Spatiotemporal patterns in the export of dissolved organic carbon and chromophoric dissolved organic matter from a coastal, blackwater river

Dina M. Leech[1] · **Scott H. Ensign**[2] · **Michael F. Piehler**[3]

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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 to 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 remained relatively low 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 $\sim$60 % of the variance. DOC and CDOM absorption loads to the Albemarle Sound ranged from 2.63×10^{10} g $year^{-1}$ and 9.84×10^{10} m^2 $year^{-1}$, respectively, in a dry year and 7.9×10^{10} g $year^{-1}$ and 2.2×10^{11} m^2 $year^{-1}$, respectively, in a wet year, which are comparable to non-blackwater rivers with larger watersheds. 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.

Keywords Chowan River · CDOM optical properties · DOC load

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✉ Dina M. Leech
leechdm@longwood.edu

[1] Department of Biological and Environmental Sciences, Longwood University, Farmville, VA, USA

[2] Aquatic Analysis and Consulting, LLC, Morehead City, NC, USA

[3] Institute of Marine Sciences, The University of North Carolina at Chapel Hill, Morehead City, NC, USA

Introduction

Dissolved organic carbon (DOC) represents a major intermediate in the global carbon cycle through its stimulation of microbial metabolism (Jaffé et al. 2008). Coastal rivers serve as vital conduits that process and transport DOC between two main carbon reservoirs—the land and the ocean. Approximately, 200–250 Tg C is delivered to the coastal ocean each year from riverine export of DOC (Cole et al. 2007; Dai et al. 2012). Of this, 6.3 Tg C $year^{-1}$ are estimated to come from rivers draining the continental 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 CO_2 evasion (Hopkinson and Smith 2005; Herrmann et al. 2015).

Chromophoric dissolved organic matter (CDOM) represents the colored fraction of DOC and is primarily derived from the leaching and degradation of vascular 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, spatio-temporal changes in the quantity and quality of CDOM are of great ecological and environmental interest.

While most rivers in the continental US predominantly export inorganic carbon, rivers in the Southeast predominantly export organic carbon (Stets and Striegl 2012). Blackwater rivers are especially prominent along the US Southeastern Coastal Plain and are distinguished by their dark brownish-orange color derived from high concentrations of chromophoric humic substances but low suspended particles (Mulholland and Kuenzler 1979; Meyer 1990). Blackwater rivers are often overlooked when estimating DOC and CDOM loads to the coastal ocean because of their relatively small watershed size and low discharge (Mulholland and Kuenzler 1979; Meyer 1990; Spencer et al. 2013). However, recent evidence suggests blackwater rivers export DOC and CDOM loads comparable to major non-blackwater coastal rivers (Alkhatib et al. 2007; Spencer et al. 2013). For example, blackwaters draining to the South Atlantic Bight are estimated to 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). Consequently, the quality and quantity of DOC and CDOM exported from blackwater rivers likely varies with season.

In the present study, we examined seasonal and spatial trends in DOC and CDOM in the Chowan River, North Carolina, which discharges 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 load and yield 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 chemical structure of CDOM exported to the Albemarle Sound based on spectral characteristics and assessed 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 km^2 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 and 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 and June when samples were collected every 2 weeks. In 2010, samples were collected from all six sites at approximately monthly intervals between January and May. In total, we collected 132 and 148 samples for DOC and CDOM measurements, respectively.

