**Spatio-temporal patterns in the export of dissolved organic carbon and chromophoric dissolved organic matter from a coastal, blackwater river**

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**Running Title**: Coastal blackwater river CDOM dynamics

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**Abstract**

We examined seasonal and spatial patterns in dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) in the Chowan River Watershed, North Carolina, a blackwater river which discharges into the second largest estuary in the United States, the Albemarle-Pamlico Estuarine System. From April 2008 – May 2010, DOC concentration did not significantly vary across seasons (range: 7.69 - 30.39 mg L-1); however, CDOM molecular size and aromaticity increased throughout the spring, decreased during the summer and fall, and was variable in the winter. Spectral slope ratios suggested microbial processing of CDOM in the spring and photodegradation of CDOM in the summer and fall. Spatially, DOC and CDOM concentrations were similar in the mainstem and at the mouths of two tributaries, Bennetts Creek and Wiccacon River, but were significantly higher upstream on the tributaries. DOC concentration was positively correlated with CDOM absorbance coefficients at 254 and 350 nm; however, these optical proxies explained only ~60% of the variance. DOC and CDOM loads to the Albemarle Sound ranged from 2.8 x 1010 g yr-1 and 8.1 x 1010 m2 yr-1, respectively, in a dry year and 8.7 x 1010 g yr-1 and 2.2 x 1011 m2 yr-1, respectively, in a wet year, which are comparable to non-blackwater rivers with larger watersheds. Our results highlight the seasonal variability in load, reactivity, and bioavailability of organic carbon exported from coastal blackwaters to estuaries, and the importance of this carbon to net ecosystem metabolism, and consequently, carbon cycling in the coastal ocean.

**Introduction**

Dissolved organic carbon (DOC) represents a major intermediate in the global carbon cycle through its simulation of microbial metabolism (Jaffe et al. 2008). Coastal rivers are vital conduits transporting DOC between two main carbon reservoirs-- the land and the ocean. Approximately 250 Tg C is delivered to the coastal ocean each year from riverine export of DOC (Cole et al. 2007). Of this, 6.3 Tg C yr-1 are estimated to come from rivers draining the conterminous United States (US) (Stets and Striegl 2012). Quantifying this exchange of carbon between rivers and the coastal ocean is essential to an accurate understanding of global carbon fluxes between the land, ocean, and atmosphere. For example, estuaries receiving increased inputs of riverine organic carbon are often shifted towards net heterotrophy, increasing CO2 evasion (Hopkinson and Smith 2005). Quantifying riverine carbon exports can also contribute to identifying anthropogenic disturbances that affect the quantity and quality of carbon transported, such as logging activity, intensive agriculture, and wastewater treatment (Hernes et al. 2008; Hossler and Bauer 2013).

Chromophoric dissolved organic matter (CDOM) represents the colored fraction of DOC and is primarily derived from the degradation of higher plant matter (Wetzel 2001). Because it absorbs sunlight within the ultraviolet and blue regions of the spectrum, numerous biological, chemical, and physical properties of inland and coastal waters are regulated by the quantity and quality (i.e., chemical character) of CDOM. These broadly include effects on microbial community dynamics, rates of biogeochemical transformations, dissolved oxygen availability, thermal stratification, and ultraviolet (UV) transparency. From a public health perspective, CDOM influences the mobilization of heavy metals, such as mercury (Dittman et al. 2009), as well as the formation of carcinogenic disinfection byproducts during drinking water treatment (Chow et al. 2007). Thus, the production, fate and transport of CDOM from land to sea are of great ecological and environmental interest.

Blackwater rivers contribute large quantities of both DOC and CDOM to the coastal ocean, relative to other systems, and are especially prominent along the US Southeastern Coastal Plain (Mulholland and Kuenzler 1979; Meyer 1990; Spencer et al. 2013). However, less is known about the quantity and quality of carbon exported from blackwater rivers compared to larger, coastal rivers with higher discharges (Mulholland and Kuenzler 1979; Meyer 1990; Spencer et al. 2013). While most rivers in the conterminous US predominantly export inorganic carbon, rivers in the Southeast predominantly export organic carbon (Stets and Striegl 2012). Furthermore, recent estimates suggest that blackwaters draining to the South Atlantic Bight deliver a CDOM load comparable to that of the Mississippi River from a region approximately 10% the size of the Mississippi watershed (Spencer et al. 2013). These large inputs of DOC and CDOM mostly originate from extensive wetlands that commonly occur along the floodplain of blackwater rivers (Mulholland and Kuenzler 1979; Meyer 1990). Due to the low slope of the coastal plain region, floodplains become inundated during periods of high discharge, typically winter to early spring, followed by extensive drying during the summer and fall (Hupp 2000).

In the present study, we examined seasonal and spatial trends in DOC and CDOM within a coastal, blackwater riverine system. Specifically, we studied the Chowan River, North Carolina and two of its tributaries, which discharge large quantities of fresh water and organic matter into the second largest estuary in the US, the Albemarle-Pamlico Estuarine System. Based on our analysis, we provide conservative estimates of DOC and CDOM loads and yields to the Albemarle Sound and compare these with other US coastal rivers as well as blackwater rivers across the globe. We also examined seasonal differences in the photoreactivity and bioavailability of CDOM exported to the Albemarle Sound based on spectral characteristics and assess the ability of commonly used CDOM optical proxies to predict DOC concentrations in coastal blackwater systems.

