

AN INTEGRATED METHOD FOR MONITORING MATERIAL TRANSPORT IN A
COUPLED LAND-ESTUARY SYSTEM FOLLOWING A DYNAMIC STORM EVENT: THE
NEUSE RIVER AND ESTUARY, NC AND HURRICANE IRENE

by

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Coastal aquatic environments are complex and dynamic systems that are influenced by both marine and terrestrial processes such as waves, tides, winds and freshwater discharge. Rivers are conduits that transport freshwater and terrestrially derived particulate and dissolved material such as sediment and dissolved organic matter (DOM) to the coastal ocean. Increased concentrations of these in-water constituents can negatively influence aquatic biota. Storm events and associated rainfall often lead to increases in the amount of terrestrial material delivered to coastal waters, however varying storm characteristics such as the location and intensity of rainfall within a river basin results in varying impacts to hydrology and material transport. Due to the dynamic nature of coastal waters, the monitoring of material transport solely by using traditional field measurements proves difficult over large areas and especially during and following storm events where the collection of field samples is often not possible. To offset this limitation, an integrated method incorporating field sampling, numerical modeling, and remote sensing was used to monitor the transport and distribution of terrestrially derived material from the Neuse River basin to the Neuse River and Neuse River Estuary (NRE) following Hurricane Irene in August 2011. Field samples were used to quantitatively characterize changes in the concentration of total suspended matter (TSM), colored dissolved organic matter (CDOM),

dissolved organic carbon (DOC) and salinity in the Neuse River and NRE; numerical modeling was used to simulate the transport and distribution of freshwater and DOC throughout the NRE; and remote sensing was used to provide unique large-scale synoptic views of suspended sediment following the storm. This integrated method was adequate in providing the spatial and temporal resolution needed to examine the land-water processes that govern the transport of material through this coupled land-estuary system. This methodology may be applicable to similar estuarine systems and can help better characterize flow and transport during and following storm events.

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by

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CHAPTER 1: EXAMINING MATERIAL TRANSPORT IN COUPLED LAND-OCEAN
SYSTEMS: AN EXAMPLE OF THE LOWER NEUSE RIVER AND NEUSE RIVER
ESTUARY, NC

1.1 Introduction

Coastal aquatic environments are complex and dynamic systems that are subject to considerable pressure from both natural and anthropogenic events such as hurricanes, sea-level rise, pollution, and changes in land-use practices. These events often have large negative impacts on coastal water quality and the frequency of these events are expected to increase as a result of continued rapid population growth and climate change. Due to the importance of coastal waters for providing numerous ecological services and supporting navigational, recreational and human habitation, it is critical that these environments are protected and maintained and as such, improving water quality is a primary goal of many coastal policy makers.

Coastal areas are also transitional zones between terrestrial and oceanic environments. The coupling of terrestrial and oceanic systems through large-scale physical processes such as winds, tides, currents, and freshwater discharge makes the monitoring of in-water constituents difficult over large surface areas, especially following dynamic storm events. Rivers are conduits that transport freshwater and terrestrial material from the land surface to coastal and oceanic waters. Due to variability in river length, discharge, and drainage basin characteristics, the type and amount of material transported by rivers throughout the world is highly variable.

Globally, the average annual river discharge to oceans is estimated at $\sim 40,000 \text{ km}^3 \text{ yr}^{-1}$ (Fekete et al., 2002) with an estimated total suspended solid (TSS) export of 19 Pg yr^{-1} (Beusen et al., 2005). An increased concentration of suspended sediment in coastal waters can significantly decrease light penetration within the water column, negatively impacting phytoplankton production (Cloern, 1987), the growth and distribution of submerged aquatic vegetation (Stevenson et al., 1993; Orth et al., 2010) and coral (Miller and Cruise, 1995). Suspended sediment also influences nutrient and pollutant dynamics through sorption and desorption processes (Oschwald, 1972).

In addition to suspended sediment, rivers transport a significant amount of carbon to the world's oceans. Approximately 590-830 Tg of total carbon is transported to the world's oceans by rivers each year as dissolved inorganic carbon (DIC) and total organic carbon (TOC), making riverine transport a significant portion of the global carbon cycle (Cole et al., 2007). Organic matter is the largest reservoir of reduced carbon on earth (Bianchi, 2011). Organic matter can exist in the aquatic environment as both particulate (POM) and dissolved (DOM) material. The dissolved fraction typically dominates the TOC pool, with an estimated export of POC to the ocean of 170 Tg C yr⁻¹ compared to about 210 Tg C yr⁻¹ as DOC (Ludwig et al., 1996). Colored dissolved organic matter (CDOM), the light-absorbing portion of DOM, is often highly correlated to DOC in rivers and coastal waters influenced by river discharge (Ferrari et al., 1996; Vodacek et al., 1997; Del Castillo et al., 1999; Del Castillo and Miller, 2008; Mannino et al., 2008; Matsuoka et al., 2012; Spencer et al., 2012). DOM regulates many water parameters and ecological processes, several of which are described in more detail in Chapters 2 and 3.

The riverine transport of sediment and carbon to coastal waters is largely dependent upon natural and anthropogenic processes occurring within drainage basins. Tectonic processes influencing climate, weathering, and topography largely control the mobilization and transport of material (McKee, 2003). Drainage basins with steep slopes experience increased particulate loads within their associated rivers. Meade (1996) reports that much of the world's river sediment is derived from tectonically active locations such as the Himalayan region, western Pacific islands, the Andes, and southern Alaska. Milliman and Syvitski (1992) suggest that basin area and maximum elevation within a river basin are the primary factors that influence sediment yield with secondary factors including climate and runoff.

Weathering and erosion of the continents represent a major sink for atmospheric carbon (Ludwig et al., 1998) and these processes provide much of the material that is transported within river systems. Sources of DOM in streams and rivers include both terrestrial (allochthonous) and in-stream (autochthonous) inputs, the importance of which can change as stream size increases (McDonald et al., 2004). Soils and terrestrial vegetation represent the major sources of allochthonous organic carbon input to streams and rivers (Thurman, 1985). The amount of carbon stored in terrestrial vegetation is on the order of carbon stored in the atmosphere and the amount of organic matter in soils is 2-3 times that stored in vegetation (Houghton, 2007). Therefore, soils represent the largest organic carbon source to streams and rivers. Accumulation and storage within a drainage basin control the amount of terrestrial organic carbon available to be eroded and transported to and within a river system. The accumulation of carbon and responses of DOC in streams can be impacted by factors such as antecedent rainfall and moisture conditions (Biron et al., 1999; Bernal et al., 2002; Inamdar et al., 2008; Turgeon and Courchesne, 2008). Ludwig et al. (1998) report that POC flux is related to sediment yield and drainage intensity while DOC flux is a function of drainage intensity, basin slope, and carbon accumulation within soils. Changes in climatic conditions, including the frequency and intensity of storm events, could lead to numerous changes within river systems that could dramatically affect the transport of terrestrially derived material (Dhillon and Inamdar, 2013). For example, more frequent and intense rain events will result in increased runoff, an important control on the export of material from within drainage basins.

As with natural perturbations within watersheds, river systems are also highly impacted by anthropogenic activity. The world's population is expected to increase to 10 billion within the century (Crutzen, 2002) and continued stress on the natural environment is expected. Meade

(1996) reports crop farming as the main anthropogenic impact that directly affects river sediment loads, especially in deforested regions. Furthermore, dam and reservoir construction have greatly altered river systems. Although humans have increased sediment transport by global rivers through deforestation and increased agricultural activity, Syvitski et al. (2005) predict a decrease in the volume of sediment that reaches the world's coasts as compared to pre-human load estimates due to reservoir retention.

Because of the many dynamic processes within drainage basins that control and alter the concentration and transport of river material and the potential negative impacts on coastal aquatic environments, it is vitally important to accurately monitor the concentration and distribution of river material discharged to coastal waters. Due to the large size and complex, dynamic nature of most coastal systems, the sole use of field sampling data often cannot provide sufficient spatial and temporal resolution to adequately examine land-water processes that govern the transport of material through a coupled land-ocean system. However, an integrated approach that utilizes field sampling, numerical modeling and remote sensing would presumably better capture the dynamics of a coastal system and provide a better understanding of material transport. Field samples provide data needed to initialize, calibrate and validate numerical models and also are necessary to develop remote sensing algorithms. Numerical modeling provides simulations that can examine the transport and fate of material under various scenarios, predictions when field samples and remote sensing data are unavailable, and three-dimensional information while remote sensing provides large-scale synoptic views. Hence, this study used an integrated approach to examine the transport of both particulate and dissolved material through the Neuse River and Estuarine System following Hurricane Irene, which made landfall in eastern

North Carolina on August 27, 2011. The research goal was to examine an increase in the flux of material through the system following a major rain event (Fig. 1.1).

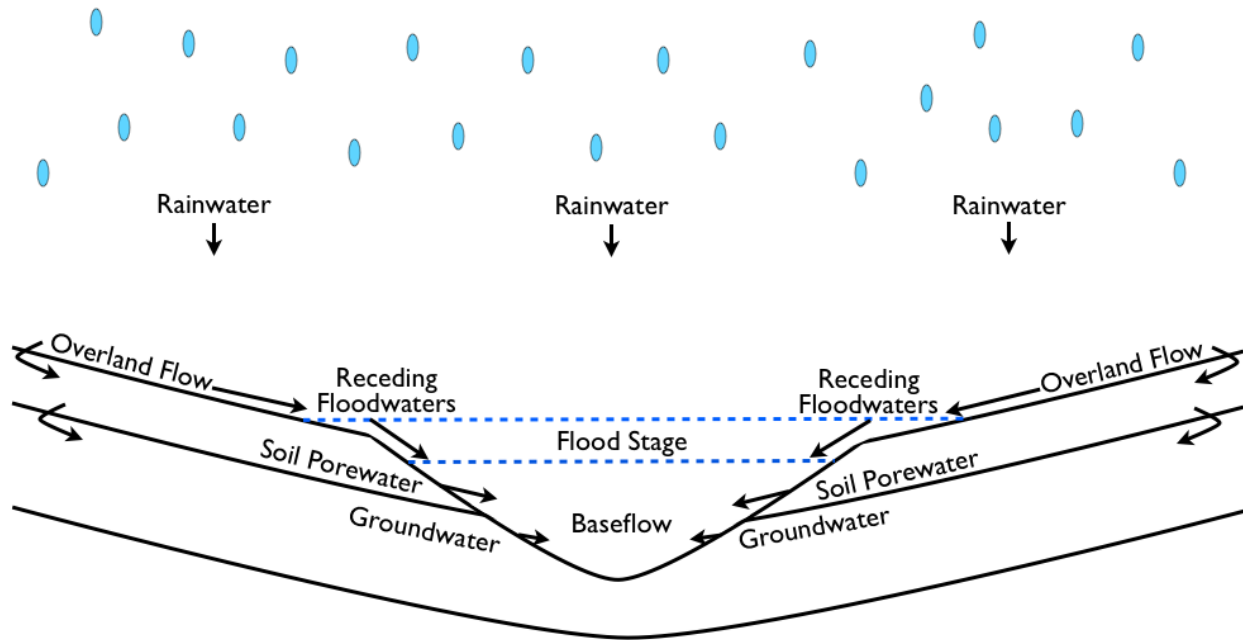


Fig. 1.1: Idealized conceptual diagram of the potential sources and general magnitudes (length of straight arrows) of material flux to a river system during and following a rain event. Curved arrows represent possible exchanges between material reservoirs.

The research design included a series of field locations established to examine *in situ* changes in suspended sediment, CDOM and DOC as well as provide data to develop remote sensing algorithms for suspended sediments, analyze the utility of previously developed remote sensing algorithms to monitor CDOM and DOC, and initialize, calibrate and validate a numerical model of DOC for the Neuse River Estuary (NRE). The work related to examining suspended sediments and the use of remote sensing to monitor material transport is presented in this chapter. A detailed description of the measurements and results of CDOM and DOC dynamics based on field measurements are described in Chapter 2: *The impact of rainfall and runoff from*

Hurricane Irene (2011) on the transport and concentration of dissolved organic matter in the lower Neuse River and Neuse River Estuary, NC, USA. The Delft3D three-dimensional numerical flow and transport model was used to simulate the transport and distribution of DOC in the NRE following Hurricane Irene. A detailed description on the use and results of these model simulations are presented in Chapter 3: *Modeling the transport of freshwater and dissolved organic carbon in the Neuse River Estuary, NC, USA following Hurricane Irene (2011)*. An overall summary discussion of this study is presented in Chapter 4: *Discussing the use of an integrated method for examining material transport in the lower Neuse River and Neuse River Estuary, NC following a hurricane.*

1.2 Methods

1.2.1 Study Site

The Neuse River and Estuarine System of eastern North Carolina is a coupled land-estuary system that transports particulate and dissolved material from the Neuse River basin (NRB) to Pamlico Sound and ultimately the Atlantic Ocean (Fig. 1.2). The Neuse River flows approximately 320 km through the Piedmont and Coastal Plain provinces of North Carolina, draining an approximately 16,000 km² watershed primarily composed of forest and agriculture. The Neuse River forms the headwaters of the Neuse River Estuary (NRE) at New Bern, NC. The NRE is a shallow drowned river valley with a depth ranging from about 3 meters at the head of the estuary to about 7 meters at the mouth. The NRE flows approximately 70 km before the system discharges directly to the southwestern portion of Pamlico Sound. Pamlico Sound is the largest portion of the Albemarle-Pamlico Estuarine System (APES), the second largest estuarine system and largest lagoonal estuary in the United States and 1 of 28 estuaries of national significance as designated by the United States Environmental Protection Agency (EPA). The APES drains an approximately 80,000 km² watershed that spans Virginia and North Carolina. Numerous riverine sources from the drainage basin exemplify the difficulties in monitoring material transport over a large surface area. High concentrations of suspended sediments are often observed throughout the system following tropical and extra-tropical storms, however the high concentrations are comparatively short-lived to the longer-term transport of DOM from the rivers and sub-estuaries (Miller et al., 2011a).



Fig. 1.2. A Moderate-resolution Imaging Spectroradiometer (MODIS) 250 m true color image of the Albemarle-Pamlico Estuarine System (APES) of eastern North Carolina displaying the major rivers and sounds. Image taken on September 10, 2011, two weeks following the landfall of Hurricane Irene.

1.2.2 Sample Collection and Measurements for Total Suspended Matter and Residual Salt on Filters

Discrete surface water samples were collected at four shoreline locations (see Fig. 2.1) within the lower reach of NRB near Hookerton, Fort Barnwell, Cowpens and Bridgeton, NC. Samples were collected prior to and following the landfall of Hurricane Irene (Aug. 27, 2011) on 14 days from Aug. 24 to Sept. 15, 2011. All stations were located on the Neuse River with the exception of Hookerton, which is located on Contentnea Creek, a tributary to the Neuse. Samples were collected and stored on ice in pre-washed 1L brown Nalgene bottles until transported to the laboratory where they were refrigerated (4°C) until analysis. Additional discrete surface water samples and data were collected over nine field expeditions from Aug. 24, 2011 to Jan. 10, 2012 at 14 stations in the upper NRE (see Fig. 2.2) as part of the bi-monthly sampling of the Neuse Estuary Monitoring and Research Program (NEMReP) from a small boat and stored following the methods for shoreline samples. An additional 50 discrete surface water samples were collected in the NRE and Pamlico Sound from a small boat on Oct. 26 and Nov. 12, 2011 (see Fig. 2.1) and stored following the methods described above.

The concentration of total suspended matter (TSM) was determined gravimetrically by filtering a known volume of sample water through pre-weighed Whatman 0.7- μm GF/F filters. Following filtration, the filters were rinsed with approximately 75 ml of Milli-Q water and stored in the dark in covered Petri dishes until dried. Filters were folded in quarters and placed in heavy-duty aluminum foil where they were dried at 103°C for 2 hours. The filters were then brought to room temperature and weighed on a high precision balance. The drying process was repeated two additional times to investigate variation in filter weight due to possible water absorption by retained salt (Stavn et al., 2009). The weight of the filter following the third drying process was used to determine TSM concentrations. Samples collected on Nov. 9 in the upper

NRE and on Nov. 12 in the lower NRE and Pamlico Sound were used to further investigate the impact of salt retention on TSM concentration. A measured volume of sample water was filtered to remove particulate material. The filtrate was then filtered through a new, pre-weighed filter that was then treated in the same manner as TSM filters. NEMReP samples collected on March 8 and April 11, 2012 were also analyzed for TSM to assess differences in concentrations as determined by filtering through 0.7- μm GF/F and Nuclepore 0.2- μm polycarbonate filters.

1.2.3 Remote Sensing

Remotely sensed data were obtained for the Moderate-resolution Imaging Spectroradiometer (MODIS) instrument. Several investigators have shown that MODIS data can be used to investigate water quality constituents in oceanic, coastal, and inland waters (e.g. Miller and McKee, 2004; Chen et al., 2007; Chen et al., 2009; Petus et al., 2010; Zhang et al., 2010). Two MODIS sensors are in operation, one each aboard the NASA TERRA and AQUA spacecraft. The TERRA and AQUA spacecraft are in near-polar, sun synchronous orbits, crossing the equator at the same local time each day (approximately 10:30 and 1:30 for TERRA and AQUA, respectively). MODIS instruments measure reflected or emitted electromagnetic energy in 36 spectral bands ranging from the blue (0.4 μm) to thermal infrared (14.4 μm) regions of the electromagnetic spectrum. Data are collected at 250 m (bands 1 and 2), 500 m (bands 3-7) and 1000 m (bands 8-36) spatial resolutions with a revisit period of nominally 1.5 days. In this study, MODIS 250 m data were used to develop a regional TSM remote sensing algorithm for the APES. The algorithm of Miller and McKee (2004), which was previously used to examine TSM throughout the dynamic APES (Miller et al., 2011b), was also used. MODIS 500 m band 3

and band 4 data were used to examine the use of band ratios for monitoring the concentration and distribution of CDOM as reported by Lunetta et al. (2009).

MODIS images of the APES were collected during clear sky days before and after Hurricane Irene to assess the mobilization, transport, and fate of material resulting from the storm. Level 0 MODIS images were acquired from the NASA Ocean Color Web (<http://oceancolor.gsfc.nasa.gov/>) and processed using the NASA SeaDAS (SeaWiFS Data Analysis System) v6.4 software. MODIS 5-minute granules were processed to Level 1A and then the region of the APES extracted. The resulting Level 1A files were processed to L1B files that contained MODIS 1 km, 500 m, and 250 m resolutions. Atmospheric correction was performed using the SeaDAS MODIS L2 File Generating Program using a white aerosol extrapolation model with 859 nm as the highest wavelength for aerosol model selection. Remote sensing reflectance and normalized water-leaving radiance products were produced for MODIS 250 m band 1 (645 nm) and band 2 (859 nm) to investigate suspended sediment. MODIS 500 m remote sensing reflectance products at band 3 (469 nm) and band 4 (555 nm) were used to investigate CDOM dynamics. The resulting L2 files were imported to ENVI 4.8 to retrieve MODIS band 1 and band 2 reflectance and water-leaving radiance and band 3 and band 4 reflectance corresponding to the locations of field sample collection and to apply the remote sensing algorithm of Miller and McKee (2004) to band 1 and band 2 images.

1.3 Results

1.3.1 Field Measurements of Total Suspended Matter and Residual Salt on Filters

Variation in TSM concentration was observed in both shoreline and mid-channel NRE locations during the study although no clear pattern was observed between TSM and freshwater discharge (Fig. 1.3). At the shoreline stations, TSM concentration showed little variation between pre-storm and post-storm samples two days (Aug. 29) following Hurricane Irene's landfall. The average TSM concentration at shoreline stations was 7.1 mg L^{-1} prior to the landfall of Hurricane Irene and 7.0 mg L^{-1} on Aug. 29. The maximum TSM concentration of 22.0 mg L^{-1} was measured at Hookerton on Sept. 5, nine days following the landfall of Hurricane Irene. At the next downstream station at Fort Barnwell, however, TSM concentration was considerably lower (about 5 mg L^{-1}). As with TSM concentrations measured at shoreline stations, no clear pattern was observed at mid-channel locations in the upper NRE. A maximum TSM concentration of 34.1 mg L^{-1} was measured pre-storm in the middle estuary and decreased to 8.1 mg L^{-1} at the same location one week later. It was often observed that samples collected closest to the mouth of the Neuse River had a lower suspended sediment concentration than most of the samples collected on the same day throughout the remaining NRE stations.

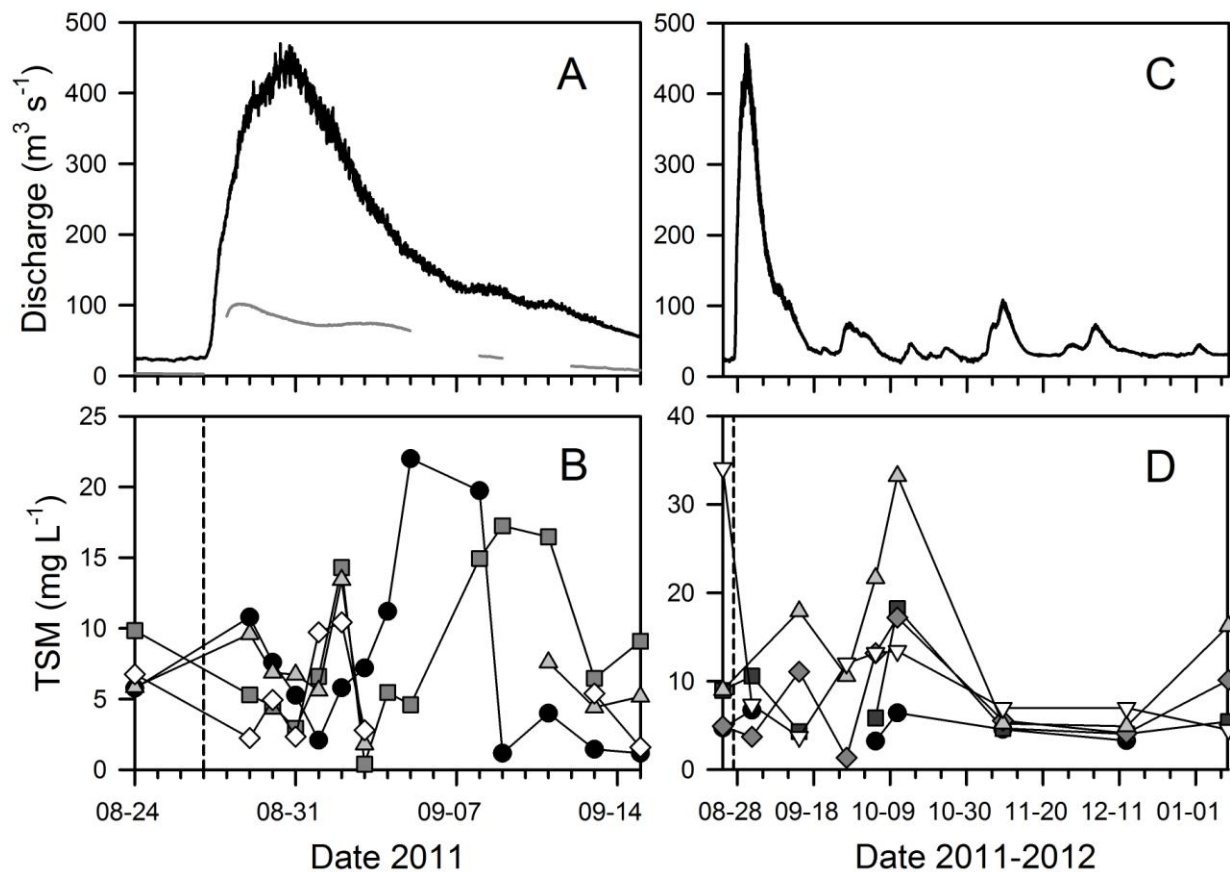


Fig. 1.3: River discharge and TSM concentration at river and estuary stations. A) River discharge measured for the Neuse River at Fort Barnwell (black line) and for Contentnea Creek at Hookerton (gray line). B) TSM measured at the shoreline stations upriver to downriver: Hookerton (●), Fort Barnwell (■), Cowpens (△), and Bridgeton (◇). C) Neuse River discharge measured at Fort Barnwell (note the longer measurement period compared to panel A). D) TSM measured in the upper to mid-estuary sections of the Neuse River Estuary obtained at NEMReP stations up-estuary to down-estuary: RR1 (●), BB2 (■), JPM (◆), BOM (△) and CHM(▽). Vertical dashed lines represent the date of Hurricane Irene's landfall.

