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Storm event impact on organic matter flux, composition and reactivity in Taskinas Creek, VA

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Storm Event Impact on Organic Matter Flux, Composition and Reactivity in Taskinas Creek, VA

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Abstract

Carbon export from the land to the ocean are an important part of the global carbon cycle, linking terrestrial watersheds and the global carbon cycle. Burial of terrestrial organic carbon represents a long term sink for atmospheric CO_2. Approximately 0.4 Pg Cy^{-1} is delivered to the global ocean from rivers, equally divided between POC and DOC. However, the amount of carbon entering the ocean is a small portion of the total amount entering rivers from the terrestrial environment, suggesting a large amount of processing in inland waters and estuaries. Most monitoring efforts have focused the processing of organic matter on baseflow conditions. However, recent studies have shown that POC and DOC exported during storm events, a small time period during a hydrologic year, can account for the majority of the annual carbon exported from small watersheds.

This dissertation identifies the impact different magnitudes of storm events have on the source, composition and reactivity of organic carbon released to downstream waters from the terrestrial environment at Taskinas Creek, Virginia. The proximity of the Creek to the York River estuary, the changes in water table at the site, along with the small size of the watershed allowing opportunity to examine the connectivity between the watershed processes and delivery of organic matter made the site ideal for identifying how hydrology and environment alter POM and DOM export and reactivity. The sources, composition and flux of DOM and POM were measured during four storm events of different magnitudes to determine how events impacted the sources and fluxes of organic matter and the % reactive DOC exported. Events of different magnitudes with varying sources of DOC and POC had similar % reactive DOC that was not predicted using excitation emission spectroscopy. The events resulted in DOC fluxes 1.5-490 fold higher than baseflow. POC fluxes for storm were 6.7-55 times higher than DOC fluxes. Although the % reactive DOC did not increase during storm event conditions, coupled with the overall flux, storm events represent a considerable pulse of % reactive DOC to downstream waters, well above baseflow levels. When considered with increases in storm intensity due to climate change, storm event fluxes of reactive OM may have broad impacts on estuaries and the global carbon cycle through changes in carbon storage.

Storm Event Impact on Organic Matter Flux, Composition and Reactivity in Taskinas Creek, VA

Chapter 1:Introduction

Carbon export from the terrestrial biosphere to the oceans is an important component of the global carbon cycle. Rivers and estuaries provide important links between terrestrial watersheds and the coastal ocean [*Bauer et al. 2013*, *Blair and Aller 2012*; *Seitzinger and Harrison 2008*] and the global cycles of carbon and nitrogen [*Aufdencampe et al., 2011; Cole et al., 2007; Battin et al., 2009; Raymond et al., 2013, Seitzinger and Harrison 2008, Meybeck 1982)*]. Burial of terrestrial carbon represents a long-term sink for atmospheric CO_2 and knowledge of the fate of terrestrial organic carbon is critical for modeling biogeochemical processes. An estimated 0.4 petagrams of carbon ($PgCy^{-1}$), evenly divided between particulate organic carbon (POC) and dissolved organic carbon (DOC) [*Richey et al., 2004*], as well as 40-65 Tg N yr^{-1} [*Seitzinger and Harrison 2008*], are delivered from rivers to the coastal ocean annually. However, previous studies using isotopes and biomarkers to examine riverine and seawater end-members have found little evidence for terrestrial OM [*Hedges et al., 1997*] in the open ocean. The amount of carbon entering the ocean from rivers is only a small portion of the total amount entering rivers from the terrestrial environment [*Aufdencampe et al., 2011*].

Indeed, the amount of terrestrial organic carbon exported to coastal waters is a small amount of the total carbon processed in inland waters and estuaries [*Cole et al. 2007, Cai 2011*]. Many estuaries are considered to be net heterotrophic, with large amounts of carbon processed within them and released as CO_2 [*Cai 2011*]. POC can be sequestered in inland systems and depositional areas, or transported and deposited in coastal systems. During transport, deposition and resuspension, DOC can be leached from POC [*Jung et al., 2014*] and processed and released as CO_2 in inland and coastal

waters [*Mayorga et al., 2005; Raymond et al., 2013*], making understanding POC and DOC sources and fluxes important. Understanding the connections between rivers, estuaries and the coastal oceans and their importance in carbon and nitrogen cycling *[Hedges et al. 1997],* is critical to developing budgets and predicting delivery and the effects of climate change on estuaries and coastal waters.

Despite the importance of DOC and POC the key factors controlling the fluxes, compositional characteristics, and reactivity of terrigenous DOM and POM in river and estuarine systems are poorly understood [*Richey et al., 2002, Eimers et al., 2008, Bellamy et al., 2005; Skelvalke et al., 2005*]. Once exported from watersheds, terrigenous organic matter (OM) components may be recycled by bacteria and respired or incorporated into microbial and higher organism food webs [*Dagg et al., 2004; del Giorgio and Pace, 2008; Nakagawa et al., 2007*] serving as carbon (C), nitrogen (N), and phosphorus (P) sources (Figure 1 [*Dagg et al., 2004, del Giorgio and Pace, 2008; Nakagawa et al., 2007; Azam et al., 1983; Pomeroy, 1974; Fenchel, 2008*]. Bacterial Growth Efficiency (BGE), the proportion of total DOC utilized that is assimilated into microbial biomass, is high in estuaries and coastal zones (~27-34%) compared to the open ocean (~15%) [*del Giorgio and Cole 2000*], indicating that terrigenous DOM delivered to rivers and estuaries may support microbial food webs [*del Giorgio and Pace, 2008; Maranger et al., 2005; Butman et al., 2007; Thottathil et al., 2008*]. Studies have shown that, once released from the preservational environment (i.e., soils, POM), even highly aged DOM, such as material sorbed to soil particles, may be rapidly consumed in aquatic settings [*Butman et al., 2007; Thottathil et al., 2008; Petsch et al., 2001, Schillawski and Petsch*

2008]. Alternatively, terrestrial DOM may be altered by abiotic processes such as photochemical transformation [*Opsahl and Benner, 1995; Moran et al., 2000]*, flocculation [*Sholkovitz , 1976*] and sorption [*Shank et al., 2005*] or remain largely unaltered as it is exported to the coastal or open ocean [*Hedges et al., 1997*].

Understanding the long-term variability in OM is complicated by climate change and its expected impacts on hydrologic conditions (i.e., increased frequency of high intensity events, changes in seasonal distribution of flow) [*Boesch et al., 2001; Kemp et al., 2005; Najjar et al., 2010; Stocker et al., 2013*]. Changes in hydrology are expected to impact the delivery of terrestrial organic matter to downstream aquatic environments [*Canuel et al., 2012*]. For example, northern hemisphere rivers have undergone a dramatic rise in the amount of DOC exported in the past 1-2 decades [*Worrall et al., 2003; Worrall et al, 2005; Evans et al., 2005*], along with increases in river water color [*Hongve et al., 2004*] and decreases in soil OM [*Knorr et al., 2005*]. In some regions, increases in river DOC flux have also been accompanied by increases in dissolved organic nitrogen (DON) [*Worrall et al., 2009*] and decreases in dissolved organic phosphorus (DOP) [*Dillon and Molot, 2005*]. Consequently, the observed variations in the subcomponents of DOM over the past 1-2 decades suggest that the net flux of DOM may be altered by climate change. Short-term and long-term variability in DOM and POM export from watersheds to rivers, estuaries and associated coastal waters may alter the sources, ages, chemical composition, and reactivity of this OM during its transport from terrestrial to aquatic systems [*Raymond and Bauer, 2000; McAllister et al., 2004; McCallister et al., 2006; Dhillon and Inamdar 2014*].

In addition to OM changes found in many regions, climate change is also expected to increase the frequency and intensity of eutrophication and hypoxia [*Diaz et al., 2001; Hagy et al., 2004; Diaz et al., 2008; Pyke et al., 2008; Najjar et al., 2010*]. In the Chesapeake Bay, climate change is predicted to increase the intensity of storms, which will increase the delivery of nutrients (N and P) that enter the Bay through runoff and stream discharge [*Najjar et al., 2010,Boesch et al, 2001; USEPA, 2000*]. Along with increased runoff, climate change will also influence the delivery of OM from land due to increased erosion and loss of wetlands through sea level rise [*Nicholls et al., 1999; Scavia et al., 2002; Neubauer and Craft, 2009*]. As a result, there is a broad need to understand climate change and its interactions with organic matter and nutrient delivery on a global basis.

Management efforts have focused on controlling and monitoring the inputs of nitrogen and phosphorus in order to avoid increased eutrophication and hypoxia within estuaries such as Chesapeake Bay. However, the focus on nutrient pollutants such as nitrogen and phosphorus has limitations for managing the problems of eutrophication and hypoxia because it neglects other potential contributions to water quality problems. Organic matter delivered from the surrounding watershed to the estuary (allochthonous OM) may fuel eutrophication and hypoxia in several ways including: (1) remineralization to inorganic forms, which subsequently stimulate primary production and lead to excess organic matter accumulation in the estuary, and (2) respiration or decomposition of allochthonous OM, which consumes dissolved oxygen. Thus, understanding the factors that control OM delivery and composition, including potential interactions with climate

change, is necessary for developing sound management practice [*Stanley et al., 2012*]. However, despite the recognized importance of DOM to the estuarine ecosystem, it is often difficult to predict how DOM delivery will impact downstream waters, since its composition is highly variable thereby influencing its chemical properties and biological availability [*McKnight et al., 1985; McKnight et al., 2001; Fellman et al., 2008; Yamashita et al., 2010*].

DELIVERY OF DOC AND POC FROM THE WATERSHED TO THE ESTUARY

In addition to active monitoring of nitrogen and phosphorus, improving our understanding of how organic matter released to rivers and estuaries varies with hydrologic conditions is necessary in order to predict, improve and manage water quality and predict changes in biogeochemistry. Until recently, monitoring efforts have focused on baseflow rather than stormflow sampling, and focus primarily on DOC fluxes when events are measured [*Jung et al., 2014*]. However, recent data suggest that storm events can account for 71-90% of the total DOM released from streams annually [*Dalzell et al., 2007; Fellman et al., 2009; Raymond and Saiers, 2010*], and increase POM fluxes by 6-8 fold [*Dhillon and Inamdar 2014*]. Recent work has suggested that DOC and POC may respond differently to storm events [*Dhillon and Inamdar 2013; Dhillon and Inamdar 2014*]. Since multiple studies have shown that DOM is readily leached from POM [*Jung et al., 2014, Butman et al., 2007, Schillawski and Petsch, 2008*] and can be an additional supply of DOC during transport and resuspension, and that POM can be a fuel for food webs and a mechanism for CO_2 sequestration, understanding the controls on POC

transport is important. Moreover, since climate change is expected to increase the variability of precipitation events and tropical cyclones may increase in frequency [*Lozano et al., 2004, Najjar et al., 2010*], there is increased need to understand how "events" influence the delivery of organic matter to estuaries. An understanding of the concentration, composition and reactivity of DOM and POM components released during storm events is needed in order to predict potential biogeochemical responses.

Recent work in rivers and streams, monitoring storm events and comparing them to baseflow events, has provided some information about how organic matter delivery and composition may be altered during storm events in various environments. Storm events have been documented to increase stream DOC and POC concentrations and flux, and POM and DOM composition [*Fellman et al., 2009; Hernes et al., 2008; Hinton et al., 1998; Buffam et al., 2001; Worrall et al., 2002; Inamdar and Mitchell, 2007, Dhillon and Inamdar 2014*]. However, the components that are altered are not constant for each storm event because the sources of DOM and POM to stream waters change depending on hydrologic conditions [*Easthouse et al., 1992; Vidon et al., 2008; Dhillon and Inamdar et al., 2014*].

Previously, knowledge of organic matter composition has been limited by the challenges associated with characterizing it fully [*Hedges et al., 2000; Minor et al., 2014; Stubbins et al., 2014*]. For POM and DOM, stable and radiocarbon isotopes in addition to C:N ratios have been successfully used to characterize sources and age of DOM and to identify changes in composition [*Sanderman et al., 2009, Raymond and Bauer* 2001]. However, a limitation of analysis at the bulk level is that it can be difficult to resolve

contributions from specific sources. Indeed, for OM, identifying and isolating the moieties has been challenging [*Hatcher et al., 2004, and references therein*], although new tools continue to be developed.

Recent work using the fluorescence of DOM, a tool borrowed from studies in marine systems [*Coble et al., 1990; Coble 1996; Coble et al., 1998; Murphy et al., 2008*], has been able to track relative contributions of organic matter from soils, vegetation, and phytoplankton to stream DOM. Differences in the excitation and emission spectra from forested, wetland and agricultural watersheds have been identified [*Stedmon et al., 2003; Fellman et al., 2008; Yamashita et al., 2010*] and used to understand how watershed characteristics impact DOM composition. Fluorescence has also been used to track how different allochthonous organic matter sources are altered along stream paths under baseflow and stormflow conditions [*McKnight et al., 2001; Ohno 2002; Stedmon and Bro, 2003; Cory and McKnight, 2005; Stedmon and Bro, 2008; Fellman et al., 2010; Jaffe et al., 2008*]. Fluorescence combined with isotopic analysis of bulk DOM has shown that groundwater contributes DOM to streams during baseflow, while DOM is generally of recent origin and from upper soil horizons, throughfall, and leaf litter during stormflow [*Aitkenhead-Peterson et al., 2005, Schiff et al., 1997; Palmer et al., 2001; McGlynn & McDonnell 2003; Worrall et al., 2003; Fraser et al., 2001*]. This change in DOM sources results in measurable changes in the composition of DOM. DOC released from upland environments during storm flow is consistently higher in humics than during baseflow [*Fellman et al., 2009*], while DOC from wetlands has been found to be more enriched in proteins and slightly depleted in humics during storm flow relative to

baseflow [*Fellman et al., 2009*]. These changes in the composition of DOM likely have an impact on its reactivity.

Experiments examining the reactivity of organic matter during storm events versus baseflow have found an overall increase in the lability of DOM released during stormflow [*Schiff et al., 1997; Fraser et al., 2001; Worrall et al., 2003*]. However, DOM lability has been found to vary with more than just streamflow. In a comparison of two storm events in wetlands and forested watersheds, biodegradable carbon (BDOC) was dependent on total stream discharge, the antecedent conditions in the watersheds, and seasonal changes in organic matter [*Fellman et al., 2009]*. Additionally, organic matter degradation may be enhanced both by the addition of nutrients from anthropogenic sources, or through photochemical reactions that produce lower molecular weight compounds [*Lindell et al., 1995; Tranvik, 1998; Moran and Zepp, 1997; Bertilsson and Tranvik, 2000, Lu et al., 201*3] and/or nutrients [*Bushaw et al., 1996; Stedmon et al., 2007*]. However, photochemical reactions do not always increase the lability of DOM in surface waters. In surface waters with large amounts of terrestrial organic matter, photochemical reactions with DOM generally increase reactivity and support bacterial growth [*Mopper et al., 1991; Moran and Zepp, 1997; Tranvik and Bertilsson, 2001*], while in regions with considerable algal production, photochemical reactions seem to decrease DOM bioavailability [*Keil and Kirchman, 1994; Naganuma et al., 1996; Tranvik and Kokalj, 1998, and Tranvik and Bertilsson, 2001*]. Additionally, sources of DOM, including POM, have varying availability of DOM components (DOC, DON, and DOP), which may impact DOM reactivity in cases where C, N, or P is limited to bacteria

[*Fellman et al., 2008a*]. Consequently, the sources of DOM and how they are controlled by hydrology and watershed characteristics are important for determining the bioavailability of DOM.

In addition to differences in the composition of DOM delivered during baseflow and stormflow, DOM and POM amounts, quality and sources may be impacted by antecedent conditions and event magnitude. While storms generally increase the amount of DOC and POC found in surface waters, differences in antecedent conditions can impact the response. Antecedent hydrologic conditions are known to impact basin storage capacity, hydraulic conductivity of soils, connectivity of surface soils and groundwater, runoff pathways, and the constituents available within the catchment for export [*Buttle et al., 2001; Soulsby et al., 2003; Welsch et al. 2001; Weiler and McDonnell, 2007; Vidon et al., 2009*]. As a result, understanding the relationship between antecedent conditions and stormflow DOC and POC is important.

However, the relationship between antecedent conditions and stormflow generated DOC is not easily predicted. In a study of Big Pine Creek, Indiana, DOC export was reduced in spring when the basin was subject to greater moisture and higher stream flow [*Dalzell et al., 2007*] compared to other times of the year. High moisture content, which tends to increase the water table, was also observed in boreal peatlands in the spring and the fall [*Jager et al., 2008*]. Within these peatlands, the high moisture content and higher water table were considered to be the factors that led to observed decreases in DOC export after storm events. Given these observations of antecedent conditions, it might be expected that DOC and nutrients should increase during storm

event following drought conditions. However, this is not necessarily the case. In studies of British rivers with substantial increases in DOC over the past decades, drought conditions did not cause an overall increase in DOC [*Worrall and Burt, 2008*]. Because upland environments do not follow a linear trend in their response to changing hydrologic conditions and DOC export, it is necessary to unravel how different topologies, magnitude of events, flowpaths and sources of DOM in uplands impact the response of DOC to changing hydrologic conditions both during the current and predicted climate.

In order to predict how organic matter associated with storm events will impact downstream waters under changing climate conditions, additional research was conducted to determine: 1) whether measurements such as excitation emission spectra (EEMs) provide useful proxies for predicting reactivity under a range of environmental conditions; 2) how storm events impact fluxes of DOC and POC and their reactivity in downstream environments where light and nutrients may be more available, and 3) whether the magnitude of storm events impacts the fluxes of POC and DOC differently.

APPROACH

Study Site

A first-order stream and sub-watershed within the Taskinas Creek watershed was chosen for the study. This stream joins the main body of Taskinas Creek, which discharges directly into the York River Estuary (Figure 2**)** and then into Chesapeake Bay. A water quality monitoring station near the mouth of Taskinas Creek is managed by the Chesapeake Bay National Estuarine Research Reserve System (CBNERRS). Within the

York River State Park, which is adjacent to Taskinas Creek, real-time weather, barometric pressure and precipitation data are provided by CBNERRS. The water table at the study site varies as a function of season and precipitation. The proximity of the Creek to the York River estuary, seasonal changes in water table at the site, along with the small size of the watershed allow an opportunity to examine the connectivity between the watershed and delivery of organic matter to streams making the site ideal for testing hypotheses about how hydrology and environment alter the export, composition, reactivity and sources of DOM and POM to downstream waters. The main chapters of this dissertation are structured around three study objectives: (1) examine DOC export and reactivity during three moderate storm events and the use of EEMS as a proxy for DOC reactivity, (2) quantify DOM flux and reactivity during a large storm event, Hurricane Irene, and (3) compare of POC fluxes during two storms of different magnitudes with similar antecedent conditions.

Chapter 2: Chapter 2 examines three small events that occurred at the study site during May, August and November of 2011. EEMS components were used to characterize initial sources of DOM, and demonstrate how those sources changed over the hydrograph for each event. Then, incubations with two treatments, one with light and microbial exposure, and the other with light, microbial and nutrient exposure, were conducted to examine DOC reactivity. Initial component composition did not predict incubation % reactive DOC results, suggesting that EEMS components are not always reliable

indicators of % reactive DOC released during storm events, particularly under light exposure.

Chapter 3*:* Chapter 3 examines the impact of a large event, Hurricane Irene, that occurred in the watershed during 2011, on DOC, DON and DOP flux and % reactive DOC export to the downstream watershed of the York River. A large component of the overall flux was reactive, but was not demonstrably more reactive than DOC exported under baseflow conditions. Additionally, EEMS components were used to characterize initial sources of DOM, and demonstrate how sources changed over the hydrograph for this event. Similar to moderate events, EEMS measurements did not predict % reactive DOC during this large magnitude event.

Chapter 4*:* Chapter 4 examines the impact one small and one large event (small event in August vs Hurricane Irene), with similar antecedent conditions, have on POC, PN and DOC. POC, PN and TSS covaried during the August event. During the Irene event, POC sources varied with rainfall and the hydrograph but did not covary with total suspended solid (TSS) concentrations. DOC, however, correlated with precipitation and discharge during Hurricane Irene. Results support work suggesting DOC sources and POC sources are distinct and vary between events.

Chapter 5: Chapter 5 summarizes the key findings of this research and discusses: 1) the ability of EEMs components to predict reactivity when photochemical reactions are

considered; 2) how large storm events impact fluxes of DOC and downstream reactivity, and 3) how the magnitude of events impact POC and DOC fluxes differently.

Overall, this work improves our understanding of the effects of hydrology, antecedent conditions, and abiotic and biotic factors on DOM and its reactivity in river and estuarine systems. This information contributes to an improved understanding the linkages between terrigeneous and marine environments and the coastal carbon budget.

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Figure 1-1. Once exported from watersheds, terrestrial DOM (brown) can be taken up by the microbial loop or remain altered and exported to the coastal ocean.

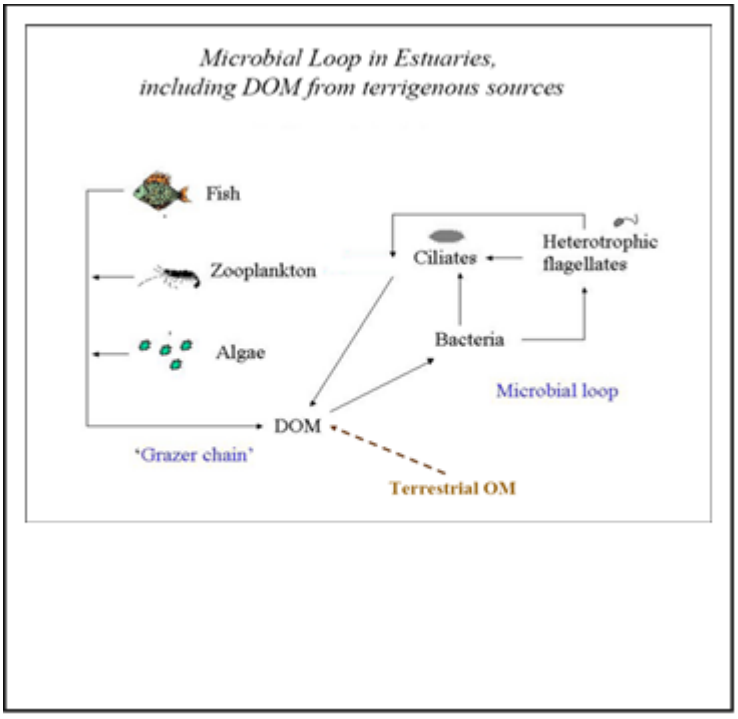
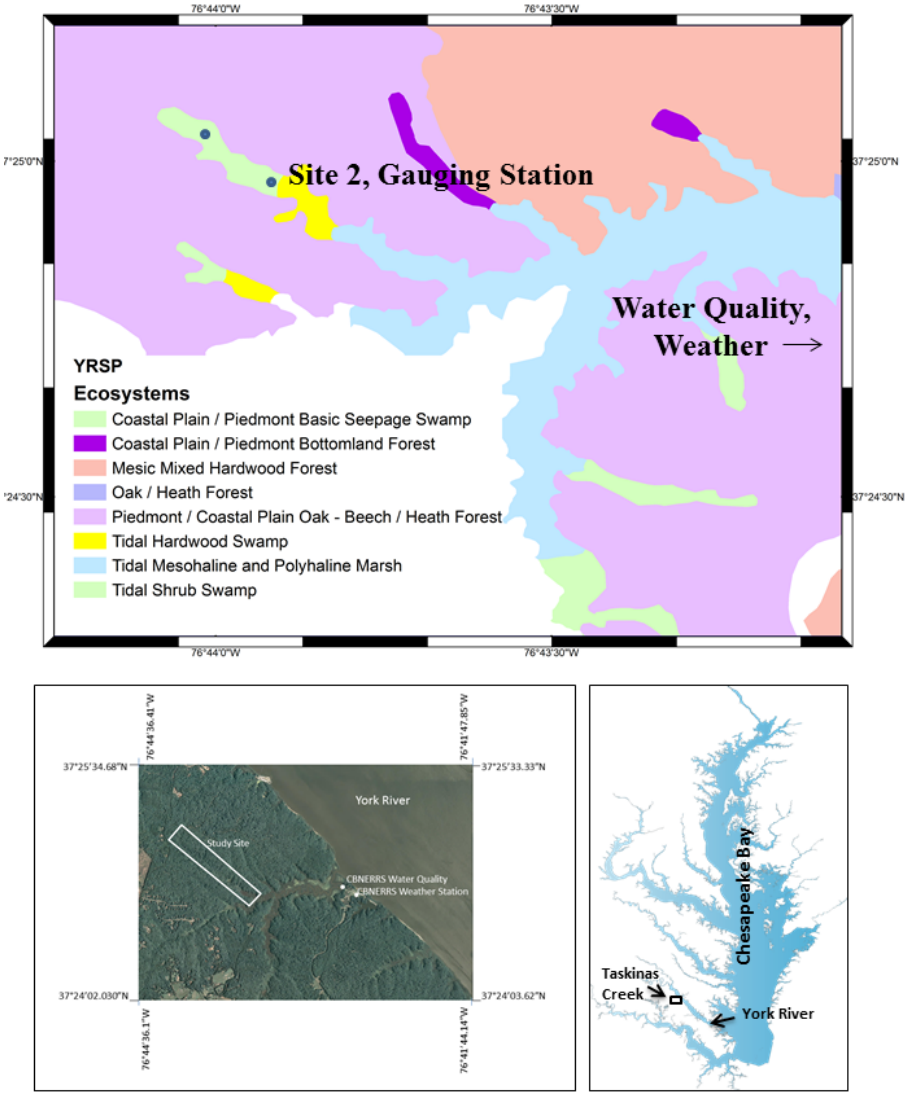


Figure 1-2. The study site at Taskinas Creek is located within a first-order stream (a), which feeds into York River (b) within the Chesapeake Bay, VA (c).



Chapter 2: Reactivity of dissolved organic carbon during baseflow and stormflow in a small stream and the use of EEMS to evaluate reactivity

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ABSTRACT

Samples were collected in a perennial stream to determine the composition of dissolved organic matter transported during moderate rain events (5-14 mm rainfall) in the watershed of Taskinas Creek, Virginia, and the impact composition had on the reactivity of dissolved organic carbon (DOC) present in stormwater flow relative to baseflow. Excitation emission spectroscopy (EEMS) was used to generate matrices for baseflow samples collected during 2009-2011 and for storm events in May 2011, August 2011 and November 2011. DOC concentrations were similar across the three events (1.85±0.44 to 3.92±2.12 mg/L) and across different stages of the hydrograph (1.83 to 2.32 mg/L during baseflow, 1.42 to 3.15 mg/L during rising limb and 2.32 to 6.32 mg/L during falling limb. These concentrations translated to total exports of DOC of 150 mg (May), 114 mg (August), and 177 mg (November). Average exported DOC during the storm events exceeded fluxes during baseflow over an equivalent time period (142 ± 39.3 vs. 79.7±31.1). Incubation experiments (7-day) were used to measure % reactive DOC with light and microbial treatments (LM) and light, microbial and nutrient amendments (LMN). Percent reactive DOC ranged from 22.3 to 90.7 in May, 19.2 to 32.1 in August and 15.0 to 86.0 in November with similar values during LM and LMN incubations ($p>0.05$), suggesting that light, not nutrients, influenced reactivity. Percent reactive DOC was also similar across stages of the hydrograph and between events, although % reactive DOC was notably higher during the rising limb of the hydrograph during May and November events. PARAFAC components showed changes in DOC composition during the rising and falling hydrograph of each event, with Component C1 dominating the total

fluorescence. However, composition of DOM as determined by PARAFAC was not correlated with % reactive DOC, and was not able to predict the reactivity of DOC at this site during LM and LMN incubations.

Keywords

DOC, Watersheds, Reactivity, Photochemical alteration, Storm Events, Baseflow, Excitation Emission Matrix, Parallel Factor Analysis (PARAFAC)

Key Points

1. DOC fluxes increased 1.5 to 2.3-fold during moderate storm event flows in Taskinas Creek, Virginia relative to baseflow conditions.
2. Incubation experiments showed no difference between % reactive DOC during LM and LMN conditions.
3. PARAFAC models showed measurable changes in the composition of DOM during the storm events. However, these changes did not correlate with changes in % reactive DOC during photochemical and microbial incubation experiments.
4. These experiments indicate that PARAFAC components previously linked to reactivity may need to be re-examined for application in systems where light is an important determinant of DOC reactivity.