**Methods**

**Study site**

The Chowan River lies within the Coastal Plain Physiographic Region, originating at the North Carolina-Virginia state border at the confluence of the Blackwater and Nottoway Rivers (Fig. 1). Approximately 80.5 km downstream it then empties into the Albemarle Sound. In total, the watershed drains an extensive network of approximately 4800 stream kilometers. Seventy five percent of the 12,665 km2 watershed is located upstream of the Chowan River in Virginia. In general, watershed topography is very flat with an underlying geology of alternating sand, silt, clay, and limestone (NCDENR 2002). The watershed is overall very rural, with only 1% of the watershed identified as urban (NCDENR 2002). Approximately 63% of the watershed is forested wetland, which includes the Dismal and Chowan Swamps (NCDENR 2002). Twenty-nine percent of the watershed is used for cultivated crops, including soybeans, corn, tobacco, cotton, and peanuts. Timber plantations and confined animal feeding operations (i.e., mostly pigs and chickens) are also found within the basin (NCDENR 2002).

Our study sites were located in the freshwater, tidal portion of the Chowan River Estuary, with two sites on the mainstem Chowan River, the Harbor and Shingle Island, and two sites on each of two smaller tributaries, Bennetts Creek and the Wiccacon River (Fig. 1). These two tributaries enter the Chowan River in between our two sites on the mainstem. Sample collection occurred during April 2008 – May 2010. In 2008, samples were collected at approximately monthly intervals between April – December from our two sites on the mainstem and at the mouths of Bennetts Creek and Wiccacon River. In 2009, we added our upstream sites on Bennetts Creek (Trotman’s Farm) and the Wiccacon River (Harrellsville) and again collected samples at monthly intervals, except between April – June when samples were collected every two weeks. In 2010, samples were collected from all six sites at approximately monthly intervals between January – May. In total, we collected 132 and 148 samples for DOC and CDOM measurements, respectively.

**Discharge estimation**

Due to the lack of gauging stations along the Chowan River, discharge was estimated based on data from the five United States Geological Survey (USGS) gauging stations within the basin, located at Potecasi Creek (2049500), Ahoskie Creek (2053500), Nottoway River (2047000), Meherrin River (2052000), and the Blackwater River (2052000). Discharge at all five of these sites was summed to determine a total daily average stream flow from the gauged portion of the watershed. These values were divided by the total gauged area (7993 km2) and then multiplied by the total area of the watershed (gauged plus ungauged or 12,665 km2) to estimate total daily watershed discharge over the course of the study. We acknowledge that this method may overestimate discharge given that the gauging stations are primarily located in the headwaters of the watershed. Nevertheless, our derived discharge is within the range of historical data recorded at a former USGS gauging station located near the mouth of the Chowan River (02053652, in operation from April 1974- March 1976).

**Sample collection and processing**

During each sampling event, river water was collected at each site in a pre-cleaned and pre-rinsed 1 L Nalgene bottle approximately 0.2 m below the surface. Bottles were immediately placed in a dark cooler on ice. All samples were collected between 09:00 h – 16:00 h in mid-channel. Samples were returned to the laboratory the same day as collection and immediately filtered through Whatman GF/F glass fiber filters (0.7 *μ*m pore size) and kept at 4oC. Filtrate used for DOC analysis was acidified with 2 mol L-1 HCl and stored in glass scintillation vials. Filtrate used for spectrophotometric analysis was stored in polypropylene and polystyrene Beckman Dickinson Falcon centrifuge tubes.

**DOC and CDOM Measurement**

DOC concentrations were measured within one month of sample collection by high temperature combustion using a Shimadzu Total Organic Carbon 5000 analyzer calibrated with potassium biphthalate. All DOC data presented are the mean of three to five replicate samples with a <2% coefficient of variation.

CDOM measurements were performed the day after sample collection. UV-Vis absorption spectra were obtained on a Shimadzu UV-mini 1240 spectrophotometer using distilled water as a blank. All scans were run at room temperature between 250 and 800 nm in a 1 cm quartz cuvette. For each sample, the average absorbance between 700- 800 nm was subtracted from the spectrum between 250 – 700 nm to remove background noise associated with baseline drift, scattering, and refractive effects (Green and Blough 1994). Corrected absorbance values were then converted to Napierian absorption coefficients using the equation, *aλ* = 2.303 x *Aλ* /*l,* where *aλ* is the absorption coefficient at wavelength *λ*, *Aλ* is the absorbance at wavelength *λ*, and *l* is the path length of the quartz cuvette in meters.

**CDOM optical proxies**

The ratio of absorbance at 254 nm to 365 nm was calculated to track changes in the relative size of CDOM molecules (modified from De Haan and De Boer 1987). The ratio decreases as molecular size increases due to stronger light absorption at longer wavelengths by high-molecular-weight CDOM. This ratio is also used as a proxy for photodegradability (Dalrymple et al. 2010), with increasing 254:365 ratios suggesting increased photodegradation of CDOM. Specific UV absorbance at 254 nm (SUVA254) was calculated by dividing the UV absorbance at 254 nm (m-1) by the DOC concentration (mg L-1) and was used as a proxy for estimating CDOM aromaticity (Weishaar et al. 2003). As SUVA254 increases, aromaticity increases, indicating CDOM inputs from terrestrial sources. Spectral slopes between 275 – 295 nm (S275-295) and 350 – 400 nm (S350-400) were determined by applying a linear fit to natural log-transformed spectral absorbance data corresponding to each spectral range. These ranges provide information regarding CDOM source, structure, and diagenesis (e.g., photobleaching, microbial degradation) (Helms et al. 2008). S*275-295* is used as a proxy for molecular weight, with decreases in slope indicating increases in molecular weight, while the ratio of S275-295 to S350-400 (SR) is used to characterize changes in CDOM source and character. The lower the SR value, the more allochthonous the sample, the higher molecular weight CDOM, the less photodegraded (Helms et al. 2014). Specifically, SR values less than one signify CDOM of terrestrial origin (Helms et al. 2008). Finally, absorbance at 350 nm was used as an estimate of CDOM concentration (*a*350) (Moran et al. 2000) while the ratio of absorbance at 350 nm to DOC concentration (*a*350:DOC) was used to estimate the contribution of CDOM to the larger DOC pool (Moran et al. 2000).