Based on the findings of previous investigators (see for example, Stavn et al., 2009), the potential impact of salt retention on GF/F filters on the determination of TSM was examined (Fig. 1.4). A near linear relationship was observed between apparent salt retained and salinity below 20 ppt. Above 20 ppt the apparent salt retained on the GF/F filters was highly variable and ranged from about 2 to over 5 mg.

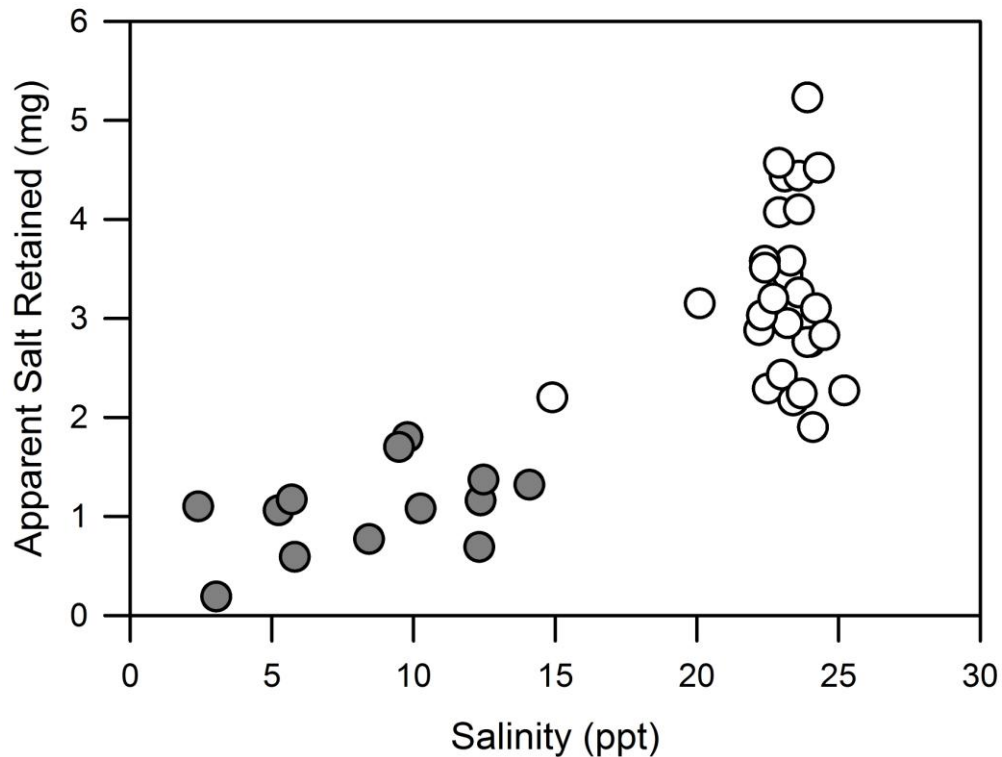


Fig. 1.4: Relationship between apparent salt retained on GF/F filters and salinity of filtered waters. Apparent salt retained refers to both salt and water of hydration. Closed circles represent samples collected at NEMReP stations on Nov. 9 whereas open circles represent samples collected in the lower Neuse River Estuary and Pamlico Sound on Nov. 12.

In addition, differences were observed in TSM concentration when using 0.7- μm GF/F or 0.2- μm polycarbonate filters at NEMReP stations. The average TSM concentration on March 8 was 6.0 and 10.6 mg L^{-1} using 0.7- μm and 0.2- μm filters, respectively. Similar results were

obtained on April 11 where the TSM concentration ranged from 7.6 mg L⁻¹ for 0.7- μ m GF/F filters to 10.9 mg L⁻¹ for 0.2- μ m polycarbonate filters.

1.3.2 Remote Sensing

Field measurements were used with processed MODIS imagery to develop a remote sensing algorithm for TSM concentration and assess the utility of a previously described algorithm to monitor CDOM. Samples collected in the lower NRE and Pamlico Sound were analyzed for TSM concentrations that were then compared to MODIS 250 m band 1 reflectance to assess the development of a TSM remote sensing algorithm. Data collected on Oct. 26 in the lower NRE and Pamlico Sound were not used in algorithm development due to contamination in the MODIS image from clouds and foam generated by high winds. Conditions on Nov. 12 were calm and clear and provided the best opportunity to evaluate the use of remote sensing to image TSM. However, no direct relationship was observed between TSM and MODIS Aqua 250 m band 1 reflectance (Fig. 1.5).

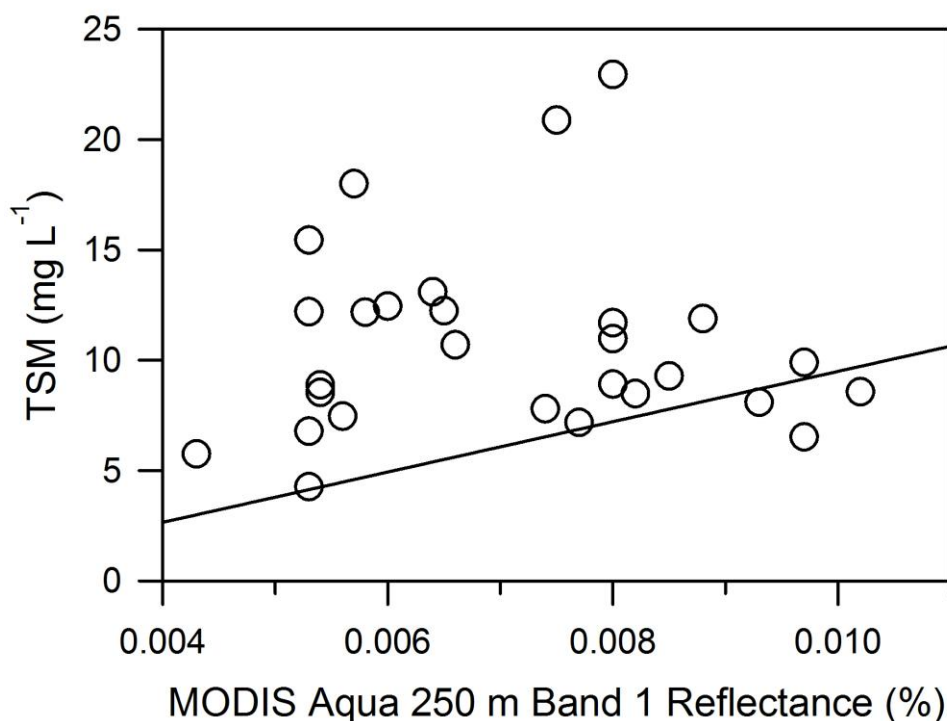


Fig. 1.5: Relationship between total suspended matter (TSM) and MODIS Aqua 250 m band 1 reflectance in the lower NRE and Pamlico Sound on Nov. 12, 2011. Locations of sample collection are shown in Fig. 2.1. The line is the least-squares fit of data from Miller and McKee (2004) described by $TSM = -1.91 + 1140.25(\text{MODIS Band 1})$.

Due to the unsuccessful development of a new, regional TSM algorithm, large-scale synoptic images of TSM concentration within the APES were created using the remote sensing algorithm of Miller and McKee (2004). These images show a significant increase in modeled TSM concentrations following the landfall of Hurricane Irene on Aug. 27, 2011 based on an increase in band 1 water-leaving radiance (Fig. 1.6). Algorithm-derived measurements indicate low TSM concentration throughout the APES prior to Hurricane Irene, ranging from about 20-25 mg L⁻¹ throughout the NRE and Pamlico Sound (Fig. 1.6A). Modeled concentrations significantly increased the day after landfall on Aug. 28 (Fig. 1.6B), ranging from 40-70 mg L⁻¹ in the NRE and up to about 75 mg L⁻¹ in Pamlico Sound. Suspended particles began to settle out

of the water column by Aug. 31 and Sept. 1 (Fig. 1.6C,D) and modeled TSM concentrations in the NRE decreased to around 10-25 mg L⁻¹. Highly complex patterns of TSM concentration are evident with the highest modeled concentrations estimated at about 55 mg L⁻¹ in the central portion of Pamlico Sound. By Sept. 10, algorithm-derived concentrations in the NRE remained around 15 mg L⁻¹ and increased to approximately 20 mg L⁻¹ in Pamlico Sound (Fig. 1.6E). Modeled TSM concentrations slightly increased in the NRE and Pamlico Sound to about 25 mg L⁻¹ on Sept. 13 (Fig.1.6F).

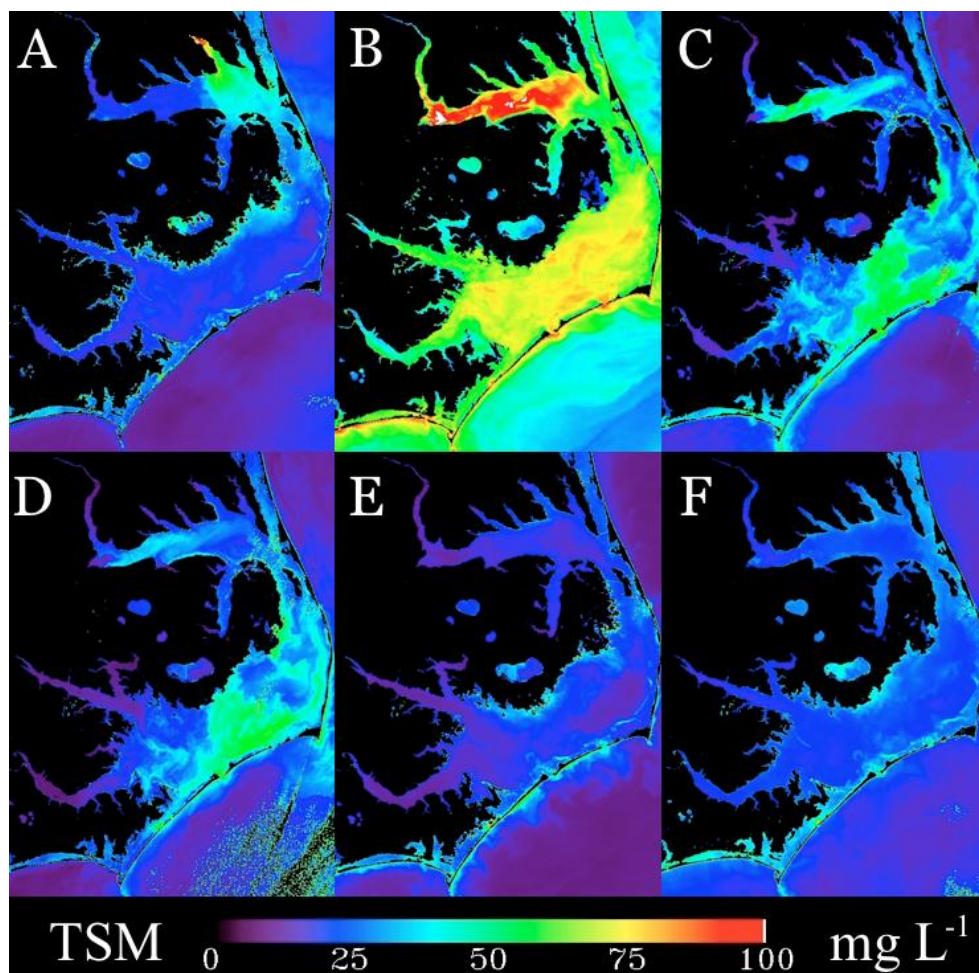


Fig. 1.6: Processed MODIS band 1 imagery of the Albemarle Pamlico Estuarine System (APES) from selected dates prior to and following the landfall of Hurricane Irene on Aug. 27, 2011 displaying the modeled concentration and distribution of total suspended matter (TSM) in mg L⁻¹ based on the algorithm from Miller and McKee (2004). A) Aug. 16; B) Aug. 28; C) Aug. 31; D) Sept. 1; E) Sept. 10; F) Sept. 13.

Similar difficulties were encountered when investigating the utility of a MODIS reflectance ratio (band 3/band 4) to monitor CDOM absorption in the NRE and Pamlico Sound (Fig. 1.7). No further analysis of MODIS data was performed to investigate CDOM.

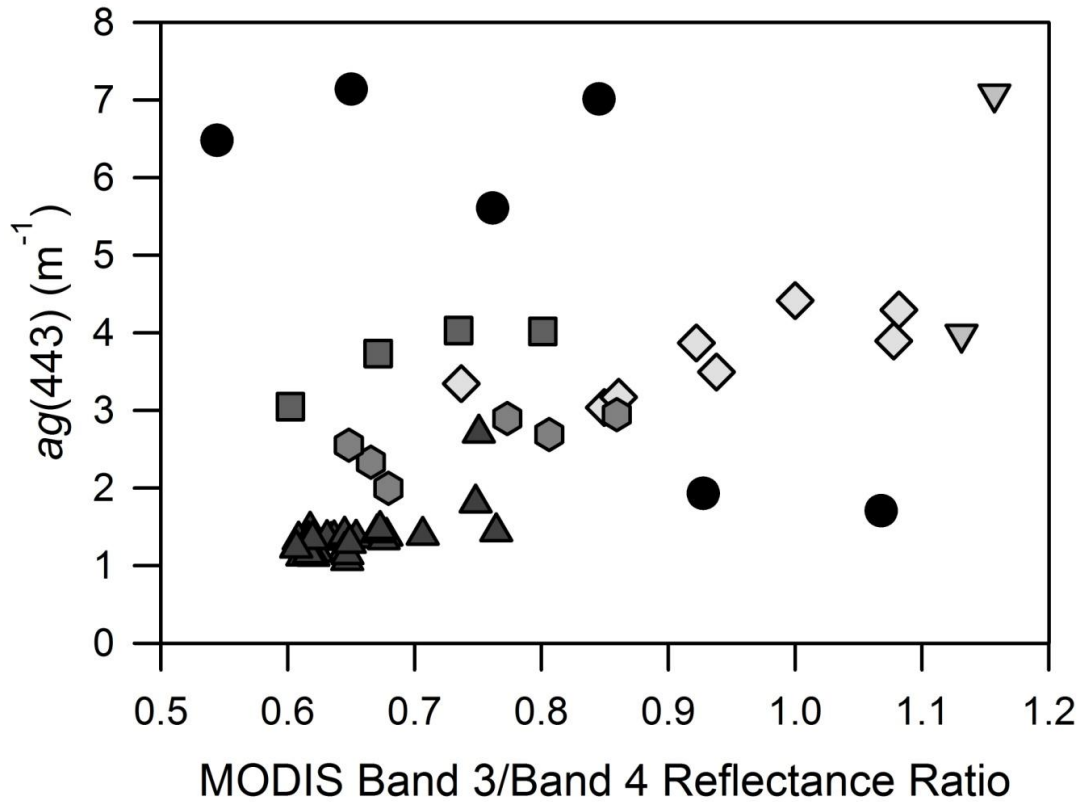


Fig. 1.7: Relationship between CDOM absorption at 443 nm ($ag(443)$) and MODIS band 3/band 4 reflectance ratio. Samples used were collected on various dates at mid-channel NEMReP stations and in the lower NRE and Pamlico Sound on Nov. 12. Samples collected at NEMReP stations varied with dates based on cloud cover and location of collection in relationship to the shoreline. Symbols indicate different dates of sample collection.

1.4 Discussion

Results based on field sampling indicate that discharge resulting from Hurricane Irene rainfall and runoff did not create a significant pulse of suspended sediment to the NRE and Pamlico Sound, suggesting that rainfall from Hurricane Irene may not have had a major impact on the concentration of particulate material transported from the Neuse River. Precipitation was focused in the lower portions of the basin and followed a drought (www.ncdrought.org), suggesting that rainfall infiltrated soils and resulted in limited overland flow and thus limited sediment mobilization and transport. Winds resulting from Hurricane Irene did, however, cause significant sediment resuspension within Pamlico Sound as observed from processed MODIS imagery. The development of a regional remote sensing algorithm to derive TSM concentration in the APES was unsuccessful presumably due to the high spatial variability in TSM concentration within MODIS 250 m pixels. This conclusion was confirmed after an analysis of 30 m Landsat Thematic Mapper (TM) imagery where visual color differences between pixels were observed. It is suggested in future studies that samples are collected from areas where relatively constant TSM concentrations are observed over a large gradient of TSM concentrations, conditions which are most commonly observed in the central portion of Pamlico Sound. It is also recommended that samples are filtered through 0.2- μm polycarbonate filters to eliminate variations in TSM concentration resulting from retained salt. Additionally, the use of a previously developed relationship between simulated MODIS band 3/band 4 ratios and CDOM in the NRE was not successful in this study. Although this method may be appropriate during low CDOM conditions, current remote sensing instruments do not provide sufficient spectral sensitivity to generate data products for waters with concentrations of CDOM as high as those frequently observed following rain events in the NRB (Miller et al., 2011a). Although MODIS data was not able to be used to its full proposed extent, it was still used to provide large-scale

views of suspended sediment throughout the APES following Hurricane Irene and provided important information that can be used to alter future algorithm development techniques.

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CHAPTER 2: THE IMPACT OF RAINFALL AND RUNOFF FROM HURRICANE IRENE
(2011) ON THE TRANSPORT AND CONCENTRATION OF DISSOLVED ORGANIC
MATTER IN THE LOWER NEUSE RIVER AND NEUSE RIVER ESTUARY, NC, USA

Prepared for Submission To: *Estuaries and Coasts*

Abstract

Colored dissolved organic matter (CDOM) and dissolved organic carbon (DOC) concentrations were analyzed in the lower reach of the Neuse River and upper-to-middle Neuse River Estuary (NRE), NC, USA following the landfall of Hurricane Irene in August 2011 to assess the impact of a rainfall event on the transport of dissolved organic matter (DOM) in a coupled land-estuary system. Within most of the system there was a rapid, significant increase in both CDOM [expressed as CDOM absorption at 443 nm, $ag(443)$] and DOC concentration following peak discharge of the Neuse River, which increased from $24 \text{ m}^3 \text{ s}^{-1}$ to $470 \text{ m}^3 \text{ s}^{-1}$ three days following peak precipitation. Maximum $ag(443)$ reached 15.51 m^{-1} in the Neuse River while in the NRE the maximum value reached 10.60 m^{-1} . CDOM was found to behave conservatively following the storm with slight increases in spectral slope coefficients (S) suggesting possible photo or microbial degradation during down-estuary transport. A strong positive relationship ($r^2 = 0.86$) was observed between $ag(443)$ and DOC covering a range of concentrations not previously reported in similar studies. This relationship could be used with advanced *in situ* instrumentation or remote sensing technologies to more accurately characterize DOM transport during and following dynamic storm events where field sampling is often not possible. Due to the impact of varying hurricane characteristics on hydrology and material transport, this work may be used to better characterize DOM export to Pamlico Sound as well as limit the amount of DOM field data necessary following future rainfall events.

2.1 Introduction

River transport of material plays an important role in the global carbon cycle. Approximately 590-830 Tg of total carbon is transported to the world's oceans by rivers each year (Cole et al., 2007) as dissolved inorganic carbon (DIC) and total organic carbon (TOC). Organic matter represents the largest reservoir of reduced carbon on Earth (Bianchi, 2011) and is mobilized and transported from terrestrial systems to aquatic environments through various processes including rainfall, runoff and flooding. Soils and terrestrial vegetation represent the major sources of allochthonous organic carbon input to streams, rivers and ultimately coastal waters (Thurman, 1985). The amount of carbon stored in terrestrial vegetation is on the order of carbon stored in the atmosphere and the amount of organic matter in soils is 2-3 times that stored in vegetation (Houghton, 2007) and hence represents the largest organic carbon source to streams and rivers. Organic matter exists in the aquatic environment as both particulate (POM) and dissolved (DOM) material, which is operationally defined as the portion of organic matter that remains on or passes through a fine-meshed filter, respectively. The dissolved fraction typically dominates the TOC pool, and in large rivers, dissolved organic carbon (DOC) is often twice the concentration of particulate organic carbon (POC) (Thurman, 1985). The annual flux of DOC from rivers to the oceans has been estimated at 360 Tg C yr⁻¹ (Aitkenhead and McDowell, 2000).

DOM is the largest oceanic reservoir of reduced carbon on earth (Hedges et al., 1992) and as such plays an important role in many global processes such as the global carbon cycle and climate change, the transport of toxic substances (Ravichandran, 2004), and the production of harmful disinfection byproducts (Richardson, 2003; Lu et al., 2009). DOM can also serve as a food source for bacteria (Tranvik, 1992), marine sponges (Yahel et al., 2003) and zebra mussels (Baines et al., 2005) and can be degraded to CO and CO₂ gas through photodegradation (Miller and Zepp, 1995), leading to a possible significant water-to-atmospheric flux of carbon (Cole et

al., 2007; Cai, 2011). In addition, the photodegradation of DOM generates lower molecular weight, labile organic matter that can be more readily utilized by aquatic bacteria (Moran and Zepp, 1997).

Colored dissolved organic matter (CDOM), also commonly referred to as gelbstoff, yellow substance or chromophoric dissolved organic matter, is the light absorbing fraction of DOM. CDOM absorption exhibits strong absorption in the ultraviolet and blue regions of the electromagnetic spectrum with exponentially decreasing absorption with increasing wavelength within the visible portion of the spectrum; optical measurements of CDOM concentration are widely used in a broad range of environments (Miller et al., 2002). CDOM absorption, particularly in coastal waters, interferes with remote sensing estimates of chlorophyll *a* (Carder et al., 1989) and is often a major control of the underwater light field in coastal systems (Markager et al., 2000; Branco and Kremer, 2005; Kostoglidis et al., 2005; Foden et al., 2008). Measurements of CDOM absorption and DOC concentration are highly correlated for many riverine and coastal waters (Ferrari et al., 1996; Vodacek et al., 1997; Del Castillo et al., 1999; Del Castillo and Miller, 2008; Mannino et al., 2008; Matsuoka et al., 2012; Spencer et al., 2012). The CDOM-DOC relationship can provide an enhanced understanding of DOC dynamics, especially during highly variable storm periods, by using frequent, *in situ* CDOM measurements (Chen, 1999; Del Castillo et al., 2001; Spencer et al., 2007; Saraceno et al., 2009; Downing et al., 2009; Pellerin et al., 2012) or large-scale synoptic estimates of CDOM concentration using remotely sensing images (Hoge and Lyon, 2002; Del Castillo and Miller, 2008; Griffin et al., 2011). Investigations of the riverine transport of organic matter to coastal waters is important to further our understanding of the coupling between terrestrial and aquatic processes as well as

enhance our understanding of how natural and anthropogenic events within coastal watersheds influence coastal DOM dynamics.

The mobilization and transport of terrestrial material is often enhanced following rainfall events where the export of DOM can account for the majority of the annual export budget (e.g. Hinton et al., 1997; Inamdar et al., 2006; Raymond and Saiers, 2010). Yoon and Raymond (2012) report the export of 43% and 31% of the annual DOC and dissolved organic nitrogen (DON) flux in only five days in a forested watershed in New York following Hurricane Irene (2011). Similarly, Avery et al. (2004) report the export of one-third and one-half of the annual river flux of DOC following Hurricane Fran (1996) and Floyd (1999) in the Cape Fear region of North Carolina. Due to expected increases in the frequency of intense hurricanes (Bender et al., 2010) and the expected increase in rainfall associated with tropical cyclones (Seneviratne et al., 2012), it is crucial to gain a better understanding of how storms currently impact coastal watersheds and associated aquatic systems to more accurately predict future changes.

