships between total suspended solid and POC had r^2 values of 0.74 and 0.88 for Irene and TS Lee, respectively (data not shown). Moreover, patterns of hysteresis for POC and total suspended sediment were nearly identical, indicating that POC and total suspended sediment are closely linked. Increased POC concentrations during rising and peak flows is most likely the signal of higher sediment inputs from rain splash and/or channel incision.

3.3. Organic Carbon Export During Irene and Lee

[15] Although both dissolved and particulate forms of organic carbon were relevant to the total carbon fluxes, DOC export was higher by a factor of approximately 2 (Table 1). During Hurricane Irene alone, the DOC flux from this cropland watershed was 12.7 kg ha^{-1}. For comparison, forested watershed export of DOC from Hurricane Irene was 3.3 kg ha^{-1} in south-central Maryland where 16 cm of rainfall fell [*Dhillon and Inamdar*, 2013] and 6.3 kg ha^{-1} in

central New York State [*Yoon and Raymond*, 2012] where 29 cm of rainfall fell. Annual DOC export from the forested watershed in Maryland, which has a similar climate to our study area averaged 10 kg ha yr^{-1} during 2008–2010 [*Dhillon and Inamdar*, 2013]. We measured more than twice this annual DOC export from our watershed during just 2 weeks in late summer 2011. DOC export during these consecutive storms was also higher than the annual export of 0.1 to 5.1 kg ha^{-1} quantified for tile-drained agricultural fields in the Midwest and 7.5 kg ha^{-1} annual DOC export typical of the mixed land use Minnesota River basin [*Dalzell et al.*, 2011]. While DOC fluxes are controlled partly by precipitation, we show that mass transport in ephemeral channels draining agricultural lands needs closer evaluation.

[16] The annual flux of C to the northern Atlantic Ocean from perennial rivers is 46 kg ha^{-1} drainage area [*Ludwig et al.*, 1996]. Given that we measured nearly this amount over just a 2 week period and that the Mid-Atlantic region commonly receives nor'easters and tropical storms that deliver ~20 cm of rainfall per event, our data indicate that event-scale export of carbon from ephemeral channels is substantial at the regional scale. There are 2.6 million ha of cropland in the Chesapeake Bay Watershed alone (CBW); if all cropland in the CBW land exported organic carbon at the same rate as our study site, then 86,000 metric tons of organic carbon could have been mobilized during this 2 week period. While we cannot definitively explain the immediate fate of the carbon exported during these tropical storms, we speculate that some may be temporarily stored in the wetlands or channel of the lower James River Estuary.

4. Conclusions

[17] During the first of two consecutive tropical storms, DOC export from an agricultural field was more than double the flux measured from forested watersheds for the same hydrologic event and larger than the annual flux measured in perennial waterways in the same climate zone. For this agricultural watershed in late summer, with a large pool of soluble organic matter in the form of both crop residues and soil components, the ratio of DOC to POC was greater than unity throughout the storms, which contrasts with the POC-dominated export shown for forested lands during extreme hydrologic events. DOC exported from the cropland watershed had a large photoreactive carbon component, which has implications for ecosystem functioning in downstream habitats. Given that croplands make up a large fraction of Earth's land surface and climate change scenarios include shifts in the frequency and magnitude of storms, more efforts are needed to evaluate how landscape modification and global change will impact terrestrial carbon cycling at watershed scale.

[18] **Acknowledgments.** The authors thank the Virginia Environmental Endowment for financial support.

[19] The Editor thanks Peter Raymond and Brent Dalzell for their assistance in evaluating this paper.

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