**DOC and CDOM loading and yield estimation**

To estimate loading of DOC and CDOM to the Albemarle Sound from the Chowan River, we multiplied our calculated daily discharge by the measured DOC concentration and *a*350 observed at our furthest downstream station on the mainstem (the Harbor) during each respective sampling month or two-week period. Calculated daily loads were summed to estimate DOC and CDOM loading for March 2008 – February 2009 (a dry year) and March 2009 – February 2010 (a wet year). These two time periods were selected in order to represent one annual cycle of all four seasons (i.e., spring, summer, fall, winter). To estimate yield, DOC and CDOM loads were divided by the area of the Chowan River Watershed.

Although the Harbor is located approximately 26 km from the mouth of the Chowan River, DOC concentrations here are representative of historical data collected at mouth. Based on information compiled from the United States Environmental Protection Agency Storage and Retrieval (STORET) database, from 1976-2006, DOC concentrations ranged from 10-15 mg C L-1 at the US-17 Bridge, which spans the mouth of the Chowan River at Edenton, North Carolina. We did not collect DOC and CDOM data at the mouth because the primary focus of our sampling efforts was to assist the state of North Carolina in to river herring restoration at our upstream locations (Leech et al. 2011).

**Statistical analyses**

All statistical tests were performed in the R statistical environment (R Core Development Team 2010). DOC and CDOM proxies were first checked for normality (Kolmogorov-Smirnov test) and homoscedasticity (Levene test). Because all variables lacked a normal distribution, Kruskal–Wallis tests combined with non-parametric Tukey-like multiple comparisons were used to examine statistical differences in DOC and CDOM across time (i.e., season) and space (i.e., sampling site). Linear regression was used to assess relationships between the maximum weekly discharge recorded the week prior to sampling and DOC and CDOM concentrations. Relationships between DOC concentrations and the CDOM optical proxies were also assessed using linear regression.

**Results**

**Summary of discharge during study period**

Discharge in the Chowan River Watershed ranged from 2 – 790 m3 s-1 and significantly varied with season (‘H’ Score (*H)*= 72.26, degrees of freedom (*df*)=3, *p* < 1.4 x 10-15) (Fig. 2). During the summer and fall (June – November), discharge was low, averaging 25 m3 s-1 + 7 standard deviation (SD). In contrast, discharge was 6.5 times greater in the winter and spring (December – May), averaging 163 m3 s-1 + 6 SD. When examined over a study year from April 2008 – February 2009 vs. March 2009 – February 2010, average annual discharge was twice as high during the second year of our study (158 m3 s-1 + 206 SD) compared to the first (70 m3 s-1 + 95 SD). This was due to a wetter summer in 2009 combined with several high discharge events occurring in late December 2009, which extended through April 2010 (Fig. 2).

**DOC concentration, load, and yield**

From April 2008 through May 2010, DOC concentration across all six sites ranged from 7.69 to 30.39 mg L-1 (Fig. 3). Despite the wide seasonal variation in river flow, linear regression revealed a weak correlation between DOC concentration and discharge when analyzed across the entire dataset (*R*2= 0.03, *p* < 0.05, *n*=118). However, when the data were parsed by season, there was a significant positive relationship between DOC and discharge during the winter (December through February, *R*2= 0.51, *p* < 7.4 x 10-06, *n*=29). This suggests that DOC is partially coupled to discharge in the winter but not spring, summer, or fall. Based on Kruskal–Wallis tests, no significant seasonal pattern in DOC concentration was observed for most sampling sites (*p*>0.05). The exceptions were our upstream sites on Bennetts Creek (Trotman’s Farm, *H*=10.28, *df*= 3, *p*=0.02) and the Wiccacon River (Harrellsville, *H*=7.94, *df*=3, *p*=0.05). At both sites, DOC concentrations were approximately 5-7 mg L-1 greater in the summer and fall (DOC concentration= 23-25 mg L-1) compared to winter and spring (DOC concentration= 16-17 mg L-1).

Spatially, DOC concentration significantly varied across sampling sites (*H*=40.09, df=5, *p* < 1.4 x 10-7). Specifically, DOC concentrations at the upstream sites on Bennetts Creek (Trotman’s Farm) and the Wiccacon River (Harrellsville) were significantly greater than the mainstem, but DOC concentrations at the mouths of the tributaries did not significantly differ from the mainstem (Fig. 3). Within Wiccacon River, DOC concentration was significantly greater at the upstream site compared to downstream by approximately 4 mg L-1 (Fig. 3). However, no significant difference in DOC concentration was observed between the up- and downstream sites within Bennetts Creek or on the mainstem (Fig. 3).

Based on biweekly to monthly DOC concentrations at our furthest downstream site (the Harbor), the DOC load to the Albemarle Sound was approximately 1.26 x 1010 g during the fall and winter of 2008-2009 (Table 1). If we assume DOC concentration was approximately 11 mg L-1 during the spring and summer of 2008, this would give an annual load of 2.83 x 1010 g yr-1. In 2009, when DOC data were collected throughout all four seasons, the annual DOC load was estimated to be 8.75 x 1010 g yr-1 (Table 1). Annual DOC yields for the same time periods were approximately 2.23 and 6.91 g m-2 yr-1, respectively. Thus, DOC loading and yield may more than double in wet compared to dry years, with the highest contributions to the Sound during the spring and winter (Table 1). The spring of 2010 was a particularly wet period with a DOC load of 1.64 x 1010 g and a DOC yield of 1.29 (Table 1).