Coastal North Carolina is susceptible to rainfall events associated with the landfall of tropical storms and hurricanes. Increased rainfall from these events results in the delivery of increased nonpoint source runoff that has been found to alter water quality and ecosystem health within North Carolina's Neuse River and Neuse River Estuary (NRE) (Paerl et al., 1998; Paerl et al., 2001; Bales, 2003; Peierls et al., 2003; Burkholder et al., 2004; Paerl et al., 2006; Wetz and Paerl, 2008). The extent of water quality degradation and associated impacts differ according to hurricane characteristics (Avery et al., 2004; Paerl et al., 2006) and in some cases the effects of a hurricane have been shown to be beneficial to the shallow estuarine system (Burkholder et al., 2004). Rain events mobilize material such as sediment, organic matter, nutrients, and pollutants from within the Neuse River basin (NRB) and deliver them to the Neuse River and NRE. This

non-point source runoff is the main cause of impacted water within the NRB (NCDENR, 2009) with sources of organic matter including topsoil, fertilizer, sewage, animal waste and croplands (Bales, 2003; Paerl et al., 2006). During extreme rain events, material from the NRB can impact Pamlico Sound and adjacent coastal waters. Large amounts of organic material were exported from the NRE following intense rainfall and regional flooding following Hurricane Fran in 1996 (Paerl et al., 1998) and following a series of hurricanes (Dennis, Floyd and Irene) that affected the area over a two-month period in 1999. Hurricanes Dennis, Floyd and Irene contributed to DOC concentrations in the Neuse River that exceeded measurements made the previous decade (Bales, 2003) and the doubling of pre-storm DOC concentrations at the mouth of the NRE (Paerl et al., 2001). The landfall of Hurricane Irene in eastern North Carolina in August 2011 provided an opportunity to continue examining how rainfall events influence the concentration and transport of DOM in the Neuse River and NRE.

As Hurricane Irene made landfall in eastern North Carolina on Aug. 27, 2011 as a category 1 hurricane, significant amounts of rainfall were delivered to the lower reaches of the NRB. Precipitation in the NRB was focused in the lower portion of the basin near New Bern, NC where accumulated rainfall reached 38 cm from Aug. 21 to Aug. 28 (Avila and Cangialosi, 2011). Hurricane Irene made landfall following months of drought conditions within the NRB (www.ncdrought.org). Antecedent moisture conditions have previously been reported to impact DOC dynamics in streams (Biron et al., 1999; Bernal et al., 2002; Inamdar et al., 2008; Turgeon and Courchesne, 2008). A series of discrete surface water samples were collected from the lower Neuse River and upper-to-middle region of the NRE prior to and following the landfall of Hurricane Irene and analyzed for CDOM and DOC to investigate the impact of rainfall on the

mobilization and transport of terrestrially derived organic material in this coupled land-estuary system.

2.2 Methods

2.2.1 Study Area

The Albemarle-Pamlico Estuarine System (APES) of eastern North Carolina (Fig. 2.1) drains about 80,000 km² from five major watersheds that span Virginia and North Carolina to form the second largest estuarine system and largest lagoonal estuary in the United States (Paerl et al., 2006). The APES is bounded to the east by the Outer Banks barrier islands, creating its lagoonal nature by limiting the exchange of water with the Atlantic Ocean through three narrow tidal inlets. Pamlico Sound covers the largest surface area of the APES at about 5,335 km² (Giese et al., 1979) and provides many ecological, recreational, and commercial services that are vital to North Carolina's economy. Two rivers, the Tar-Pamlico and the Neuse, directly discharge to Pamlico Sound. The NRB (Fig. 2.1) is the largest and most populated watershed draining directly to Pamlico Sound and is experiencing a rapid growth in population that could increase from a current estimate of 1.7 million to over 3 million by 2050 (NCDENR, 2010). The NRB consists of four sub-basins that span about 16,000 km². Two thirds of the land-cover within the watershed is composed of forest and agriculture with an additional 20% of the surface area occupied by open water or wetlands (NCDENR, 2010). The Neuse River flows approximately 320 km through the Piedmont and Coastal-Plain provinces of North Carolina before widening at New Bern, NC to form the headwaters of the NRE (Fig. 2.2). The NRE is a shallow drowned river valley that has experienced phytoplankton blooms (Pinckney et al., 1997), fish kills (Paerl et al., 1998), and bottom water hypoxia-anoxia (Paerl et al., 1998) associated with an increased loading of nutrients to the system. Potential negative impacts of terrestrially derived material on water quality are enhanced by a 1-2 month residence time of the NRE (Knowles, 1975; Robbins and Bales, 1995) and 11-month residence time of Pamlico Sound (Giese et al., 1979; Pietrafesa et al., 1986).

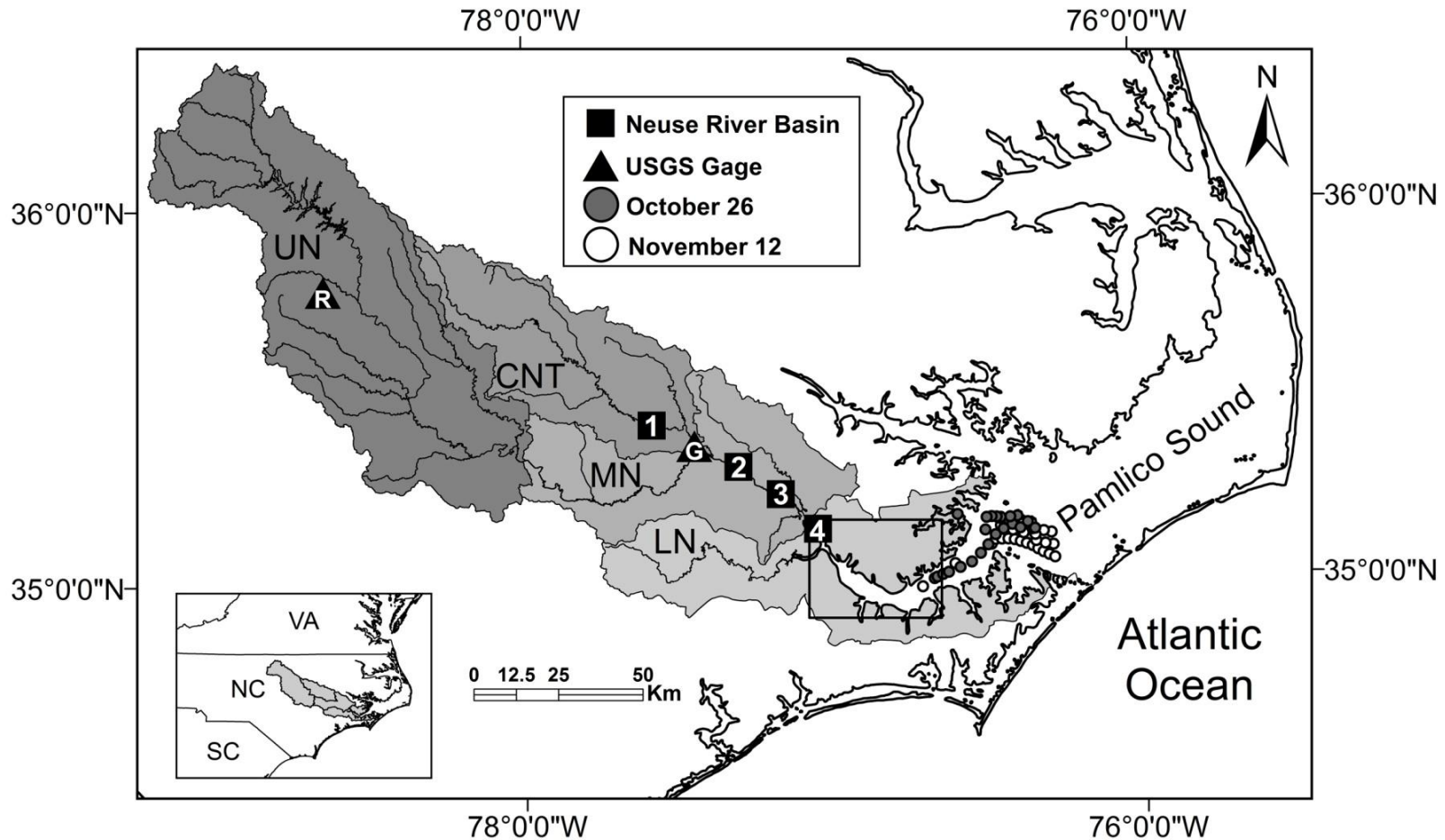


Fig. 2.1: Location map of the Albemarle Pamlico Estuarine System (APES) of eastern North Carolina showing the Neuse River basin and tributary system that connects to the Neuse River Estuary and Pamlico Sound. The Neuse River watershed is shown with sub-basins Upper Neuse (UN), Contentnea (CNT), Middle Neuse (MN), and Lower Neuse (LN). The location of shoreline stations (NRB) for surface water samples are shown as numbered black squares: 1-Hookerton, 2-Fort Barnwell, 3-Cowpens, and 4-Bridgeton. The location of surface water samples obtained from a small boat in the lower Neuse River Estuary and Pamlico Sound on Oct. 26 (closed circles) and on Nov. 12 (open circles) is also shown. USGS gage stations are represented by black triangles: R-Pigeon House Creek at Raleigh, and G-Contentnea Creek at Grifton. The black rectangle is the area of the upper Neuse River Estuary shown in Fig. 2.2.

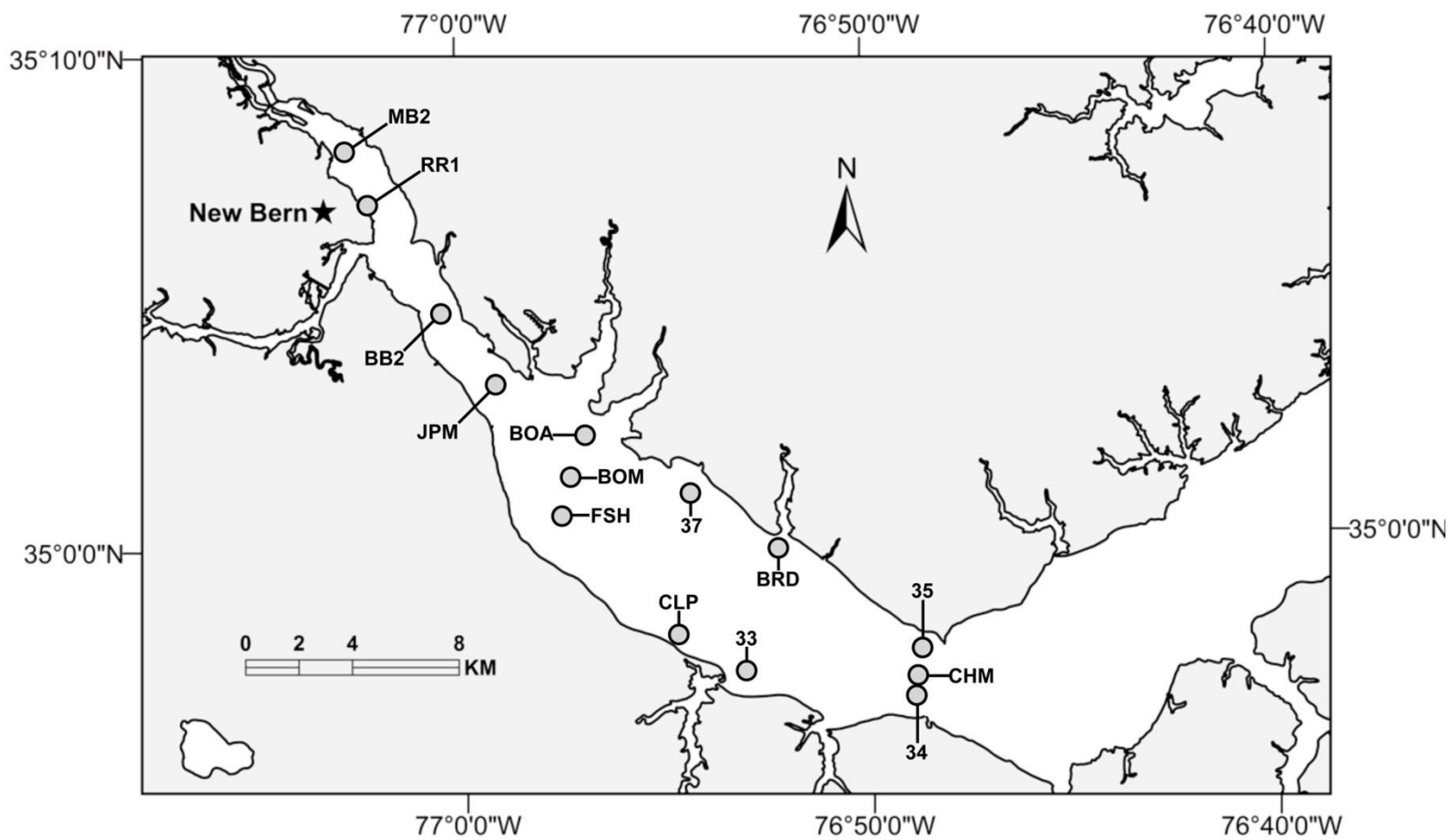


Fig. 2.2: Map of the upper Neuse River Estuary showing station locations for samples obtained as part of the North Carolina State University's Neuse Estuary Monitoring and Research Program (NEMReP). Samples were collected at NEMReP stations during nine field expeditions from Aug. 24, 2011 to Jan. 10, 2012.

2.2.2 Precipitation and Hydrology

Daily-accumulated rainfall (cm) was obtained from two United States Geological Survey (USGS) stations (Fig. 2.1). Rainfall was measured in the lower region of the NRB at Grifton, NC (USGS 02091764) and in the upper region of the NRB at Raleigh, NC (USGS 0208732534). River discharge and gage height along the Neuse River were obtained from a USGS gage station near Fort Barnwell, NC (USGS 02091814; hereby referred to as Barnwell) and a station on Contentnea Creek at Hookerton (USGS 02091500; hereby referred to as Hookerton). The Barnwell gage station is the lower most station on the Neuse River before it discharges into the NRE, while the Hookerton station measures river conditions related to Contentnea Creek, a tributary draining a NRB sub-basin that connects to the Neuse River about 10 km upstream from the Barnwell station.

2.2.3 Field Sampling and Measurements

Discrete surface water samples were collected at approximately 20 cm water depth at four locations within the lower reaches of the NRB (Fig. 2.1) prior to and following the landfall of Hurricane Irene. Samples were collected to characterize changes in material flux at different river height and volume discharge measured at the Barnwell and Hookerton gage stations. Surface water was collected from the shoreline at three stations on the lower Neuse River (Barnwell, Cowpens, Bridgeton) and one station on Contentnea Creek (Hookerton) on 14 separate days from Aug. 24 to Sept. 15, 2011. The Hookerton and Barnwell sampling sites were located near the USGS gage stations. Samples were collected and stored on ice in pre-washed 1L brown Nalgene bottles until transported to the laboratory where they were refrigerated (4°C) until analysis.

Additional discrete surface water samples were collected during nine field expeditions from Aug. 24, 2011 to Jan. 10, 2012 at 14 stations in the upper NRE (Fig. 2.2) as part of the bi-monthly sampling of the Neuse Estuary Monitoring and Research Program (NEMReP). Discrete surface water samples were collected away from the shore using a small boat and stored following the methods for NRB samples. Vertical salinity profiles were measured using a calibrated YSI 6600V2 water quality sonde. Surface salinity measurements obtained from the top 0.5 meters were used in this study.

An additional 50 discrete surface water samples were collected in the lower NRE and Pamlico Sound from a small boat on Oct. 26 and Nov. 12, 2011 (Fig. 2.1). Samples were handled and stored as described above. Salinity was measured in the laboratory on samples that were brought to room temperature using a Reichert AR200 digital handheld refractometer.

2.2.4 Colored Dissolved Organic Matter

Water samples were filtered under a gentle vacuum (< 5 mm Hg) through pre-rinsed Whatman 0.7- μm GF/F filters. Sample filtrate was collected in acid-washed 60 ml amber glass bottles with Teflon-lined caps and stored refrigerated until analysis. Samples were brought to room temperature, placed in a 1 cm quartz spectrophotometer grade cuvette, and absorbance measured from 187 to 721 nm at a 1 nm resolution using a single-path fiber optic absorption system (Miller et al., 2011a). Milli-Q water was used as a reference. Three absorbance spectra were recorded for each sample and averaged. The average absorbance values were corrected for scattering and baseline fluctuations by subtracting the average absorbance at 700 nm (Bricaud, 1981). The CDOM absorption coefficient, $a_g(\lambda)$ (m^{-1}), was calculated using:

$$a_g(\lambda) = 2.303A(\lambda)/L, \quad (1)$$

where $A(\lambda)$ is absorbance at wavelength (λ) and L is pathlength in meters (0.01 m). A is calculated as $\log_{10}(I_0/I)$, where I_0 is the absorbance of the Milli-Q reference and I is the absorbance of the sample. Spectral slope, S (nm^{-1}), was calculated using least squares linear regression of $\ln ag(\lambda)$ vs. wavelength from 300-600 nm.

2.2.5 Dissolved Organic Carbon

Approximately 20 ml of filtrate from the filtration for CDOM were transferred to pre-combusted (450° C for 4 hours) borosilicate vials with foil liner caps and acidified with 3-5 drops of 2 N hydrochloric acid. Although non-combusted filters were used, a comparison between combusted and non-combusted filters yielded only a ~1% difference in DOC concentration ($n = 13$). Acidified DOC samples were stored refrigerated until analyzed using a Shimadzu TOC-V_{CPN} Total Organic Carbon Analyzer with Autosampler (ASI-V) capabilities. DOC concentrations were determined using high temperature (680°C) catalytically-aided combustion oxidation and non-dispersive infrared detection. Calibration curves for DOC were created using standard solutions of potassium hydrogen phthalate.

2.3 Results

2.3.1 Precipitation and Hydrology

Rainfall within the NRB associated with Hurricane Irene, which followed months of drought conditions (www.ncdrought.org), resulted in rapid, significant changes in river discharge and gage height of the Neuse River and Contentnea Creek (Fig. 2.3). Daily-accumulated rainfall at Grifton, located near the confluence of Contentnea Creek and the Neuse River in the lower region of the NRB, was about 30 cm on the day of landfall while near Raleigh in the upper region of the basin, rainfall was about 2.5 cm (Fig. 2.3A).

At the Barnwell station, where the Neuse River drains about 10,100 km² of the NRB, discharge increased to a maximum of 470 m³ s⁻¹, ranking as the seventh highest peak discharge over 16 years of historical peak discharge measurements. This maximum discharge occurred on Aug. 30, three days following maximum rainfall. River discharge diminished over the following 6 days to about 130 m³ s⁻¹ before a small rainfall event on Sept. 6-7 slightly interrupted the receding trend. Discharge decreased to about 35 m³ s⁻¹ on Sept. 17 before doubling on Sept. 27-28 following small (< 5 cm day⁻¹) rainfall events in the basin (Fig. 2.3B). Gage height at Barnwell reached a maximum of 3.79 m, less than the National Weather Service (NWS) flood stage of 3.81 m (Fig. 2.3C).

River discharge at Hookerton, which drains about 1,900 km² within the Contentnea sub-basin, increased to a maximum of 102 m³ s⁻¹ on Aug. 28, just one day following maximum rainfall. Peak discharge ranked as only the 52nd highest historical peak over 85 years of peak discharge measurements. Discharge decreased to about 70 m³ s⁻¹ on Sept. 1 before slightly increasing to about 75 m³ s⁻¹ on Sept. 3 following precipitation at Grifton of about 4 cm on Aug. 29-30. Discharge receded to about 13 m³ s⁻¹ on Sept. 12 and remained less than about 10 m³ s⁻¹

for the following month (Fig. 2.3B). The maximum gage height at Hookerton reached 4.15 m and exceeded the NWS flood stage of 3.96 m for about 2.5 days (Fig. 2.3C).

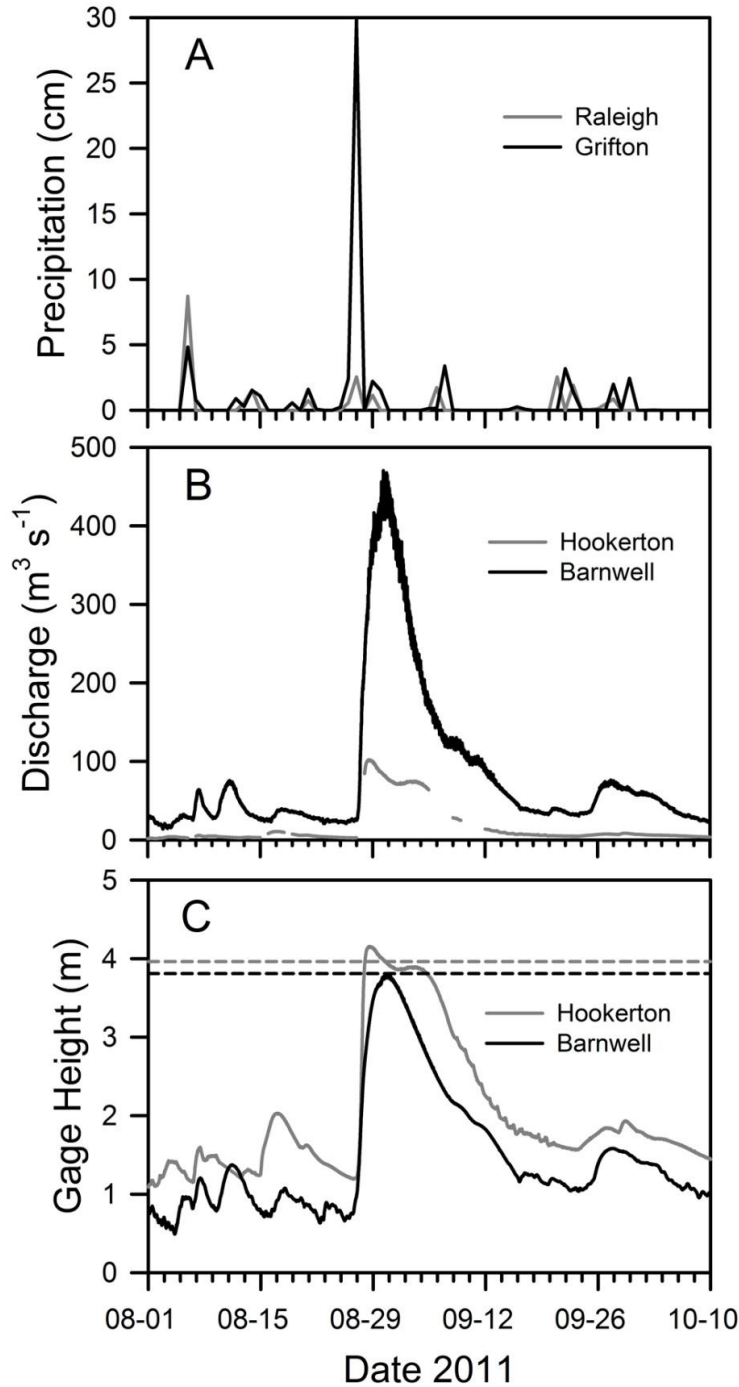


Fig. 2.3: Daily accumulated rainfall measured at United States Geological Survey (USGS) stations at Raleigh (USGS 0208732534) and Grifton, NC (USGS 02091764) (A), and river discharge (B) and gage height (C) measured at the USGS stations on Contentnea Creek at Hookerton, NC (USGS 02091500) and the Neuse River at Fort Barnwell, NC (USGS 02091814). Dashed lines in (C) represent flood stage elevations for Hookerton (gray) and Barnwell (black).

2.3.2 Colored Dissolved Organic Matter

CDOM absorption at 443 nm ($ag(443)$), used as a proxy for CDOM concentration, increased throughout the NRB and NRE from pre-storm values and reached maximum values following peak discharge (Fig. 2.4). Pre-storm values in the NRB samples averaged 5.08 m^{-1} with a maximum of 7.87 m^{-1} measured at the most upstream station at Hookerton and a minimum of 2.93 m^{-1} measured at the most downstream station at Bridgeton. Maximum $ag(443)$ at Hookerton reached 14.41 m^{-1} on Sept. 4 as the discharge of Contentnea Creek decreased to about $70 \text{ m}^3 \text{ s}^{-1}$ while maximum $ag(443)$ at Barnwell reached 12.42 m^{-1} on Sept. 5 as the discharge of the Neuse River decreased to about $165 \text{ m}^3 \text{ s}^{-1}$ (Fig. 2.4A,B). Maximum values at Cowpens (11.93 m^{-1}) and Bridgeton (15.51 m^{-1}) were measured on Sept. 3, although limited samples following this date were analyzed for CDOM due to suspected contamination. CDOM absorption decreased from the measured peaks but remained more than double the average pre-storm values on Sept. 15, averaging 11.61 m^{-1} on the final day of NRB sampling.