INTRODUCTION

Dissolved organic matter transported by streams affects water quality and ecosystem processes [*Stanley et al., 2012*] and releases CO_2 to the atmosphere as a result of heterotrophic respiration [*Cole et al., 2007; Tranvik et al., 2009*]. Storm events are known to increase DOC concentrations and stream discharge, accounting for up to 86% of the annual DOC flux from watersheds [*Raymond and Saiers 2010*]. With the probability of increased fluxes of carbon resulting from higher frequency of large storm events due to climate change [*Najjar et al., 2010*], changes in the fluxes and reactivity of DOC will likely have a significant impact on carbon export from land to the coastal ocean. DOC concentrations and sources vary across storm events as well as during the rising and falling hydrographs associated with individual storms [*Dhillon and Inamdar 2013; Inamdar et al., 2011*]. As a result, the composition and the reactivity of DOC can vary over the storm hydrograph and relative to baseflow conditions. Baseflow sources of DOC generally derive from groundwater, with most storm events causing a transition in DOC sources in streams from groundwater to throughfall, then to shallow pathways through upper soils and leaf litter, followed by recovery [*Inamdar et al., 2012; Inamdar et al., 2007*]. This changing composition and flux of DOC during storms is expected to increase DOC reactivity compared to baseflow. However, these observations are based on a relatively small number of recent studies. The changing nature of DOC composition and reactivity during storm events and the influence of storms on DOC reactivity requires further investigation in order to predict and model ecosystem responses broadly.

Recent investigations have focused on the biodegradable component of DOC (BDOC) to determine the impacts DOC fluxes have in global and regional carbon budgets and on ecosystem processes. In one stream where storm events were sampled, BDOC increased significantly during storm events for 83% of storms [*McLaughin and Kaplan 2014*]. In other locations, BDOC has also been shown to increase during storm events [*Buffam et al. 2001*], whereas in some streams, BDOC decreased during storms [*Leff and Meyer 1991; Wiegner et al., 2009*]. These differences in BDOC may be due to changes in the composition and sources of DOC during storm events [*Qualls and Haines, 1992; Neff et al., 2006; Fellman et al., 2009; Sanderman et al., 2009*] as well as other processes. Explanations for the variations in DOC reactivity during storms have included: different molecular components being utilized during events [*Sleighter et al., 2014*], variations in source environments [*Stedmon et al., 2003; Fellman et al., 2008; Yamashita et al., 2010*] and the impact of photochemistry on DOM [*Mopper et al., 2000*]. However, photochemistry is not generally considered in BDOC experiments, because BDOC experiments are usually conducted in the absence of light.

Studies using excitation-emission spectra (EEMS) have offered many insights into the composition of DOM. EEMS have been used to provide information about the sources and composition of DOM and to assess the biodegradability of DOM, with protein-like fluorophores correlating with % reactive DOC [*Balcaryczyk et al., 2009; Fellman et al., 2009; Petrone et al., 2011*]. EEMS combined with BDOC analyses, for example, have shown that humic-like and protein-like components of PARAFAC models are correlated with the relative change in reactivity [*Fellman et al., 2009a and 2009b*]. In

these cases, EEMS analysis used alone may be applied to estimate DOC reactivity. This offers tremendous benefit because EEMS analyses require only a small aliquot of water compared to BDOC incubation experiments, resulting in less field effort and lab processing compared to running BDOC experiments. However, the absence of information about the molecular signatures associated with PARAFAC components may be a limitation of EEMS analysis in some cases [*Stubbins et al., 2014*].

In a system like the York River Estuary and its watershed, where water and analytes in the subwatershed have a short transit time to the downstream estuary [*Herman et al., 2007*], identifying the reactivity of DOM is important for understanding and predicting the effects of storm events on water quality in the downstream estuary. During increases in stream discharge (Q), the small perennial streams that drain into the York have the potential to transport reactive DOC from surface soils and leaf litter. The downstream York River Estuary, like many other coastal waters, is influenced by nutrient loadings from its watershed, delivery of contaminants in stormwater runoff, and periods of low dissolved oxygen. For resource managers, including fisheries managers, understanding how DOC may fuel heterotrophs during baseflow and storm delivery is an important consideration. DOC loadings during storm events may result in the consumption of dissolved oxygen, resulting in the loss of habitat for consumer organisms [*Paerl et al., 2005*]. DOC loadings also have the potential to influence light, pH, and metabolism [*Stanley et al., 2012*]. Consequently, methods such as EEMS that provide a quick and easy assessment of DOC source and composition and the impact they may have on bioreactivity offer a great advantage. However, to our knowledge EEMS has

only been shown to be effective in determining the biodegradability of DOC in incubation studies conducted under dark conditions. Photochemistry has been shown to influence the reactivity of DOC across a range of systems [*Opsahl and Benner, 1995; Moran et al., 2000; Lu et al., 2013*], suggesting the need for studying the relationship between EEMS and DOC reactivity in the presence of light under a range of environmental conditions.

Consequently, we sampled three storm events to determine the effects of photochemistry and biodegradation on % reactive DOC, both with added nutrients that reflected conditions in the downstream estuary, and without added nutrients (i.e. under ambient nutrient concentrations). Simultaneously, we assessed whether changes in PARAFAC components were able to predict the reactivity of DOC.

METHODS

Study Site Description

The study site was located within a first order forested subwatershed of Taskinas Creek, a managed component of the Chesapeake Bay National Estuarine Research Reserve (CBNERR), which drains directly to the York River estuary, Virginia, a tributary of southern Chesapeake Bay (see Site 2; Figure 2-1). Nontidal portions of the study site, 54 ha in area, contain three dominant ecosystem types, described as oak-heath forest, oak-beech-heath forest and basic seepage swamp, which drain into a tidal hardwood swamp and a mesohaline to polyhaline marsh system (Figure 1; *Patterson 2011*). The upper reaches of the study stream lie within an oak-beech-heath forest characterized by

mesic ravine slopes and ridges dominated by a hardwood canopy (e.g., *Fagus grandifolia, Quercus var., Acer var*.) mixed with some pine (e.g., *Pinus taeda and virginiana*) and contains an understory of American holly (*Ilex opaca*) and mountain laurel (*Kalmia latifolia*) [*Myers et al. 2008*]. Downstream, the stream traverses a basic seepage swamp that exhibits temporary and seasonal flooding, and has a mixed hardwood community including red maple (*A. rubrum*), black gum (*Nyssa sylvatica*), green ash (*Fraxinus pennsylvanica*), a variety of oak (*Quercus var.*) and other more water tolerant species [*Myers et al. 2008*]. Flow continues from the seepage swamp through tidal hardwood swamp and mesohaline marsh ecosystems prior to discharge in Taskinas Creek. The sandy bottom stream is relatively well defined with short reaches of subterranean flow in the upper reaches and evidence of bed migration in the broad (~25 m) nontidal swamp floodplain.

Soils within the study site primarily consist of poorly drained soils of the Johnston complex in the nearly level (0-2 % slopes) floodplain region and deep, moderately drained Craven complex soils in regions with moderate slopes (2-10% slopes), and well drained Emporia complex soils along the adjacent steep (25-50% slopes) ravines [*Hodges et al., 1985*]. Floodplain soils have high organic content (~27%) [*Myers et al. 2008*], exhibit a high water table, and frequently flood as a result of intense rainfall. Properties of the Emporia complex soils include low organic matter content, deeper water tables (~ 0.9-1.5 m), and high erosion and runoff potentials [*Hodges et al., 1985*]. Texturally, Johnston complex surface and subsoils (upper 0.9 m) are black silt loam with fine sandy loam substratum to a depth of 1.5 m. Craven complex slopes are generally silty loam with

depths to 0.9 m [*Hodges et al., 1985*]. Surficial soils of the Emporia complex are typically fine sandy loam, with loamy subsoils and sandy clay loams extending to a depth of 1.9 m [*Hodges et al., 1985*]. This study was conducted at the downstream edge of the seepage swamp site (Figure 1), from the center of the stream channel. The channel ranged from a depth of six inches to four feet during the study period.

Hydrology

A near continuous record of stream flow from 2009-2011 was generated in the dominant stream flow channel at the most down gradient point of Site 2 (see Figure 2-1 for locations of Site 2 and gaging station) through development of a stream stage-discharge (Q) rating curve. Stream water levels at Site 2 were recorded at 15 minute intervals by a Solonist® level logger deployed in a stilling well with water levels corrected for changes in atmospheric pressure. In channel field measurements for stream Q followed both velocity-area [*Buchanan and Somers, 1969*] and salt dilution [*Moore, 2005*] methods with the selected method depending on water depth conditions. The estimated error for the velocity area method is estimated to be ~40%, with the salt dilution method resulting in ~20% error for this study site.

During the November event, the Solonist sensor was disrupted. Consequently, a second approach was used to estimate stream and floodplain Q at Site 2; the USDA/NRCS TR-55, a single-event rainfall-runoff small watershed hydrologic model was utilized [*Cronshey, 1986*]. While originally developed for agricultural and developing watersheds, TR-55 has been successfully applied to low gradient, forested

watersheds [*Corbett et al. 1997*]. TR-55 model parameters incorporated local information and reflected current pre-storm conditions; model parameters and data sources are provided in Supplemental Table 2-1. The TR-55 model estimation for this event resulted in ~45% error. The most conservative estimate of error was applied to all hydrologic modeling in this study, which was 45%.

Meteorological data were collected by the CBNERR maintained Campbell Scientific UT10 weather station located adjacent to the study site in York River State Park (Figure 1); precipitation was measured with a TE 525 tipping bucket rain gage recording at 15 minute intervals. Water level and water quality data for tidal waters within Taskinas Creek and the adjacent York River proper were collected at 15 minute intervals with YSI 6600 V2 data sondes maintained by CBNERR. Total stream discharge during baseflow and storm conditions are reported on Table 1.Temperature and photosynthetically active radiation (PAR) (mmole light energy/m^2) averaged over the seven days preceding each event, are reported on Table 2-1.

Sample Collection and Analysis

Discrete water samples were collected within the primary stream channel throughout the three events including pre-storm baseflow conditions. Samples were collected into combusted (450 °C) glass bottles at two-hour intervals using portable ISCO™ automatic samplers. Runoff and throughfall samples were collected in combusted glass bottles during storm events. Soil pore water and groundwater were collected from lysimeters and groundwater wells during baseflow conditions over the

course of the study. All samples were removed from the field, kept on ice, and filtered through pre-combusted glass fiber filters (GF/F; nominal pore size of 0.7 μm, 47mm diameter) within 48 hours of collection and initial EEMs were completed within 24 hours. DOC samples were either completed within 24 hours, or frozen at -20°C until analyses could be completed. Additionally, leaf litter from the study site was collected, dried at room temperature, and then placed in a combusted glass Erlenmeyer flask with 200 mL of DI water, stopped with a platinum-silicon stopper, and placed on a shaker table for 24 hours to leach DOC from leaf litter. The sample was then filtered similarly to the other samples.

Concentrations of DOC were measured using high temperature combustion on a Shimadzu TOC/TN-V [*Seitzinger and Sanders*, 1997; *Sharp et al.*, 1993]. Glucose was used to construct the standard curve for DOC. A consensus seawater standard from the Hansell laboratory was used to confirm accuracy. A duplicate sample for every ten samples ran was randomly selected for replicate analysis and the relative standard deviation was within 1.2% for all analyses. DOC concentrations are expressed in units of mg/L.

Incubation Experiments

Incubations were conducted on a subset of samples representing different phases of the hydrograph including baseflow (BF), rising limb (RL) and falling limb (FL). A composite sample including stream water from upstream, the sample site and the tidal York River was filtered through a 2.0 μm filter and reserved as the bacterial inoculum.

This composite inoculum was used across all experiments so that a similar microbial community was added to each sample. The prepared inoculum (5mL) was then added to 350 mL of the 0.7 μm filtered water sample. The York River estuary experiences some nutrient enhanced conditions [*Sin et al., 1999*] compared to undeveloped first order streams such as this catchment. Consequently, nutrients were added to some treatments to simulate the additional nutrient loadings found in the estuary [*Sin et al., 1999*]. Inorganic N and P were added to each treatment to raise initial concentrations by 0.03 mg/L of NH_4, 0.01 mg/L of NO_3 and 0.03 mg/L of PO_4, which was the amount required to raise concentrations to the lowest recorded average concentration in the estuary.

Two incubation treatments were used to assess the potential reactivity of stream water DOC and changes in DOM characteristics. Treatment I (LM) included microbial inoculated samples exposed to UV-A radiation, whereas Treatment II (LMN) included microbial inoculated samples exposed to UV-A radiation and supplemented nutrients (N and P). Both treatments were carried out in 500mL quartz flasks that were placed on a light table and incubated following procedures with light exposure type and quantity as described in Lu et al. [2013]. Incubations were terminated after 7 days, which was expected to coincide with a plateau in DOM concentration [*Bertilsson et al., 1999*]. This time period is greater than the total transport time through the tidal portion of Taskinas Creek, which is under seven days [*Herman et al., 2007*]. Reactive DOC was calculated as the percent change in DOC concentration relative to the initial DOC concentration [*Lu et al.*, 2013]. Reactive DOC was used to compare the reactivity of DOM under stormflow

(i.e., rising limb and falling limb hydrograph) to baseflow conditions in order to determine whether light, microbes and nutrients influenced DOM reactivity.

Fluorescence Analysis and Parallel Factor Analysis (PARAFAC)

Fluorescence was measured using a Varian Eclipse fluorescence spectrofluorophotometer and a Shimadzu UV-Vis spectrophotometer. Samples were filtered in the lab through pre-combusted 0.7 μm GF/F filters into acid washed polycarbonate bottles and stored in the refrigerator for a maximum of 24 hours prior to analysis. Samples were placed in 1-cm quartz cuvettes and then allowed to warm to room temperature. EEM spectra for each sample were generated using a Varian Eclipse excitation-emission spectrometer. Fluorescence spectra were corrected for inner filter effects [*McKnight et al.*, 2001] and then for instrument bias and Raman scattering [*Stedmon et al.*, 2003] using a previously-developed Matlab program [*Murphy et al.*, 2008]. Total fluorescence was measured as the sum of all components, measured in Raman Units, identified within the EEMS. The EEMS for the storm events, along with 300 other Taskinas Creek samples collected during baseflow and rain event conditions between 2009-2011, were compiled for use in PARAFAC. PARAFAC model analysis was used to identify the statistically important components of the EEMS as described elsewhere in detail [*Ohno*, 2002; *Stedmon and Bro*, 2008]. Storm samples were compared with runoff, throughfall, pore water, ground water and leaf litter leachate results to detect changes in composition during events that could be attributed to these different sources.

Statistical Analyses

Storm event data including DOC concentration, PARAFAC composition, total fluorescence and incubation treatment results were analyzed statistically using R version 3.0.1. Significant differences were determined using the Wilcoxon Mann-Whitney and the Kruskal-Wallis tests for non-parametric data. Linear regression was used to examine relationships between different variables, using Box-Cox transformations to improve the normality of the data as needed. The significance level between variables was set at $p<0.05$.

RESULTS

Precipitation and Stream Discharge

Rainfall associated with each event occurred over less than 24 hours. The May event occurred over 4.25 hours with a measured maximum rate of 0.19 mm min^{-1} and cumulative precipitation during the event was 9.4 mm (Table 2-1). The August event occurred over 6 hours with a measured maximum rate of 0.07 mm min^{-1} and total cumulative precipitation of 5.2 mm. The November event occurred over 7 hours with a measured maximum rate of 0.05 mm min^{-1} and cumulative total precipitation of 14.4 mm (Table 2-1). The three events were considered small events and no storm surge was generated downstream in Taskinas Creek. These events are representative of the magnitude of the majority of rain events occurring in the watershed in 2011 (Figure 2-2). Events producing greater than 15 mm of rainfall in the watershed were infrequent, representing less than 25% of events in 2011.

Antecedent conditions prior to the storm were relatively dry with each event occurring more than 4 days after the previous rain event (May=6 days, November=5 days, August=6 days). Stream base flow during this period varied from 0.0019 to 0.0029 $m^3 sec^{-1}$. Average temperature was greatest in August (25.8±4.1°C), followed by May (20.3±5.5°C) and lowest in November (11.3±6.1°C) (Table 1). PAR was greatest in May (636.4±478.4 mmole light energy m^{-2}) and declined in August (571.0.0±434.9 mmole light energy m^{-2}) and November (373.3±357.0 mmole light energy m^{-2}).

DOC Concentrations and DOM Composition During Events

DOC concentrations in May ranged from a low of 2.29 mg/L during baseflow (BF) to 3.15 mg/L during rising limb (RL), to a high of 6.32 mg/L during the falling limb (FL) of the hydrograph (Table 2- 2). In August, DOC concentrations during BF were 2.32 mg/L while RL and FL concentrations were 2.26 mg/L and 2.32 mg/L, respectively. DOC concentrations in November ranged from 1.42 mg/L during the RL of the hydrograph to a peak concentration of 2.3 mg/L during the falling hydrograph. DOC concentrations during BF in November were 1.83 mg/L. DOC concentrations were not statistically distinct from each other across the hydrograph for the three events ($p>0.05$) (BF=2.15±0.27, RL=2.28±0.87, and FL=3.65±2.32; Table2- 2). There was a trend of higher DOC concentrations in May (3.92±2.12 mg/L) relative to August and November (2.30±0.03 mg/L and 1.85±0.44 mg/L, respectively). The total flux of DOC during all events increased above baseflow values when compared to an equivalent length of time at baseflow. Total DOC flux during the May event was 150 mg, August was 114 mg, and November was 177 mg (Table 2-1).

Total fluorescence in May was 10.49 Raman Units during BF conditions. Fluorescence was 5.58 ±1.39 Raman Units during the RL and 7.75 Raman Units during the FL (Table 2-2). In August, total fluorescence was 4.3±2.6 during BF, 5.13±4.7 during the RL and 3.26±0.35 during the FL of the storm event. In contrast, during the November event, total fluorescence showed an increase from 2.8 Raman Units during BF to 4.46 Raman Units during the RL, and 5.16 Raman Units during the FL of the hydrograph. Like DOC concentrations, there was a trend of higher total fluorescence in May (8.01±2.36 Raman Units) relative to August and November (4.26±0.94 and 4.14±1.21 Raman Units, respectively) and no statistical differences across different stages of the hydrograph ($p>0.05$).

A six component PARAFAC model accounting for 91% of the variance observed across all samples was developed (Table 2-3). Prior to incubations, component 1 was most abundant for all events, with other components (C2-C6) making up a smaller portion of total fluorescence during BF conditions preceding the May, August and November events (Table 2-4). Component 1 (C1; Humic-like, A) ranged from a high of 5.58 Raman Units in May to 4.9 in August, to a low of 0.71 Raman Units in November (Table 2-4). This amount represented % relative fluorescence values of 61.3 for the initial (pre-incubation) BF sample in May, 67.2 in August, and 29.3 in November (Table 2-5). The protein-like component, Component 6, was the least abundant component of total fluorescence in the initial (pre-incubation) BF samples for all events, ranging from a high of 0.32 Raman Units in August to a low of 0.07 in November (Table 2-4), corresponding to 4.1 to 2.5% of the % relative fluorescence, respectively (Table 2-5).

PARAFAC component fluorescence showed similar distributions during stormflow (RL and FL) and between storm events (Tables 2-4 and 2-5; Figure 2-3). C1 (humic-like) was the most abundant component of total fluorescence during stormflow, as it was during BF. Both the highest and lowest values of C1 for stormflow, 2.59 and 0.42 Raman Units, occurred during RL and FL of the August event, respectively (Table 2-4). These values correspond to a % relative fluorescence of 50.9 and 33.1 for RL and FL in August, respectively (Table 2-5). Despite these variations in C1, the differences in C1 values, as determined by ANOVA for both events and over the hydrograph (BF, RL, FL), were not statistically significant. C6 (protein-like) was the least abundant component (Table 2-4), ranging from 2.0% of the relative fluorescence during FL in May to 15% of the relative fluorescence during FL in August (Table 2-5). Similar to C1, C2-C6 values were neither statistically distinct between events nor over the phases of the hydrograph (Table 2-4; Figure 2-3).

Potential sources of DOM to the stream ranged in composition (Table 2-6). Leaf litter had the highest total fluorescence at 38.18 total Raman Units. Throughfall had the lowest total fluorescence, with a total of 3.63 Raman Units, and runoff, soil pore water and groundwater had intermediate values (6.79 to 28.45 Raman Units; Table 2-6). Component fluorescence varied, with C1 being the most abundant component in all samples except leaf litter leachate, which had higher abundances of C2-C5. Soil pore waters had the highest C1 values (24.6 Raman Units), followed by storm runoff (5.77 Raman Units), and groundwater samples (3.93 Raman Units). Leaf litter leachate and throughfall had the lowest C1 values (1.47 and 1.29 Raman Units, respectively). The

elevated total fluorescence in leaf litter compared to other samples was due to contributions from C2-C5 components that ranged from 9.2-8.84 Raman Units. Other endmembers had lower total fluorescence in these groups, ranging between a low of 0.4 to a high of 1.5 in components C2-C5.

C1 ranged between 5.6 and 4.9 Raman Units in initial incubation samples for BF in May and August, which was intermediate between the groundwater and soil pore-water endmembers. May and August samples were also low in C2-C6 components, similar to both soil pore water and groundwater endmembers. In November, C1 was 0.71 Raman Units in initial incubation samples for BF, which was lower than all endmember samples and different from May and August.

Storm samples (RL and FL) for the May and August events had C1 concentrations that were lower than groundwater, but within the range of leaf litter and throughfall (Tables 2-4 and 2-6). However, concentrations of C2-C5 for the May and August events were lower than leaf litter, and similar to other endmember values. RL samples in May decreased in C1 relative to BF (1.37 Raman Units) approaching throughfall (1.29 Raman Units), followed by an increase in C1 during FL (3.45 Raman Units) that approaches groundwater values (3.93 Raman Units) (Tables 2-4 and 2-6). In August, RL samples decreased in C1 relative to BF (2.59 Raman Units) to values lower than groundwater sources (3.93±0.95 Raman Units, Table 2-6), but greater than throughfall (1.29 Raman Units) and leaf leachate (1.47 Raman Units). During FL in August, C1 decreased to 0.42 Raman Units (Table 2-4), which was lower than any

endmember measured (Table 2-6). C6 values for May and August were low ($\leq$ 0.32 Raman Units) and similar to several of the endmembers. In November, storm (RL and FL) samples were higher in C1 than BF (Table 2-4). November storm samples had C1 components values (1.1-1.2 Raman Units) that were closer to throughfall and leaf litter leachate values. C2-C6 values (0.12-0.71) for storm samples in November were similar to several endmembers, but much lower than leaf litter leachate values. Overall, the PARAFAC component concentrations suggest some difference in organic matter source across the three events (e.g., lower C1 and C6 in November than in May or August) and some change over the storm hydrograph (e.g., higher but more variable amounts of C1 during BF vs. RL and FL) (Figure 2-3).

Reactivity of DOC

Reactive DOC was present in all samples and ranged from 15.0 to 90.7%, with considerable variability across and within the storm events (Table 2-7; see Supplemental Table 2-2 for initial and final DOC concentrations). On average, there was a trend of lower % reactive DOC in August than during May and November (Figure 2-4). Average % reactive DOC for BF samples for the three events was 32.2±5.6 for LM incubations and 38.0±10.5 % for LMN incubations. Incubations of RL samples resulted in % reactive DOC values that ranged from a low of 25% for August LMN to a high of 90.7% for May LM. Rising limb incubations had an average % reactive DOC of 68.2±35.0 for LM incubations and 46.8.±22.3 for LMN incubations (Figure 2-4). Percent reactive DOC amounts associated with FL incubations ranged from a low of 15% for November LM samples to a high of 69.8% in November LMN samples (Table 2-7). Incubations of FL

samples ranged from 21.7±6.4 % reactive DOC for the LM treatment, and 35.9±28.9 % reactive DOC for the LMN treatment.

Overall, there was a trend of %DOC reactivity being higher for RL samples vs. BF and FL samples, but this was not supported statistically and reactivity was not enhanced by nutrient additions (Table 2-7, Figure 2-4).

Changes in Composition Following Incubations and Relation to % Reactive DOC

Component 1 (HMW, humic-like, A) was the most abundant component as measured in Raman Units, in the initial incubation samples (Table 2-4). Consequently, changes in C1 during incubations controlled the observed changes in total fluorescence. In May, C1 was reduced during LM and LMN incubations for all stages of the hydrograph (Final values = 2 to 51% of Initial values; Supplemental Table 2-4). Responses to LM and LMN incubations differed across the hydrograph for August samples; C1 was reduced in BF and RL samples whereas FL samples had mixed responses (no change for LM; increase in C1 for LMN). The largest changes in C1 were observed in November when BF and FL samples increased substantially during LM and LMN incubations (Table 2-4; Supplemental Table 2-2). However, C1 decreased in RL samples in November. In comparison, there was little change in C2-C6 during the incubations (Table 2-5).

Although the greatest changes in fluorescence coincided with changes in Component 1, % changes in Component 1 values did not correlate with % reactive DOC (Figure 2-5). Likewise, the smaller % changes in C2-C6 Components also did not

correlate with % reactive DOC (Figure 2-5). Additionally, % reactive DOC did not correlate with either the initial or final composition of PARAFAC components values in this study (Supplemental Figure 2-1,2- 2). Furthermore, % reactive DOC also did not correlate with the relative % fluorescence of components in the study (Supplemental Figure 2-3).

DISCUSSION

DOC Concentrations and Fluxes during Moderate Events

Several studies have noted that large storm events increase DOC concentrations in streams and rivers [*Fellman et al., 2009; Hernes et al., 2008; Hinton et al., 1998; Buffam et al., 2001; Worrall et al., 2002; Inamdar and Mitchell, 2007*]. However, across the small to moderate storm events captured by this study (<20mm of precipitation), increases in DOC concentrations were relatively small and generally restricted to the falling limb of the storm hydrograph. In May and November, DOC concentrations were elevated during FL compared to pre-storm BF conditions, while in August, there was no difference in DOC concentration across the hydrograph (Table 2-2). In previous studies, these changes in DOC concentration have been attributed to factors such as antecedent conditions, contributing regions, storm intensity, flowpaths and season [*Inmadar et al., 2011 and references therein*]. Since this study focused on moderate events, factors such as changes in storm intensity and flowpaths would not be expected to influence DOC fluxes as much as during larger storms. In other studies, the majority of which focus on events of greater magnitude, pronounced increases in DOC concentration occurred during rising limb and falling limb portions of the hydrograph, while increases in DOC

concentrations were only somewhat apparent during the FL in this study. Since precipitation was low, it may have taken longer for soils to become saturated, delaying the release of DOC until later in the hydrograph.

In addition to changes in DOC concentration, previous studies have noted changes in DOC flux that were modulated by antecedent conditions and resulted in changes in DOC composition. Consistent with previous work, DOC fluxes increased 1.5- to 2.3-fold above BF in this study (Table 1). DOC fluxes have been shown to increase more when events were preceded by dry conditions [*Inamdar et al.2011 and references therein*] and increased fluxes corresponded to changes DOM composition. Detailed characterization of endmember sources of DOM conducted for a range of events of different magnitudes and intensities have also shown that the magnitude and intensity of an event [*Inamdar et al., 2011, Inamdar et al., 2012*], in addition to antecedent conditions and season [*Singh et al., 2014*], can impact DOM composition.

Precipitation totals for events were typical of storm events in the watershed (Figure 2-2). In this study, antecedent conditions for moisture were similar (no rain 4-6 days prior to each event), as were the size (<20mm of precipitation) and intensity of events (occurring in less than 6 hours), suggesting moisture was not the reason for the differences in DOC concentration and flux between the three moderate events. Consequently, changes in DOC concentration in this study more likely arise from seasonal changes in sources of organic matter (e.g., temperature and light changes

impacting organic matter, autumn leaf fall [*Inamdar et al., 2011; Singh et al., 2014*] or from seasonal differences in the organic content of throughfall.

Both spring and fall events have been shown to have different responses to rain events, relative to summer events [*Singh et al., 2014, Inamdar et al., 2011 and 2012*]. Throughfall has also has been shown to impact DOC [*Inamdar et al. 2012*], and may be the source of variation in this study. PARAFAC composition of endmembers in the watershed showed throughfall had the lowest C1 values of all endmembers (Table 2-6). C1 was lowest in November (1.0 ± 0.26 Raman Units) and was most similar to throughfall (1.29 Raman Units; Table 2-6). In contrast, C1 was higher in May and August (3.37 and 2.64 Raman Units, respectively) and more similar to runoff and groundwater endmembers (5.77 and 3.93 Raman Units, respectively; Table 2-6). While these data are consistent with changes in sources, high frequency sampling, including continuous logging and measurement of groundwater levels, analysis of throughfall, and flowpath analysis would be required to determine the source of the variability observed during rain events in the Taskinas study system.

Total Fluorescence and PARAFAC composition during storm events

Total fluorescence in stream water samples has also been shown to change during storm events with some locations reporting an increase in total fluorescence [*Nyguen et al., 2010; Yang et al., 2015*] and increases in aromatic composition attributed to contributions from fulvic and humic sources [*Inamdar et al 2011; Caverly et al., 2013*]. In the May event there was a decrease in total fluorescence (Table 2-2) from BF to

stormflow. Total fluorescence was relatively constant during the August event, and increased during stormflow compared to BF during the November event. In May, the decreases in Cl (humic-like) component tracked total fluorescence suggesting that loss of humic materials contributed to the change in fluorescence (Table 2-4). In November, all components increased during storm events.