**CDOM characteristics, load, and yield**

In contrast to DOC concentration, CDOM proxies primarily varied seasonally rather than spatially (Fig. 4). Kruskal-Wallis tests revealed no significant patterns across sampling site for most CDOM proxies (*p*>0.05), except *a*350 (*H*=7.62, *df*=5, *p*=0.01). This suggests that CDOM of similar molecular weight and aromaticity entered the system across all six sampling sites. However, the concentration of CDOM entering the system is significantly higher at the upstream sites on Bennetts Creek (Trotman's Farm, average *a*350= 65 m-1 + 17 SD) and the Wiccacon River (Harrellsville, average *a*350= 64.15 m-1 + 23 SD) compared to sites on the mainstem and at the mouths of the two tributaries (average *a*350= 45 m-1 + 13 SD).

Significant seasonal patterns in *a*254:*a*365 (*H*=41.17, *df*=3, *n*= 140, *p* < 6.02 x 10-9), SUVA254(*H*=24.57, *df*=3, *n*=140, *p* < 1.9 x 10-5), S275-295*(H*=24.13, *df*=3, *n*=140, *p* < 2.4 x 10-5), S350-400(*H*=15.8, *df*=3, *n*=140, *p* = 0.001) and S*R*(*H*=37.83, *df*=3, *n*=140, *p* < 3.1 x 10-8) were observed across the six sampling sites. In general, *a*254:*a*365, S*275-295*, and S*R* decreased throughout the spring and early summer while SUVA254 and *S350*-400increased, indicating that CDOM was increasing in molecular size and aromaticity and subject to increased microbial degradation (Figs. 4, 5). From summer through autumn, the opposite pattern was generally observed, with *a*254:*a*365, S275-295, and S*R*increasing and SUVA254 and S350-400decreasing (Figs. 4, 5). This suggests decreases in CDOM molecular size and aromaticity as well as increased photodegradation throughout the summer and fall. In the winter, CDOM proxies displayed variable patterns between the two study years, likely related to differences in winter discharge during 2008-2009 vs. 2009-2010. Typically, *a*254:*a*365, S275-295, and S*R* increased or remained relatively high, SUVA254 decreased or remained relatively low, and S350-400 increased (Figs. 4, 5). CDOM in the winter may therefore represent a more heterogeneous mixture of molecules varying in size and aromaticity. CDOM proxies were also more variable in the winter of 2009 compared to the winter of 2008, which corresponds to higher, more variable discharge in Chowan River Watershed in the winter of 2009.

CDOM quantity, based on *a*350, also varied significantly across season (*H*=10.09, *df*=3, *p* < 0.02), but only between the summer and winter. Generally, CDOM concentrations increased throughout the spring, remained relatively constant during the early summer, and then decreased during the latter portion of the summer through fall and winter (Fig. 4). Furthermore, CDOM concentrations in the spring, summer, and fall were higher in 2009-2010 compared to data collected in 2008. The *a*350:DOC ratio suggest that CDOM comprises a larger proportion of the total DOC pool in the late spring and summer compared to the fall and winter (Fig. 4).

CDOM loading from the Chowan River to the Albemarle Sound was approximately 8.07 x 1010 m2 yr-1 during the first year of the study, which again was a relatively dry year. During the second, wetter year of the study, CDOM load increased to 2.22 x 1011 m2 yr-1. CDOM yields from the Chowan watershed for the two study years were 6.37 and 17.5 yr-1, respectively. Both load and yield were greater in the winter and spring compared to the summer and fall (Table 1).

**Relationship between DOC concentration and CDOM proxies**

A significant linear relationship was detected between DOC concentration and the CDOM proxies *a*254 (*R*2=0.59, *p* < 2.2 x 10-16,*n*=118) and *a*350 (*R*2=0.58, *p* < 2.2 x 10-16,*n*=118). Both explained approximately 60% of the variance in DOC concentration across time and space with most of the deviation from linearity observed at DOC concentrations above 20 mg L-1 (Fig. 6). S275-295 (*R*2=0.25, *p* < 4.7 x 10-9,*n*=118)and S*R* (*R*2=0.21, *p* < 1.2 x 10-7,*n*=118) were also linearly correlated with DOC concentration; however, these proxies only explained 21-25% of the variance.

**Discussion**

Estuaries that receive high inputs of riverine dissolved organic matter are often net heterotrophic (Hopkinson and Smith 2005), where increased CDOM loads reduce light availability for photosynthesis while stimulating bacterial respiration (Durako et al. 2010). Blackwater rivers may therefore represent “hotspots” in coastal carbon chemistry, with seasonal variations in the quality and quantity of DOC and CDOM influencing estuarine food web dynamics and net ecosystem metabolism.

**Spatio-temporal patterns in DOC and CDOM concentration**

DOC concentrations observed in the Chowan River and its tributaries (Fig. 4A; 7.69 to 30.39 mg C L-1) were similar to other blackwater systems in the Southeastern US, such as the Elizabeth River, VA (10-20 mg C L-1; Helms et al. 2008), the Newport River, NC (14.8 to 50.0 mg C L-1; Ensign et al., 2012), the Cape Fear River, NC (9.1-17.5 mg C L-1; Avery et al. 2003), the Edisto River, SC (mean = 11.2 mg C L-1; Hanley et al. 2013), and the St. Mary's River, FL (mean = 46.8 mg C L-1; Hanley et al. 2013). In comparison, the DOC concentrations of these Southeastern US blackwater rivers is equivalent to the tropical rivers of the Rio Negro Basin (4.8 -18.9 mg C L-1; Moreira-Turcq et al. 2003) and the Guayana Shield, Venezuala (1.2-25.5 mg C L-1; Yashimoto et al. 2010), which both drain the rich organic soils of the Amazon Rainforest. Furthermore, they are often higher than the Epulu River (5.2 – 9.0 mg C L-1; Spencer et al. 2010), which drains the tropical rainforest of the Democratic Republic of the Congo.

DOC concentrations in the Chowan River were also higher than the DOC range reported for the nearby Roanoke River, NC (2.7 - 8.8 mg C L-1; Hossler and Bauer 2013). The Roanoke River watershed is 25,294 km2 (i.e., approximately twice the size of the Chowan River watershed) and is primarily located in the Piedmont Physiographic Region. The importance of physiographic region on DOC concentration was highlighted by the much higher DOC concentration in a Coastal Plain river (Chowan) compared to a Piedmont river (Roanoke) twice its size highlights.