Samples in the NRE were collected until Jan. 10, 2012, about 4.5 months following the landfall of Hurricane Irene, to examine the long-term impact of the storm on CDOM dynamics within the system. CDOM absorption in the NRE followed a similar pattern to that observed from the shore-based river samples with a rapid increase in $ag(443)$ from pre-storm values that averaged 2.14 m^{-1} . Pre-storm values increased immediately following peak discharge on Sept. 1 to an average of 8.71 m^{-1} and remained elevated at an average of 7.86 m^{-1} further along the receding limb of the hydrograph on Sept. 14 where discharge decreased to around $60 \text{ m}^3 \text{ s}^{-1}$ (Fig. 2.4C,D). CDOM absorption decreased at all stations on Sept. 27, although discharge of the Neuse River increased to about $70 \text{ m}^3 \text{ s}^{-1}$ after a week long period where discharge averaged about $35 \text{ m}^3 \text{ s}^{-1}$. CDOM absorption continued to decrease through October sampling until Nov. 9 where average $ag(443)$ away from the head of the estuary increased by about 0.23 m^{-1} during a

rising hydrograph of the Neuse River which peaked at $108 \text{ m}^3 \text{ s}^{-1}$ the previous day. CDOM absorption in the NRE returned close to pre-storm values on Jan. 10, 2012, over four months after Hurricane Irene made landfall in the region. Within the NRE, CDOM absorption significantly decreased by dilution within 30 km of the head of the estuary as $ag(443)$ at the head and mid-estuary differed by a factor of approximately 2 throughout the study period. CDOM absorption in the lower NRE and Pamlico Sound averaged 1.51 m^{-1} and 1.36 m^{-1} on Oct. 26 and Nov. 12, respectively, with highest values measured in the lower NRE.

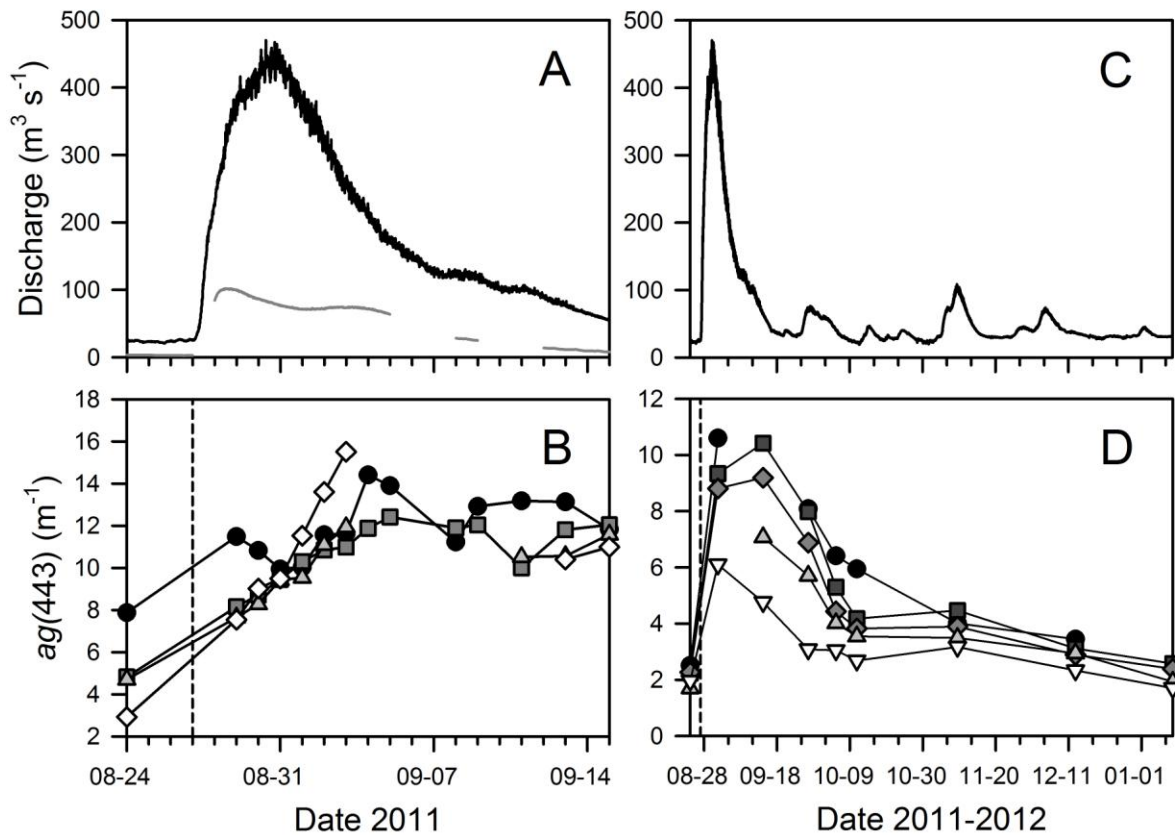


Fig. 2.4: River discharge and CDOM absorption at 443 nm ($ag(443)$). A) River discharge measured for the Neuse River at Fort Barnwell (black line) and for Contentnea Creek at Hookerton (gray line). B) $ag(443)$ measured at the shoreline stations upriver to downriver: Hookerton (●), Barnwell (■), Cowpens (△), and Bridgeton (◇). C) Neuse River discharge measured at Fort Barnwell (note the longer measurement period compared to panel A). D) $ag(443)$ measured in the upper to mid-estuary sections of the Neuse River Estuary obtained at the NEMReP stations up-estuary to down-estuary: RR1 (●), BB2 (■), JPM (◇), BOM (△) and CHM (▽). Vertical dashed lines represent the date of Hurricane Irene's landfall.

CDOM generally exhibited a conservative response within the NRE and Pamlico Sound with CDOM absorption decreasing with increasing salinity (Fig. 2.5). CDOM absorption and salinity were weakly correlated on Aug. 24 prior to the passage of Hurricane Irene when both $ag(443)$ and river discharge were low; $ag(443)$ at salinities greater than 17 ppt ranged from 1.28 m^{-1} to 2.43 m^{-1} . A strong linear relationship was observed between salinity and $ag(443)$ on sampling cruises following Hurricane Irene (Table 2.1). The higher variability in $ag(443)$ at lower salinities resulted from localized changes in the concentration of CDOM in the Neuse River end member (i.e., salinity = 0).

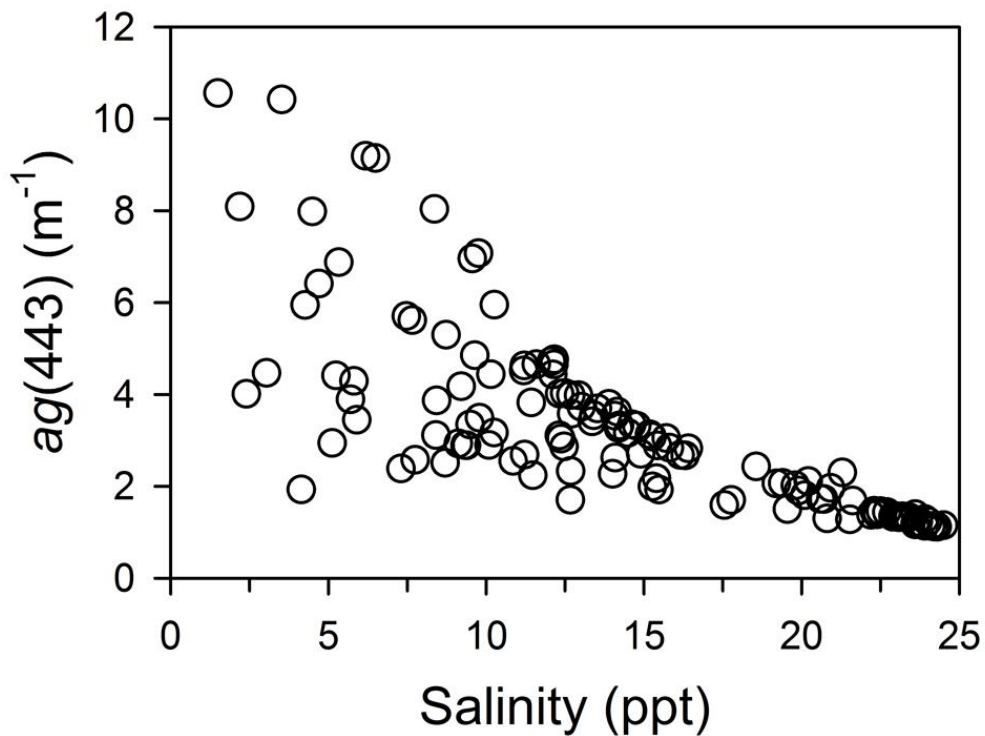


Fig. 2.5: Relationship between $ag(443)$ and salinity at all sampled NEMReP stations from Aug. 24, 2011 to Jan. 10, 2012 and at stations in the lower NRE and Pamlico Sound sampled on Oct. 26 and Nov. 12.

Table 2.1: Relationship between $ag(443)$ and salinity in the NRE and Pamlico Sound.

| Date | <i>n</i> | r^2 | Intercept | Slope |
|-------------|-----------------|-------------------------|------------------|--------------|
| 08/24/2011 | 13 | 0.33 | 2.98 | -0.059 |
| 09/14/2011 | 13 | 0.94 | 12.63 | -0.635 |
| 09/27/2011 | 13 | 0.97 | 8.98 | -0.391 |
| 10/05/2011 | 13 | 0.98 | 7.83 | -0.304 |
| 10/11/2011 | 13 | 0.98 | 6.86 | -0.256 |
| 10/26/2011 | 6 | 0.94 | 7.01 | -0.256 |
| 11/09/2011 | 13 | 0.86 | 4.87 | -0.150 |
| 11/12/2011 | 28 | 0.97 | 5.08 | -0.162 |
| 12/13/2011 | 13 | 0.96 | 4.34 | -0.151 |
| 01/10/2012 | 4 | 0.13 | 2.47 | -0.040 |

The CDOM spectral slope coefficient (S) showed little variation within the NRB as well as in the NRE and Pamlico Sound over a wide range of salinity (Fig. 2.6). For the NRB samples, S was higher in the pre-storm samples, decreased following landfall, and then increased to near pre-storm values on Sept. 15. The spectral slope was less than 0.015 nm^{-1} for all samples collected in the NRB except for the pre-storm sample collected at the mouth of the Neuse River at Bridgeton. A small upward trend in S was observed in the NRE and Pamlico Sound with increasing salinity except for a limited number of samples with a S below 0.015 nm^{-1} at salinities near 20 ppt, all of which were collected prior to Hurricane Irene's landfall.

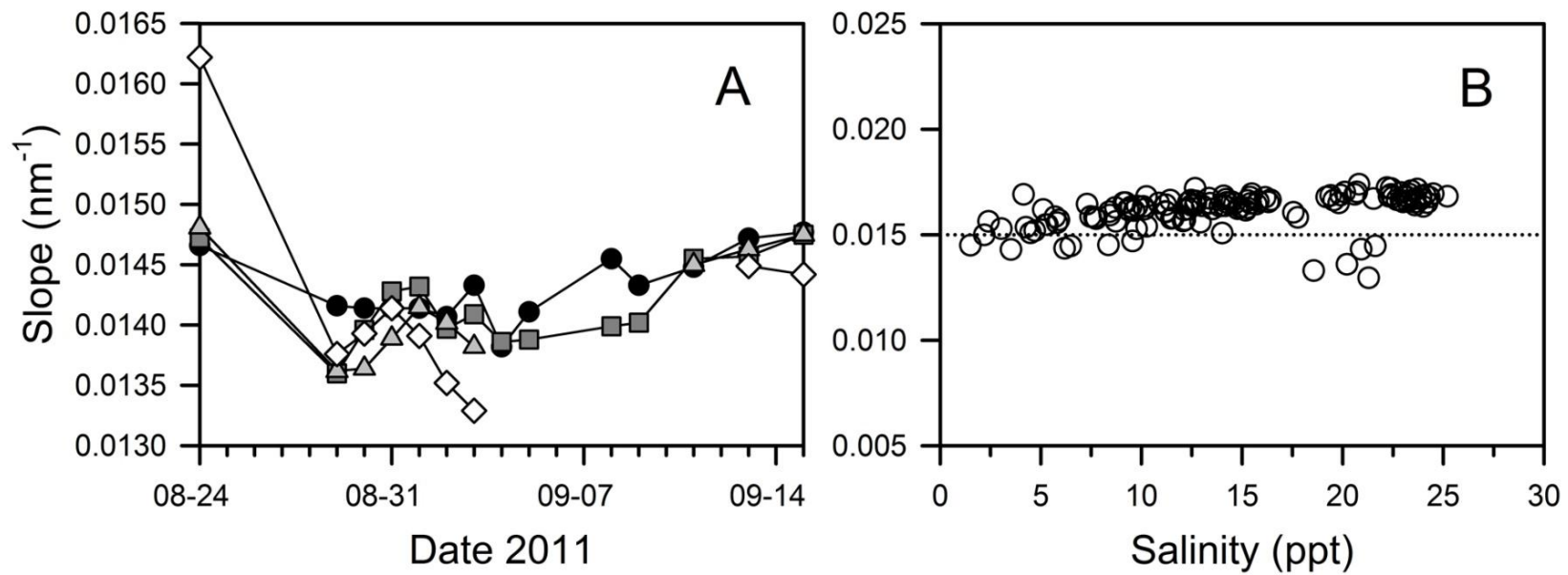


Fig. 2.6: Spectral slope characteristics at shoreline (A) and NEMReP, lower Neuse, and Pamlico Sound stations (B). Shoreline stations in (A) denoted by circles (Hookerton), squares (Barnwell), triangles (Cowpens), and diamonds (Bridgeton).

2.3.3 Dissolved Organic Carbon

A strong positive linear relationship between $ag(443)$ and DOC ($r^2=0.86$) was observed in both river and estuary samples (Fig. 2.7), and as such the response in DOC concentration following Hurricane Irene (Fig. 2.8) showed a similar pattern to that observed for CDOM. Samples collected at Barnwell and at all NRE stations on Aug. 24, the first date of sampling, were not included in the analysis due to suspected sample contamination. Pre-storm DOC concentration in the river samples averaged 8.6 mg L^{-1} and gradually increased as Neuse River discharge increased to a maximum of $470 \text{ m}^3 \text{ s}^{-1}$ on Aug. 30, three days post-landfall. DOC concentration measured for the river samples continued to increase to an average of 25.6 mg L^{-1} on Sept. 5 during the declining stage of river discharge at Barnwell (Fig. 2.8A,B). This near-linear increase in concentration was offset by exceptionally high concentrations measured at Hookerton (64.9 mg L^{-1}) and Bridgeton (42.2 mg L^{-1}) on Sept. 1, three days following maximum precipitation. Similar high values were observed in a Neuse River sample following maximum discharge resulting from Tropical Storm Nicole in 2010 (Miller et al., 2011b). DOC concentration decreased from measured maximum values but remained well above pre-storm concentrations on the final day of sampling with an average of 17.0 mg L^{-1} in the river samples almost three weeks following Hurricane Irene's landfall. An estimated $7.6 \times 10^6 \text{ kg}$ DOC were transported to the NRE from the Neuse River from Aug. 24 to Sept. 15 (see Chapter 3).

DOC concentration quickly increased within the NRE following the down-estuary transport of freshwater. Similar to CDOM, maximum DOC concentrations were measured during the receding limb of the Hurricane Irene hydrograph (Fig. 2.8C,D) with average values reaching 16.5 mg L^{-1} and 18.3 mg L^{-1} on Sept. 1 and Sept. 14, respectively. Maximum concentrations measured on Sept. 27, one month following Irene's landfall, decreased to concentrations close to those measured at the most upstream stations immediately following maximum discharge.

Concentrations continued to decrease through the end of September before the most dramatic decrease was observed on Oct. 5, over two weeks following the end of the receding Irene hydrograph, where the average DOC concentration declined to 9.7 mg L^{-1} . DOC concentration was slightly elevated at the three most downstream locations on Nov. 9 corresponding to an increase in discharge at Barnwell before concentrations decreased to the lowest measured values on Dec. 13, over three months post-landfall. The down estuary transport of DOC greatly impacted the range of DOC concentrations measured at the head and mid-estuary (Fig. 2.8D). Ranges in DOC concentration reached over 6 mg L^{-1} during September sampling except for September 14 (range of about 4 mg L^{-1}) where sampling did not occur at the most upstream station. The range in DOC concentration decreased to around 3 mg L^{-1} during October sampling while concentrations from the head to mid-estuary were uniform in November and December.

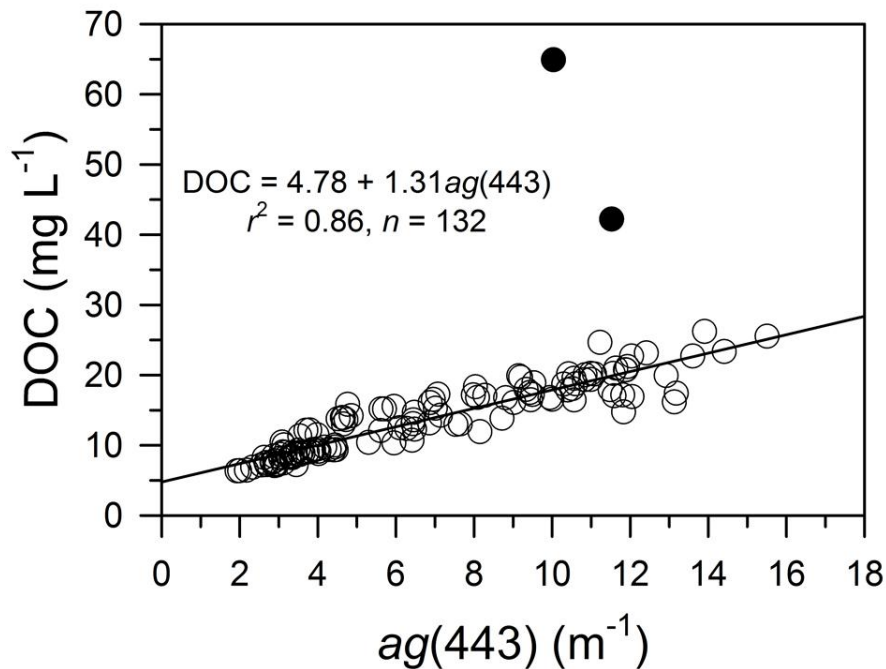


Fig. 2.7: Relationship between DOC and $ag(443)$ at shoreline and NEMReP stations following Hurricane Irene (i.e. not including pre-storm samples collected Aug. 24). The line represents the fit to the linear least squares regression. Samples shown as closed circles measured at Hookerton and Bridgeton on Sept. 1 were not included in the regression analysis.

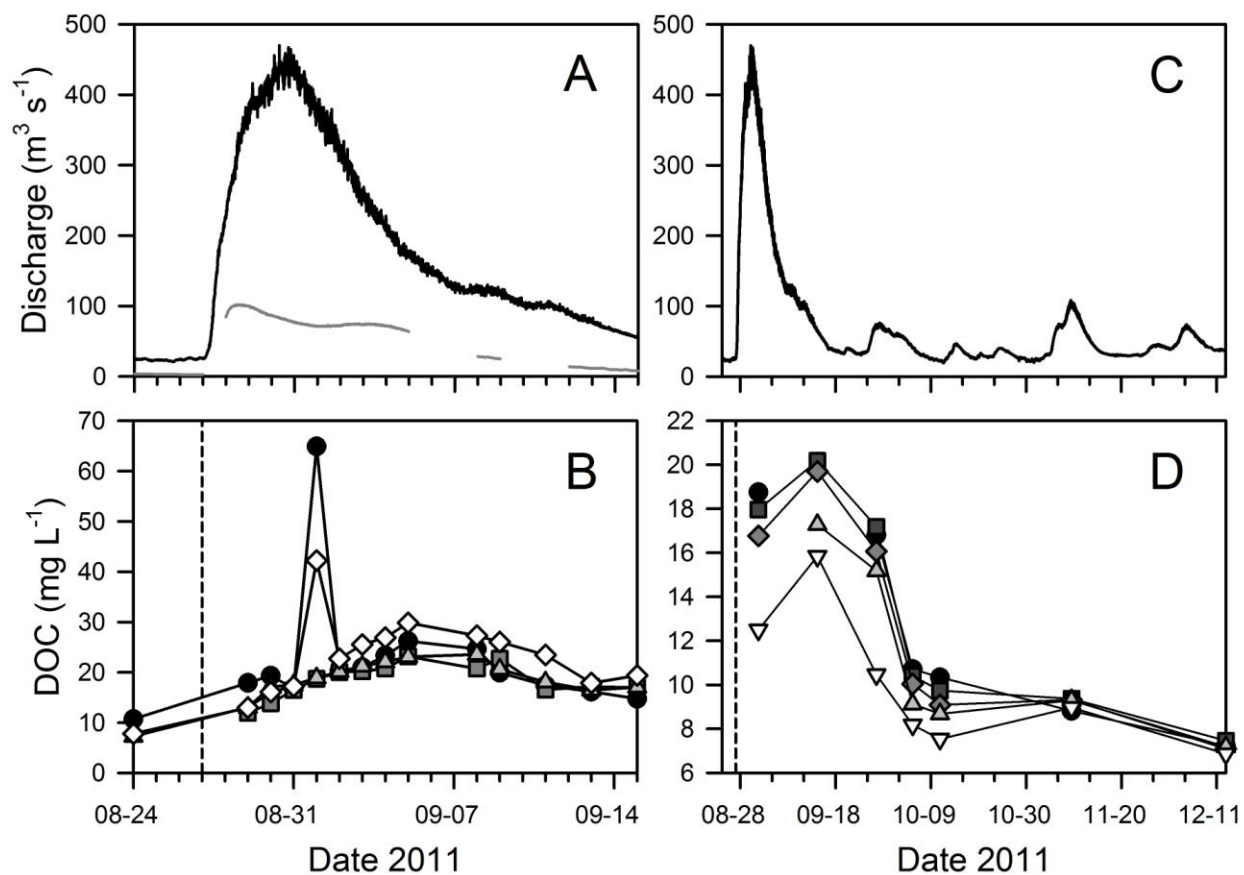


Fig. 2.8: River discharge and dissolved organic carbon (DOC) concentration at river and estuary stations. A) River discharge measured for the Neuse River at Fort Barnwell (black line) and for Contentnea Creek at Hookerton (gray line). B) DOC concentration measured at the shoreline stations upriver to downriver: Hookerton (●), Barnwell (■), Cowpens (△), and Bridgeton (◇). C) Neuse River discharge measured at Fort Barnwell (note the longer measurement period compared to panel A). D) DOC concentration measured in the upper to mid-estuary sections of the Neuse River Estuary obtained at the NEMReP stations up-estuary to down-estuary: RR1 (●), BB2 (■), JPM (◆), BOM (△) and CHM (▽). Vertical dashed lines represent the date of Hurricane Irene's landfall.

Values of $ag(443)$ and DOC were generally lower at increased discharge following Hurricane Irene at Barnwell, exhibiting a weaker coupling at lower discharge (Fig. 2.9) and indicating a delay in the transport of DOM compared to freshwater. Maximum values of $ag(443)$ and DOC were measured when Neuse River discharge was only about $160 \text{ m}^3 \text{ s}^{-1}$ while minimum values were measured when discharge reached about $382 \text{ m}^3 \text{ s}^{-1}$ on the rising limb of the hydrograph.