Seasonal differences (e.g. leaf cover) in the watershed could contribute to the observed differences in DOC composition across the three rain events. In November, there was an increase in total fluorescence (Table 2-2) as well as humic-like and fulvic-like components from BF to stormflow (RL and FL) (see results for C1 and C3 in Table 2-4). Peak leaf fall occurs during October in the study region and the November event occurred after considerable leaf fall. In a study comparing events in a small stream draining a forested watershed in the mid-Atlantic, Inamdar *et al. [2011],* noted a difference in composition between two moderate, similar sized rain events in spring and fall (<13mm). They attributed increases in DOC and the humic-like content of DOM [*Inamdar et al., 2011*], to the abundance of fresh leaf litter. Given the timing of the November event, it seems plausible that leaf litter could have contributed to the observed variation in total fluorescence and DOC. However, based on comparison to endmembers, this is uncertain. The components most uniquely elevated in leaf litter (C2-C5) increased, but not to a level beyond the amount found in throughfall, soil pore water, groundwater or runoff. Without an additional tracer for each endmember source, it is difficult to assign the exact cause of the increase in C2-C5. However, the observed changes in total

fluorescence during moderate events at Taskinas Creek are consistent with seasonal changes in organic matter sources.

Additional work on DOC composition has shown that DOC from wetland environments is enriched in protein-like components and depleted in humic-like components during storm events relative to baseflow conditions [*Fellman et al., 2009*]. However, Inamdar et al. (2011) reported a decrease in percent protein-like components in a riparian mid-Atlantic stream with excellent drainage, whereas the overall mass of percent protein-like component increased in the watershed. As noted above, the Taskinas site is characterized by excellent drainage from upland areas, but poor drainage through the riparian and wetland soils. During storm events, humic-like components, as represented by C1 in this study, decreased compared to baseflow values in May and August (Table 2-4). Protein-like C6 was correlated with C1 (Pearson's correlation coefficient=0.65, r^2=0.42). The correlation between C1 and C6 contrasts with earlier studies that found a negative correlation between protein-like and humic-like components [*Fellman et al., 2009*], and in studies where a decrease in protein-like component was found during events [*Inamdar et al., 2011*]. Differences in the composition of DOC during the rain events sampled in this study relative to those observed in previous studies could be due to differences in the flowpaths between study environments or antecedent conditions between events and study sites [*Welsch et al., 2001, Weiler and McDonnell, 2007; Fellman et al., 2009;Vidon et al., 2008; Vidon et al., 2009*]. Cross-system comparison of storm events of different magnitudes is needed to further resolve the source of these differences.

DOC Reactivity

Previous studies have shown that DOC exhibits a large range in reactivity during storm events *[Hood et al., 2006*; *Fellman et al., 2009; Inamdar et al., 2011; McLaughlin and Kaplan, 2013*]. In microbial only (BDOC only) incubations in a wetland environment, % reactive DOC ranged from 7 to 38% [*Fellman et al., 2009*]. In our study % reactive DOC was generally higher and ranged between 15.0 and 90.7% for light and bacterial (LM) incubations. The values in this study are similar to those found by Lu et al., 2013, who found % reactive DOC ranging from 4.8-91.5% in light +bacterial incubations during baseflow conditions in Virginia streams. The higher reactivity of samples in this study and the Lu et al. (2013) studies, compared to BDOC only incubations in a wetland environment, suggests potential differences in DOC reactivity either due to differences in source (wetland vs. stream samples) or the incorporation of light in the incubation studies.

DOC reactivity has also been enhanced by the addition of anthropogenic sources of DOC, nutrients, or through photochemical reactions that produce lower molecular weight compounds [*Lindell et al., 2000; Tranvik, 1998; Moran and Zepp, 1997; Bertillson et al., 1999; Bushaw et al., 1996; Stedmon et al., 2007*]. In this study, the nutrient addition did not enhance decomposition of DOC, as demonstrated by the similar average values between LM and LMN for all events (Table 2-7). This suggests that our site was not limited by nitrogen and phosphorus, or that nutrient addition levels conducted were not great enough to cause an impact. Instead, similarities in % reactive DOC between the LM and LMN incubations suggest another possibility. Interestingly,

the incubations that included UV exposure from this study did not follow the same compositional fluorescence predictors as observed in dark only incubations in other studies [*Fellman et al., 2009a and 2009b*]. In dark only incubations, humic-like components were negatively correlated with % reactive DOC while protein-like components were positively correlated with % reactive DOC, providing proxies for downstream reactivity of storm-derived DOC [*Fellman et al., 2009a and b*]. In contrast, the light and microbial incubations conducted in this study do not show any correlation between initial component composition of samples and overall DOC reactivity as measured at the conclusion of incubations (Figure 2-3). This result is similar to Lu et al. (2013), who also found no correlation between protein-like fluorescence and DOC reactivity [*Lu et al., 2013*] across several streams in the York River watershed that were sampled during baseflow conditions. Although the sample size in this study was small, a trend between % reactive DOC and %C1 and % reactive DOC and %C6 was expected for these events. Likewise there was no relationship between the absolute concentration of components and % reactive DOC (Supplemental Figures 2-2 and 2-3).

Additionally, incubations that included UV exposure did not follow the same compositional fluorescence predictors as observed in light and microbial combined incubations in other studies [*Lu et al., 2013*]. Lu et al. (2013) found higher reactivity for DOC in streams draining urban watersheds compared to those with forested watersheds, and found % DOC reactivity correlated positively to a higher percentage of components representing fluorescence from terrestrial sources. Lu et al. (2013) found no relationship between % protein-like components and % reactive DOC, but found that % humic-like

components were positively correlated to % reactive DOC. Over the three storm events studied within the Taskinas watershed for this study, there was no relationship between %reactive DOC and initial component concentrations for any component over the hydrograph (see supplemental figure 1). Also, there was no correlation between %reactive DOC and change in % component over the duration of the incubations within events, or between event hydrograph stages (Figure 2-3).

This lack of correlation between EEMS components and DOC reactivity may have occurred for several reasons. It may be that the variability between events is too high, with too small of a sample size to detect relationships between EEMS components and DOC reactivity. This is certainly possible. However, there was also no correlation within events, which should occur within this small data set, because variability caused by season and antecedent condition should not influence individual events. In order for component composition to be a reliable proxy, a robust relationship between % reactivity and component composition within a small sample size is desirable. Another reason for a lack of correlation may be related to the exposure time of the DOM to light and microbial reactions. Most photochemical incubation experiments conducted previously lasted for greater than 14 days [*Lu et al., 2013 and references therein*]. Although it could be argued that the incubations conducted for this study may have been too short to assess the total reactivity, in most cases over 20% of the DOC was lost, suggesting there was adequate time to observe a response. Several other researchers have hypothesized that previous exposure to light may impact DOM reactivity [*Lu et al., 2013; Molot and Dillon 1997*] while others have suggested other processes, such as sorption are more critical

[*Larson et al., 2007*]. Increasing the length of light exposure may have yielded stronger correlations to final reactivity. However, longer incubation times would be less relevant to Taskinas, where transit times are short (<7 days). The primary difference between sites that found a correlation between components versus this site was the addition of light to incubations, suggesting that light had an impact on the ability of EEMs to predict reactivity.

For PARAFAC components (% protein-like component, % humic-like component) to be a robust proxy for reactive DOC, even a 1-week incubation should show some correlation between the total loss of an individual component and the measured % reactive DOC, regardless of when the incubation was terminated. Here, there is no correlation with % DOC reactivity and final PARAFAC component value and reactivity. Consequently, in order to readily apply PARAFAC component composition as a proxy for DOC reactivity during storm events, more research is required to determine the impact that light exposure, seasonality, and DOM sources have on estimates of DOC reactivity over the course of a hydrologic year. Ideally, these variables should be investigated across a variety of aquatic systems that drain different land uses and respond differently to hydrologic events. Understanding the role that these factors have on DOC reactivity will enable proxies such as PARAFAC components to be applied more reliably across aquatic systems.

The lack of correlation between PARAFAC components and % DOC reactivity was unexpected. However, recent work that has attempted to characterize DOM pools by

mass spectrometry has shown that fluorescence in DOM is a small proportion of total DOM, and that there is interaction between the 'dark' pool and the fluorescent pool of dissolved organic matter. Research has shown that different DOM moieties are tracked with fluorescence [*Stubbins et al., 2014*], and that careful consideration of specific chemical components associated with fluorescence is needed. Although EEMs has proven to be a valuable tool in some environments, particularly in identifying terrestrial DOM in marine environments, it may not be appropriate to apply it uniformly to infer reactivity of DOC for all terrestrial environments and conditions without additional evaluation of the moieties it represents in each environment. New methods, such as ultrahigh resolution Fourier transform ion cyclotron mass spectrometry (FTICR-MS), in concert with EEMS may yield better interpretations because they hold the potential for identifying specific components that contribute to DOC reactivity.

CONCLUSIONS

Results from the sampling of small storm events showed a variety of responses in terms of DOC concentration and composition. Similar to previous studies, DOC released during storm events was reactive, but while DOC reactivity has been limited by nutrient availability in some systems, this was not the case in the Taskinas system. Consequently, managing nutrient delivery to the York for small events may not prevent storm-derived terrestrial DOC from potentially fueling eutrophication and hypoxia through remineralization, and respiration. This study did not find a relationship between EEMS PARAFAC components and DOC reactivity suggesting that additional work is needed to

develop proxies that can assess the combined photochemical and microbial degradation potential of released DOC across systems in the absence of incubation experiments.

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Table 2-1. Storm Event Characteristics

Storm	Length (hrs)	Cumulative Rain (mm)	Storm Q Volume (m^3)	Baseflow Time Equivalent Q Volume (m^3)[1]	DOC Export, Storm event (mg)	DOC Export, Baseflow (mg)	PAR [2] (mmole light/m^2)	Air Temperature (°C)[3]
May	4.25	9.4	42.2±19	38.7±17	150±68	101±45	636.4.5±478.4	20.3±5.5
August	6	5.2	49.8±22	47.2±21	114±51	110±50	571.0±434.9	25.8±4.1
November	7	14.4	94.2±42	51.2±23	177±53	94±42	373.3.±357.0	11.3±6.1

[1] Baseflow time equivalent Q volume, is the total amount of water discharged, compared to the event in the same month, during the same amount of time as the storm event following the baseflow condition.

[2] PAR (mmole light energy/m^2) was averaged over the seven 24 hour periods prior to each storm event, as recorded by the Chesapeake Bay National Estuarine Research Reserve. For each event, n=515, n=459, n=454.

[3] Air Temperature were averaged over the seven 24 hour periods prior to each storm event, as recorded by the Chesapeake Bay National Estuarine Research Reserve, n=767.

Table 2-2. DOC concentration and Total Fluorescence values for baseflow and storm events

Event	Hydrograph Phase	Subset	Total Fluorescence (Raman Units)	DOC (mg/L)
May	**Baseflow**		**10.49 (n=1)**	**2.29**
	Rising Limb		**5.8±1.39 (n=7)**[1]	**3.15**
		R1[2]	5.13	
		R2	5.65	
		R3	5.56	
		R4	8.5	
		R5	5.35	
		R6	5.2	
		R7	5.35	
	Falling Limb		**7.75 (n=1)**	**6.32**
	Baseflow		**4.30±2.6 (n=11)**	**2.32**
		B1	5.01	
		B2	3.19	
		B3	4.05	
		B4	3.74	
		B5	3.88	
		B6	2.4	
		B7	3.18	
		B8	11.78	
		B9	3.16	
		B10	3.97	
		B11	2.98	
	Rising Limb		**5.13±4.7 (n=6)**	**2.26**
		R1	3.15	
		R2	3.02	
		R3	3.2	
		R4	3.06	
		R5	3.66	
		R6	14.7	
	Falling Limb		**3.26±0.35 (n=4)**	**2.32**
		F1	3.23	
		F2	2.95	
		F3	3.14	
November		F4	3.74	
	Baseflow		**2.8 (n=1)**	**1.83**
	Rising Limb		**4.46 (n=1)**	**1.42**
	Falling Limb		**5.16 (n=1)**	**2.3**

[1]Mean and standard deviation for total fluorescence values for samples collected over each stage of the hydrograph. Values in parenthesis indicate the total number of samples used to calculate the mean.

[2]Samples collected sequentially over each stage of the hydrograph are listed by stage of the hydrograph (B=baseflow, R=rising limb, F=falling limb) and the order in which they were collected (B1, B2, etc.). Because the ISCO was programmed in advance of the storm, coverage was uneven across each event.

Table 2-3. Description of PARAFAC model components with characteristics based on Fellman et al. (2010).

Component	Excitation (nm)	Emission (nm)	Characteristics (based on Fellman et al., 2010)
1	<230	440-470	UVC humic-like, A[1], terrestrial HMW
2	330-355	430-460	UVC humic-like, C, terrestrial
3	<230	390-410	Autocthonous or microbial, oxidized, humic-like, correlated with aliphatic C content
4	305-330	390-420	UVA humic-like, LMW, M
5	270-280; 390-410	485-500; 495-505	UVA humic-like, fulvic acid; Soil fulvic acid, D
6	268-282	300-308	Protein-like, result of degradation processes

[1]Letters in the characteristics represent previous designations of these components in the scientific literature.

Table 2-4. PARAFAC component concentrations (Raman Units) for initial (I) samples and following 7-day incubations under photochemical and microbial (LM) and photochemical, microbial and nutrient (LMN) conditions.

		May			August			November		
Component	**Sample**	**BF**	**RL**	**FL**	**BF**	**RL**	**FL**	**BF**	**RL**	**FL**
C1	I	5.58	1.37	3.45	4.9	2.59	0.42	0.71	1.1	1.2
	LM	0.13	0.36	1.39	4.49	0.6	0.42	34.2	0.44	8.9
	LMN	0.15	0.24	0.26	1.46	0.65	7.9	37.4	0.78	27.1
C2	I	0.65	0.21	0.54	0.33	0.44	0.11	0.33	0.53	0.71
	LM	0.05	0.09	0.08	0.14	0.15	0.13	0.25	0.19	0.02
	LMN	0.05	0.09	0.08	0.14	0.13	0.17	0.3	0.15	0.26
C3	I	1.24	0.48	1.07	0.92	0.95	0.32	0.64	1	1.2
	LM	0.11	0.21	0.2	0.36	0.37	0.39	0.35	0.53	0.54
	LMN	0.11	0.28	0.18	0.35	0.42	0.58	0.46	0.4	0.55
C4	I	0.7	0.22	0.58	0.4	0.41	0.1	0.32	0.53	0.67
	LM	0.05	0.09	0.08	0.14	0.16	0.15	0.21	0.23	0.23
	LMN	0.04	0.08	0.07	0.14	0.16	0.18	0.29	0.16	0.25
C5	I	0.7	0.29	0.64	0.42	0.48	0.13	0.35	0.53	0.69
	LM	0.08	0.13	0.12	0.17	0.19	0.23	0.29	0.29	0.32
	LMN	0.07	0.15	0.1	0.17	0.18	0.33	0.37	0.23	0.37
C6	I	0.23	0.17	0.13	0.32	0.22	0.19	0.07	0.18	0.12
	LM	0.09	0.18	0.13	0.21	0.18	0.23	0.24	0.15	0.18
	LMN	0.11	0.16	0.13	0.19	0.21	0.33	0.46	0.16	0.25

BF =Baseflow, RL=Rising Limb, FL=Falling Limb LM=Light (L) and Microbial (M) Incubation, LMN= L,M and nutrient(N)

Table 2-5. EEMS % relative fluorescence for initial (I) samples and following 7-day incubations under photochemical and microbial (LM) and photochemical, microbial and nutrient (LMN) conditions.

		May			August			November		
Component	**Sample**	**BF**	**RL**	**FL**	**BF**	**RL**	**FL**	**BF**	**RL**	**FL**
%C1	I	61.3	50.1	53.8	67.2	50.9	33.1	29.3	28.4	26.1
	LM	25.5	34.0	69.5	81.5	36.4	27.1	96.2	24.0	87.3
	LMN	28.3	24.0	31.7	59.6	37.1	83.2	95.2	41.5	94.2
%C2	I	7.2	7.7	8.5	4.5	8.6	8.7	13.6	13.7	15.5
	LM	9.8	8.5	4.0	2.5	9.1	8.4	0.7	10.4	0.2
	LMN	9.4	9.0	9.8	5.7	7.4	1.8	0.8	8.0	0.9
%C3	I	13.6	17.6	16.7	12.7	18.7	25.2	26.4	25.8	26.1
	LM	21.6	19.8	10.0	6.5	22.4	25.2	1.0	29.0	5.3
	LMN	20.8	28.0	22.0	14.3	24.0	6.1	1.2	21.3	1.9
%C4	I	7.7	8.0	9.0	5.5	8.1	7.9	13.2	13.7	14.6
	LM	9.8	8.5	4.0	2.5	9.7	9.7	0.6	12.6	2.3
	LMN	7.5	8.0	8.5	5.7	9.1	1.9	0.7	8.5	0.9
%C5	I	7.7	10.6	10.0	5.8	9.4	10.2	14.5	13.7	15.0
	LM	15.7	12.3	6.0	3.1	11.5	14.8	0.8	15.8	3.1
	LMN	13.2	15.0	12.2	6.9	10.3	3.5	0.9	12.2	1.3
%C6	I	2.5	6.2	2.0	4.1	4.3	15.0	2.9	4.7	2.6
	LM	17.6	17.0	6.5	3.8	10.9	14.8	0.7	8.2	1.8
	LMN	20.8	16.0	15.9	7.8	12.0	3.5	1.2	8.5	0.9

%C is the relative % fluorescence of the PARAFAC model components (see Table 3)
Abbreviations are: BF =Baseflow, RL=Rising Limb, FL=Falling Limb, LM=Light and Microbial Incubation, LMN=Light, Microbial and Nutrient Incubation

Table 2-6. Endmember PARAFAC component composition and total fluoresence in Raman Units.

Sample	C1	C2	C3	C4	C5	C6	Total Fluorescence
Throughfall	1.29	0.49	0.71	0.44	0.44	0.25	3.63
Leaf Litter	1.47	9.25	9.24	8.84	8.94	0.33	38.18
Storm Runoff	5.77	0.96	1.50	0.92	0.92	0.27	10.35
Pore Water (n=2)	24.66 ±5.98	0.71±0.67	1.31±0.88	0.71±0.65	0.78±0.71	0.28±0.08	28.45±8.98
Groundwater (n=8)	3.93±0.95	0.53±0.29	1.04±0.52	0.56±0.29	0.58±0.31	0.16±0.02	6.79±1.65

Table 2-7. Percent reactive DOC for photochemical and microbial incubations (LM) and photochemical, microbial and nutrient (LMN) incubations of water collected during baseflow and storm events.

Month	Treatment	BF	RL	FL
May	LM	37.8	90.7	22.3
	LMN	44.5	45.7	24.1
August	LM	32.1	27.9	27.7
	LMN	25.9	25	19.2
November	LM	26.6	86.0	15.0
	LMN	43.5	69.8	69.3
All (Averages)	LM (3)[1]	32.2±5.6	68.2±35.0	21.7±6.4
	LMN (3)	38.0±10.5	46.8.±22.3	35.9±28.9

[1] The number of samples used to compute the means is provided in parenthesis.
BF =Baseflow
RL=Rising Limb
FL=Falling Limb
All =Averages of all data from each month for baseflow, rising limb and falling limb hydrograph phases, and for each treatment (LM and LMN)
±= range of mean
LM=Light and Microbial Incubation
LMN=Light, Microbial and Nutrient Incubation

Figure 2-1. Study Site Location Map depicting dominant ecosystem types, gauging station (GS), weather station (WS) and water quality station location.

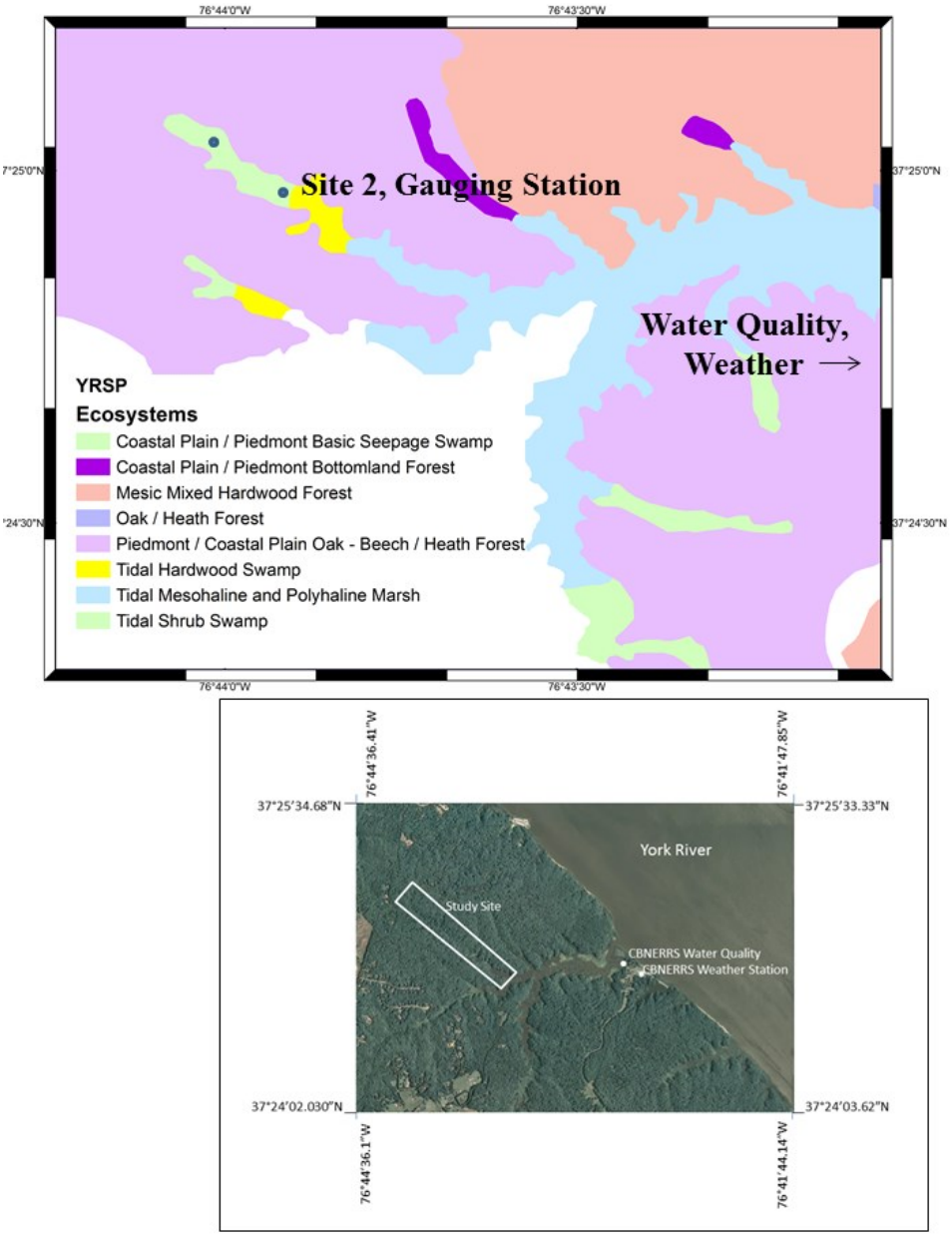


Figure 2-2. Frequency histogram displaying the frequency of different classes of rainfall during the 2011 hydrologic year at Taskinas Creek, VA.

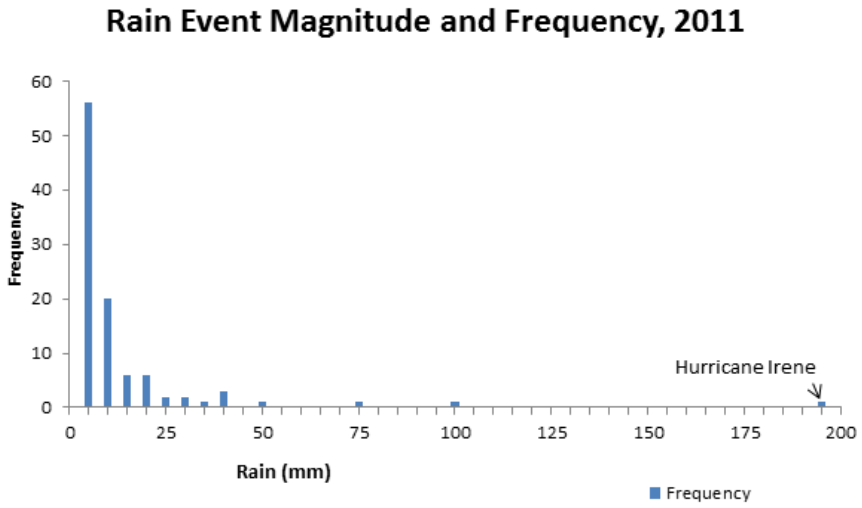


Figure 2-3. Average values for C1 and C6 (Raman Units) for the three storm events (top panels) and over the storm hydrograph (bottom panels).

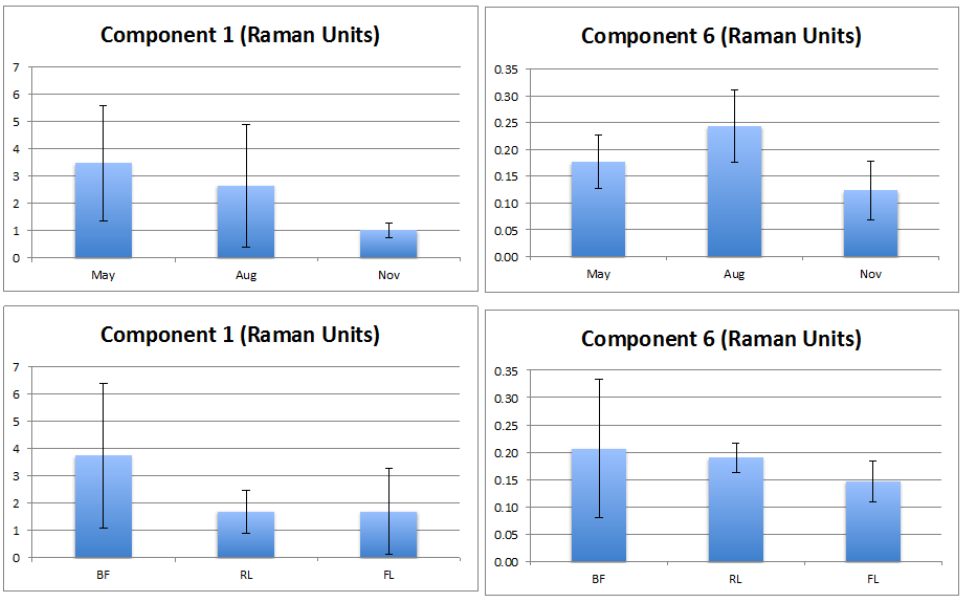
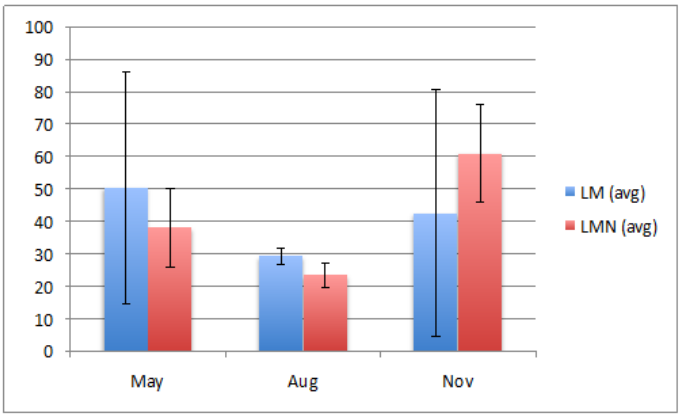


Figure 2-4. Percent reactive DOC as determined by LM and LMN incubations. The upper panel shows % reactive DOC across the three storm events and the lower panels shows % reactive DOC over the storm hydrograph.