Based on absorption coefficients at 350 nm, CDOM concentrations in the Chowan River and two representative tributaries are also characteristic of organic-rich waters, ranging from 19.9 - 95.9 m-1 (Fig. 4D). Interestingly, these values are approximately five times higher than *a*350 reported for the Atchafalaya River, Louisiana, US during the same time period as our study (4.19- 17.52 m-1; January 2009 – March 2010) (Shen et al. 2012). Because both systems have wetland-dominated floodplains, we predicted *a*350 would be of similar magnitude. However, CDOM in the Atchafalaya River may be diluted by the high volume of water diverted into the river from the Mississippi River, which accounts for ~75% of its volume (Shen et al. 2012). The *a*350:DOC ratio of the Chowan River system (1.31 - 4.94 L mg-1 m-1)suggests CDOM often represents a greater proportion of the bulk DOC pool, particularly during the summer (Fig. 4E). Comparatively, the highest value reported for the Atchafalaya River was only 2.46 L mg-1 m-1 and was observed during the fall, October – November 2009 (Shen et al. 2012). The reason for this difference in peak ratio (i.e., the Chowan in the summer and the Atchafalaya in the fall) is unknown, but may be related to differences in their annual hydrographs.

In contrast to studies citing a strong, positive relationship between DOC/CDOM concentration and discharge (Holmes et al. 2011; Lu et al. 2011), increases in DOC and CDOM were only coupled to increases in discharge in the winter. This may have been related to the large variation in discharge between the winter of 2008-2009 vs. the winter of 2009-2010. Interestingly, although not significant, DOC and CDOM appeared to exhibit the reverse pattern in the spring, decreasing in concentration with increasing discharge. In the winter, increases in DOC and CDOM with increasing discharge could be explained by a ‘first flush’, releasing organic matter that has built up on the floodplain over the summer and fall. Once removed, subsequent high discharge events in the spring act to dilute DOC and CDOM concentrations. Seasonal priming and flushing of DOC with changes in rainfall, and consequently discharge, have been reported in other systems, including the Penoboscot River, ME (Huntington and Aiken 2013) and several rivers of the United Kingdom (Worall and Burt 2007).

Nevertheless, there was overall no significant difference in DOC and CDOM concentration across season, except at the upstream sites on Bennetts Creek (Trotman’s Farm) and the Wiccacon River (Harrellsville). Here DOC and CDOM were approximately 30% greater in the summer and fall compared to the winter and spring. We hypothesize that decreased flow and increased evaporation in the summer may concentrate DOC and CDOM in the water column at these upstream sites where the channel is shallower and narrower. Furthermore, given that these sites are closer to the headwaters, DOC and CDOM are exposed to microbes and sunlight for a shorter period of time. These two factors may reduce DOC and CDOM concentrations further downstream with increased rates of mineralization (Engelhaupt et al. 2003).

Similarly, there was no significant difference in DOC and CDOM concentrations across sampling site, except at the upstream sites on the two tributaries (i.e., Trotman’s Farm and Harrellsville) (Fig. 3). From May 2009 - October 2009, DOC and CDOM concentrations at these upstream sites were generally 30-35% higher than the two stations on the mainstem as well as at the mouth of each respective tributary. Given that concentrations were similar at all six sampling sites from November 2009 – May 2010, the reduction in DOC and CDOM within each tributary during the summer/early fall may be attributed to increased photobleaching and/or microbial degradation as DOC and CDOM travel downstream (Moran et al. 2000; Helms et al. 2008). It is also possible that increased inputs of DOC-poor groundwater may have diluted DOC and CDOM concentrations. Tesoriero et al. (2004) reported that DOC concentration in the surficial aquifer averages 0.8 mg L-1 within the Chowan River watershed. Of the 127 cm of annual precipitation in the Albemarle-Pamlico Sound Basin, 25 cm moves through shallow aquifers as groundwater or baseflow (Wilder et al. 1978).

**Relationship between DOC concentration and CDOM optical proxies**

Because DOC and CDOM are central to determining the biological, chemical, and physical structure and function of aquatic ecosystems (Wetzel 2001, Jaffe et al. 2008) as well as monitoring the flux of carbon from land to the sea (Cole et al. 2007), great attention is placed on developing reliable, accurate measurements that are easily obtained. Optical indices based on the spectral characteristics of natural waters within the ultraviolet and visible wavebands have provided valuable information regarding estimates of DOC and CDOM concentration as well as their chemical character (De Haan and De Boer 1987; Weishaar et al. 2003; Helms et al. 2008). Coupling these indices with current advances in remote sensing has further enhanced out ability to calculate real-time estimates of carbon fluxes from rivers to the coastal ocean (Osburn and Stedmon 2011). Nevertheless, a potential problem with estimating carbon exports from blackwater rivers is that currently published models used to estimate DOC concentrations from spectral data generally did not include blackwater systems in their development (but *see* Weishaar et al. 2003; Helms et al. 2008).

Here absorbance coefficients at 254 and 350 nm explained approximately 60% of the variance in DOC concentration while S275-295 and S350-400only explained ~21-25% of the variance in DOC concentration. Previous studies examining a variety of non-blackwater riverine systems have reported much stronger correlations between DOC and these optical indices, often explaining > 80% of the variance in DOC concentration (Griffin et al. 2011; Spencer et al. 2012). In general, the highest DOC concentration included in most of these studies was approximately 10 mg L-1. We observed that the predictive power of *a*245 and *a*350 decreased at DOC concentrations above 15-20 mg C L-1 (Figure 6). Furthermore, the predictive power of S*275-295*, S*350-400*, and S*R* was low at all DOC concentrations in the Chowan River. This suggests that these commonly used optical indices are less reliable when estimating the DOC concentration of blackwaters with particularly high DOC loads. Inaccurate estimates of DOC concentration will consequently lead to inaccurate estimates of DOC fluxes from blackwater systems to the coastal ocean, which will lead to inaccuracies in global carbon budgets.