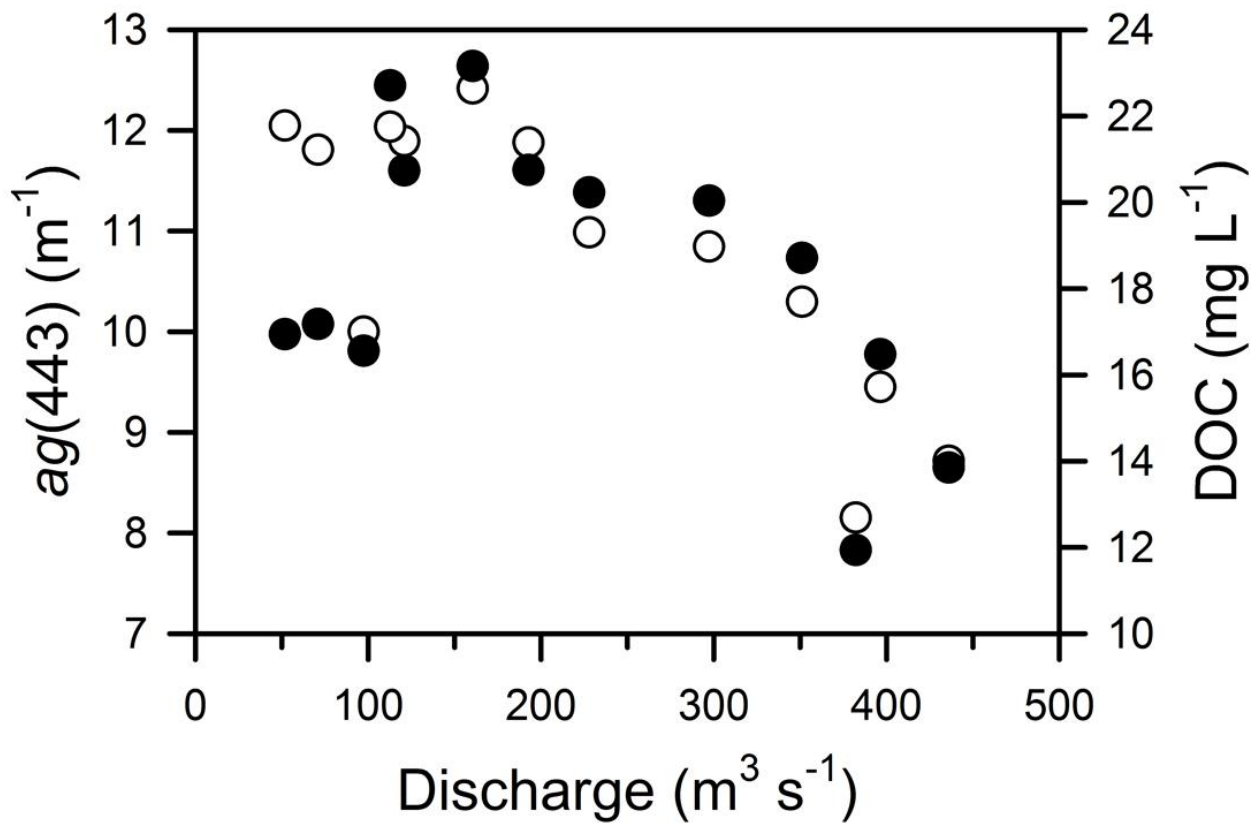


Fig. 2.9: Relationship between $ag(443)$ (○) and DOC (●) measured following Hurricane Irene at Fort Barnwell as a function of Neuse River discharge at Fort Barnwell.

2.4 Discussion

Surface water samples were collected during 2011 in the lower Neuse River and upper-to-middle NRE and analyzed for CDOM absorption and DOC concentration to assess the impact of a major rainfall event, Hurricane Irene, on the transport of DOM in a coupled land-estuary system. A significant increase in DOM concentration in the Neuse River and NRE was observed (Figs. 2.4, 2.8) that is consistent with previous studies in the NRE following Hurricanes Fran in 1996 (Paerl et al., 1998) and Dennis, Floyd, and Irene in 1999 (Paerl et al., 2001). Differences in the amount of DOM added to the system depends in-part on hurricane characteristics such as the intensity and location of rainfall and pre-storm conditions that directly affect system hydrology and material availability, localized transport, and loading (Avery et al., 2004; Paerl et al., 2006). Drought-like conditions existed in the NRB prior to Hurricane Irene's landfall (www.ncdrought.org), similar to the conditions prior to the landfall of Hurricanes Dennis, Floyd, and Irene but in contrast to the saturated conditions that existed throughout the basin prior to the landfall of Hurricane Fran. Saturated soils prior to Hurricane Fran limited soil storage capacity (Bales and Childress, 1996), likely leading to increased runoff and an enhanced capability to mobilize and transport terrestrial material; an estimated $> 14 \times 10^6$ kg TOC were associated with Hurricane Fran discharge (Paerl et al., 1998). Flooding from Hurricane Fran exceeded many unregulated peak flows measured in the 1900's with unregulated flows of the Neuse River ranging in recurrence interval from 10-50 years (Bales and Childress, 1996). Conversely, the sequential landfall of Hurricanes Dennis, Floyd, and Irene resulted in 500-year floods (Bales, 2003) and the transport of CDOM throughout the entire APES (Tester et al., 2003). Unlike the hydrological impacts from these storms, Hurricane Irene (2011) resulted in < 2 -year flood events and delivered only a small amount of DOC to the mouth of the NRE (see Chapter 3).

During this study, CDOM discharged within the NRE following Hurricane Irene was largely diluted within the uppermost 30 km of the estuary (Fig. 2.4), resulting in low CDOM waters from the mid-to-lower estuary. CDOM absorption decreased with increasing salinity throughout the NRE and Pamlico Sound (Fig. 2.5), suggesting a terrestrial DOM source. This strong relationship is a common feature in river plume regions (Kowalczyk et al., 2003) and suggests that mixing is the dominant process that decreases terrigenous DOM concentrations as it is transported down estuary. A similar relationship was demonstrated for DOC in the NRE following Hurricane Irene using a numerical model in which DOC was considered to be a passive tracer (see Chapter 3).

The small variation in the spectral slope coefficient (S) (Fig. 2.6) suggests that the composition or optical properties of CDOM did not significantly change within the observed salinity range (Del Castillo et al., 1999). The point at which changes in optical properties occur, sometimes referred to as the inflection point, is usually not observed at salinities below ~30 due to the strong influence of riverine material (Del Castillo et al., 1999; Del Castillo, 2005). Others have reported inflection points (through drastic changes in S) in oceanographic studies at salinities of 34.5 in the West Florida Shelf (Del Castillo et al., 2000) and 35.5 in the Cape Fear River Plume and Onslow Bay (Kowalczyk et al., 2003). In a more enclosed system, Puget Sound, an inflection point at a salinity of approximately 26 was reported (Coble, 1996), a value that is closer to the maximum salinity of 25.2 observed during this study. Lower S values generally indicate higher molecular weight, non-labile terrestrial CDOM that contain complex aromatic structures that may inhibit bioavailability (Amon and Benner, 1996). Higher S values often indicate photobleaching or microbial degradation which results in the loss of the higher molecular weight CDOM fraction and an increase in lability (Moran et al., 2000; Twardowski

and Donaghay, 2002). Although minimal, the small increase in S with increasing salinity may suggest a decrease in the DOM molecular weight due to an increased exposure to sunlight (e.g., photobleaching) and microbial degradation during down-estuary transport as observed by Osburn et al. (2012). Stratified conditions in the NRE due to high freshwater discharge (see Chapter 3), accompanied with a decrease in turbidity (Osburn et al., 2012), could have increased the probability of CDOM photobleaching in NRE surface waters following Hurricane Irene.

There are limited previous studies that provide CDOM concentrations in the Neuse River, NRE, and Pamlico Sound. A summary of basin-wide baseflow CDOM and DOC data is provided by Vähätalo et al. (2005), who reported average $ag(300)$ throughout NRB streams and the NRE at 37.8 m^{-1} and 27.5 m^{-1} , respectively. Values for $ag(300)$ and DOC at Hookerton and Fort Barnwell by Vähätalo et al. (2005) are compared to values found in this work in Table 2.2. These similar results suggest that natural and anthropogenic changes in the NRB from 2002 to 2011 have not resulted in a significant change in the baseflow river input or properties of CDOM and DOC to the Neuse River and Contentnea Creek.

Table 2.2: Comparison of hydrologic, CDOM and DOC parameters reported in this work to that of Vähätalo et al. (2005).

| Location | Source | Flow ($\text{m}^3 \text{ s}^{-1}$) | $ag(300)$ (m^{-1}) | S (nm^{-1}) | DOC (mg L^{-1}) |
|---------------|------------------------|--------------------------------------|-------------------------------|--------------------------|----------------------------|
| Hookerton | Vähätalo et al. (2005) | 3.91 | 92.0 | 14.4 | 11.3 |
| | This study | 3.40 | 69.8 | 14.7 | 10.7 |
| Fort Barnwell | Vähätalo et al. (2005) | 31.71 | 46.2 | 15.1 | 7.4 |
| | This study | 25.42 | 41.2 | 14.7 | 11.1* |

*Calculated using equation from Fig. 2.7.

Woodruff et al. (1999) measured $ag(400)$ within the NRE, Pamlico River Estuary (PRE), and Pamlico Sound to evaluate the use of AVHRR satellite images as a means to monitor light

attenuation within Pamlico Sound. Average $ag(400)$ of 4.4 m^{-1} , 4.1 m^{-1} , and 1.9 m^{-1} were reported for the NRE, PRE, and Pamlico Sound, respectively with a maximum $ag(400)$ in the NRE and Pamlico Sound of 14.9 m^{-1} and 5.0 m^{-1} . During this study the maximum $ag(400)$ was about 22 m^{-1} in the NRE and 4.2 m^{-1} in Pamlico Sound (excluding samples collected Oct. 26 and Nov. 12 in the lower NRE). Woodruff et al. (1999) did not report the dates of sample collection and therefore a comparison with river discharge and rainfall amounts as done in this study is not possible. Using airborne laser-induced fluorescence measurements, Tester et al. (2003) mapped the relative abundance of CDOM distributed within the entire APES and adjacent coastal waters following Hurricanes Dennis, Floyd, and Irene in 1999 and a year later during a period of no hurricane activity. High CDOM abundance was observed within much of the APES following the three Hurricanes due to the prolonged flooding of marshes and peat-rich areas. A more typical CDOM distribution of uniformly low CDOM abundance in the Sounds and higher abundance in the rivers and estuaries was observed a year later following no hurricane activity.

Our results indicate a strong positive relationship between $ag(443)$ and DOC following Hurricane Irene (Fig. 2.7), and to our knowledge, this relationship spans the largest range of CDOM absorption and DOC concentration previously reported in similar studies (Ferrari et al., 1996; Vodacek et al., 1997; Del Castillo et al., 1999; Del Castillo and Miller, 2008; Mannino et al., 2008; Matsuoka et al., 2012; Spencer et al., 2012). A direct relationship between CDOM and DOC can provide a means to track DOC transport over large coastal areas using optical remote sensing instruments (Del Castillo, 2005; Del Castillo and Miller, 2008). This approach is a valuable tool for examining coastal carbon dynamics as well as providing an opportunity to examine DOC flux following major weather events that often make the collection of field data difficult. Previously, Lunetta et al. (2009) found good relationships between CDOM and

simulated remote sensing reflectance ratios in the NRE and Pamlico Sound. However, the use of remote sensing within the NRE and Pamlico Sound may be limited to baseflow conditions when CDOM concentration is low because current remote sensing instruments do not provide the spectral sensitivity necessary to accurately measure the reflectance of high CDOM waters as are frequently observed in the NRE following storm events (Miller et al., 2011b). Nevertheless, the CDOM-DOC relationship developed for the NRE may presumably be applied to the adjacent PRE given the similar values in DOM concentration between the two systems (Woodruff et al., 1999), providing a means to examine DOC transport dynamics in two major watersheds that discharge directly to Pamlico Sound.

While this study demonstrates the coupling of a major rainfall event and the transport of terrestrially derived organic matter from the landscape of the Neuse River watershed to the Neuse River and to the NRE, the measurements made and other data available (e.g. remotely sensed imagery) cannot provide a detailed understanding of the transformation and fate of CDOM and DOC. Although CDOM absorption provides a quantitative measure of organic matter, absorption measurements do not provide detailed information of the organic matter source. Spectral slope coefficients have been used to characterize terrestrial and marine sources and to identify changes in the optical properties of organic matter. However, to provide more detailed information on the source and transformations of CDOM, spectral fluorescence excitation-emission matrices (EEM) would greatly augment this endeavor (see for example, Osburn et al., 2012). Additionally, there is a great need for enhanced remote sensing instruments with the capabilities to detect high CDOM waters in order to examine the highly dynamic nature of CDOM and DOC flux in coastal systems such as the APES following major rain events.

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CHAPTER 3: MODELING THE TRANSPORT OF FRESHWATER AND DISSOLVED
ORGANIC CARBON IN THE NEUSE RIVER ESTUARY, NC, USA FOLLOWING
HURRICANE IRENE (2011)

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Abstract

Hydrodynamic and transport models are useful tools that aid in understanding complex flow and the distribution of material over large geographic areas and during extreme weather events. Here we describe the use of a three-dimensional numerical flow and transport model (Delft3D) to simulate freshwater and dissolved organic carbon (DOC) transport over a 22-day period in the Neuse River Estuary (NRE), NC, USA following intense precipitation and river discharge resulting from Hurricane Irene (Aug. 2011). Inputs of freshwater discharge, DOC concentration, salinity, water temperature, wind speed and direction, bathymetry, and water level elevation at an open model boundary were used to initialize and simulate flow and DOC transport. The model was calibrated and validated using field measurements of water level elevations, vertical salinity profiles, and surface DOC concentrations in the estuary. Results indicate differences in the intensity of the freshwater and DOC plumes as they traveled down estuary due to a lag time between maximum discharge and DOC concentration in the river input; the maximum DOC concentration of 29.9 mg L^{-1} was reached almost one week following maximum discharge. The DOC plume only slightly influenced the lower estuary near the open model boundary by the end of the model run, increasing initial DOC concentrations by about 3 mg L^{-1} . Results also indicate cross-channel gradients in salinity and DOC concentration due to persistent winds following the storm. Techniques described here could be applied to similar estuarine systems to better characterize flow and transport during and following dynamic storm events where field measurements are often unattainable.

3.1 Introduction

Organic matter is the largest reactive reservoir of reduced carbon on Earth (Bianchi, 2011) and exists in the aquatic environment as both particulate and dissolved material. The major source of allochthonous organic matter to the coastal ocean is organic rich soils and plant material within watersheds (Thurman, 1985). The riverine transport of this terrestrially derived organic matter makes up a significant portion of the global carbon cycle as rivers annually transport an estimated 200-530 Tg of total organic carbon (TOC) to the coastal ocean (McKee, 2003 and references therein). The delivery of TOC to the coastal ocean is partitioned as 138-288 Tg C yr⁻¹ of particulate organic carbon (POC) and 214-360 Tg C yr⁻¹ of dissolved organic carbon (DOC) (McKee, 2003 and references therein). During periods of high river discharge or in rivers with high sediment loads, the ratio of POC to DOC can be equal, however in large rivers the concentration of DOC often dominates and the amount of POC is commonly only half that of DOC (Thurman, 1985). Dissolved organic matter (DOM) is the largest oceanic reservoir of reduced carbon (Benner et al., 1992) with seawater DOC containing nearly as much carbon as the atmospheric CO₂ pool (Hedges, 1992 and references therein).

The transport of large concentrations of terrestrially derived DOM by rivers can significantly influence the overall quality and ecological processes of coastal waters. For example, DOM can serve as a food source to marine invertebrates (Yahel et al., 2003; Baines et al., 2005) and bacteria (Tranvik, 1992) and control water column light availability (Markager and Vincent, 2000; Kostoglidis et al., 2005; Foden et al., 2008). In addition, colored dissolved organic matter (CDOM), the light absorbing fraction of DOM, is known to interfere with remote sensing estimates of chlorophyll *a* in coastal waters (Carder et al., 1989). The photoreactive nature of DOM can lead to the formation of CO₂ and CO (Miller and Zepp, 1995), thereby

creating a possibly significant water to atmospheric flux of carbon (Cai, 2011). Additionally, DOM has been found to be associated with the transport of toxic substances (Ravichandran, 2004) and the production of harmful disinfection byproducts (Kitis et al., 2002; Wang et al., 2007; Chow et al., 2011). Although DOM plays a significant role in many coastal environments, there remains an important need to gain a better understanding of the coupling processes and transport and fate of terrestrially derived DOM in coastal waters.

The Albemarle-Pamlico Estuarine System (APES) of eastern North Carolina (Fig. 3.1), the second largest estuarine system and largest lagoonal estuary in the United States, is an important asset that provides many ecological services that are vital to the state's economy. The APES drains an approximately 73,400 km² watershed with the majority of freshwater discharge coming from four rivers (Chowan, Roanoke, Tar and Neuse) primarily draining the Piedmont and Coastal-Plain regions of North Carolina (Miller et al., 2011a). The APES is bounded to the east by the Outer Banks barrier island system, resulting in a limited exchange of APES water with the Atlantic Ocean through three major tidal inlets. Pamlico Sound is the largest major water body occupying ~5,335 km² of the APES surface area and supports important commercial and recreational fishing industries. The Tar and Neuse River watersheds connected to Pamlico Sound drain approximately 25,640 km² (Giese et al., 1979). The Neuse River drains the largest and most populated watershed directly draining to Pamlico Sound, flowing ~320 km through the Piedmont and Coastal-Plain provinces of North Carolina and draining approximately 16,000 km² dominated by agriculture and forest (Stow et al., 2001; Whitall et al., 2003). The Neuse River broadens at New Bern, NC to form the headwaters of the Neuse River Estuary (NRE). The NRE (Fig. 3.2) is a shallow drowned river valley with an average depth of 4.6 meters (Matson et al., 1983) that flows ~70 km before discharging into the southwest region of Pamlico Sound. Due to

the few narrow inlets of the APES, the resulting small (≤ 10 cm amplitude (Wells and Kim, 1991; Benninger and Wells, 1993)) astronomical tides play a limited role on the hydrodynamics within the NRE (Luettich et al., 2000; Luettich et al., 2002). With a limited tidal influence, water and material transport within the system is mainly forced by winds (Luettich et al., 2000; Wells and Kim, 1991) and river discharge (Wells and Kim, 1991).

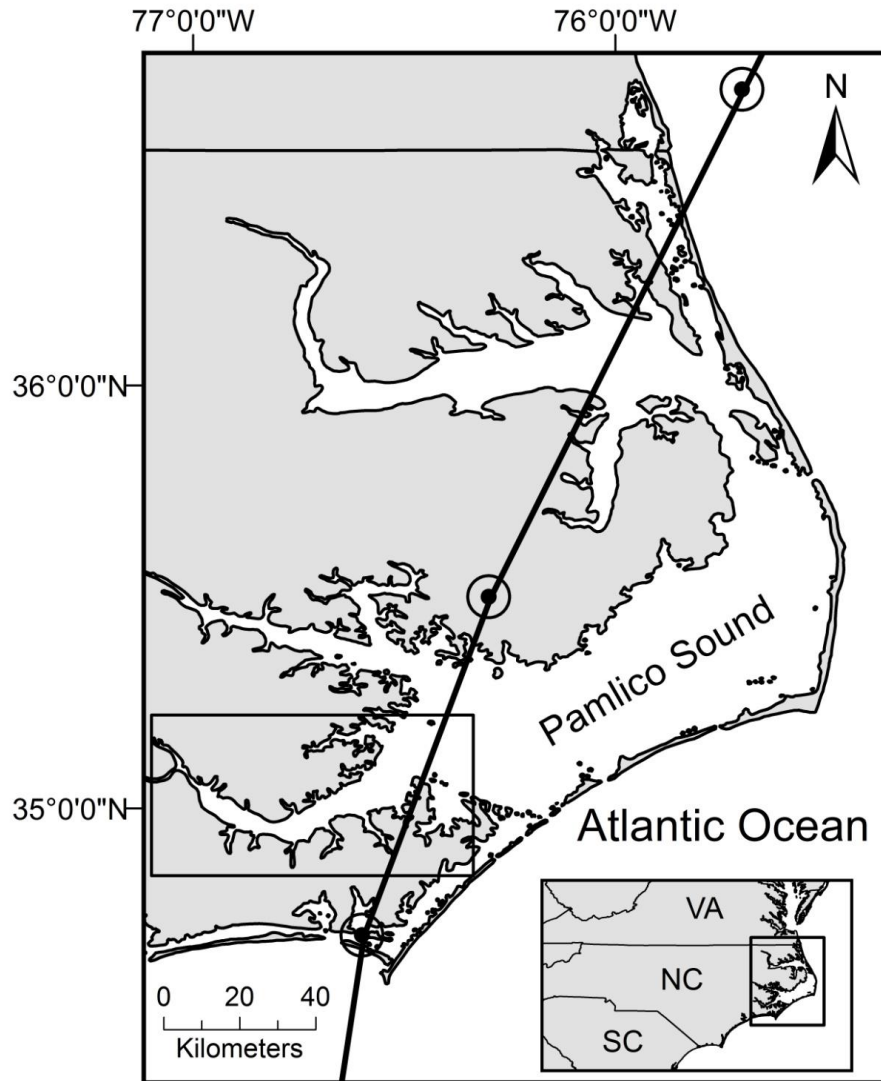


Fig. 3.1: Map of the Albemarle-Pamlico Estuarine System (APES) showing the track of Hurricane Irene (black line) through eastern North Carolina. The circles indicate the storm’s location at 1200 UTC Aug. 27, 1800 UTC Aug. 27 and 0000 UTC Aug. 28 from south to north, respectively. Black box denotes the Neuse River Estuary (NRE), shown in detail in Fig. 3.2.

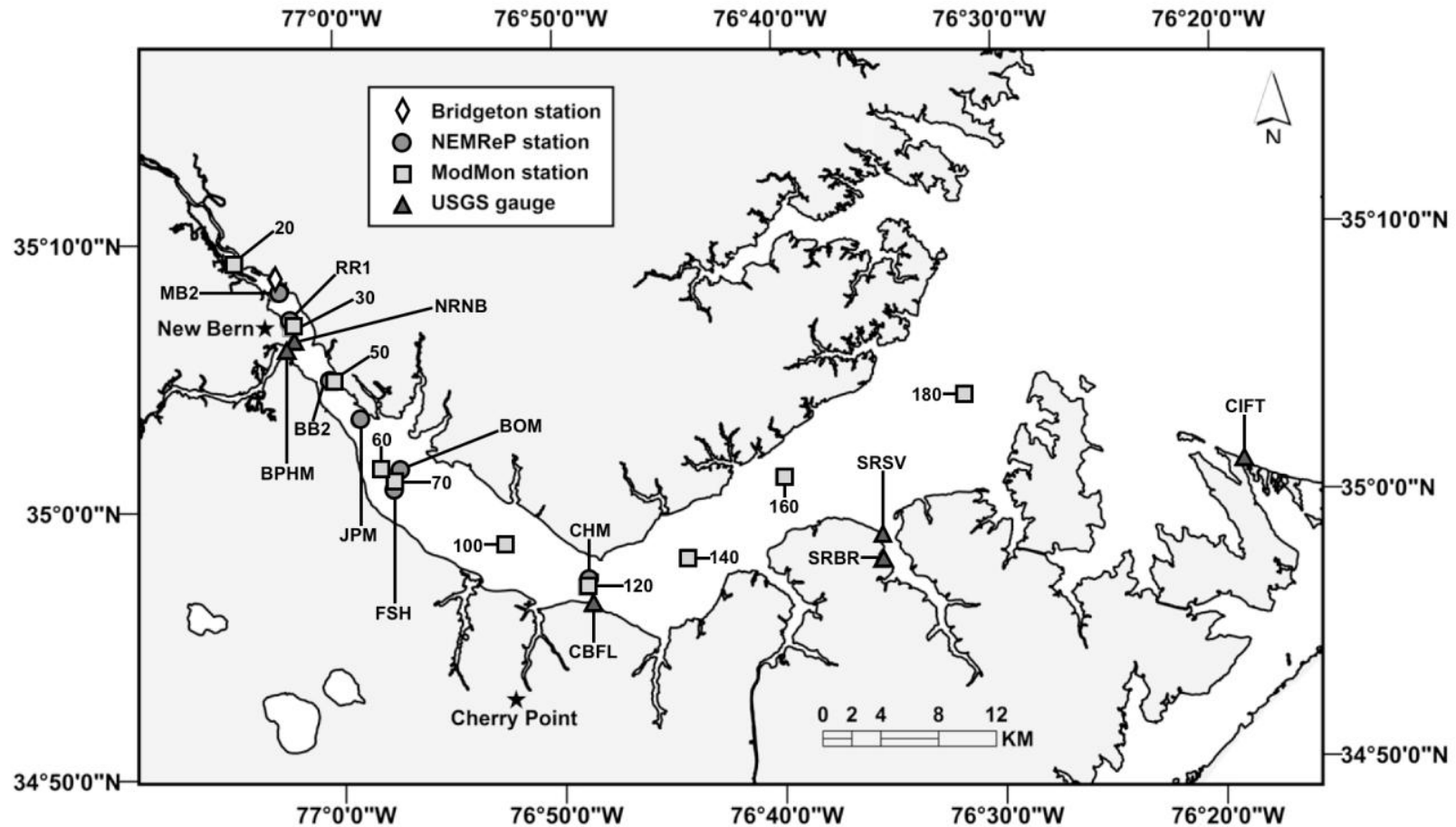


Fig. 3.2: Location map of the NRE showing the stations where data were collected and used for model input, calibration, or validation. USGS storm tide and rapid deployment streamgages are indicated by the stations labeled NRNB (Neuse River at New Bern), BPHM (Bridgpoint Hotel and Marina), CBFL (Cherry Branch Ferry Landing), SRSV (South River Sportsman's Village), SRBR (South River Boat Ramp) and CIFT (Cedar Island Ferry Terminal).