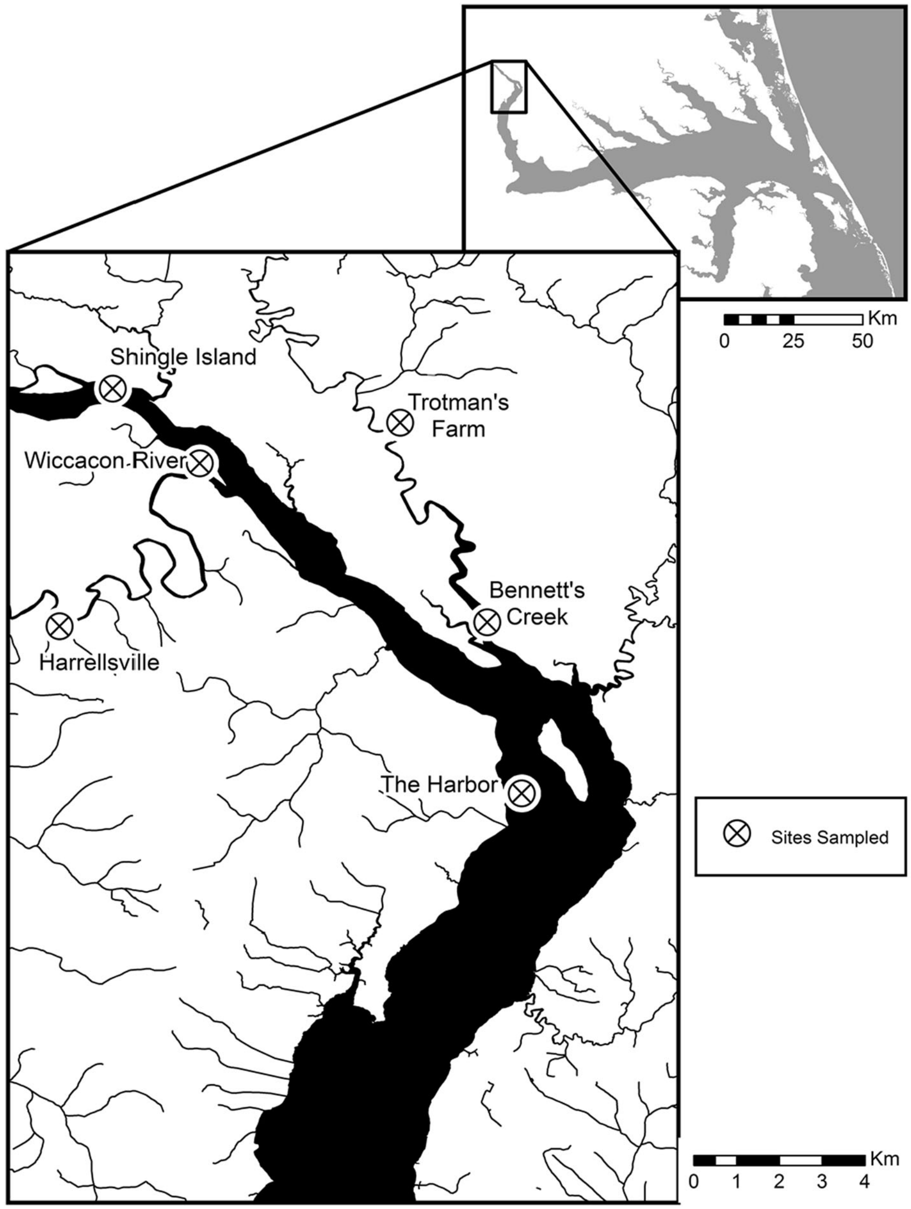

Fig. 1 Map of the six sampling sites along the Chowan River, North Carolina, United States. *Inset* shows the point of discharge into the Albemarle Sound, North Carolina

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 km^2) and then multiplied by the total area of the watershed (gauged plus ungauged or 12,665 km^2) to estimate total daily watershed discharge over the course of the study. We further used this method to estimate daily discharge in Chowan River from March 2005 to February 2015 to determine how our two study years compared to annual discharge values for the river. Over this 10-year period, discharge ranged from 1.53–5.45 km^3 $year^{-1}$ with a median of 3.06 km^3 $year^{-1}$. Therefore, March 2008–February 2009 represented a relatively ‘dry’ year (2.36 km^3 $year^{-1}$) while March 2009–February 2010 represented a ‘wet’ year (5.45 km^3 $year^{-1}$, highest annual discharge in the last 10 years).

We acknowledge that this method may underestimate discharge given that four of the gauging stations are located approximately 90 km upstream 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 to March 1976). Moreover, we tested our method of estimating discharge using historical data from our five gauged stations during the April 1974–March 1976 time period. The historical gauge often recorded oscillating negative followed by positive discharge values, which are reflective of the tidal influence at the mouth of the Chowan River (Supplemental Material). Our method did not predict these oscillation events; however, during periods of consistent outflow, our model generally estimated discharge within ±5–20 % of the gauged reading (Supplemental Material).

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 09:00–16:00 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 µm pore size) and kept at 4 °C. 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 50 mL polypropylene and polystyrene Beckman Dickinson Falcon centrifuge tubes.