**Spatio-temporal patterns in CDOM chemical character**

CDOM optical proxies displayed distinct variations across season but not sampling site. Thus, CDOM quality appears to vary in a similar manner over time at all our stations, with no significant differences observed between the mainstem and the two tributaries. However, based on significant differences in *a*350 across sampling site, the concentration entering the river was highest upstream on the two tributaries. Values for the *a*254:*a*365 ratio, SUVA254, S*275-295*, S*350-400* and S*R*were equal, if not higher, than those reported in other blackwater river networks (Figs. 4, 5) (Helms et al. 2008; Shen et al. 2013; Spencer et al. 2013). In general, CDOM molecular weight and aromaticity increased throughout the spring and early summer, decreased in the late summer and fall, and remained relatively low in the winter. These patterns are consistent with seasonal fluctuations in CDOM character observed in other riverine systems (Shen et al. 2012). In the spring and early summer, increasing water temperatures stimulate microbial metabolism for preferentially smaller, labile dissolved organic compounds, leaving behind more complex, aromatic organic matter (Moran et al. 2000). In the Chowan River, increasing rates of microbial respiration during this time period are suggested by our observation of decreasing dissolved oxygen levels (Leech et al. 2011) as well as decreases in S*R* (Fig. 5C; Helms et al. 2008).

Decreases in CDOM aromaticity and molecular size during the late summer and fall is likely related to increases in exposure to UV radiation, which photodegrades CDOM into smaller, organic compounds (Wetzel 2001). This is corroborated by the observed increases in S*R* (Fig. 5; Helms et al. 2008). Additionally, increases in organic carbon derived from live and decomposing phytoplankton may contribute CDOM of lower aromaticity and size to the bulk CDOM pool (Romera-Catillo et al. 2010), although some debate the contribution of phytoplankton exudates to CDOM (Rochelle-Newall and Fisher 2002). Chlorophyll-*a* concentrations were particularly high in the Chowan River and its tributaries during the summer and fall (i.e., range = 10 – 55 *µ*g L-1; Leech et al. 2011), suggesting the presence of phytoplankton biomass. In the winter, wetland soils become inundated with rising water levels. This results in anaerobic conditions that can inhibit microbial breakdown of small, labile organic compounds, increasing their subsurface runoff into nearby rivers and streams (Guillemette and del Giorgio 2011). Moreover, rates of microbial metabolism in rivers and streams are generally reduced with colder water temperatures, allowing labile compounds to persist and be transported downstream.

Land use practices may also explain spatio-temporal changes in the characteristics of riverine DOC and CDOM. For example, agricultural croplands have been demonstrated to release more labile DOM compared to forests or wetlands (Wilson and Xenopoulos 2009). The Chowan River Watershed is approximately 29% cropland and has at least 34 animal confinement operations that are permitted to release wastewater into the Chowan River (NCDENR 2002). We did not specifically examine connections between agricultural practices and CDOM reactivity and bioavailability. However, our upstream stations on Bennett’s Creek and the Wiccacon River were both adjacent to croplands with riparian buffers and did not show significant differences in CDOM optical properties from our other sampling locations, which are surrounded primarily by swampland. Identifying changes in CDOM reactivity and bioavailability with land use change may be challenging in the Chowan River Basin given the heterogeneity of cropland interspersed with swampland. Furthermore, forested wetlands dominate the watershed (i.e., 63% landcover), particularly surrounding the main channel in the upper to middle reaches (NCDENR 2002).

**Chowan River DOC and CDOM export to the Albemarle Sound**

DOC and CDOM exports to the Albemarle Sound from the Chowan River ranged from 2.83 x 1010 g yr-1 and 8.07 x 1010 m2 yr-1, respectively, in a dry year and 8.75 x 1010 g yr-1 and 2.22 x 1011 m2 yr-1, respectively, in a wet year. These loads are comparable to other blackwater rivers in the Southeastern US with similar annual discharge, such as the Edisto River (DOC load= 4.13 x 1010 g yr-1, CDOM load = 8.93 x 1010 m2 yr-1; Spencer et al. 2013). Furthermore, they are similar to DOC and CDOM exports from major US rivers with larger watersheds and higher annual discharges, including the Potomac and Susquehanna Rivers (Stets and Striegl 2012; Spencer et al. 2013). Spencer et al. 2013 recently noted that riverine systems with wetland-dominated watersheds (i.e., Androscoggin, Atchafalaya, Edisto, Mobile, and Penobscot) are disproportionately important with respect to CDOM flux. Moreover, unlike most rivers in the conterminous US, the blackwater rivers of the southeast primarily export organic carbon rather than inorganic carbon (Stets and Striegl 2012). Annual DOC and CDOM yields ranged from 2.23 g m-2 yr-1 and 6.37 yr-1, respectively, in a dry year and 6.91 g m-2 yr-1 and 17.5 yr-1, respectively,in a wet year. Again, these yields are comparable to other blackwater systems, and perhaps more importantly, are higher than most major non-blackwater rivers in the US, including the Mississippi River (DOC and CDOM yield = 0.72 g m-2 yr-1 and 1.25 yr-1, respectively; Spencer et al. 2013).