Potential negative impacts from the transport, distribution and fate of terrestrially derived material within the system may be increased by the 1-2 month residence time of the NRE (Knowles, 1975; Robbins and Bales, 1995) and 11-month residence time of Pamlico Sound (Giese et al., 1979). For example, persistent phytoplankton blooms (Paerl et al., 1995; Pinckney et al., 1997), fish kills (Paerl et al., 1998), and bottom water hypoxia-anoxia (Paerl et al., 1998) within the NRE, associated with eutrophication driven by nutrients and materials derived from within the NRE watershed (Paerl et al., 1995), has led to long-term monitoring of select water quality parameters (excluding DOM) within the NRE.

The concentration of materials transported from terrestrial to aquatic environments by rivers often increases following precipitation events or rapid snowmelt (Hinton et al., 1997; Boyer et al., 1997, 2000; Buffam et al., 2001; Inamdar et al., 2004, 2006; Raymond and Saiers, 2010). Rain events often mobilize and transport both particulate and dissolved material (e.g. nutrients, sediment, organic matter) from North Carolina's coastal watersheds and deliver this material to the streams and rivers that drain to the APES. It is well documented that rain events can significantly influence the water quality and organic matter loading to the NRE (e.g. Paerl et al., 1998; Paerl et al., 2001; Bales, 2003; Burkholder et al., 2004; Paerl et al., 2006; Wetz and Paerl, 2008). Much of this understanding was derived from studies that examined the mobilization and transport of organic material within the Neuse River and NRE following a series of tropical systems (Hurricanes Dennis, Floyd, and Irene) that impacted coastal North Carolina in 1999. The unprecedented floodwaters resulting from these tropical systems exported large amounts of organic material (Bales, 2003) such that these storms may have had a long-term effect on DOC concentrations within the NRE (Christian et al., 2004). Following the storms, DOC concentrations at the mouth of the NRE roughly doubled the pre-storm concentrations of

6.0 - 8.4 mg L⁻¹ (Paerl et al., 2001). Similarly, Paerl et al. (1998) report that greater than 14 X 10⁶ kg of organic carbon were transported to the NRE following Hurricane Fran in September 1996. These elevated amounts of organic carbon led to fish kills via hypoxia and anoxia throughout the study area. These previous studies demonstrate the coupling between rainfall events, increased loadings of terrestrially derived organic material and system response of the NRE and APES.

Because of the potential increase in the frequency of intense Atlantic tropical cyclones (Bender et al., 2010) and the projected increase in heavy rainfall associated with tropical cyclones (Seneviratne et al., 2012), it is vitally important to develop a better understanding of how storms currently impact the organic matter transport to coastal waters such as the APES. Hurricane Irene, which directly affected eastern North Carolina in August 2011, provided an opportunity to further investigate the impact of tropical systems on the hydrodynamics and transport of organic matter within the NRE. Hurricane Irene made landfall near Cape Lookout, NC on Aug. 27, 2011 as a category 1 hurricane with maximum winds of 39 m s⁻¹. Maximum sustained winds and maximum gusts (Fig. 3.3) near the middle NRE at Cherry Point (Fig. 3.2) were measured at 23 m s⁻¹ and 31 m s⁻¹, respectively (Avila and Cangialosi, 2011). Within the Neuse River basin (NRB), the highest accumulated (Aug. 21-28) amount of rainfall, 38 cm, was measured at New Bern (Avila and Cangialosi, 2011). During the same time period, the accumulated rainfall at Grifton, NC, located ~50 km upstream from New Bern, was 34 cm with the majority (32 cm) falling during an approximately 30 hour time frame from Aug. 26 to Aug. 27 (Fig. 3.3).

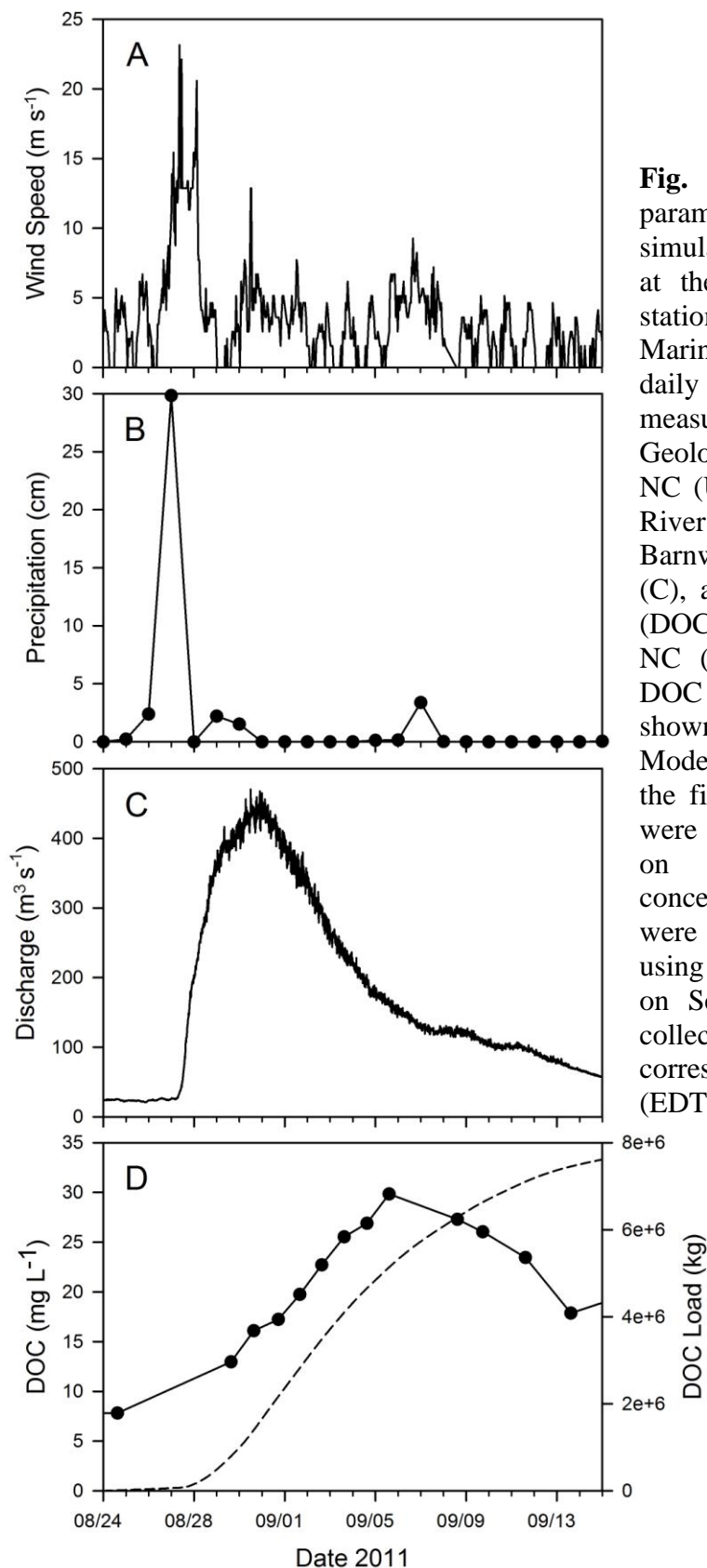


Fig. 3.3: Values of select parameters used during the model simulation. Wind speed measured at the National Weather Service station KNKT, Cherry Point Marine Corps Air Station, NC (A), daily accumulated rainfall measured at the United States Geological Survey station, Grifton, NC (USGS 02091764) (B), Neuse River discharge measured at Fort Barnwell, NC (USGS 02091814) (C), and dissolved organic carbon (DOC) concentration at Bridgeton, NC (solid line) (D). Cumulative DOC loading at Bridgeton, NC is shown as the dashed line in (D). Model DOC concentrations prior to the first measurement on Aug. 24 were set to 7.8 mg L⁻¹ as measured on Aug. 24; model DOC concentrations used after Sept. 13 were set to interpolated values using the concentration measured on Sept. 13 and a field sample collected on Sept. 15. All dates correspond to UTC except panel B (EDT).

In this study, a three-dimensional numerical model (Delft3D) was used to simulate the hydrodynamics, salinity distribution, and transport of terrestrially derived DOC within the NRE resulting from the impact of Hurricane Irene. This model was used to improve our understanding of a coupled terrestrial-aquatic system during and following a dynamic storm event and establish the techniques that could be applied to examine material transport within the NRE and similar coastal systems following future storms.

3.2 Delft3D

Delft3D is a hydrodynamic model that solves the non-steady state, shallow-water equations using a finite difference scheme (Lesser et al., 2004). Lesser et al. (2004) provide a detailed description of the development of the 3-dimensional flow and transport model and a review of several validation studies. In previous works, Delft3D has been used to simulate sand transport (Elias et al., 2006) and plume dynamics in the coastal ocean (Mulligan et al., 2010). For this study, the model grid was constructed in spherical coordinates with an average resolution of approximately 200 X 140 meters. The model used 10 vertical layers described by bathymetrically-following σ -coordinates (Phillips, 1957) within a domain extending about 80 km from the head of the NRE near Bridgeton, NC (Fig. 3.2) to an open boundary at the intersection of the NRE and Pamlico Sound (Fig. 3.4). Inputs of freshwater discharge, DOC concentration, salinity, temperature, wind speed and direction, bathymetry, and water level elevation at the open boundary were used to simulate flow and DOC transport.

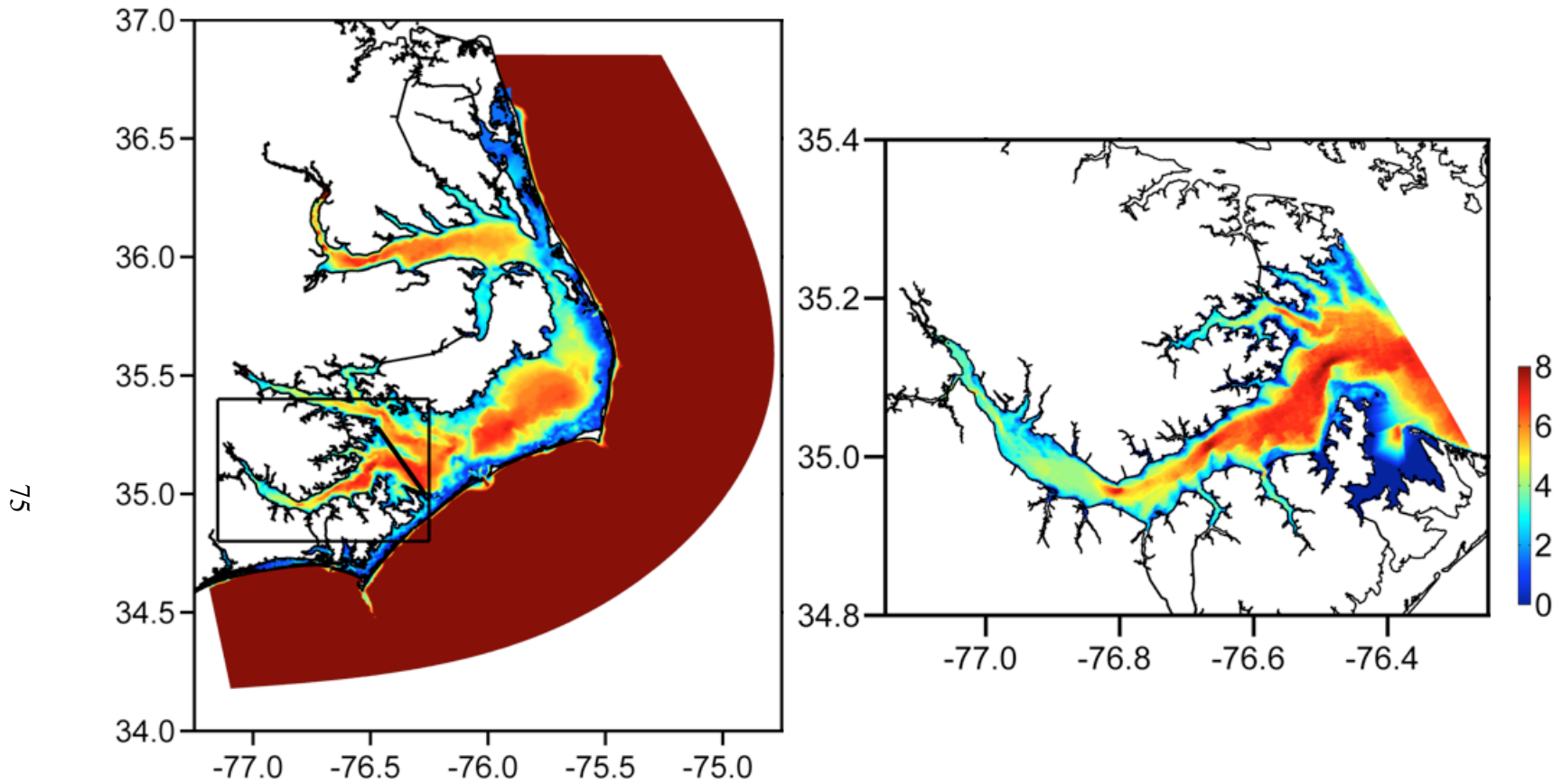


Fig. 3.4: The large-scale model domain for the APES showing system bathymetry in meters (left panel). The black box denotes the area enlarged in the right panel of the NRE indicating the model domain and bathymetry of the estuary.

To simulate freshwater input to the NRE from the Neuse River, river discharge was measured from Aug. 24 to Sept. 15 (Fig. 3.3) at a USGS gaging station near Fort Barnwell, NC, located ~30 km upstream from the head of the NRE at New Bern. To account for the ungaged discharge between Fort Barnwell and the model discharge point, the measured discharge at Fort Barnwell was increased by a factor of 1.15 to account for the ungaged basin area at New Bern (11,620 km²) as a fraction of the gaged basin area measured at Fort Barnwell (10,100 km²). Model input of river discharge, and consequently terrestrially derived DOC, was located only at the head of the NRE ~2 km upstream of Bridgeton. All other potential inputs of freshwater and DOC were not considered as they were not measured. The temperature of the freshwater discharge was set to 25°C.

DOC was modeled as a conservative tracer that entered the NRE through the simulated river discharge. DOC concentrations were measured using discrete surface water samples collected from ~20 cm water depth from the shoreline at Bridgeton during 14 field expeditions from Aug. 24 to Sept. 15. Water samples were collected and stored on ice in pre-washed 1L brown Nalgene bottles until transported to the laboratory where they were refrigerated (4°C) until analysis. Samples were then filtered under a gentle vacuum (< 5 mm Hg) through pre-rinsed Whatman 0.7- μ m GF/F filters. The sample filtrate was collected in acid-washed 60 ml amber glass bottles with Teflon-lined caps from which approximately 20 ml were transferred to pre-combusted (450°C for 4 hours) borosilicate vials with foil liner caps and acidified with 3-5 drops of 2 N hydrochloric acid. DOC samples were refrigerated until analyzed using a Shimadzu TOC-V_{CPN} Total Organic Carbon Analyzer. These DOC concentrations were linearly interpolated at 15-minute intervals between dates of sample collection to correspond to USGS river discharge measurements. Calculated loadings at 15-minute intervals were summed to provide a cumulative

DOC load estimate (kg) from the Neuse River to the NRE during the model simulation period. Additional surface water samples for DOC concentration were collected from a small boat on Sept. 1 and Sept. 14 as part of the bi-monthly sampling of the Neuse Estuary Monitoring and Research Program (NEMReP) along a central transect of the NRE (Fig. 3.2). Surface water samples were also collected at the NEMReP stations on Aug. 24 following the storage and filtering methods of DOC samples and CDOM absorption measurements made according to Miller et al. (2011b). DOC concentrations were then calculated from a previously established DOC – CDOM absorption relationship at 443 nm for the NRE (see Chapter 2). An average DOC concentration of 7.0 mg L⁻¹ derived from these samples was used to set the initial DOC concentration throughout the entire model domain and at the open model boundary for the entire simulation period.

Vertical salinity profiles were measured in the NRE using a YSI Model 6560 conductivity/temperature probe by the Neuse River Estuary Modeling and Monitoring Project (ModMon) (Fig. 3.2) on Aug. 24, Aug. 30, and Sept. 6. NEMReP also measured vertical salinity profiles on Sept. 14 using a calibrated YSI 6600V2 water quality sonde. To initialize the model salinity, the model domain was first partitioned into horizontal segments based on location to the nearest ModMon station. The initial salinity for a given depth within a model segment was then set to the estimated average salinity at that depth from the corresponding ModMon station measured on Aug. 24 (Fig. 3.5A). Salinity at the open boundary was set to 25 ppt for the duration of the model run based on salinity at the most downstream ModMon station (Station 180) on Aug. 24. Similarly, ModMon data collected on Aug. 24 was used to set the initial temperature within the estuary and throughout the entire model simulation at the open boundary to 28°C.

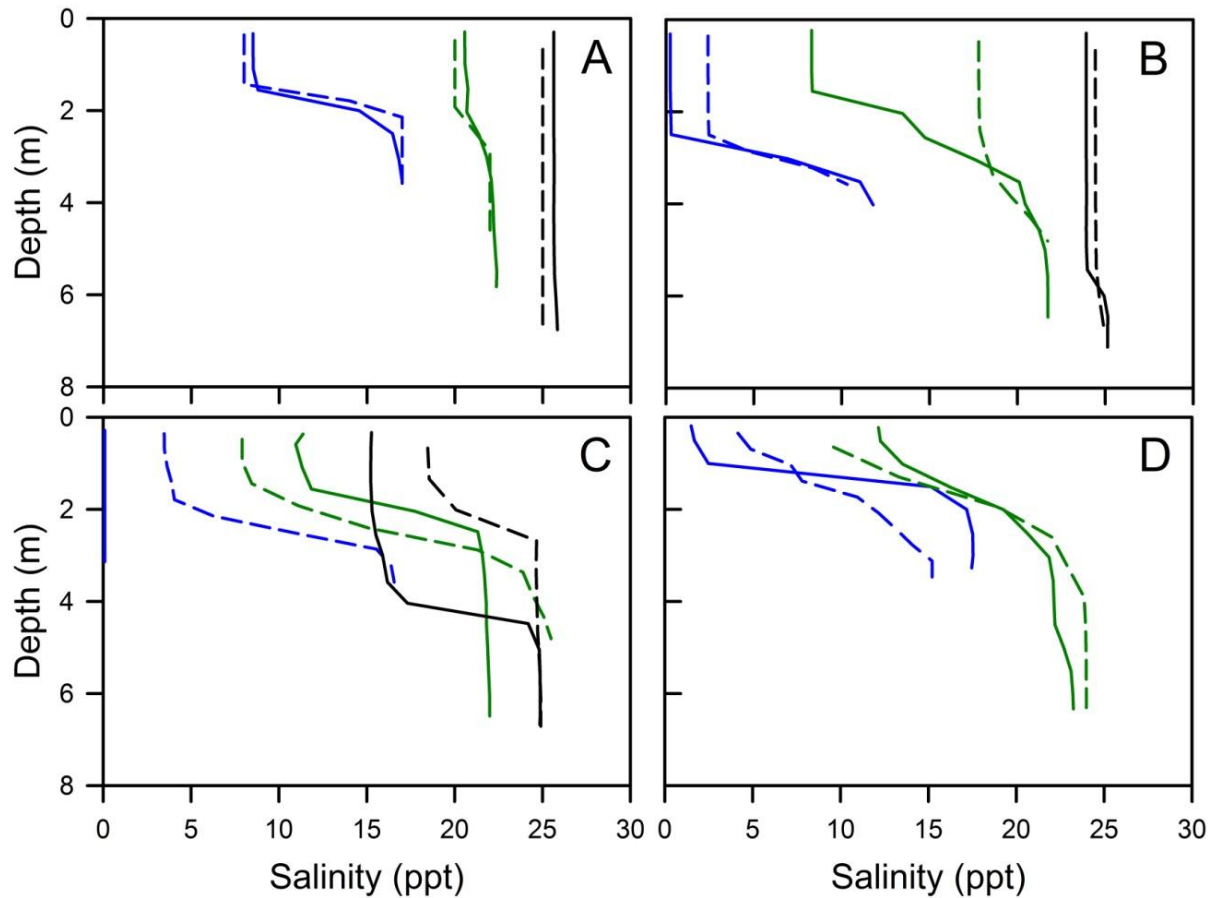


Fig. 3.5: A comparison of measured (solid lines) and modeled (dashed line) vertical salinity profiles on Aug. 24 (A), Aug. 30 (B) and Sept. 6 (C) for representative mid-channel Modmon stations located up-estuary (30, blue lines), mid-estuary (120, green lines) and lower-estuary (180, black lines) and on Sept. 14 (D) for similar NEMReP stations located up-estuary (MB2, blue lines) and mid-estuary (CHM, green lines).

Winds are a major factor influencing NRE hydrodynamics due to the limited tidal variations throughout the system (Luettich et al., 2002). Hurricane Irene winds were simulated from Aug. 24 to Aug. 29 using a parametric vortex model developed from the theory of Holland (1980) and hurricane track parameters (e.g., position of the eye, radius to maximum winds, maximum wind speeds, central pressure, ambient pressure) provided by the National Hurricane Center (Avila and Cangialosi, 2011). Winds estimated by the model were calibrated to match observations at three North Carolina sites: Cape Lookout, Cape Hatteras, and Duck (Mulligan, personal communication). Winds measured at the National Weather Service (NWS) Station KNKT at the Cherry Point Marine Corps Air Station were used to develop a spatially uniform wind field from Aug. 29 to Sept. 15 when Hurricane Irene winds no longer influenced the model domain.

Since the NRE cannot be modeled as a closed system due to its connection with Pamlico Sound, hydrodynamic and transport conditions at an open model boundary were defined. Water level elevation at the open boundary was determined using a vertically averaged model with a coarse grid that simulated conditions throughout the entire APES (Fig. 3.4). The larger APES model (~350 X 285 meter average resolution) provided a time-series of water level elevation at the intersection of the NRE and Pamlico Sound resulting from wind-driven storm surge that was used as input to the higher-resolution NRE grid (Fig. 3.4) at the open boundary. High-resolution bathymetry of the NRE and Pamlico Sound were acquired from the NOAA National Ocean Service's estuarine bathymetry digital raster dataset. To complete model initialization, default physical parameters including background vertical eddy viscosity and horizontal eddy viscosity and diffusivity were used (Delft Hydraulics, 2010).