DOC and CDOM measurement

DOC concentrations were measured as non-purgeable organic carbon within 1 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 and 800 nm was subtracted from the spectrum between 250 and 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, $a_\lambda = 2.303 \times A_\lambda / l$, where a_λ is the absorption coefficient at wavelength λ, A_λ 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 254–365 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 increasing potential for photodegradation of CDOM. Specific UV absorbance at 254 nm ($SUVA_{254}$) 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 $SUVA_{254}$ increases, aromaticity increases, indicating CDOM inputs from terrestrial sources. Spectral slopes between 275–295 nm ($S_{275–295}$) and 350–400 nm ($S_{350–400}$) 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 $S_{275–295}$ to $S_{350–400}$ (S_R) is used to characterize changes in CDOM source and character. The lower the S_R value, the more allochthonous the sample, the higher molecular weight CDOM, the less photodegraded (Helms et al. 2014). Specifically, S_R 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 absorption loading and yield estimation

To estimate loading of DOC and CDOM absorbance to the Albemarle Sound from the Chowan River, we used our measured DOC concentration and *a*350 observed at our furthest downstream station on the mainstem (the Harbor). Calculated daily loads for DOC and CDOM absorbance were estimated using the load estimator (LOADEST) program (Runkel et al. 2004) from 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). Note that DOC load is presented as a traditional mass flux (e.g., g C $year^{-1}$) while CDOM absorption load represents the delivery of absorptive property over time (e.g., m^2 $year^{-1}$, Spencer et al. 2013). To estimate yield, DOC and CDOM absorption 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 the mouth. Based on information compiled from the United States Environmental Protection Agency Storage and Retrieval (STORET) database, from 1976 to 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 was to assist the state of North Carolina in their efforts to restore river herring populations 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). Given that discharge was only estimated for the mouth of the Chowan River, the relationship between discharge and DOC and CDOM concentration were assessed with linear regression only at our furthest downstream site, the Harbor. Relationships between DOC concentrations and the CDOM optical proxies were also assessed using linear regression. A Moran's I test was performed to test for possible spatial autocorrelation in the dataset. Weak negative dispersion was detected in DOC concentration (Moran's $I = -0.05$, $p < 0.0001$) as well as absorbance at 254 (Moran's $I = -0.07$, $p < 0.0001$) and 350 nm (Moran's $I = -0.06$, $p < 0.0001$). Moran's I values for the CDOM quality parameters ranged -0.01 to 0.003 with p values greater than 0.05. Linear regression models should therefore be minimally affected by spatial autocorrelation.

Results

Summary of discharge during study period

Discharge in the Chowan River Watershed ranged from 2–790 m^3 s^{-1} and significantly varied with season ['H' Score $(H) = 72.26$, degrees of freedom $(df) = 3$, $p < 0.0001$] (Fig. 2). During the summer and fall (June–November), discharge was low, averaging 25 m^3 s^{-1} ± 7 standard deviation (SD). In contrast, discharge was 6.5 times greater in the winter and spring (December–May), averaging 163 m^3 s^{-1} ± 6 SD. When examined over a study year from April 2008–February 2009 vs. March 2009–February 2010, average daily discharge was twice as high during the second year of our study (158 m^3 s^{-1} ± 206 SD) compared to the first (70 m^3 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).

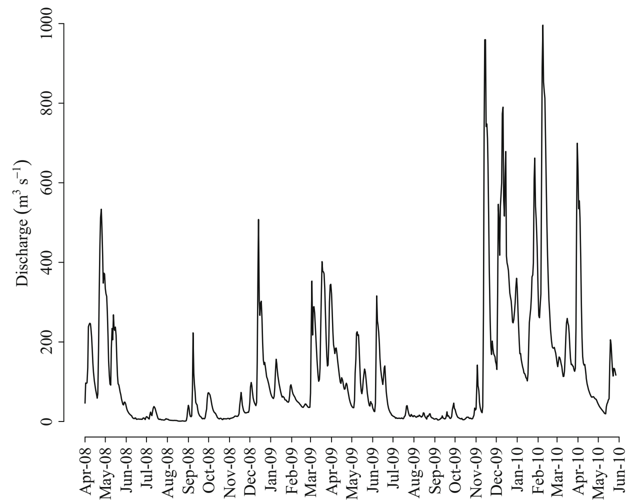

Fig. 2 Discharge (m^3 s^{-1}) for the Chowan River between April 2008 and May 2010. Due to the lack of gauging stations on the Chowan River, discharge was estimated from the five upstream gauging stations within the watershed, as described in the methods. Note the particularly low periods of discharge in the summer compared to the winter and spring

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, only a moderate relationship between DOC concentration and discharge was observed at our furthest downstream site ($R^2 = 0.24$, $p < 0.02$, $n = 20$). 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}).