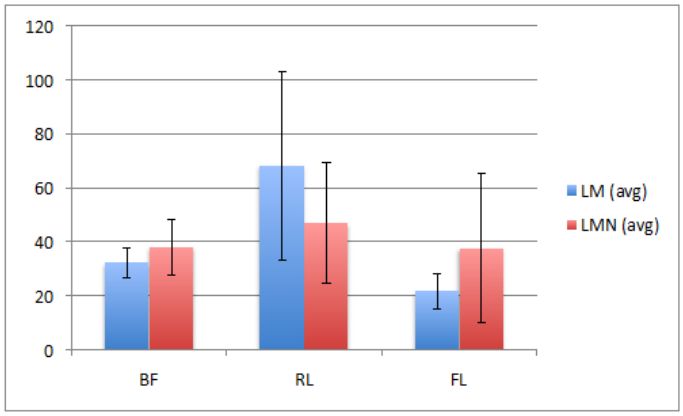
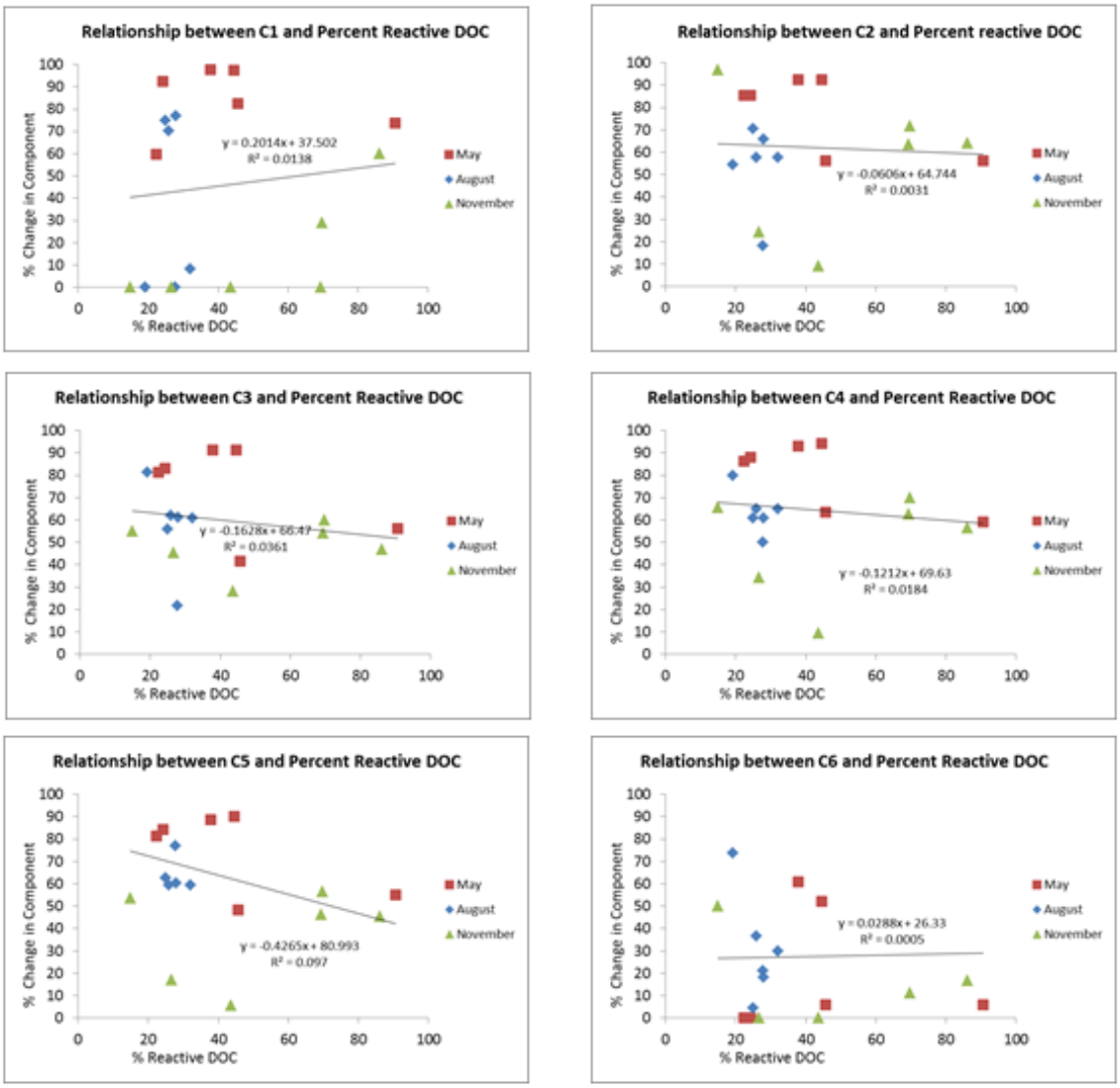


Figure 2-5. Correlations of percent reactive dissolved organic carbon with individual dissolved organic matter components during three moderate storm events during the 2011 hydrologic year at Taskinas Creek, VA.



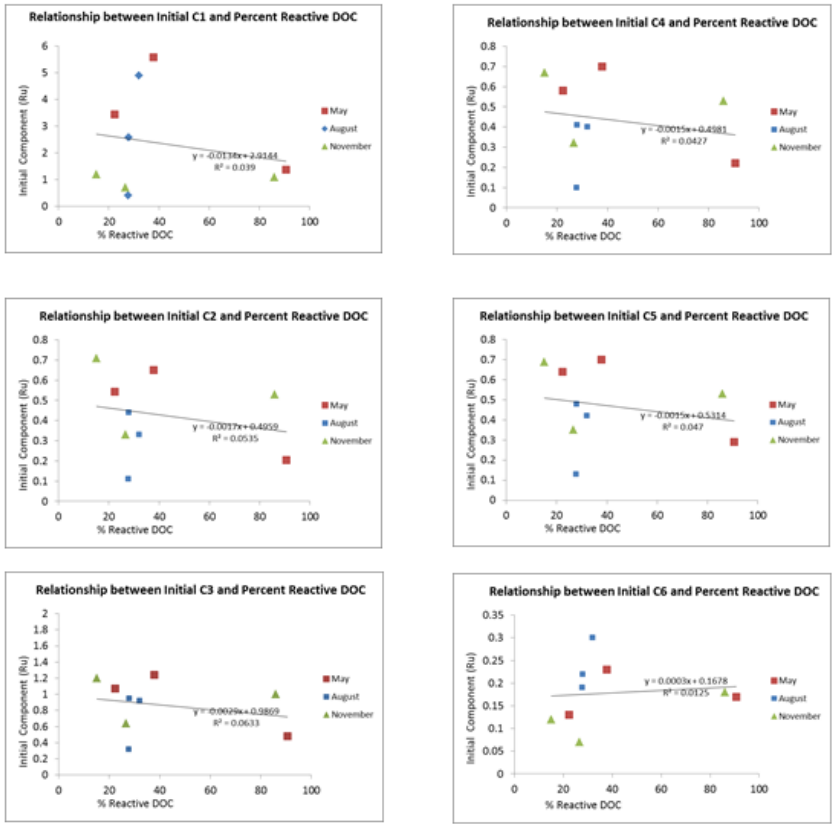
Supplemental Table 2-1. TR-55 model parameters and data sources.

Model Parameter	**Sampling Site**	**Data Source**
Rainfall (cm) Rainfall duration (hr)	0.14 7	Onsite rainfall time distribution (CBNERR 2011);10-yr Onsite rainfall distribution; 6 hr period
Watershed delineation (ha) Water flow paths (m) Soil classification Vegetation	28 Seepage Swamp	Developed 0.6 m DEM and ArcGIS watershed tool ArcGIS Flow direction tool Patterson 2011
Runoff curve number (CN) Hydrologic soil group (HSG) Cover type Cover type treatment Hydrologic condition Antecedent runoff condition (ARC)	54 A/D Woods None Good	USDA
Time of concentration (T_c)	0.01	Cronshey 1986
Weighted (K_m)	0.431	
Reach friction slopes	0.009	Field measured
Contribution channels	1	

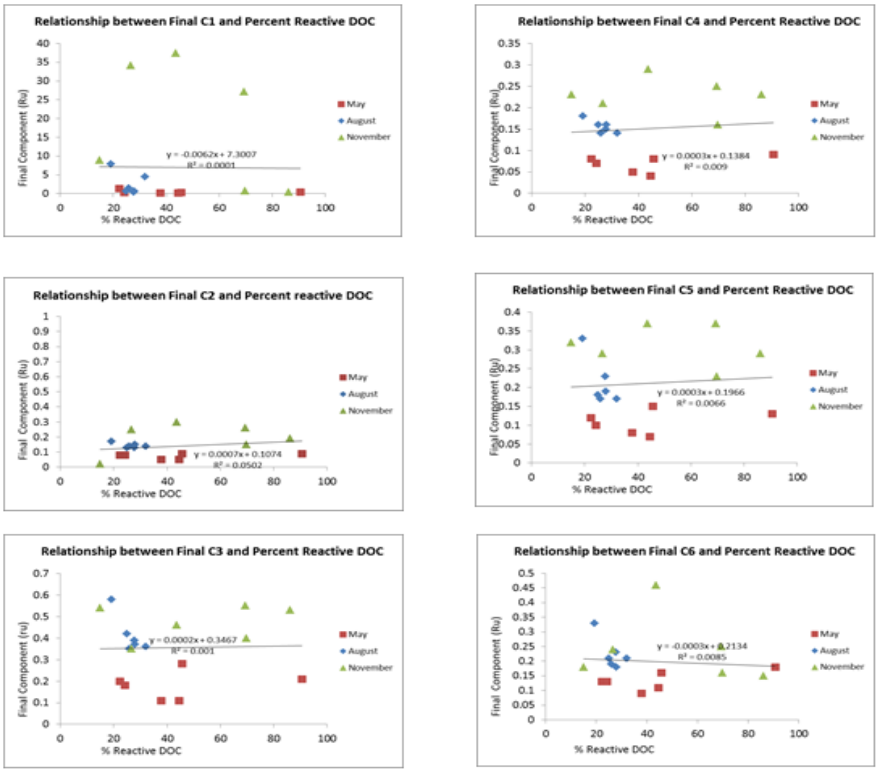
Supplemental Table 2. Initial (pre-incubation) and final (post-incubation) values for Total Fluorescence, C1(humic-like) and C6 (protein-like), DOC concentrations and % Reactive DOC.

Stage	Treatment	Month	Total Fluorescence	Initial C1 (RU)	Final C1 (RU)	Initial C6 (RU)	Final C6 (RU)	Initial DOC	Final DOC	%Reactive DOC
BF	I	May	9.10	5.58		0.2		191.1		
BF	LM	May	0.51	5.58	0.13	0.2	0.1	191.1	118.8	37.8
BF	LMN	May	0.53	5.58	0.15	0.2	0.1	191.1	105.9	44.5
BF	I	August	7.27	4.9		0.3		193.2		
BF	LM	August	5.51	4.9	4.49	0.3	0.2	193.2	131.2	32.1
BF	LMN	August	2.45	4.9	1.46	0.3	0.2	193.2	143.1	25.9
BF	I	Nov	2.42	0.71		0.1		152.6		
BF	LM	Nov	35.5	0.71	34.2	0.1	0.2	152.6	112.0	26.6
BF	LMN	Nov	95.2	0.71	37.4	0.1	0.5	152.6	86.2	43.5
RL	I	May	2.74	1.37		0.2		526.8		
RL	LM	May	1.06	1.37	0.36	0.2	0.2	526.8	49.2	90.7
RL	LMN	May	1.00	1.37	0.24	0.2	0.2	526.8	286.0	45.7
RL	I	August	5.09	2.59		0.2		193.4		
RL	LM	August	1.65	2.59	0.6	0.2	0.2	193.4	139.4	27.9
RL	LMN	August	1.75	2.59	0.65	0.2	0.2	193.4	145.0	25.0
RL	I	Nov	3.87	1.1		0.2		191.3		
RL	LM	Nov	1.83	1.1	0.44	0.2	0.2	191.3	26.7	86.0
RL	LMN	Nov	1.88	1.1	0.78	0.2	0.2	191.3	57.8	69.8
FL	I	May	6.41	2.74		0.1		262.5		
FL	LM	May	1.92	2.74	1.39	0.1	0.1	262.5	203.8	22.3
FL	LMN	May	0.82	2.74	0.26	0.1	0.1	262.5	199.1	24.1
FL	I	August	1.27	0.42		0.2		188.4		
FL	LM	August	1.55	0.42	0.42	0.2	0.2	188.4	136.3	27.7
FL	LMN	August	9.49	0.42	7.9	0.2	0.3	188.4	152.2	19.2
FL	I	Nov	4.59	1.2		0.1		118.3		
FL	LM	Nov	10.2	1.2	8.9	0.1	0.2	118.3	100.6	15.0
FL	LMN	Nov	28.8	1.2	27.1	0.1	0.3	118.3	36.3	69.3

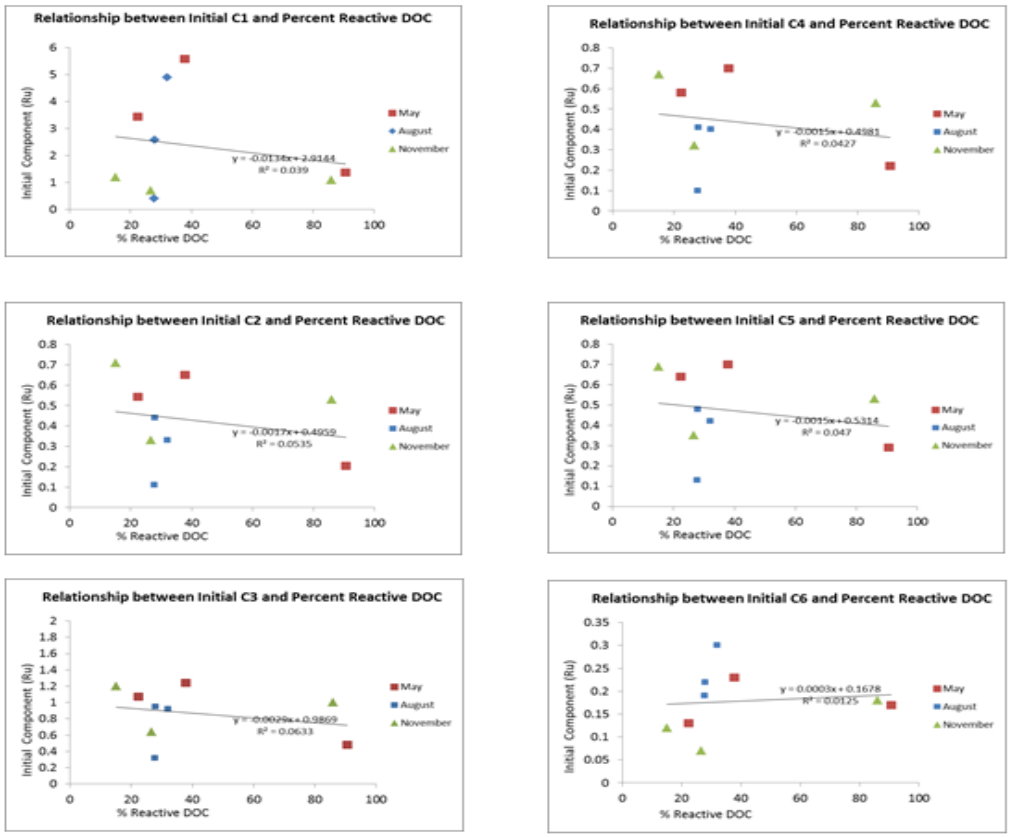
Supplemental Figure 2-1. Correlations of percent reactive dissolved organic carbon with initial PARAFAC EEMS component values during three moderate storm events during the 2011 hydrologic year at Taskinas Creek, VA.



Supplemental Figure 2-2. Correlations of percent reactive dissolved organic carbon with final PARAFAC EEMS component values during three moderate storm events during the 2011 hydrologic year at Taskinas Creek, VA.



Supplemental Figure 2-3. Correlations of percent reactive dissolved organic carbon with relative % fluorescence values during three moderate storm events during the 2011 hydrologic year at Taskinas Creek, VA



Chapter 3: Influence of Hurricane Irene on the Flux, Composition and Reactivity of Dissolved Organic Matter in a Mid-Atlantic Perennial Stream, USA

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ABSTRACT

Dissolved organic carbon (DOC) dynamics, including flux, composition and reactivity along with nutrients were examined in runoff from a Mid-Atlantic coastal, forested sub-watershed during Hurricane Irene, categorized as a 25-50 year event. During the event, the creek system experienced a 118- to 122-fold increase in discharge and exported 300 to 320 kg of DOC and 8.3 to 8.9 kg of dissolved organic nitrogen (DON), which represented 440- to 490- and 280- to 300- fold increases over baseflow conditions, respectively. Fluorescence excitation-emission matrices (EEMs) with parallel factor (PARAFAC) analysis was used to evaluate the composition of dissolved organic matter (DOM) and laboratory incubations were used to measure reactivity. The source of DOM shifted in composition and increased in high molecular weight (HMW), humic-like terrigeneous components during the storm event. Laboratory experiments showed that DOM was reactive, both with and without the addition of nutrients. Reactivity of DOM was not correlated with any particular component determined from the results of PARAFAC analysis of EEMs. Together, higher fluxes of DOM and its increased lability during portions of the stream hydrograph indicate that storm events have the potential to impact downstream water quality and biogeochemistry.

Keywords

DOC, DON, Watersheds, Reactivity, Photochemical alteration, Storm Events, Baseflow, Excitation Emission Matrix, Parallel Factor Analysis

Key Points

1. Hurricane Irene, a large storm event, caused an increase in flux of DOC and DON that was 460 to 490 and 280 to 300 times baseflow, respectively.
2. Incubation experiments showed that this organic matter was reactive in the presence of light.
3. The combination of increased flux and reactivity of DOC delivered during Hurricane Irene suggests that this storm event had the potential to impact water quality in the downstream estuary.

INTRODUCTION

Historically, terrigenous dissolved organic matter (DOM) was considered to be refractory relative to aquatic derived DOM due to the low reactivity of some of its components [*Aarnos et al*., 2012; *Benner*, 2003; *Thurman*, 1985]. However, more recent work indicates that terrigenous DOM is processed within streams and rivers as well as within estuaries and coastal waters [*Cai*, *2011*] on timescales comparable to water transport and mixing [*Battin et al*., *2009*]. *Aufdenkampe et al*. [2011], for example, showed that rivers receive, transport and process the equivalent of terrestrial net ecosystem production in their watersheds. The reactivity of terrigenous OM is further supported by observations that rivers and estuaries are the highest emitters of CO_2 per unit area [*Cole and Caraco*, *2001*; *Richey et al., 2002*]. It has also been suggested that terrigenous DOM may stimulate primary production through its remineralization to inorganic nutrients [*Bianchi et al., 2009*] and exacerbate coastal hypoxia [*Rabalais et al., 2010; Seitzinger and Sanders, 1997*].

Because of the importance of terrestrial DOM in aquatic systems and its variable reactivity, research has compared sources of terrestrial and aquatic organic matter (OM) in supporting estuarine and coastal metabolism [*McCallister et al., 2004; Raymond and Bauer, 2000*] and the impact microbial and photochemical processes may have on terrestrial DOM reactivity [*Kirchman*, *2003; Lu et al., 2013; Moran and Zepp, 1997; Osburn et al., 2009*]. Additionally, previous studies have investigated seasonal alterations in terrestrial DOM [*Eimers et al., 2008; Fellman et al., 2009b*] and transformations during transport from watersheds [*Brooks et al., 2007; Butman et al., 2007; Raymond and Saiers, 2010*]. This body of work has shown that sources of OM, their seasonal

variations, hydrologic flowpaths, and microbial and photochemical transformations impact the bioavailability of terrigenous DOM in rivers [*Wiegner et al., 2009*]. However, information about how these processes are impacted by large-scale storm events has only not been investigated within the study system presented here.

Within the mid-Atlantic region, climate change is expected to increase the episodicity and intensity of precipitation events, and large-scale storms (e.g. tropical cyclones) are expected to increase in frequency [*Lozano et al., 2004; Najjar, 2010*]. Two types of large-scale storms impact the mid-Atlantic region: extratropical storms (e.g., nor'easters) and tropical cyclones (e.g., hurricanes) [*Mallin and Corbett, 2006*]. The environmental effects of these large-scale storms include: nutrient loading, chemical pollution, changes in algal production, hypoxia, fish kills, benthic organism impacts, spread of non-native species, microbial pathogens and damage to important habitats such as emergent wetlands, underwater grasses and solitary coral [*Mallin and Corbett, 2006; Tomasko et al., 2006*]. These large storms also vary in their impact based on their unique attributes, including: point of landfall, time of landfall, trajectory path, areal extent, wind speed, speed of passage and rainfall [*Inamdar et al., 2011; Mallin and Corbett, 2006*]. Therefore, it becomes increasingly important to enhance our understanding of the effects of storms on the delivery and processing of terrestrial DOM and improve our ability to predict how alterations in storm frequency and intensity will impact aquatic biogeochemistry [*Boesch, 2001; Kemp et al., 2005; Najjar, 2010*].

Recently, more attention has been given to storm events because export of DOM from watersheds during such events can be as much as 71-90% of the total DOM released from streams annually [*Dalzell et al., 2007; Fellman et al., 2009a; Raymond and Saiers,*

2010; Yoon and Raymond, 2012]. Previous studies have documented that the quantity, sources and degradation state of DOC are dramatically altered during storm and flooding conditions [*Bianchi et al., 2013; Inamdar et al., 2011; Raymond and Saiers, 2010; Vidon et al., 2008; Yoon and Raymond, 2012*]. Dissolved organic nitrogen (DON) concentrations are also altered during storm events, but DON does not co-vary with DOC, suggesting that DOC and DON pools are either derived from different sources or display differential reactivity during storm events [*Inamdar et al., 2008*]. DON in some watersheds may primarily be derived from throughfall and the forest floor while DOC is derived from throughfall, the forest floor and soils [*Inamdar and Mitchell, 2007*]. The overall contributions of DON appear to be related to the antecedent conditions in the watershed and total precipitation during the storm event [*Inamdar et al., 2008*], which causes variations in flowpaths. The amount of DOC and DON, as well as the ratio between the two, provides clues about the reactivity of DOM released during events through insight into the composition of DOM. However, concentrations alone do not indicate the reactivity of DOM delivered during storm events.

Developments in fluorescence spectroscopy have allowed DOM composition during storm events to be studied in greater detail [*Fellman et al., 2010; Inamdar et al., 2012*]. These studies have reported differences in stream DOM composition during storm versus baseflow conditions. In a study using microbial incubations, Fellman et al. (2010) noted an increase in the reactivity of DOM during stormflow conditions and found it related to the % protein and % humic-like fractions of DOM. This observation led others to measure the humic-like and protein-like components to assess the reactivity of DOM during events [*Inamdar et al., 2011 and 2012*]. These studies suggest that the

compositional differences observed in the relative percent of fluorescence components impact the reactivity of organic matter due to processes that occur during transport or in more nutrient rich downstream waters [*Inamdar et al., 2011; Nguyen et al., 2013*]. In addition, the composition and the reactivity of DOM is known to be impacted by microbial and photochemical processing of DOM and may be enhanced by the addition of nutrients.

This study builds upon previous work by combining flux measurements of DOC and DON, analyses of DOM composition, and laboratory incubation experiments conducted from stream water obtained during a large storm, Hurricane Irene, that impacted the mid-Atlantic region in late August 2011. Observed differences in DOM composition and flux measured during this large storm event are evaluated for their potential to impact the reactivity of organic matter during and after transport downstream. During transport from the non-tidal creek to the downstream estuary, there is opportunity for alteration of OM by microbial and photochemical processes and through the addition of nutrients. The use of excitation-emission matrix (EEMS) fluorescence and associated parallel factor (PARAFAC) analysis to show compositional changes corresponding with DOC reactivity following incubations is also examined.

METHODS

Study Site Description

The study site was located within a first order forested sub-watershed of Taskinas Creek, a managed component of the Chesapeake Bay National Estuarine Research Reserve (CBNERR), which drains directly to the York River estuary, Virginia, a tributary of southern Chesapeake Bay (see Figure 3-1). Non-tidal portions of the study site, 54 ha

in area, contain three dominant ecosystem types, described as oak-heath forest, oak-beech-heath forest and basic seepage swamp, which drain into a tidal hardwood swamp and meso-polyhaline marsh system (Figure 3-1; [*Patterson 2011*]). The upper reaches of the study stream lie within an oak-beech-heath forest characterized by mesic ravine slopes and ridges dominated by a hardwood canopy (e.g., *Fagus grandifolia, Quercus var., Acer var*.) mixed with some pine (e.g., *Pinus taeda and P. virginiana*) and contain an understory of American holly (*Ilex opaca*) and mountain laurel (*Kalmia latifolia*). Downstream, the stream traverses a basic seepage swamp that exhibits temporary and seasonal flooding, and has a mixed hardwood community including red maple (*A. rubrum*), black gum (*Nyssa sylvatica*), green ash (*Fraxinus pennsylvanica*), a variety of Oak (*Quercus var.*) and other more water tolerant species. Flow continues from the seepage swamp through tidal hardwood swamp and mesohaline marsh ecosystems prior to discharge in Taskinas Creek. The sandy bottom stream is relatively well defined with short reaches of subterranean flow in the upper reaches and evidence of bed migration in the broad (~44 m) non-tidal swamp floodplain.

Soils within the study site primarily consisted of poorly drained soils of the Johnston complex in the nearly level (0-2% slopes) floodplain region and deep, moderately drained Craven complex soils in regions with moderate slopes (2-10% slopes), and well drained Emporia complex soils along the adjacent steep (25-50% slopes) ravines [*Hodges et al., 1985*]. Floodplain soils have a relatively high organic matter content, exhibit a high water table, and frequently flood as a result of intense rainfall. Properties of the Emporia complex soils include low organic matter content, deeper water tables (~ 0.9-1.5 m), and high erosion and runoff potentials. Texturally,

Johnston complex surface and subsoils (upper 0.9 m) are black silt loam with fine sandy loam substratum to a depth of 1.5 m. Craven complex slopes are generally silty loam with depths to 0.9 m. Emporia complex surficial soils are typically fine sandy loam, with loamy subsoils and sandy clay loams extending to a depth of 1.9 m. For this study, two stormwater sampling stations were established, Site 1 at the up-gradient oak-beech-heath forest and seepage swamp interface and Site 2 located at the downstream edge of the seepage swamp site (Figure 3-1). On an areal basis, Sites 1 and 2 accounted for 53 and 47 percent, respectively, of the sub-watershed used for this study.

Hydrology

A near continuous record of stream flow from 2009-2011 was generated in the dominant stream flow channel at the most down gradient point of Site 2 (see Figure 3-1 for gaging station location) through development of a stream stage-discharge (Q) rating curve that was supplemented with a Manning equation approach [*Arcement and Schneider, 1989*] when water levels exceeded bankfull conditions resulting in floodplain Q; this approach is referred to as the stage-Manning method throughout this manuscript. Stream water levels at Site 2 were recorded at 15 minute intervals by a Solonist® level logger deployed in a stilling well with water levels corrected for changes in atmospheric pressure. In channel field measurements for stream Q followed both velocity-area [*Buchanan and Somers, 1969*] and salt dilution [*Moore, 2005*] methods with the selected method depending on water depth conditions. Manning equation inputs included 0.009 for slope, a floodplain Manning coefficient (K_m) of 0.10 with extrapolated values of area and hydraulic radius based on continuous field measured water levels and basin geometry. A second approach to estimate stream and floodplain Q, at both Sites 1

(ungaged) and 2 (gaged), utilized the USDA/NRCS TR-55, a single-event rainfall-runoff small watershed hydrologic model [*Cronshey, 1986*]. While originally developed for agricultural and developing watersheds, TR-55 has been successfully applied to low gradient, forested watersheds similar to the system used in this study [*Corbett et al. 1997*]. TR-55 model parameters incorporated local information and reflected current pre-storm conditions; model parameters and data sources are provided in Table 3-1.

Meteorological data were collected by the CBNERR maintained Campbell Scientific UT10 weather station located adjacent to the study site in York River State Park (Figure 3-1); precipitation was measured with a TE 525 tipping bucket rain gage recording at 15-minute intervals. Water level and water quality variables for tidal waters within Taskinas Creek and the adjacent York River proper were collected at 15-minute intervals with YSI 6600 V2 data sondes maintained by CBNERR.

Sample Collection, Analysis and Flux Calculations

Discrete water samples were collected within the primary stream channel at Sites 1 and 2 throughout Hurricane Irene including pre- and post-storm baseflow conditions. It should be noted that due to equipment malfunction, samples were only collected for the first 24 hours at Site 1 as compared to 48 hours at Site 2. Samples were collected into combusted (450 °C) glass bottles at two-hour intervals using portable ISCO™ automatic samplers. Samples were removed from the field, kept on ice, and filtered through pre-combusted glass fiber filters (GF/F; nominal pore size of 0.7 μm, 47mm diameter) within 48 hours of collection.

Concentrations of DOC and total dissolved nitrogen (TDN) were measured using high temperature combustion on a Shimadzu TOC/TN-V [*Seitzinger and Sanders, 1997;*

Sharp et al., 1993]. Glucose was used to construct the standard curve for DOC and KNO_3 was used to construct the standard for TDN. A consensus seawater standard from the Hansell laboratory (U. Miami) was used to confirm accuracy. A Lachat autoanalyzer was used to measure dissolved inorganic nitrogen (DIN) species (NO_3^-, NH_4^+, NO_2^-) and phosphorus (PO_4^{-3}). A duplicate sample for every ten samples ran was randomly selected for replicate analysis and the relative standard deviation was within 1.2% for all analyses. DON was calculated as the difference between TDN and DIN. The percentage of error reported for calculating DON was the propagated error for uncertainty associated with the DIN and TDN measurements. Carbon and nutrient concentrations are expressed in units of mg/L as C, N and P, respectively. Time interval mass flux, typically at two-hour intervals, was determined as the product of the discrete sample constituent concentration and associated continuous discharge, with the sample collection time representing the mid-point for the discharge period. Interval fluxes were summed to determine stage interval and event fluxes.