Following model initialization, Delft3D was used to simulate water level elevations, salinity distributions, and DOC transport in the NRE from Aug. 24 to Sept. 15, 2011 using a 0.5-minute time step. Delft3D used the k - ϵ turbulence closure scheme (Lesser et al., 2004) with bottom friction expressed using a Chezy roughness coefficient of $65 \text{ m}^{1/2} \text{ s}^{-1}$. Observation points were added to the model grid to record simulated results at ModMon and NEMReP stations at 10-minute intervals. Delft3D was calibrated by changing the default values for background vertical eddy viscosity to $1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and the horizontal eddy viscosity and diffusivity to $0.1 \text{ m}^2 \text{ s}^{-1}$ to obtain the best agreement between modeled and observed salinity profiles at ModMon and NEMReP stations (Fig. 3.5B-D). Model hydrodynamics were validated by comparing water level elevations at six locations within the model domain (Fig. 3.2) to USGS observations collected from Aug. 25 to Sept. 2 by five storm tide sensors and 1 real-time rapid deployment streamgage. Storm tide sensors recorded water pressure at 30-second intervals and were converted to water level. The real-time rapid deployment streamgage, located at New Bern, recorded water level elevations at 15-minute intervals with the data uploaded every hour to the USGS for near real-time analysis (McCallum et al., 2012). Data from storm tide sensors were analyzed at 10-minute intervals to match model output whereas all data measured by the rapidly deployed streamgage were used to compare model estimates to USGS measurements. Modeled DOC concentrations were validated using DOC water samples collected at NEMReP stations on Sept. 1 and Sept. 14.

3.3 Results

To evaluate the performance of Delft3D for simulating the hydrodynamics and conservative transport of DOC within the NRE following Hurricane Irene, simulated water level elevations and DOC concentrations were compared with field observations. In general, the model performed well when compared to measured values at selected locations within the NRE.

Modeled water level elevations were compared to similar water level elevation data recorded at six USGS gage sensors located within the model domain (Fig. 3.6). There is good agreement between simulations and field measurements particularly at the upper estuary sites where changes in water level elevation were highest. These data indicate an increase in water level elevation of up to ~2 m above mean sea level (MSL) within the NRE as easterly winds generated from Hurricane Irene forced water from Pamlico Sound into the NRE. Additionally, the model results capture a rapid decrease in water level elevation of ~1.5 m below MSL caused by persistent northwesterly winds as the northward track of Hurricane Irene progressed through the center of the APES (i.e. east of the NRE) (Mulligan, personal communication). During the passage of Hurricane Irene, model estimates of water level elevation near the head of the estuary were higher compared to down estuary locations due to the funneling of water through the narrowing width of the estuary. The estimated maximum range in water level elevation was 3.63 m (2.13 m to -1.50 m) at New Bern (Fig. 3.6A) while the estimated minimum range in water level elevation was 1.34 m (0.77 m to -0.57 m) at Cedar Island (Fig. 3.6F).

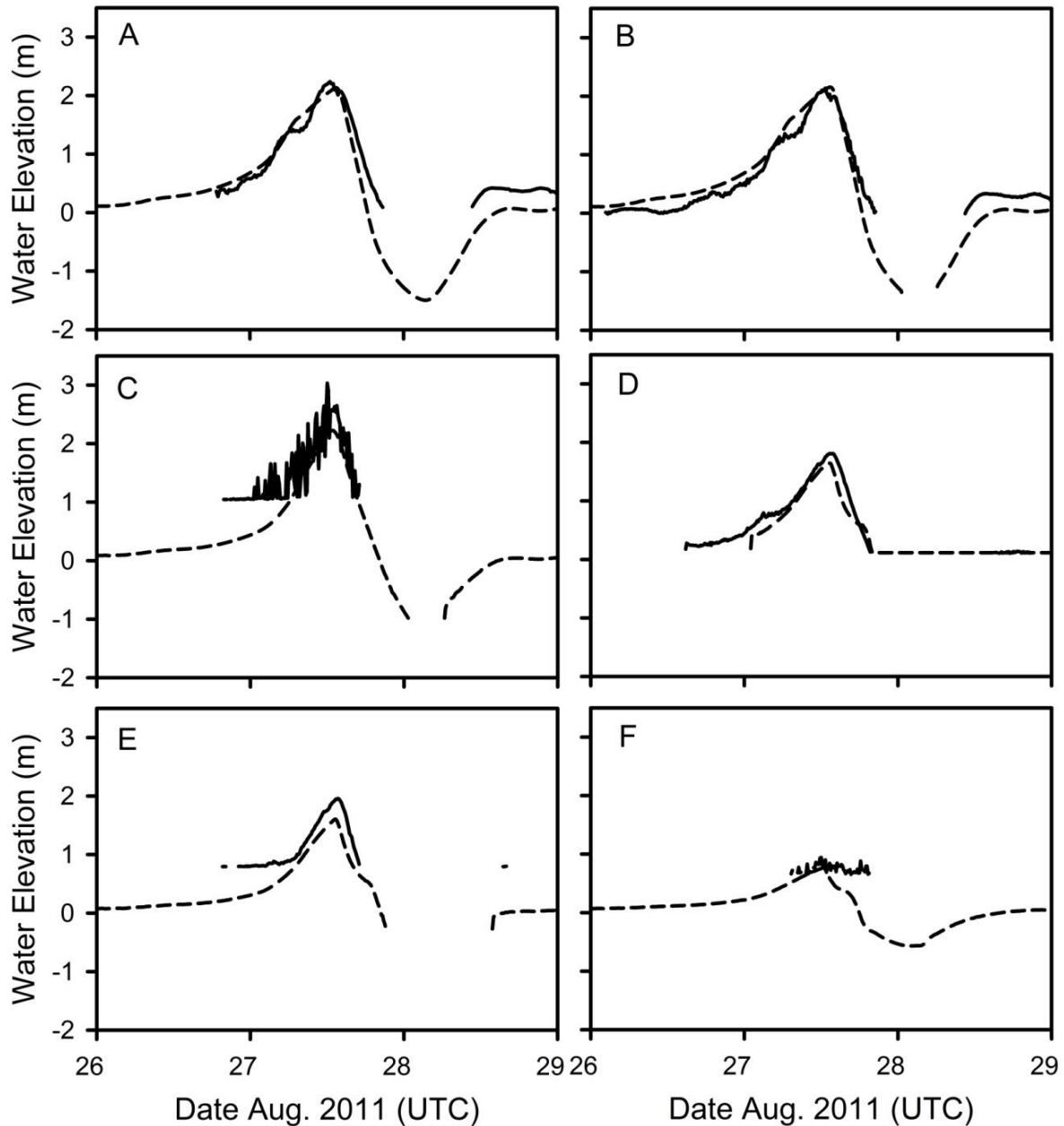


Fig. 3.6: A comparison of measured (solid line) and modeled (dashed line) water level elevations from Aug. 26 to Aug. 29 for the USGS storm tide and rapid deployment streamgages NRNB (A), BPHM (B), CBFL (C), SRBR (D), SRSV (E) and CIFT (F) shown in Fig. 3.2. The lack of streamgage data is due to a minimum water level that could be detected by sensors. Similarly, a lack of model estimates is due to a threshold depth (10 cm) below which hydrodynamic calculations were not made. The threshold depth for a cell was recognized and predictions removed when model simulations of water level elevation remained at a constant minimum. The threshold depth was commonly reached on Aug. 28 when westerly winds forced water from the NRE to Pamlico Sound.

To assess the model's ability to simulate DOC transport, model estimates of DOC were compared to measured DOC concentrations of surface water samples obtained from the main channel NEMReP stations on Sept. 1 and Sept. 14 (Fig. 3.7). In general, there was good agreement between model estimates of DOC and field measurements, particularly when the location of the primary freshwater plume generated by Hurricane Irene is considered. For example, the strongest correlation between modeled and field DOC concentrations occurred near the head of the estuary on Sept. 1 with the model underestimating field concentrations by an average of only 0.8 mg L^{-1} and at the mid-estuary stations on Sept. 14 where the difference between model and field values averaged only 0.3 mg L^{-1} . The largest average differences in model estimates and surface field measurements were 3.2 mg L^{-1} at the mid-estuary stations on Sept. 1 and 2.3 mg L^{-1} at the stations near the head of the estuary on Sept. 14.

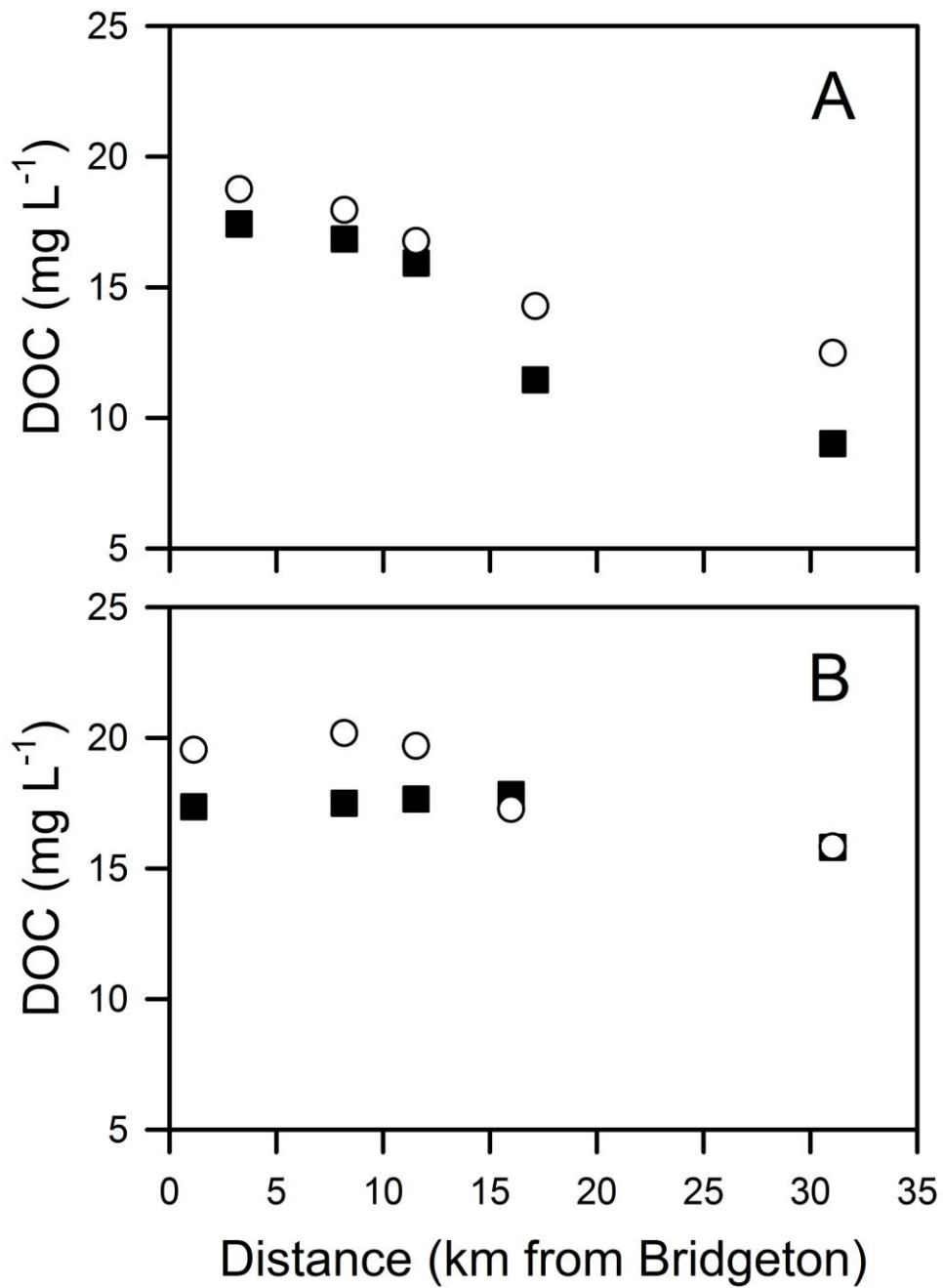


Fig. 3.7: A comparison of measured (open circles) and modeled (black squares) DOC concentrations along the upper-to-middle NRE at main channel NEMReP stations on Sept. 1 (A) and Sept. 14 (B).

Based on river discharge measured at Fort Barnwell, the calculated freshwater inflow into the NRE increased from a near drought-like baseline flow of around $28 \text{ m}^3 \text{ s}^{-1}$ on Aug. 24 to a maximum of $540 \text{ m}^3 \text{ s}^{-1}$ on Aug. 30, three days after the landfall of Hurricane Irene. This rapid, large increase in river discharge resulted from the large amount of rain associated with Hurricane Irene falling within the lower NRB during a short time period (Fig. 3.3). Accumulated rainfall increased from less than 0.5 cm beginning on Aug. 25 as the outer bands of Hurricane Irene impacted the area to about 30 cm on Aug. 27, the day of landfall. No accumulated rainfall was measured on Aug. 28 after the direct effects of Hurricane Irene had moved out of the area. Accumulated rainfall on Aug. 29 and Aug. 30 reached about 2.2 and 1.5 cm, respectively. Calculated freshwater inflow decreased rather quickly from Aug. 30 to Sept. 7 to $\sim 150 \text{ m}^3 \text{ s}^{-1}$, then decreased slowly to around $65 \text{ m}^3 \text{ s}^{-1}$ on Sept. 15, the last day of model simulations.

Simulations of surface salinity for the NRE model domain and vertical salinity profiles estimated at field stations at the upper-estuary (Station 30), mid-estuary (Station 120) and lower-estuary (Station 180) are shown for several dates of the model run in Fig. 3.8. These results show the down estuary transport of freshwater in the NRE following Hurricane Irene. The immediate impact of Hurricane Irene on Aug. 27 (day of landfall) and Aug. 28 was to vertically mix the water column causing small decreases in salinity on Aug. 28 as a plume of lower salinity water was located along the primary channel of the estuary. Starting Aug. 29, the freshwater from Irene was evident as a surface ($\sim 2 \text{ m}$) plume in the upper estuary that decreased in thickness in the mid-estuary; the thickness of the freshwater plume continued to increase in the upper and mid-estuary regions as it traveled as a large surface plume (i.e., small cross-channel variation) through Sept. 3. At this time, the lower estuary showed no apparent change in salinity from the input of freshwater related to the passage of Hurricane Irene. By Sept. 4, a near-surface layer of

freshwater existed throughout the NRE. Again, the thickness of the plume decreased down estuary and the surface plume began to become restricted to the southern shore of the estuary as a higher salinity filament of water began to develop along the northern shore. This pattern, the transport of freshwater along the southern shoreline and a strong cross-channel gradient in salinity (lower surface salinities-southern shore, higher surface salinities-northern shore), continued until Sept. 8. Persistent winds of about $5 - 9 \text{ m s}^{-1}$ (Fig. 3.3) from the south-southeast occurred in the region from Sept. 4 to Sept. 9. The depth to which these winds vertically mixed the water column may have increased from a southerly-to-northerly direction due to increased fetch of the system, thereby generating the cross-channel variation in surface salinities. On Sept. 10 to the end of the model run on Sept. 15, freshwater continued to enter the system (138 to $65 \text{ m}^3 \text{ s}^{-1}$), wind speed decreased and wind direction became more variable. Cross-channel variation in salinity became far less pronounced and a surface freshwater plume existed throughout the NRE. This surface plume reached the open boundary of the model domain on Sept. 13 and remained through Sept. 15.

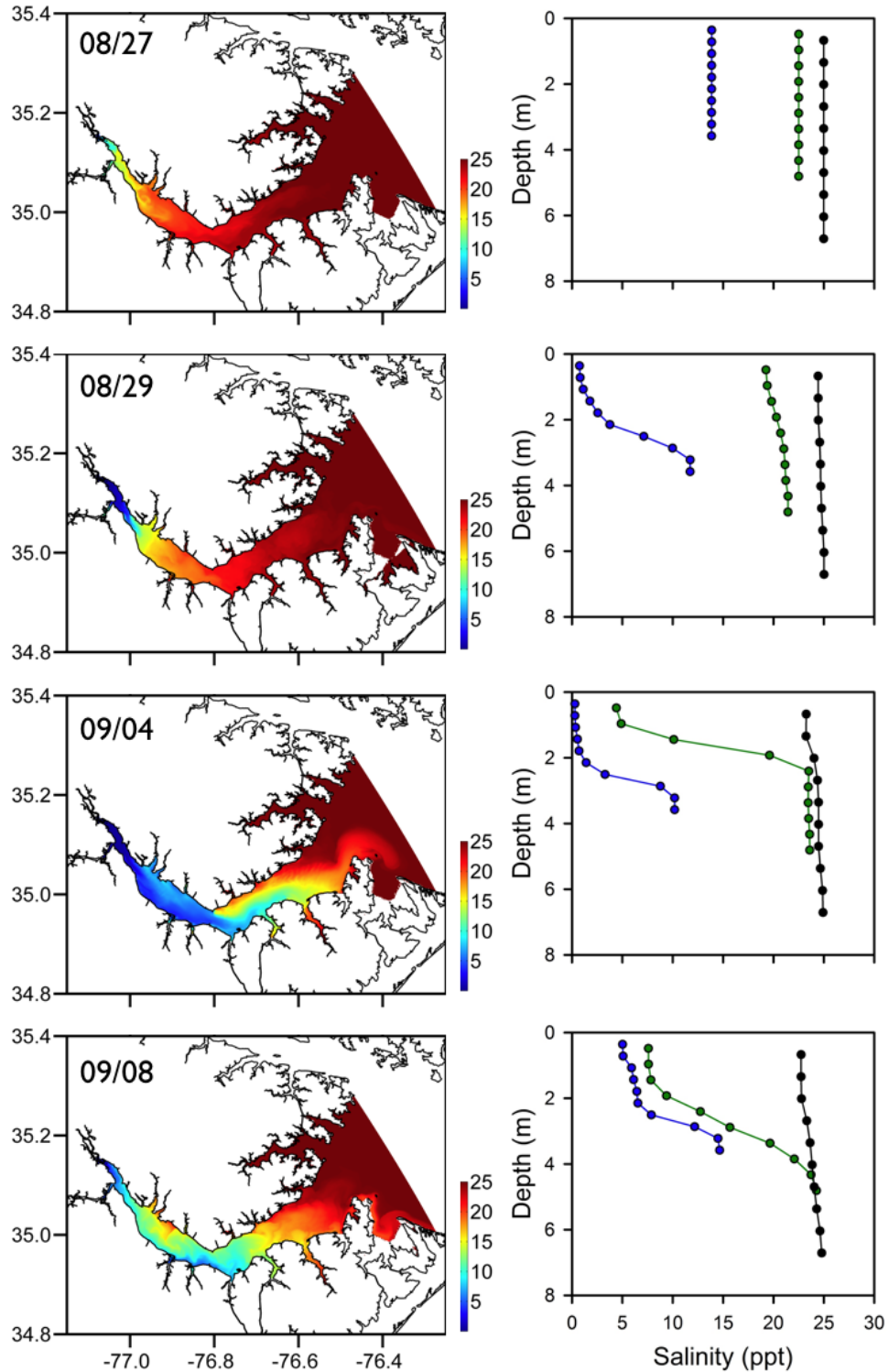


Fig. 3.8: Modeled surface salinity (ppt) distributions and vertical salinity profiles in the NRE on selected dates. The simulated vertical salinity profiles are shown for ModMon stations 30 (blue lines), 120 (green lines) and 180 (black lines) that correspond to about 4 km, 30 km and 60 km along the estuary from the river discharge point near Bridgeton.

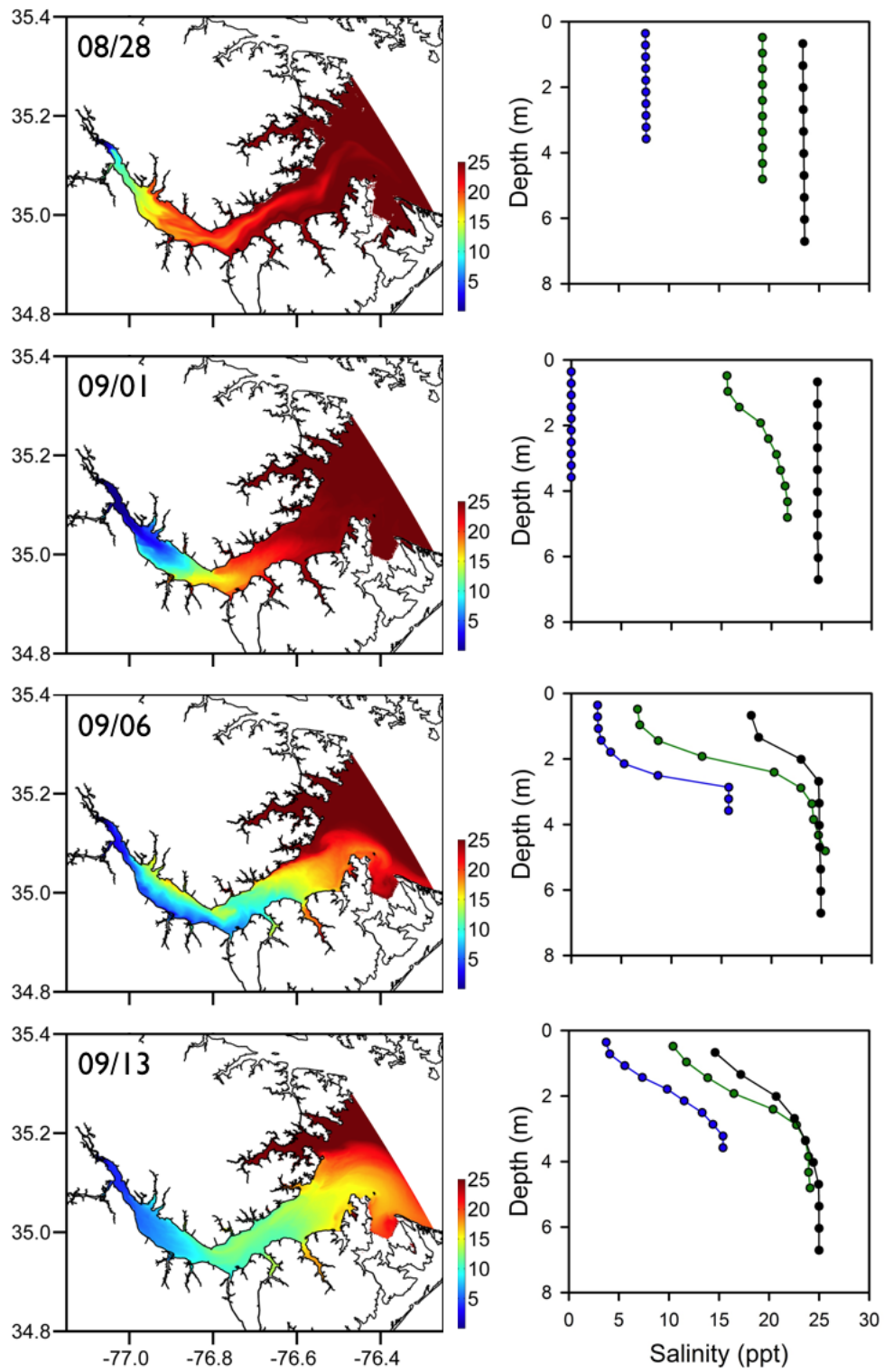


Fig. 3.8 cont.

DOC input into the model at the discharge point was driven by measured DOC concentrations at the head of the estuary (Fig. 3.3). DOC quickly increased from an initial value of 7.8 mg L^{-1} to 13.0 mg L^{-1} on Aug. 29, and then increased in a near linear fashion to a maximum of 29.9 mg L^{-1} measured on Sept. 5. The maximum DOC concentration corresponded to a decreased rate in calculated freshwater inflow of about $190 \text{ m}^3 \text{ s}^{-1}$. Following the maximum DOC input on Sept. 5, DOC concentration remained over 23 mg L^{-1} until Sept. 11, decreasing to about 18 mg L^{-1} on Sept. 13. The final DOC concentration used as input to the model was calculated at 19.4 mg L^{-1} based on a field measurement taken on Sept. 15. An estimated $7.6 \times 10^6 \text{ kg}$ DOC entered the NRE from the Neuse River during the simulation period (Fig. 3.3).