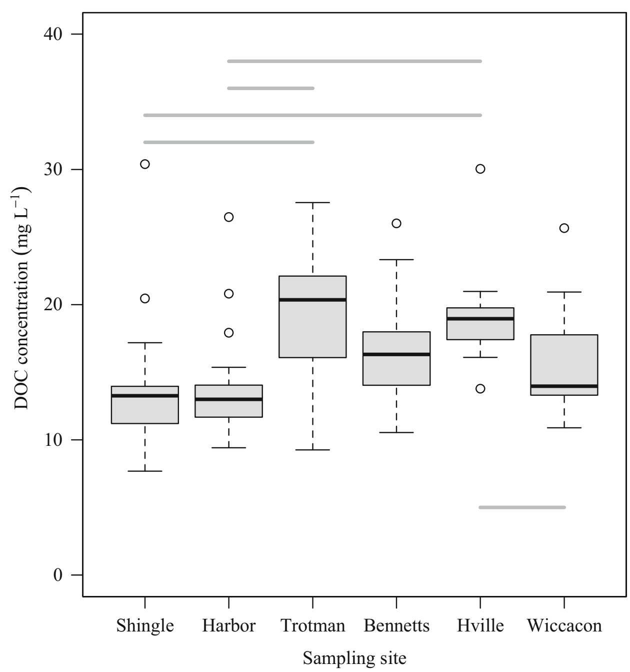

Fig. 3 Boxplots of the DOC concentrations (mg L^{-1}) observed during the two-year study across the six sampling sites. Based on a Kruskal–Wallis test, DOC concentration significantly varied across station ($H = 40.09$, $df = 5$, $p < 0.0001$), with DOC concentrations at the upstream sites on Bennetts 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 ($p < 0.05$)

Spatially, DOC concentration significantly varied across sampling sites ($H = 40.09$, $df = 5$, $p < 0.0001$). 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 1.05×10^{10} 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 2.63×10^{10} g year^{-1}. In the second study year (Spring 2009–Winter 2010), when DOC data were collected throughout all four seasons, the annual DOC load was estimated to be 7.90×10^{10} g year^{-1} (Table 1). Annual DOC yields for the same time periods were approximately 2.13 and 6.23 g m^{-2} year^{-1}, respectively (Table 1). 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. The spring of 2010 (i.e., March–May 2010) was a particularly wet period with a DOC load of 1.64×10^{10} g season^{-1} 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 $a350$ ($H = 7.62$, $df = 5$, $p = 0.01$). This suggests that CDOM of similar molecular weight and aromaticity entered the system across all six sampling sites. However, the absorbance of CDOM entering the system is significantly higher at the upstream sites on Bennetts Creek (Trotman's Farm, average $a350 = 65$ m^{-1} ± 17 SD) and the Wiccacon River (Harrellsville, average $a350 = 64.15$ m^{-1} ± 23 SD) compared to sites on the mainstem and at the mouths of the two tributaries (average $a350 = 45$ m^{-1} ± 13 SD).

Significant seasonal patterns in $a254$:$a365$ ($H = 41.17$, $df = 3$, $n = 140$, $p < 0.0001$), $SUVA_{254}$ ($H = 24.57$, $df = 3$, $n = 140$, $p < 0.0001$), $S_{275–295}$ ($H = 24.13$, $df = 3$, $n = 140$, $p < 0.0001$), $S_{350–400}$ ($H = 15.8$, $df = 3$, $n = 140$, $p = 0.001$) and S_R ($H = 37.83$, $df = 3$, $n = 140$, $p < 0.0001$) were observed across the six sampling sites. In general, $a254$:$a365$, $S_{275–295}$, and S_R decreased throughout the spring and early summer while $SUVA_{254}$ and $S_{350–400}$ increased, indicating that CDOM was increasing in molecular size and aromaticity and subjected to microbial degradation (Figs. 4, 5). From summer through autumn, the opposite pattern was generally observed, with $a254$:$a365$, $S_{275–295}$, and S_R increasing and $SUVA_{254}$ and $S_{350–400}$ decreasing (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, $a254$:$a365$, $S_{275–295}$, and S_R increased or remained relatively high, $SUVA_{254}$ decreased or remained relatively low, and $S_{350–400}$ 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 2009–2010.