Incubation Experiments

Incubations were conducted on a subset of samples representing different phases of the hydrograph including baseflow (taken August 15, 2011), rising limb, falling limb and post-storm baseflow conditions. A composite sample including stream water from Sites 1 and 2 and the tidal York River was filtered through a 2.0 μm filter and reserved as the bacterial inoculum. This composite inoculum was used across all experiments so a uniform distribution of microbial communities was added to each sample. Samples for incubation were filtered through precombusted 0.7 μm glass fiber filters. The prepared inoculum (5 mL) was then added to the 0.7 μm filtered water sample. The York River

estuary experiences different nutrient conditions *[Sin et al., 1999]* compared to undeveloped first order streams such as this catchment. Consequently, nutrients were added to simulate the additional nutrient loadings found in the estuary *[Sin et al., 1999]*. Inorganic N and P were added to each treatment to raise initial concentrations by 0.03 mg/L for NH_4, 0.01 mg/L for NO_3 and 0.03 mg/L for PO_4, which was the equivalent of the minimum values in the estuary. Total nitrogen and phosphorus were measured at the start of nutrient incubations and compared to recommended values for sustaining aquatic growth and vegetation suggested by NOAA/EPA [*Waters, 1988*]. Initial PO_4 and TDN levels met these guidelines, indicating that nutrient incubation experiments were started without limiting conditions. Following the incubation experiments, PO_4 and TDN still fell within these guidelines (PO_4>0.01 mg/L; TDN>0.1mg/L), indicating that nutrients were not limiting in supplemental nutrient incubations described below.

Two incubation treatments assessed the potential reactivity of stream water DOC and changes in DOM characteristics during baseflow and storm conditions. Treatment I (LM) included microbial inoculated samples exposed to UV-A radiation, whereas treatment II (LMN) included microbial inoculated samples exposed to UV-A radiation and supplemented nutrients (N and P). Both treatments were carried out in 500 mL quartz flasks that were placed on a light table and incubated following procedures described in [*Lu et al., 2013*], and terminated after 7 days. Replicates of each treatment were not conducted due to limitation in sample volume collected. Following incubations, DOM and DIN species were measured as previously described. Reactive DOC, calculated as a percent change of initial concentrations [*Lu et al., 2013*], was used to determine if LM

and LMN treatments caused DOM components to be more or less labile. Reactive DOC was calculated as a percent decrease relative to initial concentrations [*Lu et al., 2013*].

Fluorescence Analysis and Parallel Factor Analysis (PARAFAC)

Fluorescence was measured using a Varian Eclipse fluorescence spectrofluorophotometer and a Shimadzu UV-Vis spectrometer. Samples were filtered in the lab through pre-combusted 0.7 μm GF/F filters into acid washed polycarbonate bottles and stored in the refrigerator for a maximum of 24 hours prior to analysis. Samples were placed in 1-cm quartz cuvettes and then allowed to warm to room temperature. Excitation-emission matrices (EEMS) were generated using a Varian Eclipse excitation-emission spectrometer. Fluorescence spectra were corrected for inner filter effects [*McKnight et al., 2001*] and then for instrument bias and Raman scattering [*Stedmon et al., 2003*] using a previously-developed Matlab program [*Murphy et al., 2008*]. The EEMS for the Irene storm event, along with 300 other Taskinas Creek samples collected during baseflow and rain event conditions between 2009 and 2011, were compiled for use in parallel factor (PARAFAC) and other analyses. PARAFAC model analysis was used to identify the statistically important components of the EEMS as described elsewhere in detail [*Ohno, 2002; Stedmon and Bro, 2008*]. In addition to PARAFAC analysis, the spectra were examined using several indices that were observed from the generated EEMS. The fluorescence index (FI), the ratio of emission of fluorescence between 470 nm and 520 nm at an excitation of 370 nm [*Cory and McKnight, 2005; Fellman et al., 2010; McKnight et al., 2001*], was used to distinguish between microbial and terrestrially derived DOM. The freshness index, the ratio of fluorescence intensity at 380 nm divided by the emission intensity between 420 nm and

435 nm, at excitation 310 nm [*Parlanti et al., 2000*] was used to distinguish between recently derived and more decomposed DOM [*Wilson and Xenopolous, 2009*] and allowed the relative age of organic matter in surface waters to be determined; oldest DOM values approaching 0 and the youngest approaching 1. In addition, the humification index (HIX), as modified by Ohno [*Ohno, 2002*] to be the area under the Em spectra from 435 to 480nm divided by the peak area of 300-345nm+435-480nm at ex 254nm, was used to assess the extent to which the DOM had transformed into stable OM fractions. Based on previous study results, values that differed by more than 10% for HIX [*Ohno et al., 2007*], 10% for Freshness Index [*Petrone et al., 2011*], and 7% for Fluorescence Index [*Johnson et al. 2011*], were considered distinct from each other.

Statistical Analyses

Stages of the hydrograph and incubation treatment results were analyzed in the programming language R, version 3.01, using the Wilcoxon Mann-Whitney and the Kruskal-Wallis test for non-parametric data. Linear regression was used to examine correlations between different variables, using Box-Cox transformations to improve the linearity of the data as needed. The significance level between variables was set at $p \leq 0.05$. Samples used in hydrograph analysis were binned into pre-storm baseflow, rising limb, crest, recession limb and post-storm baseflow segments following basic graphical hydrograph separation technique and inflection point identification [*Brodie and Hostetler 2005*].

RESULTS

Hydrology

Defined by a minimum inter-event time of 1 hour, local rainfall associated with Hurricane Irene occurred over a 24 hour period (8/27/11 at 3:15am to 8/28/2011 at 3:15am EST) and resulted in a local cumulative total of 18.3 cm. Varied rainfall intensity resulted in a multi-peaked hyetograph, with intensities <10 $mm \bullet hr^{-1}$ accounting for 37 percent of the rainfall, >10-20 $mm \bullet hr^{-1}$ for 25 percent and >20 $mm \bullet hr^{-1}$ for the remaining 38 percent; maximum measured rainfall rate was 8.6 $mm \bullet 15min^{-1}$. The storm generated a pressure low of 977 mbar and sustained high wind speeds between 7-8 m/sec (peak wind speed 16.9 m/sec) [*System(CBNERRS), 2012*].

Hurricane Irene produced a storm surge of 1.0-1.1 m within Taskinas Creek and the York River proper (Station: Clay Bank; ~9 km down river of Taskinas Creek). Within the larger adjacent riverine system, as represented by the CBNERR Clay Bank continuous water quality station, the storm surge resulted in sustained elevated salinity levels over multiple tidal cycles followed by a multi-day recession driven by watershed freshwater inflows [*System(CBNERRS), 2012*]. In contrast, salinity levels near the mouth of Taskinas Creek depict an immediate and dramatic decrease during and after the storm surge, indicating rapid and substantial watershed runoff. Despite the measurable storm surge at the mouth of Taskinas Creek, water levels in the study stream did not indicate backflow of water at the gaging station.

Antecedent conditions prior to the storm were relatively dry with August 2011 rainfall totals prior to the storm (>26 days) of 18.1 mm and, with the exception of a single 0.3 mm event, no rainfall during the prior 7 days [*System(CBNERRS), 2012*]. At the

downstream Site 2, average base flow condition prior to rain-induced runoff was 0.0016 m^3 sec^{-1}. In response to Hurricane Irene, the stream exhibited a somewhat complex storm hydrograph pattern at Site 2 (Figure 3-2b). Based on the stage-Manning method, total storm related Q, as determined by discharge over the 39.25 hour period required for the return of pre-storm base flow conditions, was on the order of 20,400 m^3, exhibited a peak Q of 0.79 m^3sec^{-1} and resulted in a runoff : precipitation ratio (R/P) of 0.21.

TR-55 model results indicated peak Q's of 0.32 and 1.14 m^3sec^{-1} for Site 1 and 2 reaches, respectively, with an integrated watershed peak discharge of 1.44 m^3sec^{-1} at Site 2 (Figure 3-2). Storm related Q for reach 1 was 2700 m^3 and 16,800 m^3 for reach 2, resulting in a watershed total Q of 19,500 m^3. Resulting R/P values were 0.05 for reach 1, 0.16 for reach 2 and 0.21 for the integrated watershed.

Analyte Concentrations and Fluxes

Time series concentrations for DOC, DON, DIN and PO_4 for Sites 1 and 2 are provided in Figures 3-3a and 3-3b, with averaged concentrations of DOC, TDN, DON, DIN and PO_4 for different stages of the hydrograph provided in Table 3-2. Over the storm hydrograph, DOC concentrations varied from 3.5-19 mg/L at Site 1 (Figure 3-3a) in the upper mesic hardwood region and 5.8-17 mg/L at Site 2 (Figure 3-3b) in the downstream seepage swamp region. DOC concentrations increased with stream flow with average crest stage concentrations of 18 and 16 mg/L at Sites 1 and 2, respectively (Table 3-2), representing an increase 22 and 6.9 times pre-storm baseflow (0.79 mg/L and 2.3 mg/L).

TDN concentrations varied from 0.24-0.42 mg/L at Site 1 and 0.36-0.49 mg/L at Site 2 (Figure 3-3a and b), with average values at the crest showing an increase of 2.3 and 2.8 times pre-storm baseflow (Table 3-2). DON ranged from 0.22-0.41 mg/L at Site 1 and

0.25-0.47 mg/L over the storm hydrograph (Figure 3a and b), with average crest values that were 2.8 and 220 times pre-storm baseflow (Table 3-2). DON dominated the dissolved nitrogen pool during stormflow at both sites, representing 75-99% of the TDN pool at Site 1, and 70-99% of the TDN pool at Site 2. DOC and DON concentrations co-varied over the storm hydrograph and exhibited a significant linear relationship at both Site 1 ($m=42.6$, $r^2=0.63$, $p=.003$) and Site 2 ($m=41.60$, $r^2=0.91$, $p=.001$). During storm influenced flow, concentrations of DIN ranged from 0.01 to 0.03 mg/L(Figure 3-3a) at Site 1 and 0.01 to 0.06 mg/L at Site 2 (Figure 3-3b), with average concentrations at the crest of the storm that were 250-fold higher than pre-storm baseflow values at Site 1, and an approximate 15-fold decrease from pre-storm baseflow concentrations at Site 2 (Table 3-2). Storm influenced PO_4 concentrations varied from 0.01 to 0.06 and 0.02 to 0.06 mg/L at Sites 1 and 2 (Figure 3a and b), respectively. In contrast to DOC and DON, PO_4 concentrations decreased with streamflow with crest stage samples, diluted by a factor of 7.0 at Site 1 and by a factor of 1.5 at Site 2.

Total fluxes and areal yields of DOC, TDN, DIN, DON and PO_4 at Site 2 are reported in Table 3-3. Site 2, in addition to having contributions from the non-tidal forested seepage swamp includes the contributions from Site 1, which are contributions from the upper hardwood forested reaches. Total exported amounts for DOC were 300-320 kg; TDN was 8.0-9.4 kg, DON was 8.3-8.9 kg, DIN was 0.53-0.62 kg and PO_4 was 0.45-0.37 kg. In addition, Irene related solute fluxes are compared to pre-storm baseflow flux rates. Storm DOC flux over a 39.25 hour period was 460 to 490 times baseflow during the equivalent time period; DON flux was 280 to 300 times baseflow; TDN was

210 to 220 times baseflow; DIN was 59 to 69 times baseflow; and PO_4 was 74 to 90 times baseflow (Table 3-3).

DOM Composition During Hurricane Irene

A six component PARAFAC model was developed that accounted for 91% of the variance associated with DOM composition in the stream samples collected for this study (Table 3-4). Component 1 (Terrestrial derived, humic-like, A) was the most abundant component at both Site 1 and Site 2 (Figure 3-4a). At both sites, Component 1 increased during the rising limb of the hydrograph at Site 1, but did not strongly correlate with discharge for the remainder of the hydrograph ($r^2 \leq 0.8$ or $p > 0.05$, Table 3-5). At Site 2, Component I initially decreases, then increases with the remainder of the rising limb. Component 1 does not correlated with discharge during the hydrograph. The other components, with the exception of Component 6, also increased during the rising limb (Figure 3-4b and 3-4c). Component 6, a protein-like component, remained low and showed little change during the storm event, with the exception of during the crest and the falling limb where modest increases were noted for both sites (Figure 3-5b). Components 2, 4 and 5 decreased during the falling limb in contrast to component 3, which remained stabilized at its near maximum level throughout the storm hydrograph (Figure 3-4b, c). Component 2 correlated with Q during the crest and falling limb at Site 2 (Table 3-5).

Properties and reactivity of DOM (i.e., fluorescence, freshness and humification) over the storm hydrograph were described by initial, pre-incubation samples (Table 3-6). Given that initial sample fluorescence (FI) and humification (HIX) indices were similar between Site 1 and Site 2 for the rising, crest and recession stages of the hydrograph, it

was expected that post-storm baseflow indices at Site 1, where samples were not collected, were similar to Site 2. Measured values of FI over the storm hydrograph ranged from 1.76 to 1.96, with elevated values associated with post- storm baseflow conditions suggesting microbial sources of DOM during those periods. Minimal variation in FI occurred between sites (<3%) and within a site (~10%) for the entire storm hydrograph.

At Site 1, initial freshness index values ranged from 0.44 to 0.59, decreasing over the rising to falling hydrograph (Table 3-6). In contrast, at Site 2, freshness index values were similar over the entire hydrograph, equaling 0.48, until post-storm baseflow when elevated values of 0.94 were measured. Consequently, at Site 1, the freshness index indicates an initial pulse of younger, fresher organic matter occurring during the rising limb that does not persist over the event. However, at Site 2, the storm hydrograph shows a delay in the arrival of younger organic matter, with it appearing only after the storm as baseflow conditions were resumed.

Providing information as to the relative stability of DOM, HIX values ranged from 0.92 to 0.96 during the storm hydrograph stages at both Sites 1 and 2 and dropped to 0.48 during post storm baseflow at Site 2. Minimal variation (0-4%) in HIX was observed between sites over the storm hydrograph, as compared to a >50% difference between post-storm baseflow and other hydrograph stages, indicating that the storm event generally brought in an influx of older and more stable (humified) DOM.

DOC Reactivity and Changes in Composition

Reactive DOC, expressed as a percent change from pre-incubation concentrations, by storm hydrograph stage and incubation treatment are presented in Table 3-6 and Figure 3-6. Pre-storm baseflow samples ranged from 24-28 % and 26-32 % reactive DOC

at Sites 1 and 2, respectively. All storm associated samples (defined as rising hydrograph, crest, and falling hydrograph) contained reactive DOC resulting in measureable reductions of DOC during incubations of 13 to 33% for water collected at the hardwood forest site (Site 1) and 10 to 47% at the seepage swamp site (Site 2) (Table 3-6, Figure 3-6a,b). Overall, reactive DOC decreased during the rising hydrograph relative to pre-storm baseflow (17.5 ± 4.1 for rising vs. 27.5 ± 3.4 for pre-storm baseflow) (Figure 3-6a), followed by an increase above rising limb values during the crest and falling limb (29.8± 15.3 and 26.8 ± 8.3) (Table 3-6, Figure 3-6a). The lowest %reactive DOC values were observed during post-storm baseflow (Site 2 = 2.5 ± 0.7) (Table 3-6, Figure 3-6a,c). Samples with the highest variability included crest samples (coefficient of variance (COV)=51.3%) and falling limb samples (COV=30.9%) (Figure 3-6a).

The variability found in averaged storm incubations was examined by site (Figure 3-6b), by incubation treatments (LM and LMN) (Figure 3-6c) and averaged across site and treatments for the crest and falling hydrograph samples (Figure 3-6d). Pre-storm % reactivity was similar at Site 1 and Site 2 (26.0±2.8, 29.0±4.2). Both Site 1 and Site 2 declined in % reactive DOC during the rising hydrograph compared to pre-storm baseflow values, (14±1.4, 21.0±0.0), with more reactive DOC at Site 2 during this stage of the storm. % reactive DOC increased during the crest and falling limb of the hydrograph (Figure 3-6b). Falling limb samples show Site 1 samples (20±1.4) contain lower % reactive DOC compared to Site 2 samples (33.5±4.9). However, distinctions between DOC reactivity for Site 1 (31.0±2.8) and Site 2 (28.5±26.2) during the crest could not be determined, due to the high variability in the samples when grouped by LM and LMN treatments (COV=9.03%, 91.9%).

Due to the variation found in crest samples when LM and LMN treatments were grouped (Figure 3-6a,b), the LM and LMN treatments were examined separately over the hydrograph (Figure 3-6c). Incubations for both LM and LMN treatments showed a decrease in % reactive DOC during the rising limb (17.0±5.7 for LM, 18.0±4.2 for LMN) compared to pre-storm baseflow (28±5.7 for LM, 27.0±1.4 for LMN) incubations (Figure 3-6c). The variability made it difficult to detect between-site differences for the LM and LMN treatments.

Because variability was so large in grouping treatments by site, or by incubation, one additional grouping was examined. In many studies, and initial flush of the system during the rising limb of the hydrograph has shown a change the delivery of nutrients and DOC that differs from the remainder of the hydrograph and may be related to the composition of sources accessed during the rising limb [*Boyer et al., 1997; Hornberger et al., 1994*]. Consequently, rising limb samples were considered separately from the remainder of the hydrograph and crest and falling samples were grouped together (Figure 3-6d). Then, averaged LM and LMN treatments for the storm hydrograph (minus rising limb samples) were examined by Site, in order to determine if there were differences in % reactive DOC by site and treatment over the remainder of the hydrograph. No discernible difference was found between Site 1 LM and LMN samples, which were 24±7.1 and 27±8.5 % reactive DOC, respectively. However, Site 2 LM samples contained 20±14.1 % reactive DOC, while Site 2 LMN samples had a greater amount of %reactive DOC (42.0 ± 7.1). % reactive DOC at Site 1 LM samples (24±7.1) was similar to Site 2 LM samples (20±7.1 %). However, % reactive DOC for Site 2 LMN samples (42.0 ± 7.1) was higher than for Site 1 LMN samples (27±8.5) (Figure 3-6d).

Overall, there was a trend of decreasing % reactive DOC during the rising hydrograph compared to pre-storm samples, followed by an increase in reactivity over the crest and the falling limb of the hydrograph (Figure 3-6a). The LM and LMN treatments yielded similar levels of %reactive DOC at both sites pre-storm baseflow and rising limb. However, LMN treatments resulted in higher % reactive DOC at Site 2 vs. Site 1during the crest and falling stages.

Changes in Composition During Incubations

In general, Component 1 (HMW, humic-like, A) had the highest intensities, as measured in Raman Units (Table 3-7, Figure 3-5a). All components decreased during the incubations of pre-storm baseflow samples, as did total fluorescence. Rising limb samples show a decrease in total fluorescence for both treatments and sites. In both treatments and sites, C1 & C3 components decrease, whereas C2, C4, 5 and 6 have small increases. The greatest change in component fluorescence occurs for the C1 component, which reduces from 5.9 Raman Units at Site 1, to 0.95 and 0.99 Raman units for LM and LMN treatments, respectively (Figure 3-5c,d). Similar responses were observed for Site 2, with C1 being reduced from 5.97 to 0.97 and 0.91 Raman units for LM and LMN, respectively. Decreases in C3 are more modest; at Site 1, C3 values were reduced from 1.07 to 0.97 and 0.99 Raman units for LM and LMN treatments, respectively. C3 responded similarly at Site 2, with a reduction from 1.22 to 0.97 and 0.89 Raman units for LM and LMN, respectively. In summary, the greatest loss of intensity during incubations of rising limb samples was caused by reductions in Component 1 (HMW, humic-like, A) while there was little change in components C2, C4, C5, and C6.

LM and LMN incubations of crest samples at Site 1 showed a gain in all components, but particularly for Component 1 (Table 3-7, Figure 3-5c,d). LM and LMN incubations of crest samples from Site 1 resulted in increases in C1 (I=6.65, LM=226.8 and LMN = 221). Components 2-6 also increase during incubations of crest samples from Site 1 and show the greatest increase from initial conditions compared to all other incubations. In contrast, all components decreased during incubations of crest samples at Site 2 (Table 3-7).

LM and LMN incubations of samples from the falling limb hydrograph differed from one another by site and treatment (Table 3-7, Figure 3-5). At Site 1, Components 1-6 increased during the LM incubation, but decreased during the LMN incubations. At Site 2, all components decreased during the LM incubation, whereas all components, except C1 and C6, decreased during the LMN incubations.

Despite changes in component compositions, which in the majority of incubations were due to changes in Component 1, incubation experiments resulted in the production of fresher (higher Freshness Index) and less humified organic matter (lower HIX) for all storm samples (Table 3-6). Pre-storm samples followed this trend in freshness and HIX, except for Site 1 LMN samples, which decreased in freshness. Post storm samples showed different trends with incubations at Site 2 resulting in DOM that was less fresh (lower Freshness Index) and more humified (higher HIX) (Table 3-6).

Because C1 was the dominant component, and C6 is most commonly used to assess reactivity in other studies, Initial, LM and LMN sample values for C1 and C6 components were plotted in graphs (Figure 3-5a-f.) At Site 1, C1 values for the initial

samples were similar across most of the hydrograph but increased ~two-fold during the Falling hydrograph (Figure 3-5a). Following incubation, C1 increased over 8-fold for the crest (LM and LMN) and falling limb (LM) incubations (Figure 3-5c,e).C1 does not show a similar trend during Site 1 falling limb LMN incubations. At Site 2, C1 was similar across the hydrograph but increased during the post-storm (Figure 3-5a). Following incubation, C1 decreased in all LM treatments but increased in the LMN treatments of Falling Limb and Post-Storm baseflow samples (Figure 3-5e). In the initial samples, C6 was higher for the Crest and Falling Limb samples at both sites (Figure 3-5b). Following incubation, C6 increased in stormflow samples at Site 1, particularly during the Crest (LM and LMN) and Falling Limb (LM) (Figure 3-5d) but showed little change in the LMN incubations (Figure 3-5f).

DISCUSSION

Hydrologic Responses to Hurricane Irene

Hurricane Irene made landfall in North Carolina's Outer Banks as a Category 1 hurricane on the morning of August 27, 2011, and then re-emerged offshore of the lower Chesapeake Bay in Virginia, skirting the Delmarva Peninsula as a marginal Category 1 hurricane. In the south east portion of coastal Virginia, the average return period for tropical storm with this wind strength is on the order of 4 years [*Keim et al., 2007*]. Consequently, an estimated 25 storms of this magnitude can be expected in this region in the next 100 years.

This hurricane resulted in 18.3 cm of precipitation at the study site over a 24 hour period, representing 17% of the local total annual rainfall in 2011 and 15% of the regional annual long term average of 121 cm. Average recurrence interval for the volume

of this storm's precipitation was between 25 (17.3cm) and 50 (20.2 cm) years [*Bonnin et al. 2009*], suggesting that although storms of this force are frequent (~25 in 100 years), the amount of precipitation is unusual, (between 2-4 events in 100 years). This event also entered the Tidewater region study site during moderate drought conditions. The Palmer Severity Index values ranged from -1.97 to -2.71 from February to July preceding this event. The three weeks prior to the event, in August, also indicated moderate drought [*Center 2015*].

TR-55 results generated a maximum peak Q of 1.44 m^3sec^{-1} with a total Q Volume of 19,700 m^3, with other peaks following rainfall, while the stage-Manning approach generated a peak Q of 0.79 m^3sec^{-1} with a total Q of 20,400 m^3, also including subpeaks mirroring rainfall (Figure 3-2). The stage-Manning approach measured in-stream measurements while the stream was in bank during the storm. Once the stream went out of bank, discharge was estimated using the Manning equation. In contrast, TR-55 used Manning estimates from the start of rainfall and until the end of the event. The TR-55 included parameters to estimate initial storage, and once storage was full, routed the rest of rainfall directly to stream discharge. In contrast, the stage-Manning approach measured actual conditions and responses in the stream, until out of bank conditions occurred when estimates were then required. The large peak in TR-55 compared to the stage-Manning model suggests more storage occurred in the basin than was estimated by the TR-55 model. TR-55 also does not allow for the channel overflowing and filling the surrounding basin, as the stage-Manning model does. The smaller peak in the stage-Manning model with the discharge rising steadily and sooner than the TR-55 model suggests more storage in the watershed, with additional surrounding areas contributing to

flow after the rain event occurs. Consequently, the TR-55 model has a slightly lower discharge despite having a large peak Q when compared to the stage-Manning approach. It is likely the actual values of Q are somewhere between the two model estimates, so the range of values are considered when examining the total flux of solutes.

The runoff ratios for each model were 0.21 for the stage-Manning model and 0.20 for the TR-55 model. These models have somewhat similar ratios compared to other work. Corbett et al. (1997), utilizing TR-55, reported somewhat similar runoff ratios, ranging from 0.25-0.35, for a dry forested coastal South Carolina watershed receiving rainfall between 150-200 mm over a 24- hour period. Work in a forested watershed in the southeastern Coastal Plain of South Carolina found mean event runoff ratios were higher for wet periods than for dry conditions [*La Torre Torres et al., 2011*]. In a long term study (1964-1976) storms with >100 mm rainfall, with low previous 5 day (0.0) and 30 day (33-42 mm) rainfall had R/P values ranging from 0.04-0.19, while the mean R/P for all dry period storms was 0.21 [*La Torre Torres et al., 2011*].

Some of the differences between the models developed for Hurricane Irene here and at other sites may derive from variable source areas. There are variable runoff volumes between higher forest elevations versus lower elevations with saturated seepage areas. Corbett et al (1997) found that during heavy rainfall simulations (>100 mm) saturated forest soil reduced infiltration rates to near zero and produced high runoff volumes per area, similar to the results generated by impervious surfaces. La Torre Torres et al. (2011) reported that for a low gradient southeastern Coastal Plain forested watershed in South Carolina, shallow saturated overland flow was the dominant runoff generation mechanism. At Taskinas Creek, it took several hours after rainfall started

before peak Q occurred at the upland forest Site 1. However, during the course of the event, once peak Q was reached at both Site 1 and Site 2, stream discharge mirrored rainfall, suggesting infiltration ceased and saturated overland flow from rainfall had become the dominant runoff source. Consequently, the differences in R/P at Taskinas Creek and other study sites could be due to variation in source elevations.

Stream DOM Composition, Flux and Reactivity

Hurricane Irene delivered a large increase over baseflow flux for DOC and DON discharge from the unnamed perennial stream, while PO_4 and DIN decreased. These changes in fluxes for storm events are in keeping with other studies. In previous studies, DOC has been shown to increase by 100-400% above baseflow, and events often account for the majority of export of DOC and DON during a hydrologic year [*Hinton et al., 1997; Inamdar et al., 2012; Raymond and Saiers, 2010*].

In the uppermost portion of the watershed, DOC concentrations reached maximum values with the peak of the hydrograph (8/27/2011 14:15), while DON concentration peaked later (Figure 3-3). In contrast, at downstream Site 2, DOC and DON concentrations peaked with the rising hydrograph. In a study of forest and wetland environments, Inamdar et al. [*Inamdar et al., 2008*] found DON and DOC concentrations are dependent on the storm event and the source of DOM. They found that DON lagged behind DOC when DON was being added from soils rather than throughfall. This suggests that in the upland portion of the watershed represented by Site 1, soils are being accessed and contribute to the DOM pool during the onset of the storm event. It also suggests that downstream, there is greater connectivity between the stream and the

watershed initially, consistent with the more saturated soils that characterize the seepage swamp region, as there was no lag in DOC and DON concentrations.

These observations of DOC and DON concentrations are supported by observations of the geomorphology at the field sites. The upstream portion, Site 1, is a single channel with a steep gradient. In a similar system, Inamdar [*Inamdar et al., 2011*] reported that sources of DOM over a hydrograph followed a predictable pattern based on an end-member mixing model for their study system. Caverly also found a predictable pattern in ephemeral streams during Hurricane Irene, where initial flow is from runoff, followed by organic matter released from soils as rainfall infiltrates soils and contributes to the stream channel [*Caverly et al., 2013*]. However, Inamdar's system is more similar to this one, although it is smaller system. In that system, DOM is derived from throughfall/rainfall initially, followed by leaf litter leachate, then soil and groundwater sources comprise the recession limb of the hydrograph. This is likely what was observed at Site 1. In contrast, the downstream portion, Site 2, is a braided stream in a wide floodplain and is a wetland with regularly saturated soils. This greater connectivity of surface water to surface soils is apparent, as there is no lag between DOC and DON concentrations. At Site 2, unlike in the upstream Site 1, there is no observable lag between throughfall/rainfall contributions and leaf litter/soil source contributions to stream DOM.