Simulations of surface DOC concentrations for the NRE model domain and vertical DOC profiles estimated at ModMon field stations at the upper-estuary (Station 30), mid-estuary (Station 120) and lower-estuary (Station 180) are shown for several dates of the model run in Fig. 3.9. No appreciable changes in DOC concentrations within the NRE occurred until Aug. 30 when a surface plume of DOC was observed at the head and upper reach of the estuary. During Sept. 1-2, DOC concentrations in the upper estuary continued to increase to over 15 mg L^{-1} and were constant throughout the water column. A shallow surface plume of DOC became evident in the mid-estuary on Sept. 2 that increased concentrations to 12.3 mg L^{-1} on Sept. 3, a concentration that remained the minimum at the mid-estuary throughout the remainder of the model run. A surface plume of DOC returned to the upper estuary on Sept. 3 and reached a maximum around 25 mg L^{-1} on Sept. 6 and remained over 15 mg L^{-1} , more than twice the initial concentration, for the remainder of the simulated period. A shallow ($< 2 \text{ m}$) plume of only slightly elevated DOC concentrations ($< 10 \text{ mg L}^{-1}$) was first observed in the lower estuary on Sept. 5 and showed small variations in concentration until a maximum surface concentration of

about 10 mg L^{-1} was estimated on Sept. 15. The depth of the near-surface DOC plume throughout the NRE closely followed those modeled for the freshwater plume. Surface DOC concentrations exhibited cross-channel plume characteristics from Sept. 4-10, similar to simulated surface salinity; higher DOC waters migrated close to the south shore toward the lower estuary while lower DOC waters were observed along the north shore from the upper-to-lower estuary regions. By Sept. 15, the entire upper and mid-estuary was enriched in surface DOC concentrations ($> 15 \text{ mg L}^{-1}$), although the major portion of the DOC surface plume did not reach the open model boundary.

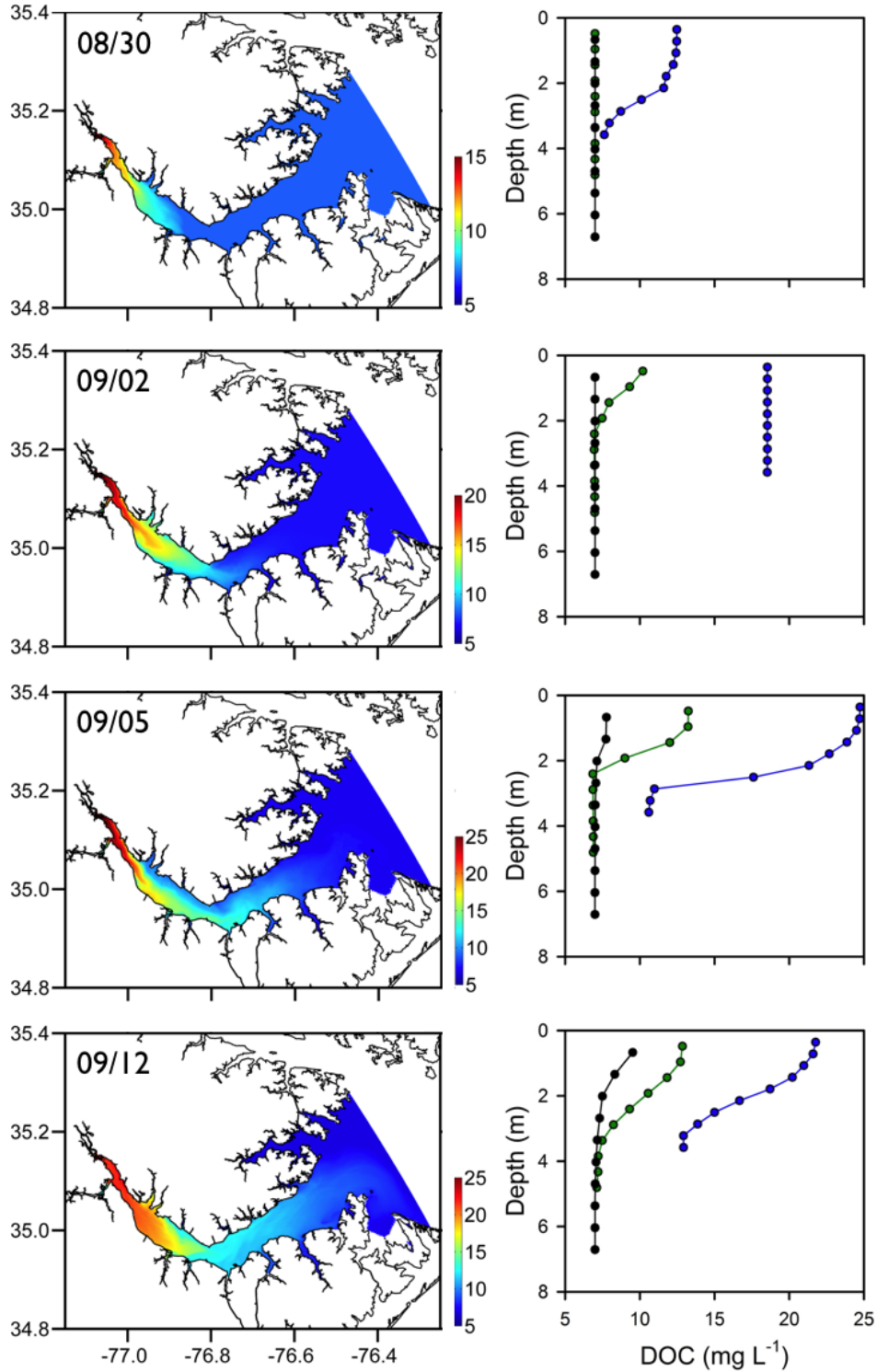


Fig. 3.9: Modeled surface DOC concentrations (mg L^{-1}) and vertical DOC profiles in the NRE on selected dates. The simulated DOC profiles are shown for ModMon stations 30 (blue lines), 120 (green lines) and 180 (black lines) that correspond to about 4 km, 30 km and 60 km along the estuary from the river discharge point near Bridgeton. Note scale changes in modeled surface DOC concentrations.

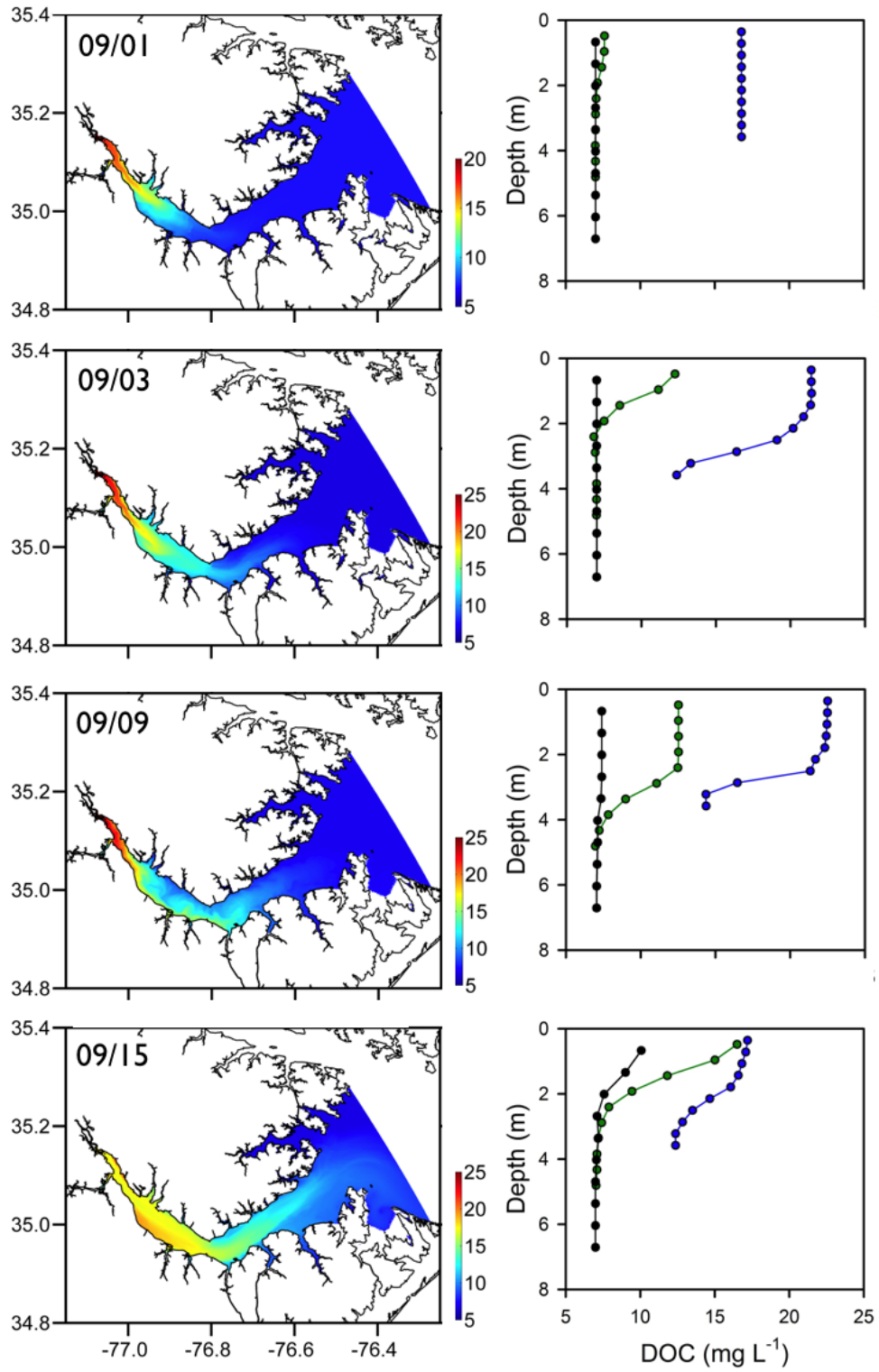


Fig. 3.9 cont.

3.4 Discussion

The three-dimensional numerical flow model, Delft3D, was calibrated to simulate the distribution and transport of terrestrially derived DOC within the NRE following the landfall of Hurricane Irene in coastal North Carolina on August 27, 2011. In general, the model was able to accurately simulate the horizontal and vertical distribution of the freshwater (i.e. salinity) and DOC plumes within the NRE that entered the upper estuary over a three-week period (Aug. 24 – Sept. 15). Differences were observed in the dynamics of the freshwater and DOC plumes due to a lag in the timing of the maximum freshwater discharge and maximum input of DOC; freshwater discharge reached a maximum almost one week prior to maximum DOC concentration. This lag could represent upriver sources of DOC within the watershed and the time needed for DOC and other material to be transported from the land to the river and then downriver to the estuary. An observed lag time in maximum DOC concentration has been observed in other studies and has been attributed to the delayed contribution from organic rich soil water, lag from stem flow, delayed saturation of wetlands and peatlands, and isolation of saturated areas within the basin (Brown et al., 1999; Hagedorn et al., 2000; Hangen et al., 2001; Inamdar et al., 2004).

Our model indicated that following Hurricane Irene, the freshwater and DOC plumes did not progress simply as broad, estuary-wide plumes, but became elongated plumes that followed the southern shore as they progressed toward Pamlico Sound. The development of cross-channel variation in surface salinity and DOC concentration with low salinity, higher DOC water along the southern shore and higher salinity, lower DOC water along the northern shore was attributed to persistent winds and near constant wind direction from the south-southeast that vertically mixed the water column in the cross-channel direction. This explanation may also account for

the apparent up-estuary movement of the leading edge of the freshwater plume around Sept. 6. That is, the down estuary edge of the plume was mixed more as the depth and width (i.e., fetch relative to southerly winds) of the estuary increased. The greater mixing diluted the plume edge to salinity values closer to that of Pamlico Sound, with the exception of a narrow, lower salinity plume along the southern shore (short fetch) that continued to migrate to the model boundary. These simulations suggest that given the freshwater volume discharge to the NRE from Hurricane Irene and the meteorological conditions that followed, wind-driven mixing was the dominant process that controlled the horizontal (cross-estuary and along-estuary) and vertical distribution of DOC concentration throughout the estuary. Although mixing in estuaries is largely controlled by density differences from salinity and water temperature, the small variations observed in water temperature at individual stations (0-3°C) indicate that salinity was more important in inducing density driven flows.

Although Hurricane Irene caused major increases in freshwater discharge and DOC concentrations from baseline conditions, the amount of rainfall, volume discharge, and DOC loading generated by the passage of Hurricane Irene was not as significant as the impacts of Hurricanes Dennis, Floyd, and Irene (1999) and Hurricane Fran (1996). Our results indicate an estimated 7.6×10^6 kg DOC were exported to the NRE during the three-week simulation period. This DOC loading is roughly 19 times more than would have been transported given constant pre-storm conditions. Although model results indicated that concentrations in the upper estuary significantly increased from initialized values, modeled concentrations increased only about 3 mg L⁻¹ in the lower estuary and at the open model boundary on Sept. 15 from the influence of the outer extent of the DOC plume. In contrast, the accumulation of rainfall in the upper NRB following Hurricanes Dennis, Floyd, and Irene over a two month period in 1999 reached 66% of

the average annual rainfall (Bales et al., 2000) and resulted in an increase in DOC concentration at the mouth of the NRE to more than 14.4 mg L^{-1} (Paerl et al., 2001). The transport of organic carbon delivered by Hurricane Irene in 2011 also appears to be less than that delivered by Hurricane Fran in 1996. Although Paerl et al. (1998) estimate that more than $14 \times 10^6 \text{ kg}$ of TOC were transported following Hurricane Fran, their estimates were not partitioned in separate POC and DOC loadings, and hence a direct comparison with findings cannot be made. However, assuming that higher amounts of DOC are transported than POC from terrestrial sources following storms impacting the NRB (Christian et al., 2004; Paerl et al., 2006), the amount of DOC flux to the NRE from Hurricane Fran would surpass that transported during Hurricane Irene in 2011. Saturated soils resulting from high rainfall in the basin prior to Hurricane Fran and the rapid sequence of Hurricanes Dennis, Floyd, and Irene (1999) following drought conditions greatly differ from rainfall prior to and following Hurricane Irene (2011) and should serve as a major factor controlling the mobilization of terrestrial carbon and its transport to the river system.

Although Delft3D simulated the physical processes and DOC transport reasonably well within the system based on comparisons with field data, future modeling efforts could be improved. Data from pre-existing field programs were critical in providing observations for model comparison, however a higher sampling frequency (e.g. daily) and additional field observations including current velocity profiles would have provided a means to more accurately calibrate and validate the model. Apart from traditional field measurements, the use of remotely sensed ocean color data and regional DOC algorithms could also improve model calibration and validation by providing unique large-scale surface data. However, current remote sensing instruments do not provide sufficient spectral sensitivity to generate data products for waters

with concentrations of CDOM as high as those frequently observed following rain events in the NRB (Miller et al., 2011c).

Similarly, freshwater discharge and DOC concentrations contributed by tributaries, particularly the larger tributaries, to the NRE should be included. It was determined, using the model to test the sensitivity of the system by adding additional freshwater discharge points, that there was no significant impact on local salinity or DOC concentrations from additional freshwater sources. However, estimated values of these inputs were used since field measurements were not available. Additional improvements could be achieved by coupling the Delft3D DOC model to a watershed-based hydrologic model to estimate freshwater inflow within the different basins of the watershed given measured, or modeled, rainfall following different tropical and extra-tropical (Nor'easters) events. Lastly, although long-term monitoring projects operate within the NRE, continuous monitoring of select parameters in Pamlico Sound would provide more accurate open boundary conditions and improve model estimates.

Due to the size and complexity of the APES and the rivers and sub-estuaries draining coastal North Carolina watersheds, adequately monitoring the transport of freshwater and terrestrial material to these coastal waters only using field measurements is extremely difficult and costly. The use of a numerical model provided results unattainable using traditional field measurements. The model presented here demonstrates that a successful simulation of freshwater and conservative tracer transport could be obtained using limited data from pre-existing monitoring programs and may be used to fill data needs between bi-weekly or monthly measurements. Our successful use of Delft3D for the NRE suggests that this modeling approach could be expanded and applied to the adjacent Tar-Pamlico River basin and Pamlico River

Estuary to better characterize freshwater and organic matter transport following storm events from the two major watersheds that directly drain into the Pamlico Sound.

Acknowledgements

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CHAPTER 4: DISCUSSING THE USE OF AN INTEGRATED METHOD FOR EXAMINING
MATERIAL TRANSPORT IN THE LOWER NEUSE RIVER AND NEUSE RIVER
ESTUARY, NC FOLLOWING A HURRICANE

An integrated approach that incorporated traditional field samples, a numerical model and remotely sensed images was used to examine material transport in the Neuse River and Neuse River Estuary (NRE) following Hurricane Irene (2011). The Neuse River and NRE is an example of a coupled land-estuary system that transports both terrestrially derived particulate and dissolved material to a larger water body and then ultimately to the ocean. The size and dynamic nature of the system, however, makes the monitoring of important in-water constituents (e.g., sediment, carbon, nutrients) difficult over the large surface area and especially during and following storm events that mix the water column, alter the system's hydrology, and deliver material to the river network via rainfall, runoff and flooding. Although this system has been studied in detail with respect to the consequences of eutrophication, there are few examples of how storms influence the transport of terrestrial material and how this material is distributed throughout the NRE and Pamlico Sound. As it is expected that the frequency of intense hurricanes and rainfall associated with hurricanes and tropical storms will increase due to climate change (Bender et al., 2010; Seneviratne et al., 2012), there is a critical need to understand how storms currently impact material transport in this and other coupled land-ocean systems in order to predict future changes. The limited information from previous work within the Neuse River and NRE on the transport and distribution of terrestrial material may be due in part to not using an integrated approach that maximizes the utility of field samples that, as shown in this study, provided significantly more information when used to support modeling and remote sensing efforts than information extracted from field samples alone.

Field sampling provided the framework for this study and was used to characterize the transport of dissolved organic matter (DOM) in the Neuse River and NRE. This effort clearly demonstrates that rainfall events can dramatically alter the concentration of dissolved organic

carbon (DOC) and colored dissolved organic matter (CDOM) within the system. Field samples not only allowed for the quantification of DOM, but also were used to characterize changes in DOM composition during down-estuary transport, confirm conservative behavior with respect to salinity, and define a strong relationship between CDOM and DOC. Field samples, however, provided data at low spatial and temporal resolutions as samples analyzed for DOM in the NRE were collected only in the upper-to-middle portions of the estuary once or twice monthly; this sampling frequency is common to many studies. Although field samples provided necessary and useful information to understand how storms influence the concentration and transport of terrestrially derived material, the utility of data derived from field samples was greatly enhanced when the data were used with numerical modeling and remote sensing technologies.

Numerical modeling was beneficial in providing simulations of the concentration and transport of DOC during and immediately following Hurricane Irene, a time when the collection of field samples was not possible. Field samples collected at the mouth of the Neuse River and throughout the NRE by the ModMon and NEMReP programs provided vital information that was needed to initialize, calibrate, and validate the Delft3D numerical flow and transport model. Field samples analyzed for DOC, however, were only collected in the upper-to-middle NRE and thus were unable to characterize changes in the concentration and distribution of DOC in the lower estuary near the confluence with Pamlico Sound. Delft3D accounted for this lack of data by simulating down-estuary transport and providing estimates along the length of the NRE at depth and at a high temporal resolution. The accuracy of model estimates suggests that the model can be used to predict DOC transport between bi-monthly field expeditions and provide results at high spatial and temporal resolutions when the use of remote sensing is not possible due to either cloudy conditions or from a lack of instrument spectral sensitivity.

Data from field samples were also required to investigate the relationship between particulate and dissolved material concentrations and Moderate-resolution Imaging Spectroradiometer (MODIS) remotely sensed images. MODIS instruments provide frequent, large-scale synoptic views of the Albemarle Pamlico Estuarine System (APES), and the use of validated remote sensing algorithms would provide unique information on the distribution and concentration of sediment and carbon throughout the system that could not be obtained from field sampling or model simulations. Although numerical modeling provided results at a high spatial and temporal resolution for the NRE, it is difficult to apply the model over the entire APES due to computational limits. Unfortunately, the development of a local algorithm for suspended sediments to monitor suspended particulate material was not successful, a result that is attributed to the high spatial variability of suspended matter in the location where samples were collected. Imagery was, however, able to confirm the observation from field sampling that a large sediment pulse from the Neuse River to the NRE and Pamlico Sound did not occur following Hurricane Irene. MODIS images also provided information on the distribution and relative concentration of particulate material following different wind events. Hopefully, these images will provide an insight on locations within the APES where alternate sampling methods can be applied that will lead to an improved relationship between field measurements and remotely sensed data. The rapid settling of particulate material in the APES following Irene, combined with high riverine DOM concentrations, suggests terrestrial sources (overland flow, soil porewater, groundwater) and a limited contribution of DOM from particle desorption.

As with particulate material, difficulties were encountered when employing a previously developed relationship between CDOM and MODIS data. This result was attributed to the extremely high concentrations of light-absorbing DOM that limited reflectance to values below

the sensitivity of the instrument and atmospheric correction algorithms. For this reason, the use of remote sensing to monitor DOM within the NRE and Pamlico Sound may be limited to baseflow conditions when CDOM concentration is low as current remote sensing instruments do not provide the spectral sensitivity necessary to accurately measure the reflectance of high CDOM waters as are frequently observed in the NRE following rainfall events.

This study demonstrated that the use of an integrated method provided data and predictions at an increased spatial and temporal resolution needed to adequately characterize the impacts of a hurricane and associated rainfall on the transport of terrestrially derived material in a coupled land-estuary system; however, this study also demonstrated that the methods used should be expanded in future studies. Field samples within the Neuse River basin could be collected at locations near the USGS gaging stations at Kinston and Grifton, NC to more accurately characterize the relationship between discharge and material transport following future rain events as these parameters are linked to the location and intensity of rainfall within the basin. Samples should also be analyzed for DOM fluorescence to provide more detailed information of DOM sources and transformations. It would also be beneficial to collect field samples for DOC along the entire length of the NRE to provide for more accurate calibration and validation of the transport model; DOC concentrations collected regularly at ModMon stations would be more beneficial than samples collected only in the upper-to-middle estuary at NEMReP locations. Furthermore, it is recommended that the model employed in this study be more rigorously validated following a future storm event to confirm the accuracy of the model's physical parameters. The Delft3D model could also be applied to the adjacent Tar-Pamlico River and Pamlico River Estuary (PRE) to better characterize the transport of material from both of the major sub-estuaries that discharge directly to Pamlico Sound. However, due to a lack of

monitoring programs in the PRE, sampling cruises would have to be undertaken with measurements for water quality parameters and vertical salinity profiles. Similar to the model used in this work, field samples could be collected at the mouth of the Tar River at Washington, NC to force the transport of DOC to the PRE. Lastly, model simulations of DOC could be further validated through visual comparisons with remotely sensed imagery. Although it is recognized that current remote sensing data may not be able to provide accurate estimates of DOM in the NRE and Pamlico Sound, the development of a successful suspended sediment algorithm is still possible. It is recommended that suspended sediment samples be collected in the central portion of Pamlico Sound where the spatial variability of particulate material appears to be low while the collection of data over a wide range of concentrations is possible.

Overall, this study demonstrated that storms play an important role in the transport of terrestrially derived material to estuaries and the coastal ocean and that the use of an integrated method to maximize the utility of field samples provided a unique and comprehensive data set that accurately characterized material transport in the Neuse River and NRE following Hurricane Irene (2011). The continued use of this integrated method can be used to more accurately characterize the concentration and distribution of terrestrially derived material in various land-estuary systems and would be especially useful to characterize changes during and following dynamic storm events. Continued study within this and other systems is crucial to more accurately define the impacts of rainfall events on coupled systems as variations in storm characteristics and natural and anthropogenic processes within drainage basins could significantly alter transport dynamics and result in a wide range of impacts to coastal aquatic environments.

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