The Albemarle Sound is a shallow, lagoonal estuary (average depth = 5 m) with no direct connection to the Atlantic Ocean, resulting in low salinity (annual average = 5 ppt). Recent estimates of primary production and net ecosystem metabolism in the Albemarle Sound could not be located. However, primary production in the Albemarle-Pamlico Estuarine System generally ranges from 50 – 500 g C m-2 yr-1 (Hopkinson and Smith 2005). DOC exports from the Chowan River are therefore estimated to be 2.4 – 18% of primary production in a dry year and 7.5 – 56% of primary production in a wet year. Colored water and reduced light transparency likely contribute to Albemarle Sound primary production being on the lower end of the range for similar systems. Moreover, because of the Albemarle Sound’s low salinity, dissolved organic carbon exports from the Chowan River and its other blackwater tributaries (i.e., the Alligator, Little, North, Pasquotank, and Perquimans Rivers) are less likely to flocculate, increasing the probability of this carbon becoming incorporated into the estuarine food web or photomineralized. Interestingly, Smith and Brenner (2005) noted that photodegraded CDOM from three blackwater rivers stimulated estuarine bacterial respiration, growth, and total DOC consumption. However, photodegraded CDOM was more likely to be metabolized catabolically (i.e., respired) than anabolically (i.e., incorporated into biomass). In the case of the Chowan River and the Albemarle Sound estuaries, this would occur in the latter summer and early fall. Large inputs of labile dissolved organic matter from the Chowan River in the winter may be particularly important to supporting the estuarine food web of the Albemarle Sound.

**Global relevance of DOC export from blackwater rivers**

Recent estimates of DOC loads from blackwater rivers, including those presented here for the Chowan River, highlight their relevance to global carbon fluxes from land to sea. As shown in Alkhatib et al. (2007), DOC exported from blackwater rivers is comparable to non-blackwater rivers with catchment areas several orders of magnitude larger. Furthermore, unlike non-blackwater rivers, DOC export from blackwater rivers does not consistently increase with increasing catchment size. Comparing the DOC export from several blackwaters worldwide, we found a large variation in export between rivers with similar catchment areas (Fig. 7). Not surprisingly, discharge is more critical to determining total DOC export in coastal blackwater rivers (Fig. 8). Together, these 16 blackwater rivers alone represent approximately 5% of the DOC exported to the coastal ocean. This is based on the assumption that current estimates of total riverine carbon exports are correct. However, our study suggests these estimates appear to underestimate the contributions of small blackwater rivers. Global DOC export from blackwater rivers is likely highly significant in the global carbon budget and warrants further investigation. Our results further emphasize that the quality of dissolved organic matter exported by blackwater rivers is seasonally dynamic, and more investigation is needed to understand how these varying inputs affect carbon processing and transport through the coastal ocean.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Time Period | Season | Discharge  (km3 season-1)  (km3 yr-1) | DOC Load  (g season1)  (g yr-1) | | DOC yield  (g m-2 sn-1)  (g m-2 yr-1) | | *a*350  Load  (m2 season-1)  (m2 yr-1) | | | | | *a*350  yield  (season-1)  (yr-1) | | | | |
| March 2008 - February 2009 | spring | 1.34 | --- | --- | | | 4.69 x 1010 | | | | | | 3.70 | | | |
| summer | 0.08 | --- | --- | | | 3.86 x 109 | | | | | | 0.30 | | | |
| fall | 0.21 | 2.31 x 1009 | 0.18 | | | 6.07 x 109 | | | | | | 0.48 | | | |
| winter | 0.72 | 1.03 x 1010 | 0.81 | | | 2.38 x 1010 | | | | | | 1.88 | | | |
|  |  |  |  | | |  | | | | | |  | | | |
| total | 2.37 | ~2.83 x 1010 | ~2.23 | | | 8.07 x 1010 | | | | | | 6.37 | | | |
|  |  |  |  |  | | |  | | | | | |  | | | |
| March 2009 – February 2010 | spring | 1.24 | 1.45 x 1010 | 1.24 | | | 5.02 x 1010 | | | | | | 3.96 | | | |
| summer | 0.33 | 4.48 x 1009 | 0.34 | | | 1.68 x 1010 | | | | | | 1.33 | | | |
| fall | 0.82 | 1.16 x 1010 | 0.97 | | | 2.91 x 1010 | | | | | | 2.29 | | | |
| winter | 2.83 | 5.69 x 1010 | 3.89 | | | 1.26 x 1011 | | | | | | 9.92 | | | |
|  |  |  |  | | |  | |  | | | | | |
| total | 5.23 | 8.75 x 1010 | 6.91 | | | 2.22 x 1011 | | | | 17.50 | | |
|  |  |  |  |  | | |  | | | | |  | | | |
| March –  May 2010 | spring | 1.13 | 1.64 x 1010 | 1.29 | | | 3.86 x 1010 | | | | | 3.05 | | | |
|  |  |  |  | | |  | |  | |  | | | | | | |

**Table 1**. Seasonal DOC and CDOM loads and yields to the Albemarle Sound from the Chowan River between March 2008 – May 2010. Loads and yields are based on the estimated daily DOC concentration and *a*350 at our furthest downstream site on the Chowan River (the Harbor), which is approximately 26 km from the Sound. Seasonal discharge for the Chowan River Basin is also provided. DOC data were not collected in the spring and summer of 2008. Dashes indicate the corresponding lack of DOC load and yield data for these time periods. (sn= season)

**Figure Legends**

**Figure 1**. Map of the six sampling sites along the Chowan River, North Carolina, United States. Inset shows the point of discharge into the Albemarle Sound, North Carolina.

**Figure 2**. Discharge (m3 s-1) for the Chowan River between April 2008 – May 2010. Due to the lack of gauging stations on the Chowan River, discharge was estimated from the five upstream gauging stations within the watershed, as described in the methods. Note the particularly low periods of discharge in the summer compared to the winter and spring.