DOM composition as revealed by EEMs indices and PARAFAC component analysis provides support that the initial pulse of DOC and DON was from throughfall followed by increasing inputs from soils over time. Similarly, Caverly et al. (2013), in a study of ephemeral input during Hurricane Irene found that rainfall generated initial

runoff that led to inputs of fulvic-like components from soils as flow increased, using specific ultraviolet absorbance (SUVA). As DOM increased during the storm event, all fluorescence components except C6 increased (Figure 3-4b and c). Component 1 (humic-like, HMW terrestrial), the most abundant component, increased at both sites and remained elevated during the falling hydrograph. Over the storm hydrograph, there was little change in the fluorescence index (Table 3-6). However, both sites experienced a decrease in the freshness index and an increase in HIX during the storm event. This indicates the addition of less fresh and more humified organic matter sources, reflecting potential contributions from soils. Later, post-storm baseflow values are fresher but more humic-like (Table 3-6), suggesting access of humic organic matter from a younger source, consistent with change in flow path. High HIX values, such as those found in this study, have been correlated with soil DOM [*Kalbitz et al., 2003*] as well as with high molecular weight DOM from surficial soils [*Vidon et al., 2008*]. The HIX values observed in our study, along with changes in DOM components and fluxes of DON and DOC during Hurricane Irene, support that the majority of the DOM during the event is from near surface and surficial DOM sources, as found in previous studies [*Fellman et al., 2009b; Inamdar et al., 2012; Wiegner et al., 2009*].

Incubations showed that DOC decreased in reactivity compared to baseflow during the rising limb, and then rebounded later in the storm event hydrograph. Post storm baseflow had less % reactive DOC than pre-storm baseflow. Site 1 reactivity was more consistent, having less difference in LM and LMN % reactive DOC. Investigation into potential causes for the variability in % reactive DOC during the crest and falling limb of the hydrograph suggest that Site 2 DOC may be nutrient limited (Figure 3-6).

Sampling and incubation was limited, although grouping of crest and falling limb incubations yield higher % reactive DOC than other incubations, additional sampling and investigation is required to conclude this. Here, EEMs falls short in determining the cause of the changes and variability seen in reactivity, as there was no uniform response in EEMs to changes in percent reactivity. We expected protein-like fluorescence (C6) to vary with reactivity, as it has in other studies [*Fellman et al., 2009a*], yet it remains constant while the humic-like C1 component varies and C2-C5 components vary over the hydrograph. This suggests it is the fluorescence of the humic-like component (C1), rather than the protein-like component (C6) that may impact reactivity in this study system. The use of light in the incubation studies may have caused this response as in other studies [Chapter 2 and references therein], accessing pools of DOM previously not observed under microbial only incubations. Compound specific analysis, NMR, or other chemical compositional analyses would have been helpful to explain these differences, but was beyond the scope of this study.

Impact of Storm DOM Reactivity on Adjacent Receiving Waters

The reactivity seen in storm samples has implications for the downstream estuary, especially when considered along with the elevation in the total flux of DOC exported from events compared to export during baseflow conditions. The residence time of a water mass in Taskinas Creek is less than a day, while in the York River, it is about 40 days from West Point to the mouth [*Herman et al., 2007*]. The total delivery of DOC during Irene was 296 to 319 kg over a 39.25 hour period. When the applying the total % reactive DOC as determined from incubation experiments (~ 27.5 for baseflow, ~25% for stormflow), it means that the event delivered 73-80kg kg of carbon as compared to 0.18

kg during 39.25 hr antecedent baseflow conditions. This delivery of reactive DOC during Irene is approximately 400-444 times the amount of reactive DOC delivered during baseflow conditions in the estuary. Although nutrient addition experiments were inconclusive, % reactive DOC seemed to increase in the later stages of the hydrograph at Site 2 in the LMN treatments. Because nutrient enhanced conditions occur in the York, the reactivity of the DOM released may increase as materials are transported downstream into the estuary where light and nutrient availability increase. However, further research is required to determine the extent of the reactivity of storm DOM in the estuary.

Although the reactivity and flux of storm derived DOC may overestimate reactivity, as DOC was exposed to both microbial and photochemical decomposition the flux is considerably greater than expected from baseflow fluxes conducted under the same parameters. Although some of the breakdown of DOC may occur during transit to the estuary through transit along the tidal creek, most of it is likely to occur downstream in the estuary or coastal ocean. The breakdown and respiration of DOC by heterotrophs consumes oxygen and releases carbon dioxide, depleting the oxygen supply in surrounding waters. Loadings of DOC during Hurricane Irene were 400-444 times baseflow values and had the potential to cause significant oxygen depletion in downstream waters as has been observed in other systems [*Peierls et al., 2003; Hagy et al., 2004; Tomako et al., 2006*]. This would particularly be the case if additional unstudied streams in the York River watershed contribute comparable amounts of reactive DOM during large events. Consequently, the reactive pool of DOC from this, and other large events, was capable of being transported downstream, stimulating primary and secondary production, and contributing to low oxygen zones within the

York. Given the expected increase in frequency and intensity of large storms due to climate change, consideration of the effects of DOC loadings on receiving waters warrants further study, and potentially, management [*Stanley et al., 2011*].

CONCLUSIONS

Hurricane Irene caused a large flux of DOC, DON, and PO_4 as well as changes in DOM sources over the duration of the storm hydrograph. The largest component of DOM fluorescence was high molecular weight, humic-like material. The changes in flux and DOM sources also led to changes in the reactivity of DOM released, though they did not correlate with any one component measured by EEMS PARAFAC. This suggests that future studies should not rely solely on fluorescence of DOM to determine the potential reactivity of terrestrial organic matter during storm events.

Results from the incubation studies showed that DOC components were reactive during storm and baseflow conditions and when exposed to combined photochemical, microbial and nutrient rich treatments. The responses to light and nutrients suggest that DOM from this first order creek may be able to stimulate primary and secondary production downstream. The average storm DOC reactivity ranged between 18-25%. Together, with the large fluxes of DOC, DON and PO_4 during storm events, this reactive organic matter has the potential to impact downstream water quality by stimulating primary production and/or increasing oxygen demand, which could contribute to hypoxia. This study shows that the addition of nutrients may also enhance the reactivity of OM, likely exacerbating oxygen reduction, requiring this also to be considered in ecosystem management when planning for the impacts of climate change.

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Table 3-1. TR-55 model parameters and data sources.

Model Parameter	Site 1	Site 2	Data Source
Rainfall (cm)	18.2	18.2	On-site rainfall time distribution (CBNERR 2011);10-yr on-site rainfall distribution; 24 hr period
Rainfall duration (hr)	24	24	
Watershed delineation (ha)	26	28	Developed 0.6 m DEM and ArcGIS watershed tool
Water flow paths (m)			ArcGIS Flow direction tool
Soil classification			
Vegetation	Hardwood Forest	Seepage Swamp	Patterson 2011
Runoff curve number (CN)	36	54	USDA
Hydrologic soil group (HSG)	B	A/D	
Cover type	Woods	Woods	
Cover type treatment	None	None	
Hydrologic condition	Good	Good	
Antecedent runoff condition (ARC)			$RCN_{dry} = (4.2*RCN_{avg}) \div (10-(0.058*RCN_{avg}))$
Time of concentration (T_c)	0.04	0.01	Cronshey 1986
Weighted (K_m)	0.218	0.431	
Reach friction slopes	0.012-0.014	0.009	Field measured
Contribution channels[1]	3	1	

Table 3-2. Stream solute concentrations by hydrograph stage for Site 1 and 2. Mean values, in mg/L, are presented with standard deviation and sample size (N) shown parenthetically.

Site and Stage	DOC	TDN	DON	DIN	PO_4^{3-}
Site 1					
Pre-storm[1]	0.79	0.15	0.15	4.0×10^{-5}	0.07
Rising	7.35 (4.8,5)	0.24 (0.06,5)	0.22 (0.07,5)	0.03 (2.15,5)	0.06 (0.01,5)
Crest	17.58 (1.5,3)	0.42 (0.05,3)	0.41 (0.05,3)	0.01 (0.01,3)	0.01 (0.01,3)
Peak	19.37 (-,1)	0.38 (-,1)	0.37 (-, 1)	0.02 (-,1)	0.02 (-,1)
Falling	15.06 (0.90,3)	0.39 (0.01,3)	0.38 (0.01,3)	0.01 (0.02,3)	0.01 (0.02,3)
Post-storm[1]	1.06 (-,1)	0.29 (-,1)	0.29 (0,1)	0.01 (-,1)	0.34 (-,1)
Site 2					
Pre-storm[1]	2.3	0.20	2.0×10^{-3}	0.20	0.03
Rising	9.5(3.57,5)	0.36 (0.07,5)	0.29 (0.08,5)	0.07 (0.07,5)	0.03 (0.01,5)
Crest	15.77 (1.29,3)	0.46 (0.03,3)	0.44 (0.03,3)	0.02 (0.01,3)	0.02 (0.01,3)
Peak	17.17 (-,1)	0.49 (-,1)	0.47 (-,1)	0.02 (-,1)	0.02 (-,1)
Falling	15.97 (0.73,3)	0.47 (1.36,3)	0.44 (1.79,3)	0.04 (0.60,3)	0.02 (0.01,3)
Post-storm[1]	10.4 (2.1,12)	0.37 (0.03,12)	0.33 (0.05,12)	0.05 (0.03,12)	0.09 (0.01,12)

[1]Pre-Storm and Post-Storm indicate pre-storm and post-storm baseflow.

Table 3-3. Calculated storm and baseflow analyte fluxes, in kg, for Site 2.

Site 2	**DOC**	**TDN**	**DON**	**DIN**	**PO_4^{3-}**
Baseflow					
39.25 hr Flux (kg)	0.65	0.042	0.03	0.009	.005
39.25 hr Yield (kg/ha)	0.012	0.0008	0.0006	0.0002	8.9×10^{-5}
Storm Influenced					
Event Flux (kg)	300-320	8.9-9.4	8.3-8.9	0.53-0.62	0.45-0.37
Event Yield (kg/ha)	5.8-5.9	0.16-0.18	0.15-0.16	0.01	0.01
Storm Flux : Baseflow Flux	457-492:1	212-224:1	277-297:1	59-69:1	74-90:1
Storm Yield : Baseflow Yield	483-492:1	220-225:1	250-267:1	5:1	112:1

Table 3-4 . Description of PARAFAC model components. The model was based on characteristics described in Fellman et al. (2010).

Component	Excitation (nm)	Emission (nm)	Characteristics (based on Fellman et al., 2010)
1	<230	440-470	UVC humic-like, A, terrestrial HMW
2	330-355	430-460	UVC humic-like, C, terrestrial
3	<230	390-410	Autochthonous or microbial, oxidized, humic-like, correlated with aliphatic C content
4	305-330	390-420	UVA humic-like, LMW, M
5	270-280; 390-410	485-500; 495-505	UVA humic-like, fulvic acid; Soil fulvic acid, D
6	268-282	300-308	Protein-like, result of degradation processes

Table 3-5. Summary Statistics between PARAFAC components and Q

		r^2	p	m	intercept
Site 1, Rising Limb					
	C1	0.34	1.20E-02	0.0874	6.82
	C2	0.76	5.00E-02	0.0008	0.80
	C3	0.54	1.55E-01	0.0005	1.32
	C4	0.70	1.00E-02	0.0007	0.82
	C5	0.59	1.20E-02	0.0005	0.81
	C6	0.38	3.00E-04	1.00E-05	0.12
Site 1, Crest and Falling Limb					
	C1	0.77	2.70E-01	4.40E-03	12.9
	C2	0.73	1.69E-05	4.00E-04	1.96
	C3	0.08	1.10E-06	-5.00E-05	2.20
	C4	0.07	5.33E-06	3.00E-04	1.80
	C5	0.44	8.35E-07	1.00E-04	1.70
	C6	0.21	1.00E-05	-9.00E-06	0.13
Site 2, Rising Limb					
	C1	0.23	7.00E-02	2.10E-03	3.46
	C2	0.65	9.70E-02	7.00E-04	1.091
	C3	0.57	1.37E-01	5.00E-04	1.46
	C4	0.61	1.19E-01	5.00E-04	1.13
	C5	0.62	1.13E-01	5.00E-04	1.12
	C6	0.64	1.02E-01	-4.00E-05	0.12
Site 2, Crest and Falling Limb					
	C1	0.37	4.85E-12	9.00E-03	9.35
	C2	**0.82**	**1.44E-15**	**3.00E-04**	**1.44**
	C3	0.01	2.77E-17	1.00E-05	1.95
	C4	0.73	8.71E-16	2.00E-04	1.42
	C5	0.74	1.21E-18	1.00E-04	1.40
	C6	0.33	8.91E-15	-8.00E-06	0.12

Table 3-6. Fluorescence Index (FI), Freshness Index, Humification Index (HIX) and Total Fluorescence for samples collected over the storm hydrograph. Initial (pre-incubation) and final (post-incubation) values are provided for LM (light + microbes) and LMN (light + microbes + nutrients) treatments.

	Fluorescence Index		**Freshness Index**		**Humification Index**		**Total Fluorescence**		**% Reactive DOC**
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	
Pre-Storm Baseflow									
Site 1-LM	1.48	1.3	0.51	0.61	0.85	0.78	8.23	0.68	24
Site 1-LMN	1.48	1.2	0.51	0.45	0.85	0.78	8.23	1.00	28
Site 2-LM	1.47	>3	0.48	0.55	0.93	0.92	14.9	0.51	32
Site 2-LMN	1.47	>3	0.48	0.49	0.93	0.87	14.9	0.51	26
Rising Hydrograph									
Site 1-LM	1.85	2	0.59	0.94	0.92	0.76	8.89	5.76	13
Site 1-LMN	1.85	1.27	0.59	0.86	0.92	0.75	8.89	5.93	15
Site 2-LM	1.81	1.45	0.48	0.82	0.96	0.82	8.96	5.42	21
Site 2-LMN	1.81	1.09	0.48	0.59	0.96	0.8	8.96	5.50	21
Crest Hydrograph									
Site 1-LM	1.85	1.65	0.45	0.51	0.96	0.86	15.9	265.8	29
Site 1-LMN	1.85	1.55	0.45	0.52	0.96	0.84	15.9	264.7	33
Site 2-LM	1.8	1.46	0.48	0.58	0.96	0.85	14.6	5.04	10
Site 2-LMN	1.8	1.44	0.48	0.68	0.96	0.87	14.6	9.51	47
Falling Hydrograph									
Site 1-LM	1.76	1.37	0.44	0.69	0.96	0.82	22.5	95.5	19
Site 1-LMN	1.76	1.34	0.44	0.54	0.96	0.83	22.5	1.23	21
Site 2-LM	1.79	1.63	0.48	0.64	0.96	0.86	10.2	4.11	30
Site 2-LMN	1.79	1.27	0.48	0.54	0.96	0.86	10.2	20.9	37
Post- Storm									
Site 2-LM	1.96	1.54	0.94	0.6	0.48	0.81	14.9	7.33	3
Site 2-LMN	1.96	1.34	0.94	0.49	0.48	0.82	14.9	13.6	2

Table 3-7. DOC reactivity, as measured by Raman Units, by PARAFAC components for light + microbial (LM) and light + microbial + nutrient (LMN) incubations at Sites 1 and 2.

Hydrograph Phase &		**Site 1**			**Site 2**	
PARAFAC Components	Initial	LM	LMN	Initial	LM	LMN
Pre-Storm Baseflow						
C1	5.02	0.17	0.47	5.58	0.13	0.15
C2	0.59	0.05	0.05	6.51	0.05	0.05
C3	1.15	0.18	0.19	1.14	0.11	0.11
C4	0.63	0.05	0.06	0.70	0.05	0.04
C5	0.59	0.05	0.05	0.70	0.08	0.07
C6	0.25	0.18	0.18	0.23	0.09	0.11
Total Fluorescence	8.23	0.68	1.00	14.9	0.51	0.53
Rising Limb						
C1	5.90	0.95	0.99	5.97	0.97	0.91
C2	0.59	0.97	0.99	0.82	0.97	0.92
C3	1.07	0.97	0.99	1.22	0.97	0.89
C4	0.63	0.97	0.99	0.90	0.97	0.93
C5	0.58	0.97	0.99	0.91	0.98	0.94
C6	0.12	0.93	0.98	0.14	0.65	0.91
Total Fluorescence	8.89	5.76	5.93	8.96	5.42	5.50
Crest						
C1	6.65	226.8	221.00	4.81	0.90	3.69
C2	2.10	7.07	8.35	2.12	0.79	1.16
C3	2.05	12.12	13.55	2.33	0.75	1.25
C4	2.00	6.77	7.78	2.06	0.84	1.15
C5	1.96	7.45	8.25	2.05	0.86	1.17
C6	1.14	5.64	5.72	1.22	0.90	1.09
Total Fluorescence	15.9	265.9	264.7	14.6	5.04	9.51
Falling Limb						
C1	12.28	80.84	0.35	3.91	0.79	14.22
C2	2.24	2.57	0.06	1.24	0.59	1.29
C3	2.51	4.13	0.00	1.31	0.50	1.56
C4	2.15	2.56	0.11	1.32	0.70	1.29
C5	2.10	2.81	0.36	1.34	0.74	1.36
C6	1.23	2.59	0.35	1.06	0.79	1.21
Total Fluorescence	22.5	95.5	1.23	10.2	4.11	20.9
Post Storm Baseflow						
C1				8.74	5.50	11.50
C2				1.33	0.27	0.33
C3				2.01	0.63	0.68
C4				1.32	0.29	0.31
C5				1.37	0.41	0.48
C6				0.13	0.23	0.26

Figure 3-1. Study site location map depicting dominant ecosystem types, gaging station (GS), weather station (WS) and water quality station locations.

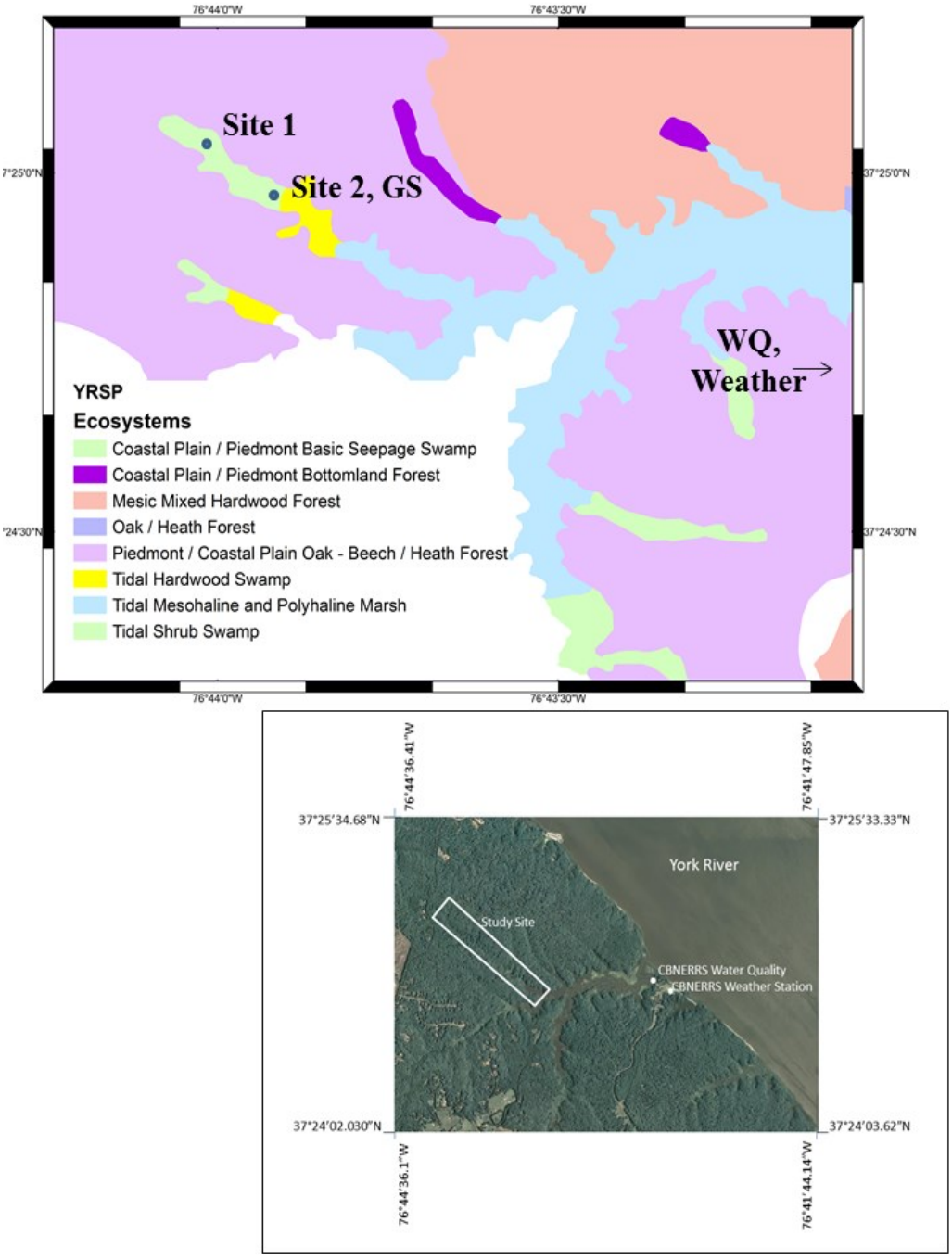
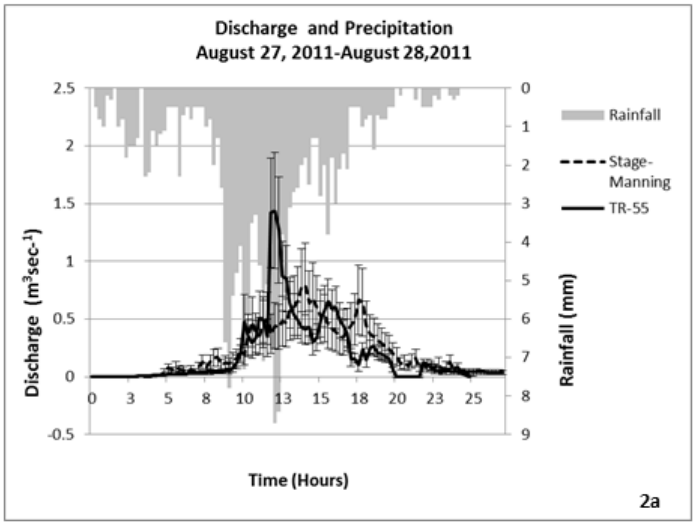


Figure 3-2. Hyetograph of Hurricane Irene rainfall and calculated discharge at Sites 1 and 2.



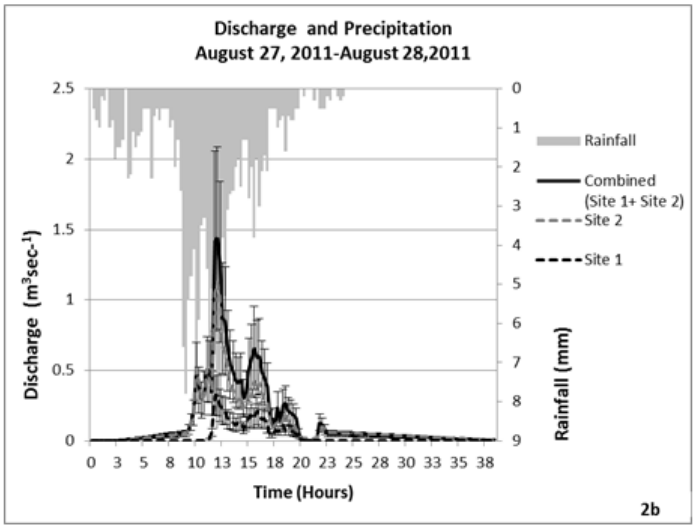
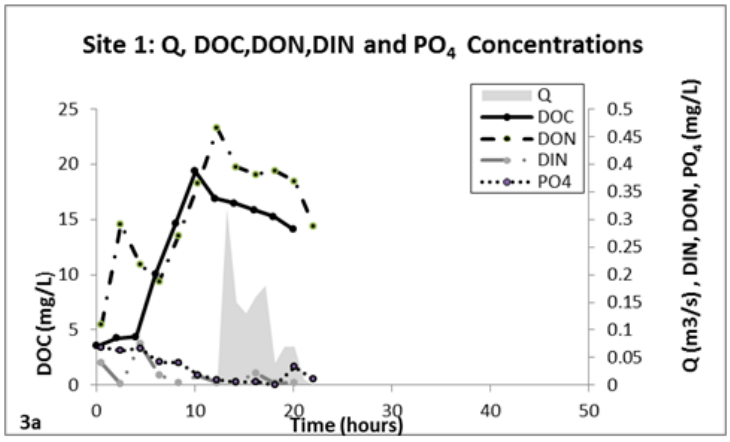


Figure 3-3. Concentrations of DOC, DON, DIN,TDN and PO4-3 along with calculated Q during Hurricane Irene at Sites 1(a) and 2(b).



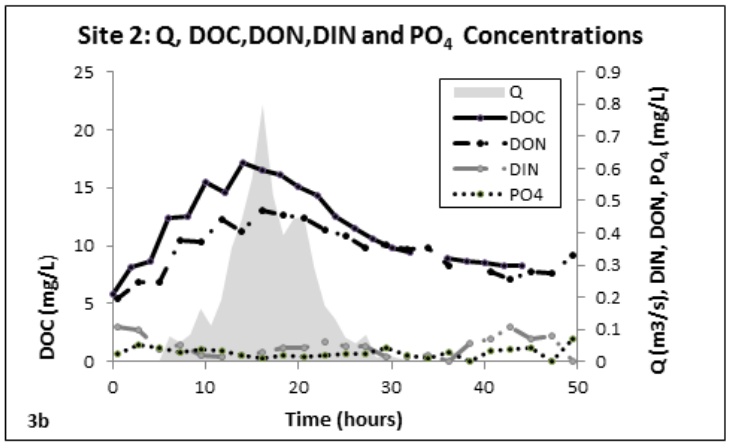


Figure 3-4. Measured PARAFAC Component values along with calculated Q during Hurricane Irene. Q and Component I (Terrestrial derived, humic-like, A) at Sites 1 and 2 (a), Additional Components(2-6) at Site 1 (b) and Additional Components (2-6) at Site 2 (c). Descriptions of the components are provided in Table 4. Note that the ranges for the left and right axes differ across the three panels.

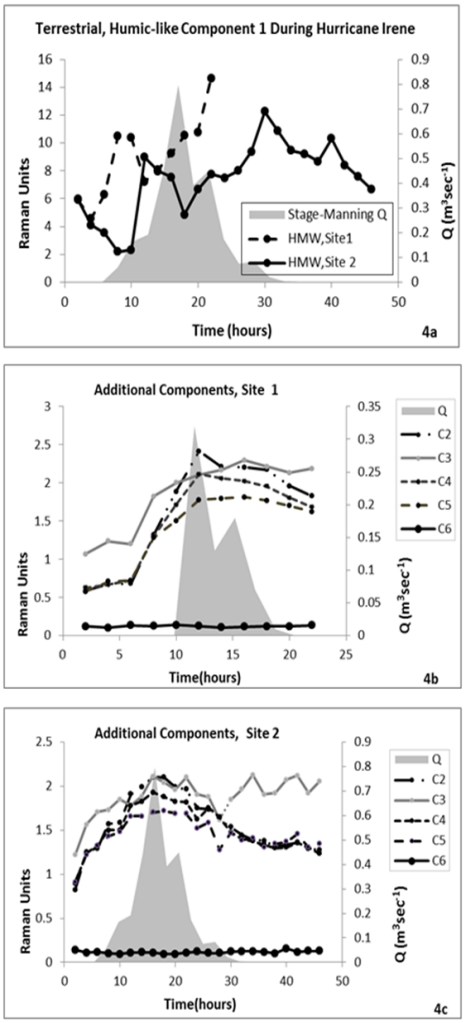


Figure 3-5. Measured PARAFAC Components C1 and C6 during LM and LMN incubations. Initial C1 values at Sites 1 and 2 (a), Initial C6 values at Sites 1 and 2 (b), LM results for C1 at Sites 1 and 2 (c), LM results for C6 at Sites 1 and 2(d), LMN results for C1 for Sites 1 and 2 (e) and LMN C6 results for Sites 1 and 2 (f).