**Figure 3**. Boxplots of the DOC concentrations (mg L-1) observed during the two-year study across the six sampling sites. Based on a Kruskal–Wallis test, DOC concentration significantly varied across station (*H*=40.09, *df*=5, *p* < 1.4 x 10-7), with DOC concentrations at the upstream sites on Bennetts Creek (i.e., Trotman’s Farm) and the Wiccacon River (i.e., Harrellsville (Hville)) significantly greater than the mainstem. DOC concentrations at the mouths of the tributaries did not significantly differ from the mainstem. Gray lines highlight the sites that significantly differ from one another (*p* < 0.05).

**Figure 4**. Boxplots of (A) DOC concentration (mg L-1) and (B) CDOM optical proxies *a*254:*a*365, (C) SUVA254, (D) *a*350, (E) *a*350:DOC across time. From April 2008 through December 2008, data were complied from the two sites on the mainstem and at the mouths of the two tributaries. Beginning in February 2009, data were compiled from all six sampling sites. Samples for DOC analysis began in September 2008. Boxplots are color-coded by season to highlight seasonal patterns.

**Figure 5**. Boxplots of the spectral slopes between (A) 275-295 nm and (B) 350-400 nm as well as (C) the spectral slope ratio (S*R*). From April 2008 through December 2008, data were complied from the two sites on the mainstem and at the mouths of the two tributaries. Beginning in February 2009, data were compiled from all six sampling sites. Boxplots are color-coded by season to highlight seasonal patterns.

**Figure 6**. Relationship between DOC concentrations and CDOM absorption coefficients (*a*254, *a*350, respectively) within the blackwater Chowan River, North Carolina, United States.

**Figure 7**. DOC export vs. catchment area for several blackwater rivers. Data are from Alkhatib et al. (2007), Baum et al. (2007), Hanley et al. (2013), Hopkinson et al. (1998), Moore et al. (2011), and Spencer et al. (2013).

**Figure 8**. DOC export vs. discharge for several blackwater rivers. DOC export data are from Alkhatib et al. (2007), Baum et al. (2007), Hanley et al. (2013), Hopkinson et al. (1998), Moore et al. (2011), and Spencer et al. (2013). Because the Rio Negro was a large outlier, it was omitted from the plot.

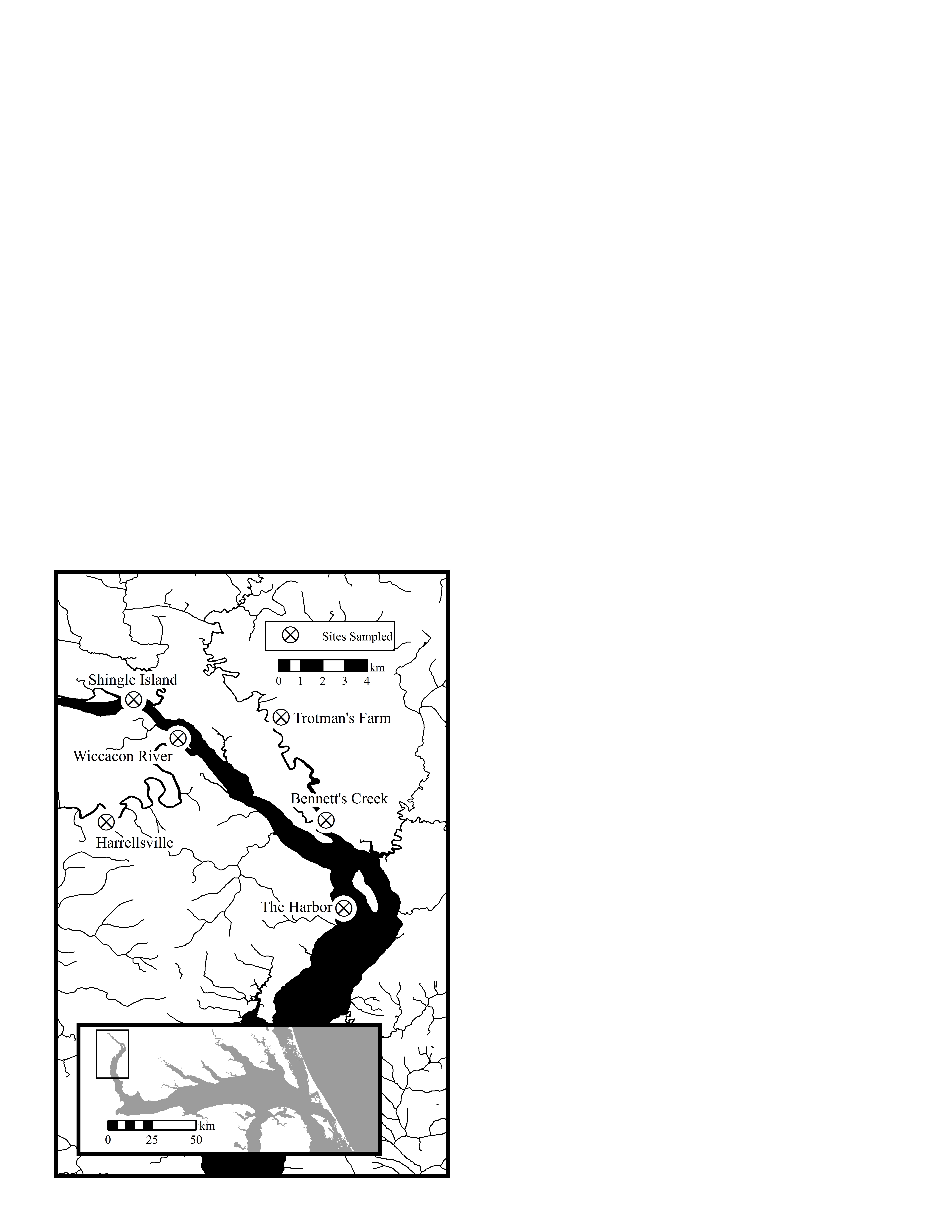


Fig. 1

Fig. 2



Fig. 3



Fig. 4



Fig. 5



Fig. 6

Fig. 7

Fig. 8