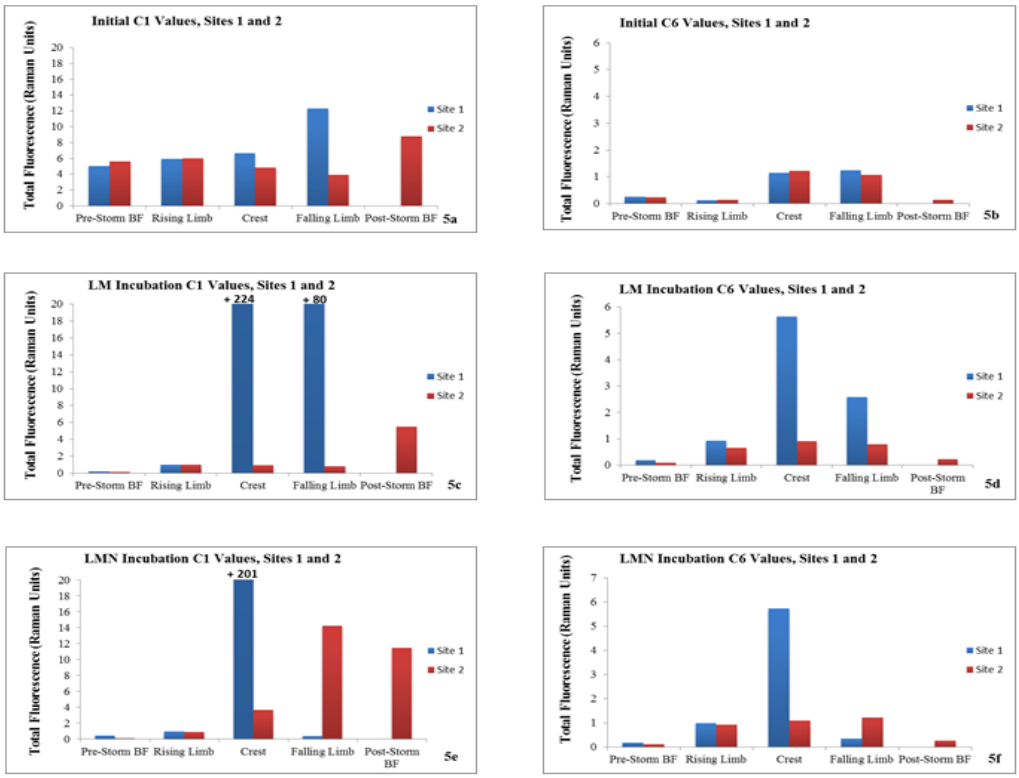
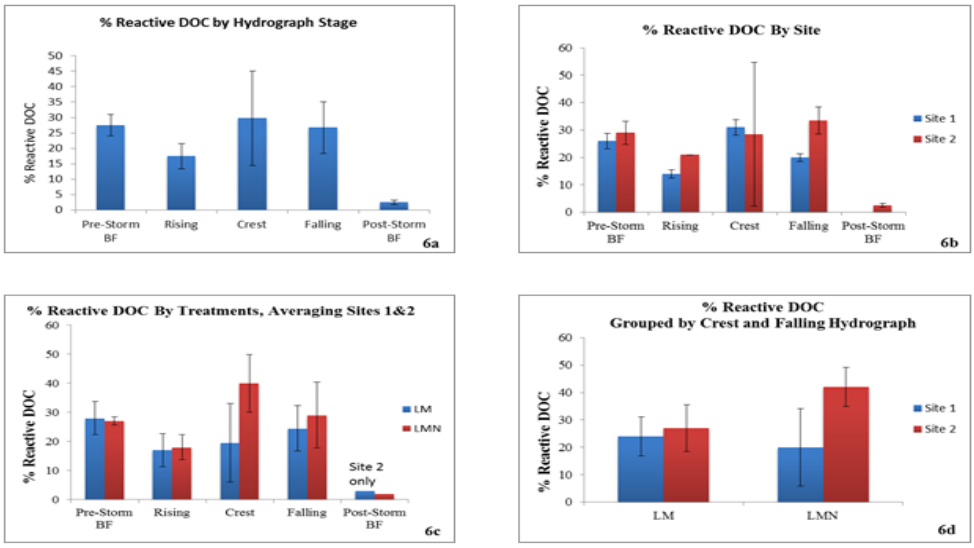


Figure 3-6. Measured % reactive DOC for pre-storm, rising, crest, falling and post-storm conditions at Site 1 and Site, per incubation treatment. Panels include averaged % reactivity grouped for all events and sites by hydrograph (a), grouped by site (b), grouped by incubation treatment (LM and LMN) (c) and crest and falling limb hydrograph samples grouped by site and treatment (d).



Chapter 4: A comparison of POC and DOC during two summer storms in a small stream

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ABSTRACT

Particulate organic carbon (POC) and dissolved organic carbon (DOC), as components of total organic carbon (TOC) are important parts of the global carbon cycle, connect the terrestrial environment with the global ocean during riverine transport. Storm events are responsible for a disproportionate portion of the POC and DOC released to downstream waters, accounting for up to 80% of the total annual released. Consequently, two storm events of different magnitudes, but similar antecedent conditions were collected during two summer events in a temperate, Mid-Atlantic perennial stream to determine the concentration and flux of total suspended solids (TSS), particulate organic carbon (POC), particulate nitrogen (PN), and dissolved organic carbon (DOC) and how they varied with sources of TOC (as measured by stable isotopes and C:N) during two different rain events. For both events, DOC, TSS, POC, and PN concentrations and fluxes increased during the events, with Hurricane Irene concentrations resulting in fluxes of DOC, TSS, POC and PN several times the smaller August event. During the August event, TSS, POC and PN (Pearson's correlation >0.6, p value <0.05) covaried, while during the Hurricane Irene event, they did not. Instead, different sources of TSS, POC and PN were noted. This suggests the magnitude of the storm events, independent of antecedent conditions which were similar for both events, can result in fluxes of TSS from distinct terrestrial sources undetectable by use of stable isotopes alone and challenging to discern using C:N ratios. Although identifying the differences in total POC and DOC yield require intensive sampling, this is critical as these distinctions can have an impact on downstream water quality.

Keywords

DOC, POC, TSS, PN, Antecedent conditions, Summer, Watersheds, Storm Events

Key Points

1. The ratios of POC:TSS and PN:TSS for two storm events with similar antecedent conditions revealed distinct terrestrial sources, as confirmed by field observations.

2. The POC flux resulting from the two events is not a linear relationship with storm magnitude, although the net flux of POC increased with storm intensity.

INTRODUCTION

Carbon export from the terrestrial biosphere to the oceans is an important component of the global carbon cycle and rivers and estuaries provide important links between terrestrial watersheds and the coastal ocean [*Blair and Aller 2012*; *Seitzinger and Harrision 2008*] and the global cycles of carbon and nitrogen [*Aufdencampe et al., 2011; Cole et al., 2007; Battin et al., 2009; Raymond et al., 2013, Seitzinger and Harrison 2008, Meybeck 1982)*]. Burial of terrestrial carbon represents a long-term sink for atmospheric CO_2 and knowledge of the fate of terrestrial organic carbon is critical for modeling biogeochemical processes. An estimated 0.4 petagrams of carbon a year ($PgCy^{-1}$), evenly divided between particulate organic carbon (POC) and dissolved organic carbon (DOC) [*Richey et al., 2004*] and 40-65 $TgN\ yr^{-1}$ [*Seitzinger and Harrison 2008*], are delivered from rivers to the coastal ocean annually. The amount of terrestrial organic carbon exported to coastal waters is a small amount of the total carbon processed in inland waters and estuaries [*Cole et al. 2007, Cai 2011*] and many estuaries are considered to be net heterotrophic, with large amounts of carbon processed within them and released as CO_2 [*Cai et al. 2011*]. Due to the connections between rivers, estuaries and the coastal oceans and their importance in carbon and nitrogen cycling *[Hedges et al. 1997],* it is critical to understand how changes in terrestrial carbon and nitrogen cycling impact estuaries, and consequently, coastal waters.

Small watersheds are an important source of soil and vegetation-derived DOM and POM to downstream waters, and are important determinants of the rate and pattern of

nitrogen export to estuaries due to their greater connectivity to coasts [*Seitzinger and Harrison 2008]*. Storm events, particularly events with high rainfall intensity that cause erosion [*Warrick et al., 2012*] can deliver large fluxes of sediment to downstream estuaries, and through wind and wave action, can cause resuspension of sediments within estuaries [*Palinkas et al., 2014; Duval et al., 2013*]. This, together with leaching of DOC [*Bauer at al., 2013, Keil et al., 1994*] greatly impacts the delivery of carbon and nitrogen to downstream waters. Export of terrestrial organic matter from small watersheds is known to be greatly influenced by storm events, accounting for 70-80% of the total annual export of DOC [*Raymond and Saiers 2010, Bauer at al.2013*] and >80% of the total POC exported annually and a large component of nitrogen [*Bauer et al. 2013*, *Dhillon and Inamdar 2014, and references therein*]. Recent studies have used high frequency measurements to compare the responses of POC and DOC during storm events [*Jung et al., 2015, Jeong et al., 2012, Ward et al. 2012; Dhillon and Inamdar 2013*]. Large exports of POC that exceed the amount of DOC released during storm events have been observed, with variations in the behavior of DOC and POC based on season [*Dhillon and Inamdar 2014*] and the magnitude of storm events. In most studies, POC concentration peaks before DOC [*Dhillon and Inamdar 2014;Oeurung et al., 2011*]. In other, larger events, POC concentration remains elevated after large storm events [*Dhillon and Inamdar 2014*] while DOC declines.

Recent work has also found differences in POC response between large, closely spaced events, and by season [*Dhillon and Inamdar, 2014*]. Larger events release more POC, and become more depleted in POC over time [*Dhillon and Inamdar, 2014*].

Summer events release more sediment and POC than autumn events, perhaps due to the intensity of the events [*Dhillon and Inamdar, 2014*]. Comparisons between events in small watersheds are often hampered by different watershed antecedent conditions, especially those caused by seasonal differences in organic matter present. Less work had been conducted to review changes in PN during events. Additional work to understand the causes of differences in POC and PN response are needed to constrain the global carbon and nitrogen budgets and understand the differential responses of POC and PN for events of different magnitudes, antecedent conditions, and seasonal parameters. Here, we examine two closely spaced events with very similar antecedent conditions occurring in late-summer to understand the response and magnitude of POC and PN fluxes to event magnitude in a stream draining a small watershed in the mid-Atlantic.

METHODS

Study Site Description

The study site was located within a first order forested subwatershed of Taskinas Creek, a managed component of the Chesapeake Bay National Estuarine Research Reserve (CBNERR), which drains directly to the York River estuary, Virginia, a tributary of southern Chesapeake Bay (see Figure 4-1). Nontidal portions of the study site, 54 ha in area, contain three dominant ecosystem types, described as oak-heath forest, oak-beech-heath forest and basic seepage swamp, which drain into a tidal hardwood swamp and a mesohaline to polyhaline marsh system (Figure 4-1; *Patterson 2011*). The upper reaches of the study stream lie within a oak-beech-heath forest characterized by mesic ravine slopes and ridges dominated by a hardwood canopy (e.g., *Fagus grandifolia, Quercus*

var., Acer var.) mixed with some pine (e.g., *Pinus taeda and virginiana*) and contains an understory of American holly (*Ilex opaca*) and mountain laurel (*Kalmia latifolia*) [*Myers et al. 2008*]. Downstream, the stream traverses a basic seepage swamp that exhibits temporary and seasonal flooding, and has a mixed hardwood community including red maple (*A. rubrum*), black gum (*Nyssa sylvatica*), green ash (*Fraxinus pennsylvanica*), a variety of oak(*Quercus var.*) and other more water tolerant species [*Myers et al. 2008*]. Flow continues from the seepage swamp through tidal hardwood swamp and mesohaline marsh ecosystems prior to discharge in Taskinas Creek. The sandy bottom stream is relatively well defined with short reaches of subterranean flow in the upper reaches and evidence of bed migration in the broad (~25 m) nontidal swamp floodplain.

Soils within the study site primarily consist of poorly drained soils of the Johnston complex in the nearly level (0-2 % slopes) floodplain region and deep, moderately drained Craven complex soils in regions with moderate slopes (2-10% slopes), and well drained Emporia complex soils along the adjacent steep (25-50% slopes) ravines [*Hodges et al., 1985*]. Floodplain soils have high organic content (~27%) [*Myers et al. 2008*], exhibit a high water table, and frequently flood as a result of intense rainfall. Properties of the Emporia complex soils include low organic matter content, deeper water tables (~ 0.9-1.5 m), and high erosion and runoff potentials [*Hodges et al., 1985*]. Texturally, Johnston complex surface and subsoils (upper 0.9 m) are black silt loam with fine sandy loam substratum to a depth of 1.5 m. Craven complex slopes are generally silty loam with depths to 0.9 m [*Hodges et al., 1985*]. Surficial soils of the Emporia complex are typically fine sandy loam, with loamy subsoils and sandy clay loams extending to a depth

of 1.9 m [*Hodges et al., 1985*]. This study was conducted at the downstream edge of the seepage swamp site (Figure 1), from the center of the stream channel. The channel ranged from a depth of six inches to four feet.

Hydrology

Precipitation records and barometric pressure readings were recorded at 15 minute intervals at the CBNERR weather station located adjacent to the study site in York River State Park (Figure 4-1). A near continuous record of stream flow from 2009-2011 was generated in the dominant stream flow channel at the most down gradient point through development of a stream stage-discharge rating curve; see Figure 1 for locations of stream gaging and rainfall collection stations. Stream water levels were recorded at 15 minute intervals by a Solonist® level logger deployed in a stilling well with water levels corrected for changes in atmospheric pressure. In channel field measurements for stream discharge followed both velocity-area [*Buchanan and Somers*, 1969] and salt dilution [*Moore*, 2005] methods.

Sample Collection and Analysis

Discrete water samples were collected within the primary stream channel throughout the two events. Samples were collected into combusted (450 °C) glass bottles at two-hour intervals using portable ISCO^{TM} automatic samplers. Samples were removed from the field, kept on ice, and filtered through pre-combusted glass fiber filters (GF/F; nominal pore size of 0.7 μm, 47mm diameter) within 48 hours of collection.

Concentrations of DOC were measured using high temperature combustion on a Shimadzu TOC/TN-V [*Seitzinger and Sanders*, 1997; *Sharp et al.*, 1993]. Glucose was used to construct the standard curve for DOC and KNO_3 was used to construct the standard for TDN. A consensus seawater standard from the Hansell laboratory (U. Miami) was used to confirm accuracy. A duplicate sample for every ten samples ran was randomly selected for replicate analysis and the relative standard deviation was within 1.2% for all analyses.

For particulates, 50-300 mL were filtered through pre-combusted Whatman GF/F glass fiber filters. The filters were dried at 55°C for 24 hours. Total suspended solid (TSS) measurements were made by subtracting the filter weight after 24 hours of drying from the initial filter weight. Samples were then placed in an HCL dessicator for 24 hours, dried again at 55°C for 24 hours, then packed into tin capsules and combusted. C and N concentrations were measured using a Carlo Erba Elemental Analyser. Stable carbon and nitrogen isotope values ($\delta^{13}C$ and $\delta^{15}N$) were measured with a Costech ECS 4010 CHNSO Analyzer (Costech Analytical Technologies, Inc.) interfaced to a Delta V Advantage Isotope Ratio Mass Spectrometer with the Conflo IV interface (Thermo Electron North America, LLC). All stable isotope values are reported compared to standard reference material (USGS 41). Replicates were run every ten samples, and variance between replicates was less than 5%.

Time interval mass fluxes were determined as the product of the discrete sample constituent concentration and associated continuous discharge, with the sample collection

time representing the mid-point for the discharge period (generally 1.5 hours during the August event, and 4 hours during the Irene event). Interval fluxes were summed to determine stage interval and event fluxes.

Statistical Analyses

Concentrations of POC, TSS, PN and DOC as well as event precipitation and discharge results were analyzed in the programming language R, version 3.01. Pearson's correlation was used to examine correlations between different variables. The significance level between variables was set at $p \leq 0.05$. Samples were binned into rising limb, crest, and falling limb segments following basic graphical hydrograph separation technique and inflection point identification, as described in preceding chapters.

RESULTS

Hydrologic Attributes of the Storm Events

Two events were sampled for this study (Table 4-1). Both storms occurred during Summer 2011, and the two represented one of the smallest and one of the largest events for the entire watershed (Chapter 2, Figure 2-2) during 2011. The August event, preceding Hurricane Irene, was responsible for 5.2mm of precipitation, while the Hurricane Irene event was responsible for 183 mm of precipitation. Total discharge during each event was 49.2 m^3 and 19,600-20,400 m^3 for August and Hurricane Irene. The maximum 15-minute rainfall intensities were 1.3mm and 45mm for the August and Hurricane Irene events, respectively. Peak discharge was 2.2×10^{-3} and $1.4 m^3 sec^{-1}$ for August and Hurricane Irene (Figure 4-2). The runoff ratios for the August and Hurricane Irene events were 4.0×10^{-6} and 0.21. Both events experienced similar summer

antecedent conditions, as prior to both events, little recorded rainfall occurred (API7, 0.3-3.3mm), and the region was experiencing a drought (Chapter 3). Average daily temperature during each event was also similar, with an average of 26±3 °C during the August event, and 24±1 °C during Hurricane Irene. There was little difference in baseflow discharge before each event (Table 4-1, AR24, 0.0018-0.0016 m^3sec^{-1}).

Storm Concentrations of TSS, POC, PN, DOC

Concentrations of TSS, POC, DOC and PN increased during both events (Table 4-2). Flow-weighted mean TSS concentrations were 165.99 ± 49.8mg/L during August and 943.7-950.3 ± 218.8 mg/L during Hurricane Irene. Flow-weighted mean POC concentrations (125.68 mg/L±38.07 in August; 300±171 mg/L rising limb Irene; 12±10 mg/L falling limb Irene; average 100.8-104.8 ±191.9 mg/L during Hurricane Irene) were a fraction of these amounts, representing 76±5.9% of August TSS, and 21 ± 26.6 %of TSS during Hurricane Irene (Table 4-2). TSS was composed of ~65± 32.5% less POC during Hurricane Irene, compared to the August event. Flow-weighted PN concentrations ranged from 7.13±3.13 mg/L during the August event to 5.13-6.68±10.21 mg/L during Hurricane Irene. DOC concentrations were 2.29 ± 0.03 mg/L and 15.6 mg/L ±3.28 during the August and Hurricane Irene events, respectively, and were much smaller than POC concentrations. POC concentrations were 53±13 and 18±27 times higher than DOC during the August and Irene events, respectively.

TSS includes POC and PN, and other minerals and analytes not measured in this study. POC concentration is the largest fraction of TSS in this study, ranging from 11-

76% of TSS, but correlations with TSS did not occur for both events (Table 4-3). In the August event POC and TSS correlate for the entire event, but they do not during Hurricane Irene. POC, PN and TSS also correlate with each other and with total precipitation during the August event. However, POC and TSS do not correlate with discharge during the August event. In contrast, during Hurricane Irene, POC and TSS do not (Table 4-3) correlate with each other, with precipitation, or with discharge (Table 4-3) over the whole event. PN shows a negative correlation with discharge and precipitation during Hurricane Irene (Table 4-3).

Comparing the concentrations of the variables by stage shows some differences between events. TSS concentrations, when compared by hydrograph stage for each event, show a slight increase at the crest and then decline during the rising limb for the August event. TSS for the Irene event follows the same pattern. TSS values for Hurricane Irene are 4.5-8.7 times TSS values for the August event (Figure 4-3a).

POC and PN concentrations showed different trends than TSS. During the August event, POC concentrations peaked at the crest and decreased during the falling limb (Figure 4-3b). POC concentrations decreased over the hydrograph for Hurricane Irene (Figure 4-3b). During August, PN declined from the rising limb to the crest of the hydrograph, then increased during the falling limb (Figure 4-3c), which is opposite to POC values during August. PN was negatively correlated with Q and precipitation during the August event (Table 4-3). PN concentrations followed the same trends as POC during Hurricane Irene, decreasing to levels below detection during the falling limb of the

hydrograph (Figure 4-3c). Interestingly, C:N ratios during the events are similar during both events 19.1±2.98 during August and 17.8±0.89 during Hurricane Irene (Figure 4-3d), although because of the low (below detection) concentration for nitrogen, during the falling limb of Hurricane Irene, C:N ratio could not be calculated.

Because studies have noted a correlation between TSS and rainfall intensity [*Dhillon and Inamdar 2014,Warrick et al. 2012*], and samples for Irene began to approach nondetectable limits after the crest of the hydrograph that could have reduced correlation, the earlier part of the hydrograph during Hurricane Irene was evaluated to determine if TSS, POC and PN had a relationship near the beginning of the event. During the first ten hours of rain, POC and PN concentrations showed a strong negative correlation with precipitation and discharge (Table 4-4). TSS concentrations showed a moderate correlation with Q and a weak correlation with precipitation (Table 4-4).

Storm Event Stable Isotope Values

$\delta^{13}C$ values were similar ($p>0.05$) across the events and between stages of the hydrograph (Figure 4-3e). Average $\delta^{13}C$ values were -28.7 ± 0.2 for August and -27.8 ± 0.7 for Hurricane Irene. $\delta^{15}N$ values were similar during the rising limb and the crest for the August event and during Hurricane Irene (Figure 4-3f), and there was no significant difference between the two events (-0.85± 2.5, 0.55± 0.73). During the falling limb in August, $\delta^{15}N$ values were lower than rising limb and crest samples. Because nitrogen concentrations were very low, values for $\delta^{15}N$ were not available for Hurricane Irene

during the falling limb (Figure 3f). $\delta^{13}C$ and $\delta^{15}N$ values did not correlate with discharge or precipitation (Table 4-3).

DISCUSSION

Sediment Sources During Storm Events

Several other studies have noted a relationship between supply, flowpath, and the source of sediments during baseflow conditions and storm events [*Dhillon and Inamdar, 2014, Warrick et al. 2012, Sanderman et al., 2009*]. High intensity events change flowpaths, remove surface layers of litter and erode more mineral rich layers, essentially changing the sources of particulate organic matter in the process. The numbers of events also impacts the supply of POC. As subsequent storms occur, easily erodible POC is removed. In a Mid-Atlantic stream, consecutive storms eroded more labile, organic-rich surface soil layers through short rain events followed by more intense storm events, until, eventually sediments that were carbon and nitrogen poor and likely from mineral soils, were delivered during Tropical Storm Lee [*Dhillon and Inamdar, 2014*]. In small mountainous rivers (SMR) light rainfall eroded loose dry soil, while intense rainfall generated overland flow that cut through soil, potentially generating debris flow from different layers [*Warrick et al., 2012*], changing the POC sources available. In some cases, rainfall creates so much discharge that the POC and sediment is delivered and buried in coastal margins, bypassing processing in rivers entirely [*Goldsmith et al., 2008*].

In this study, relationships between TSS, POC and PN differed across the two events, suggesting variation in sources, supply, or flowpaths (Table 4-2, Figure 4-3). During the August event, TSS, POC and PN covaried with one another, with POC and PN making-up ~76.0% ±5.9% and 4.0±3.0 of TSS, respectively. The ratio of POC:TSS is higher than reported by Meybeck [*Meybeck 1982*] for large rivers. However, Taskinas is a small watershed with greater connectivity to soils and other sources, which could potentially account for the higher proportion of POC:TSS found relative to large rivers [*Meybeck 1982*]. In contrast to the August event, during the Hurricane Irene event, POC and PN made-up a smaller fraction of TSS, with POC and PN comprising only 11±27%and 2.0±2.0% of TSS. These differences in the proportion of POC:TSS and PN:TSS suggest that a change in supply, flowpath, or sources caused lowered POC and PN contributing to TSS during Hurricane Irene, but not during the August event.

It is unlikely that supply of organic matter was the cause of the difference in TSS, POC and PN. The August event was a low intensity, short duration event, as were the events following the August event, but preceding the Irene event, as shown by 7 day antecedent precipitation (API7, Table 4-2). Field observations before and after the August event, and prior to the Irene event showed little change in soil and leaf litter distribution. In another Mid-Atlantic watershed during the same time period, depletion of supply of organic rich layers did not occur until after Hurricane Irene and was observed in the watershed during the remnants of Hurricane Lee [*Dhillon and Inamdar 2014*]. Consequently, other explanations of changing POC:TSS proportions were considered.

Stable isotope data and C:N data did not show differences in sources between the two events. Both $\delta^{13}C$ and $\delta^{15}N$ values and C:N ratios are consistent with a terrestrial source, although the ratio of TSS:POC for each event suggests differences in source. (Figure 4-3) Observations at the field site before and after each event support the idea that sources and flowpaths, rather than supply of POC, differed across the events, despite stable isotope data and C:N data showing only a terrestrial source for both events (Figure 4-3). Comparison of the study system before and after the August event indicated that there were no discernible changes in streamflow path or obvious changes in surface runoff locations. In contrast, after Hurricane Irene, in the upper portions of the watershed, the stream channel was deeper (~0.5m), and leaf litter and other debris had been deposited well above previous stream bank height throughout the creek. Additionally, fragments of bivalve fossils along with grey sand from the underlying Chesapeake Group formation [*Hobbs 2009*] had been washed out and deposited along the floodplain of the stream, suggesting erosion of deeper, older deposits outcropping along the creek. Erosion during high intensity events has been reported at other sites *[Warrick et al., 2014, Dhillon and Inamdar 2014]*. Additional erosion was confirmed by activation of ephemeral channels that showed fresh paths through leaf litter and the underlying soil after the event was completed. Development of new flowpaths, along with the intensity of the event, likely caused a change in source. The change in flowpaths was, however, not independent of changes in sources. Changes in sources likely changed as new flowpaths developed as a result of overland flow increasing discharge and eroding and cutting channels into mineral soils.

These observations are consistent with the idea that differences in the relationships between POC, PN, and TSS between the storms are likely due to a combination of changes in sources and flowpaths. During Hurricane Irene, PN negatively correlates with Q and precipitation during the rising limb of the event, while TSS shows a moderate correlation with Q and a weak correlation with precipitation during the rising limb. POC shows a negative correlation with Q and a positive correlation with precipitation (Table 4-4). This suggests, initially, sources of POC are similar to the August event, and then they change and the source becomes less concentrated in POC. After this change in source, TSS, POC and PN no longer correlate with discharge or precipitation(Table 4-3). This is likely when the soil and leaf litter source is depleted and more contributions from mineral soil occur, or, alternatively when flowpaths have cut through soil layers and caused erosion of mineral sediments from lower layers.

However, despite visible changes in flowpath and source, there was little change in $\delta^{13}C$ values. The values remained characteristic of terrestrial sources (vegetation and soil). This may reflect a limitation in the application of the stable isotopes to this study since terrestrial sources such as vegetation, detritus, and soil have similar isotope values [*Raymond and Bauer, 2001; Cloern et al. 2002*]. As a result, the erosion of different types of terrestrial organic matter would likely not be identified using stable isotope values. DOC data from the field site show that DOC composition changed over both the August and Irene hydrograph, suggesting POC source may have changed as well. During the August event, EEMS spectroscopy showed a decrease from 4.9 to 0.42 Raman Units in the C1 component (Chapter 2), consistent with a change in source from groundwater to

throughfall. In contrast, C1 components decrease from 5.58-3.91 Raman Units despite intense throughfall during Hurricane Irene (Chapter 3). This suggests DOC sources change from groundwater sources during baseflow to a combination of sources that may include soil pore waters and throughfall as the event progressed. This combination is unlikely during August, as DOC composition is depleted in C1. Furthermore, a change in source for POC during Irene is supported by baseflow concentrations of DOC. Soil pore water during baseflow conditions is more enriched in DOC than groundwater (Supplemental Table 4-1). In other studies, leaching of DOC from surrounding soils, along with leaching of nitrogen, led to particulates depleted in OC and TN [*Sanderman et al., 2009*]. This observation at other sites, along with the DOC concentrations observed at this site, suggests that layers at lower depths may have similar concentrations to those seen in the later portions of the Hurricane Irene event. This explanation is consistent with results from previous studies, which showed that changes in sources between larger and smaller events resulted in different flowpaths resulting in erosion and differences in POC and TSS, reflecting those deeper layers [*Dhillon and Inamdar 2014; Jung et al., 2012*].

POC, DOC, TOC and PN exports

In this study, POC exports exceeded DOC exports for both events, suggesting that storm events influence these C pools differently. The range of DOC exported was 0.9kg C to 300-320 kg C while POC was 4.95 kg C to 2400-2060 kg C, resulting in an export of total organic carbon (TOC) between 5.8 kg and 2700-2400kg (Table 4-2). This corresponded to 0.002 kg/ha to 5.8-5.9 kg/ha for DOC and 0.092 kg to 38-45 kg/ha for POC, or a TOC export between 0.094 kg C ha^{-1} and 51 kg C ha^{-1}. POC was over 80% of

the total organic carbon (POC+DOC) exported during each event. In another Mid-Atlantic watershed, Hurricane Irene was responsible for exports of 21 kg C ha^{-1} of POC and 3.3 kg C ha^{-1} or 25 kg C ha^{-1} [*Dhillon and Inamdar 2013*]. DOC and POC exports were also higher than an agricultural watershed located in James City County, VA. There, DOC export was 13 kg C ha^{-1} POC export was 6 kg C ha^{-1}, and TOC export was 19 kg C ha^{-1} [*Caverly et al., 2013*]. The differences between these locations are likely due to site factors such as land use, slope and total precipitation differences that occurred at different locations during the event. Taskinas Creek has steep slopes with easily eroded outcroppings of mineral soils compared to the other locations, which led to different amounts of DOC leaching and erosion of POC rich layers during the event.

PN also shows differences in concentration and flux between events. For the Hurricane Irene samples, PN followed a trend similar to POC. Concentrations of POC and PN decrease over the course of the hydrograph for Hurricane Irene (Figure 4-3). However, for the August event, POC and PN are the inverse of each other (Table 4-3 Figure 4-3). The crest samples for the August event are more enriched in carbon compared to nitrogen, suggesting a different source of particulate in the crest of the hydrograph compared to other samples (Figure 4-3b and c). It may be that during the smaller event, the more depleted source observed during Hurricane Irene begins to contribute POC, and then the rainfall and erosion were reduced enough to end that source contribution. In contrast, during Irene, the intensity of the rainfall and runoff allow erosion of that source to contribute to TSS throughout the falling limb of the hydrograph.

Otherwise, PN average concentrations are similar to POC, and are lower during Irene compared to August (Table 4-2).

Downstream Implications

Several studies have studied the desorption of carbon and other sorbed analytes from soil, sediment and rock matrices [*Keil et al., 1994*; *Butman et al.,2007; Schillawski and Petsch 2008*]. In many cases, once the preservational environment of the POC is altered, DOC is released and is highly reactive and can be rapidly consumed in aquatic settings [*Butman et al., 2007;Thottathil et al., 2008; Schillawski and Petsch 2008*]. During storm events, DOC concentrations increase, suggesting DOC is leached from leaf litter and soils as water moves through the watershed, which has been observed in many other studies [*Fellman et al., 2009; Sanderman et al., 2009; Inamdar et al., 2014*]. Companion studies (Chapters 2 and 3) show that this DOC is reactive and represents a large potential flux downstream. The fluxes of POC released and transported downstream during the two storm events studied here, were also large and derived from different sources. Understanding these variations in source and POC and PN contributions are critical, as during transport into the estuary, desorption of C and N from POC and PN may occur as the sediment is exposed to salinity [*Hedges et al., 1997*]. Additionally, POC influences the food web and food supply, as well as burial of atmospheric CO_2.

Understanding how desorption of DOC, as well as the reactivity of the desorbed DOC, from the total POC component of sediments delivered during these events will be an important part of understanding downstream dynamics in the future. In Chesapeake

Bay, the sediment plumes from large events, such as Hurricane Isabel, are pronounced and can last for several months [*Brasseur et al., 2008*]. During such time, leaching and consumption of DOC from sediments, in addition to the initial flux of DOC from large events, can have a large impact on estuarine food webs [*Hedges and Keil 1997; Bauer et al., 2013*]. During Hurricane Irene, large plumes of sediment were not observed in the Bay [Palinkas et al., 2014]. Instead, sediment plumes occurred a few days later, when the remnants of Tropical Storm Lee created an additional flushing of the region [Palinakas et al., 2014]. Consequently, POC and DOC were subject to resuspension, deposition, and degradation and other processes during that time period. Evaluating such interactions for these events, in addition to understanding DOC and POC, is critical for developing a thorough understanding of the impact of events on water quality.

CONCLUSIONS

Comparison of two events spaced two weeks from each other, in the absence of complicating differences in antecedent conditions, provided a unique opportunity to examine how magnitude of events can impact DOC and POC fluxes, as well as the composition of total suspended sediments during storm events. The results show:

•The two rain events can cause differences in the POC and PN composition of total suspended sediments, as well as in DOC flux. The larger event causes a reduction in the ratio of POC:TSS and PN:TSS.

•The variation in the POC and PN content of TSS is likely due to changes in terrestrial TSS sources caused by greater discharge leading to erosion and change in flowpaths to less organic rich layers.

• POC and DOC need to be studied in greater detail during storm events in order to determine the impact POC and DOC dynamics have downstream.

This comparison of two summer events highlights the enormous variability between storm events in a single watershed. The response for small events is distinct from large events, and both are distinct from baseflow conditions. Understanding the dynamics of each are important when considering the impacts of changing climate on the region, as both impact estuarine and stream dynamics.

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Table 4-1. Storm Event Characteristics

Storm	Duration	Precipitation			Streamflow discharge			
		Amount (mm)	Maximum Intensity (mm)	API7 (mm)	Amount (m^3)	Peak (m^3 sec^{-1})	Runoff Ratio	AR24 (m^3 sec^{-1})
August	6	5.2	1.3	0.3	49.2	2.2×10^{-3}	4.0×10^{-6}	0.0018
Irene	39.25	183	45	3.3	19600-20,400	0.79	0.21	0.0016

Table 4-2. Storm Event Storm Average Event Fluxes, Concentrations, and Yields

Event	Analyte	Mass Transported (kg)	Flow weighted mean concentration (mg/L)	Maximum Concentration (mg/L)	Ratios	Yield (kg/ha)
AUGUST						
	TSS	6.54	160±50	208.7		0.121
	POC	4.95	126±38	154.9		0.092
	PN	0.28	7.1±2.8	8.96		0.001
	DOC	0.09	2.3±0.03	2.32		0.002
	[POC]:[TSS]				0.76	
	[PN]:[TSS]				0.04	
	[POC]:[TOC]				0.98	
	[POC]:[DOC]				54.9	
	[DOC]:[TOC]				0.02	
IRENE	TSS	19300-18600	950-940±220	1134.8		360-340
	POC	2400-2060	105-101±190	468.4		45-38
	PN	130-105	6.7-5.1±12	27.4		2.4-1.9
	DOC	300-320	15-16±3.3	17.2		5.8-5.9
	[POC:TSS]				0.11	
	[PN:TSS]				0.02	
	[POC]:[TOC]				0.87	
	[POC]:DOC]				6.7	
	[DOC:POC]				0.15	

[]=Concentration, in mean (mg/L).

Table 4-3. Pearson's Correlation for Storm Events

Event	Parameter	TSS	PN	POC	CN	DOC	$\delta^{13}C$	$\delta^{15}N$
August								
	Q	0.25	**0.71**	0.43	**0.79**	NA	-0.06	-0.03
	Precipitation	**0.70**	**0.84**	**0.75**	**0.66**	NA	-0.12	-0.004
	POC	**0.98**	**0.68**	-	0.36	NA	**-0.77**	0.03
	PN	0.35	-	**0.68**	**0.91**	NA	**-0.99**	**0.63**
	$\delta^{15}N$	0.33	**0.63**	0.32	**0.60**	NA	0.37	-
	$\delta^{13}C$	**-0.73**	-0.09	**-0.77**	**-0.90**	NA	-	0.37
Irene								
	Q	0.37	**-0.77**	-0.17	**0.99**	**0.80**	-0.02	-0.01
	Precipitation	0.30	**-0.90**	0.01	**-0.96**	**0.64**	-0.01	0.14
	POC	0.13	**0.99**	-	**-0.78**	-0.25	**0.62**	**0.6**
	PN	0.11	-	**0.99**	**-0.79**	-0.27	0.59	**0.56**
	$\delta^{15}N$	**0.87**	0.56	**0.60**	NA	-	0.43	-
	$\delta^{13}C$	**0.73**	0.59	**0.62**	NA	-	-	0.43

Bolded values indicate significant correlations, as determined by Pearson's R.
NA=Data unavailable,- indicates space with the same parameter on the chart

Table 4-4. Pearson's Correlation for first ten hours, Hurricane Irene

Event	Parameter	TSS	PN	POC
Irene				
	Q	**0.42**	**-0.77**	**-0.76**
	Precipitation	**0.32**	**-0.90**	**0.89**

Bolded values indicate significant correlations, as determined by Pearson's R.
NA=Data unavailable,- indicates space with the same parameter on the chart

Figure 4-1. Study Site Location Map depicting dominant ecosystem types, gauging station (GS), weather station (WS) and water quality station locations.

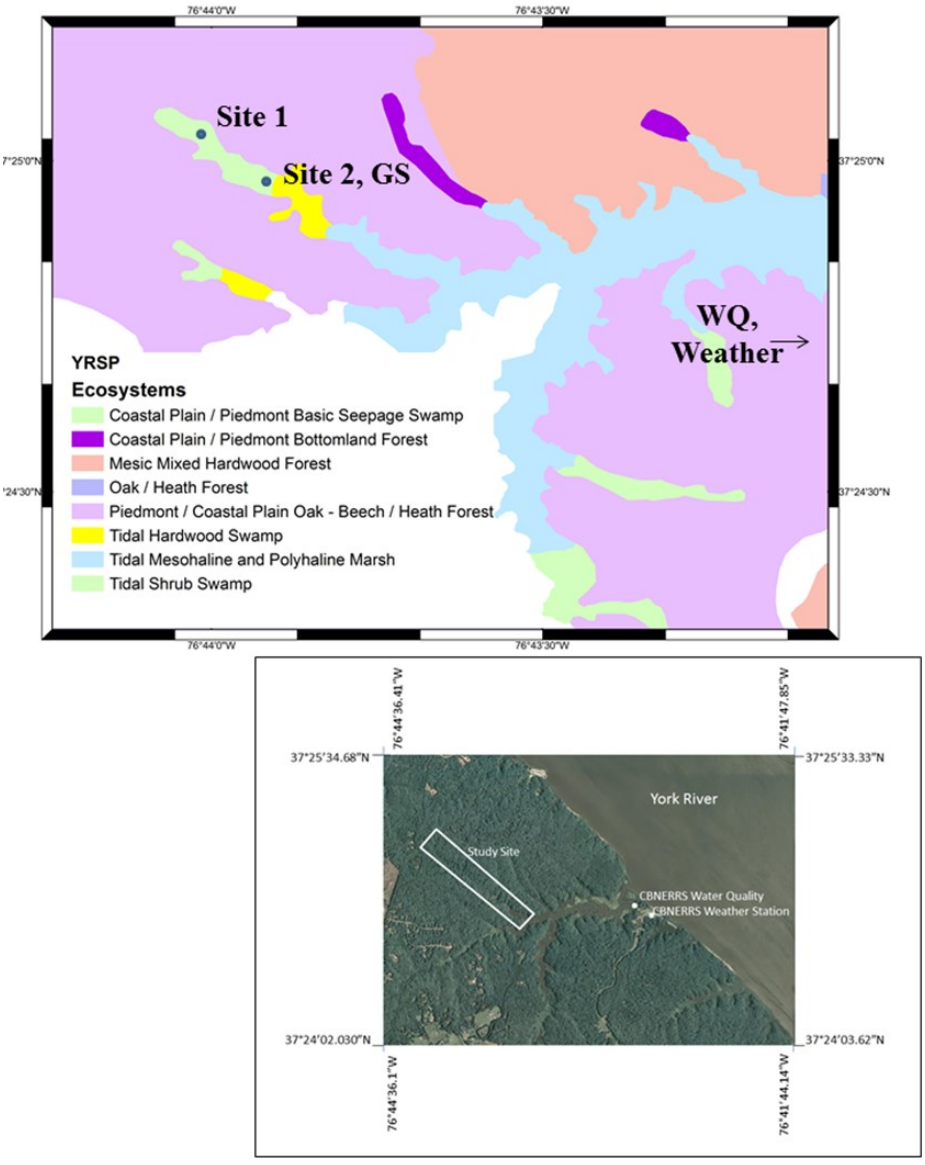
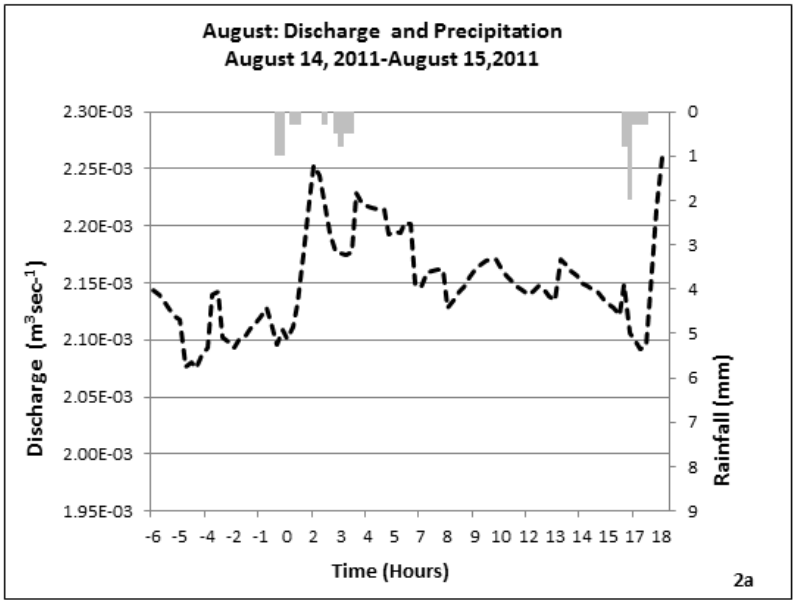


Figure 4-2. Hyetograph of August Event (a) and Hurricane Irene Event (b).



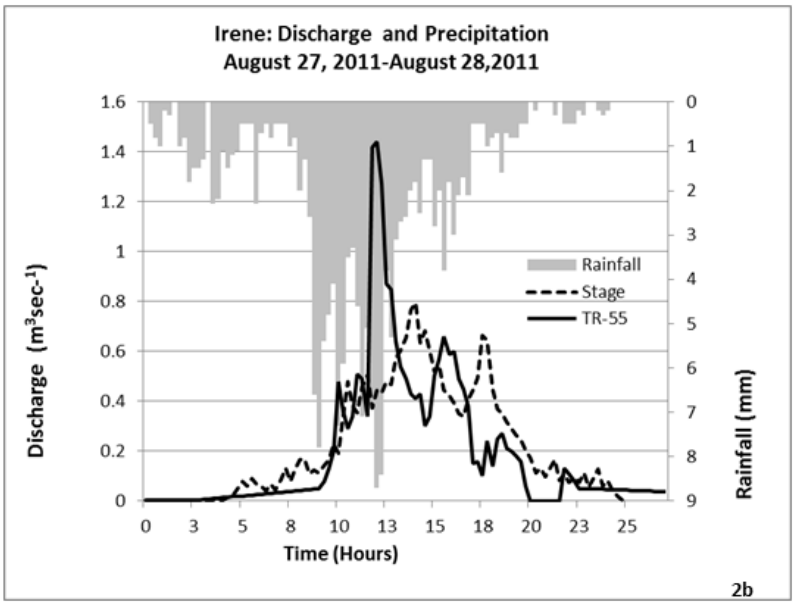
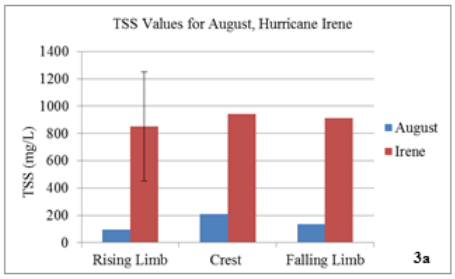
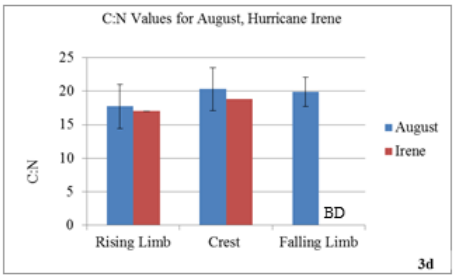
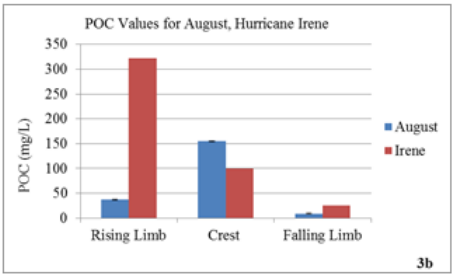
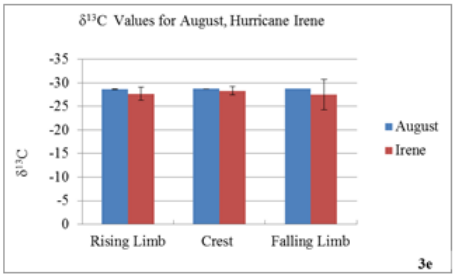


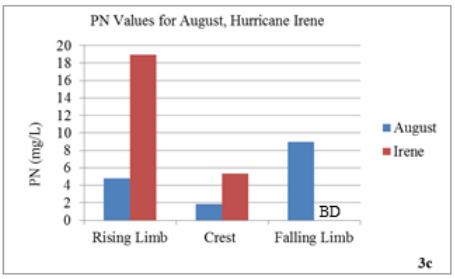
Figure 4-3. Analyte values by hydrograph stage during the August and Hurricane Irene events.











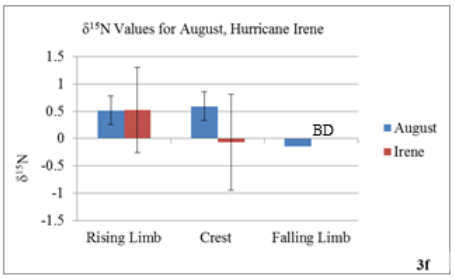
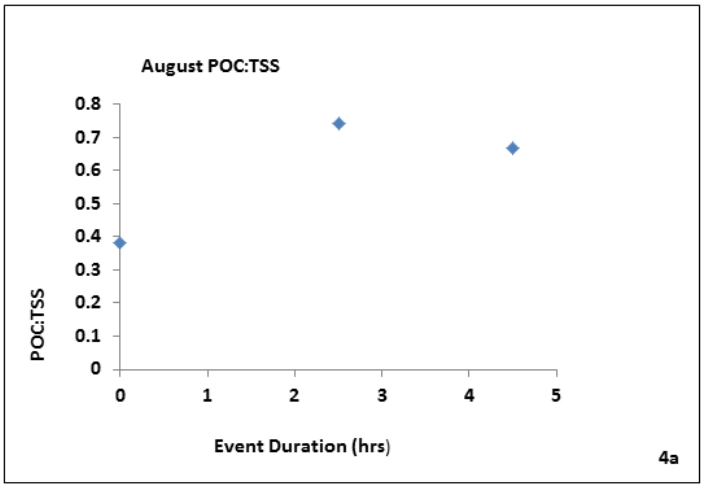
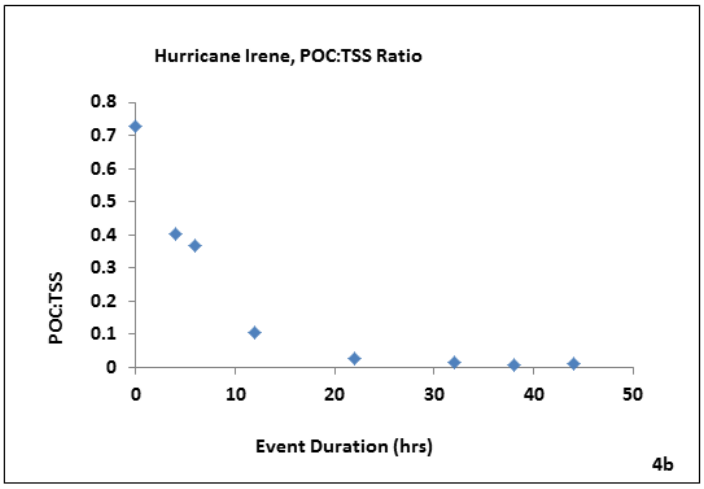


Figure 4-4. POC:TSS during the August and Hurricane Irene events.





Chapter 5:Conclusions

SUMMARY

In the past five years, the considerable fluxes of DOC and POC from rivers and the increase of these fluxes during rain events, have become well documented [*Raymond and Yoon 2012, Inamdar et al., 2013, Dhillon and Inamdar 2014, and many others*]. Carbon budgets have shown that the amount of carbon delivered to the oceans from rivers is actually only a small portion of the amount of carbon entering rivers from the terrestrial environment [*Aufdencampe et al., 2011*], and that there are high rates of respiration and processing within rivers and estuaries [*Cole and Caraco 2001, Richey et al., 2002*]. Some of this processing within rivers has been attributed to biodegradable organic carbon coming from a variety of different sources during rain events using new techniques such as fluorescence characteristics [*Fellman et al., 2010, Inamdar et al., 2014*]. However, there have been few assessments of %reactive DOC during events to determine the sources of % reactive DOC, how DOC reactivity varies with event size and OM sources during events, and few studies documenting relationships between POC and DOC sources to storm flux. This study examined a small stream in Taskinas Creek, in Virginia to: (1) determine source of % reactive DOC during small storm events using fluorescence, (2) examine the sources, flux and changes in % reactive DOC and fluorescence composition during a large event (3) determine sources of POC and DOC found in events of different magnitudes, but similar antecedent conditions. This chapter will discuss some of the implications of the data presented and potential directions for future research.

This dissertation has shown that rain events, even small ones, change the flux and concentrations of dissolved and particulate organic carbon above what can be delivered during baseflow conditions. This result is similar to findings from studies of larger events [*Dhillon and Inamdar 2014, Raymond and Saiers, 2010, Raymond and Yoon, 2012*]. Additionally, small, moderate events, as described in Chapter 2, representing only a few mm of total precipitation, change the total amount of % reactive DOC delivered downstream. Although the % reactive DOC in these events was not greater than baseflow reactivity when incubations included light exposure, when considered with the increase of overall flux of DOC, this storm event release of organic matter becomes important (Figure 5-1). Some of this % reactive DOC may fuel respiration contributing to hypoxia downstream. POC transported downstream may also leach reactive DOC during transport or resuspension of sediment. Once DOC is respired it becomes CO_2, taking simple upstream leaching and erosion from a local and regional concern to a global one.

The current concentration of atmospheric CO_2 is higher than experienced on earth for the past 800,000 years and is increasing at a rate that is an order of magnitude faster than has occurred for millions of years [*Doney et al., 2009, Doney et al., 2012*]. Atmospheric CO_2 is presently at a level that threatens the pH balance of global oceans, impacting marine life. CO_2 is also at level that has caused an increase in global temperature and an increase in extreme weather [*Stocker 2013*]. Storm events are a major mechanism of heat transfer to the poles from the equator during rising temperatures. Consequently, the leaching of reactive DOC, adding more CO_2 back to the atmosphere and increasing storm

intensity is a positive feedback to climate change. In the Chesapeake Bay, storm intensity and, consequently, rainfall are anticipated to increase [*Najjar 2010*], so the processes observed in this study, which control flux of reactive DOC from this watershed to this estuary, are of importance Climate change is anticipated to alter primary productivity in the Chesapeake Bay through variations in nutrient, sediment and organic matter supply [*Canuel et al., 2012*].This study quantifies some of the hydrologic impacts leading to those changes [*Canuel et al., 2012*].

This predicted increase in storm intensity may result in more extreme weather events as described in Chapter 3 and in Chapter 4. The flux of DOC associated with this 25-yr storm event was more than 450 times above baseflow fluxes for the same time period. The % reactive DOC released for this event, as seen for smaller events (Chapter 2), was also not greater than what was observed during baseflow. However, because of the sheer magnitude of flux from these events, their downstream impact is much greater than those events in Chapter 2 (Figure 5-1).

This dissertation was unique in that it assessed the reactivity of DOC during storm events using incubation experiments, subjecting DOC to photochemical reactions as well as microbial processes. During these incubations, it was discovered that for this data set, the EEMS components did not correlate with the % reactive DOC from incubations, and so EEMS component could not be used to assess the % reactive DOC for other events where incubations were not conducted during the hydrologic year. This was surprising, as % reactive DOC had been successfully used to track reactive BDOC previously.

However, EEMS was useful in identifying changes in source over the hydrograph, as had been done in other studies.

Additionally, this dissertation shows that the sources of POC and DOC are not the same for all events. Recent studies, since the commencement of this dissertation, have shown this as well. Jung [*Jung et al. 2014*] and Dhillon and Inamdar [*Dhillon and Inamdar et al. 2014*] demonstrated that POC and DOC have different responses to the hydrograph, and attributed the difference to distinct sources due to changes in antecedent conditions and timing of events. In this study, there was a unique opportunity to examine events of different magnitudes during the same antecedent conditions. The results suggest the magnitude of the event, while simply increasing leaching of DOC from similar sources, can cause very different POC source contributions.

LIMITATIONS AND FUTURE WORK

This study was limited to one field site and a few storm events that occurred during the study period. To truly understand changes in season, antecedent conditions, and their impacts on DOC reactivity throughout the hydrologic year, as well as intensive study of the watershed over many years is essential. Additionally, the variation within this watershed, as well as variation observed within other watersheds, suggests intensive study and knowledge of multiple systems within one region is critical for understanding how organic matter sources vary over time.

Additionally, this study only examined the reactivity of DOC released during events and under very limited parameters of nutrient concentration, light levels and temperature. Varying levels of nutrients, different light levels and different temperature

are all known to change the release of DOC and the % reactive DOC [*Lu et al., 2013*, *Bauer et al., 2013*]. For example, storm events during the winter and autumn have been shown to have different composition than summer and early spring events [*Dhillon and Inamdar 2014*]. Assessing how this impacts % reactive DOC will be critical for predicting future carbon budgets. Additionally, this study does not attempt to determine all of the interactions, such as sorption and desorption, altering the flux of percent reactive DOC released to downstream waters from the upland portion of Taskinas Creek. Future studies exploring this connectivity would be helpful in determining event impacts.

Future studies also need to examine and understand how POC loads, which often surpass DOC fluxes, impact downstream reactivity, and consequently, water quality. POC fluxes from the small watershed studied are gross fluxes released during the event, and are likely not the net export into the downstream York River. During transport, POC can be buried, resuspended, and can sorb and desorb organic matter. Future research should also examine the sediment transport dynamics during large events to understand total export of POC during such events. Furthermore, additional site specific study to determine how DOC and POC net flux and, consequently, total reactive organic carbon are impacted by changes in water temperature, salinity, pH, nutrient, light and microbial community exposure are needed to effectively model downstream impact of these events. Linking storm event fluxes from headwaters to their impact downstream within estuaries needs to be conducted on a larger scale, over the entire watersheds, to truly model and understand the impact large events will have on estuarine ecology during this period of climate change.

Overall, this work improves our understanding of the effects of hydrology, antecedent conditions, and abiotic and biotic factors on DOM and its reactivity in river and estuarine systems. This information contributes to an improved understanding the linkages between terrigeneous and marine environments and the coastal carbon budget.

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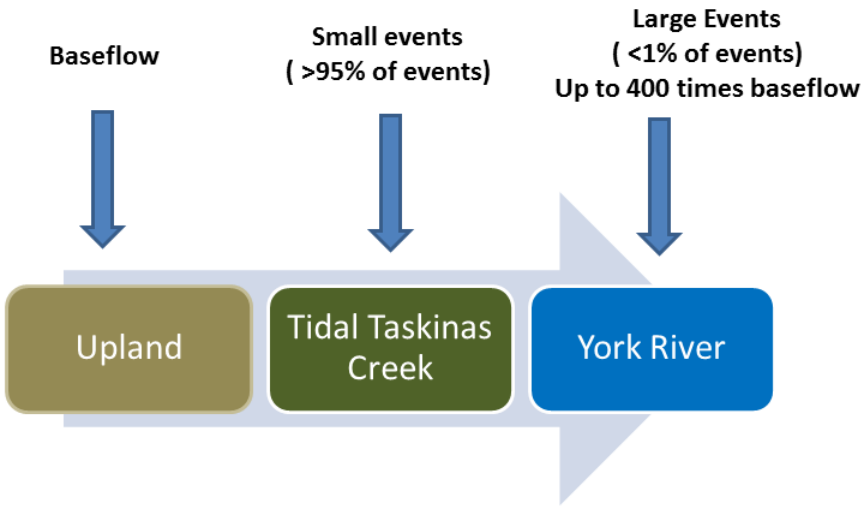
Figure 5-1. DOC and POC released from uplands has different impacts dependent on the size of events. Due to the short residence time in uplands, small events deliver important fluxes of reactive DOC to downstream waters, with large event DOC fluxes being most significant for the downstream York River. POC, as it is deposited, resuspended, and buried, will be important to ecosystems throughout each phase of the hydrograph.



Appendices

Appendices to the dissertation are electronic, and include: excitation emission spectra, hydrological data, measured analytes, and weather station data recorded by the Chesapeake Bay National Estuarine Research Reserve System in Virginia.

Appendices are permanently available at the W&M Digital Archive at: https://digitalarchive.wm.edu/handle/10288/21796.

Vita

Sarah Schillawski Cammer was born in Auburn, NY, in 1978. She graduated from Auburn High School in 1996. She attended Bryn Mawr College and earned a B.A. in geology in 2000. She completed a M.S. in geosciences from the University of Massachusetts, Amherst, in 2007. In August 2015, she earned a Ph.D. in marine science at the College of William and Mary, School of Marine Science.