CDOM absorbance at $a350$ also varied significantly across season ($H = 10.09$, $df = 3$, $p < 0.02$), but only

Table 1 Seasonal DOC and CDOM loads and yields to the Albemarle Sound from the Chowan River between March 2008 and May 2010 calculated using the load estimator (LOADEST) program

Time period	Season	Discharge (km^3 $season^{-1}$) (km^3 $year^{-1}$)	DOC load (g $season^1$) (g $year^{-1}$)	DOC yield (g m^{-2} $season^{-1}$) (g m^{-2} $year^{-1}$)	*a*350 load (m^2 $season^{-1}$) (m^2 $year^{-1}$)	*a*350 yield ($season^{-1}$) ($year^{-1}$)
March 2008–February 2009	Spring	1.34	–	–	6.45×10^{10}	5.10
	Summer	0.08	–	–	3.18×10^{9}	0.25
	Fall	0.21	2.42×10^{09}	0.15	6.82×10^{9}	0.54
	Winter	0.72	8.06×10^{9}	0.72	2.39×10^{10}	1.89
	Total	2.37	$\sim 2.63 \times 10^{10}$	$\sim$2.13	9.84×10^{10}	7.77
March 2009–February 2010	Spring	1.25	1.67×10^{10}	1.32	5.46×10^{10}	4.31
	Summer	0.33	4.49×10^{09}	0.35	1.77×10^{10}	1.40
	Fall	0.86	1.27×10^{10}	1.00	3.61×10^{10}	2.85
	Winter	3.01	4.51×10^{10}	3.56	1.12×10^{11}	8.85
	Total	5.45	7.90×10^{10}	6.23	2.20×10^{11}	17.50
March–May 2010	Spring	1.13	1.84×10^{10}	1.45	3.86×10^{10}	3.05

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). Estimates may underestimate DOC and CDOM absorption load/yield given the lack of exact discharge measurements at the mouth of the Chowan River

between the summer and winter. Generally, CDOM absorbance 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 absorbance in the spring, summer, and fall were higher in 2009–2010 compared to data collected in 2008.

CDOM absorption loading from the Chowan River to the Albemarle Sound was approximately 9.84×10^{10} m^2 $year^{-1}$ during the first year of the study, which again was a relatively dry year. During the second, wetter year of the study, CDOM absorption load increased to 2.2×10^{11} m^2 $year^{-1}$. CDOM yields from the Chowan watershed for the two study years were 7.77 and 17.5 $year^{-1}$, 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 ($R^2 = 0.59$, $p < 0.0001$, $n = 118$) and *a*350 ($R^2 = 0.58$, $p < 0.0001$, $n = 118$). 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 15 mg L^{-1} (Fig. 6). When each site was analyzed individually, CDOM proxies *a*254 and *a*350 best predicted DOC concentration at the upstream site on Bennetts Creek (Trotman's Farm), explaining 79 % of the variance, and least on the mainstem at Shingle Island and the Harbor, explaining only 12 and 19 % of the variance, respectively. $S_{275-295}$ ($R^2 = 0.25$, $p < 0.0001$, $n = 118$) and S_R ($R^2 = 0.21$, $p < 0.0001$, $n = 118$) 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; Herrmann et al. 2015), 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. Here, the quality and quantity of DOC and CDOM exports from the blackwater Chowan River to the Albemarle Sound varied systematically over time, but not space, and were comparable to major non-blackwater rivers with larger watersheds and higher discharge. We were also surprised to learn that commonly used optical indices, based on CDOM absorbance, did not always accurately predict the DOC concentration of blackwaters. Together, these findings suggest blackwater rivers warrant closer consideration when modeling global carbon budgets.

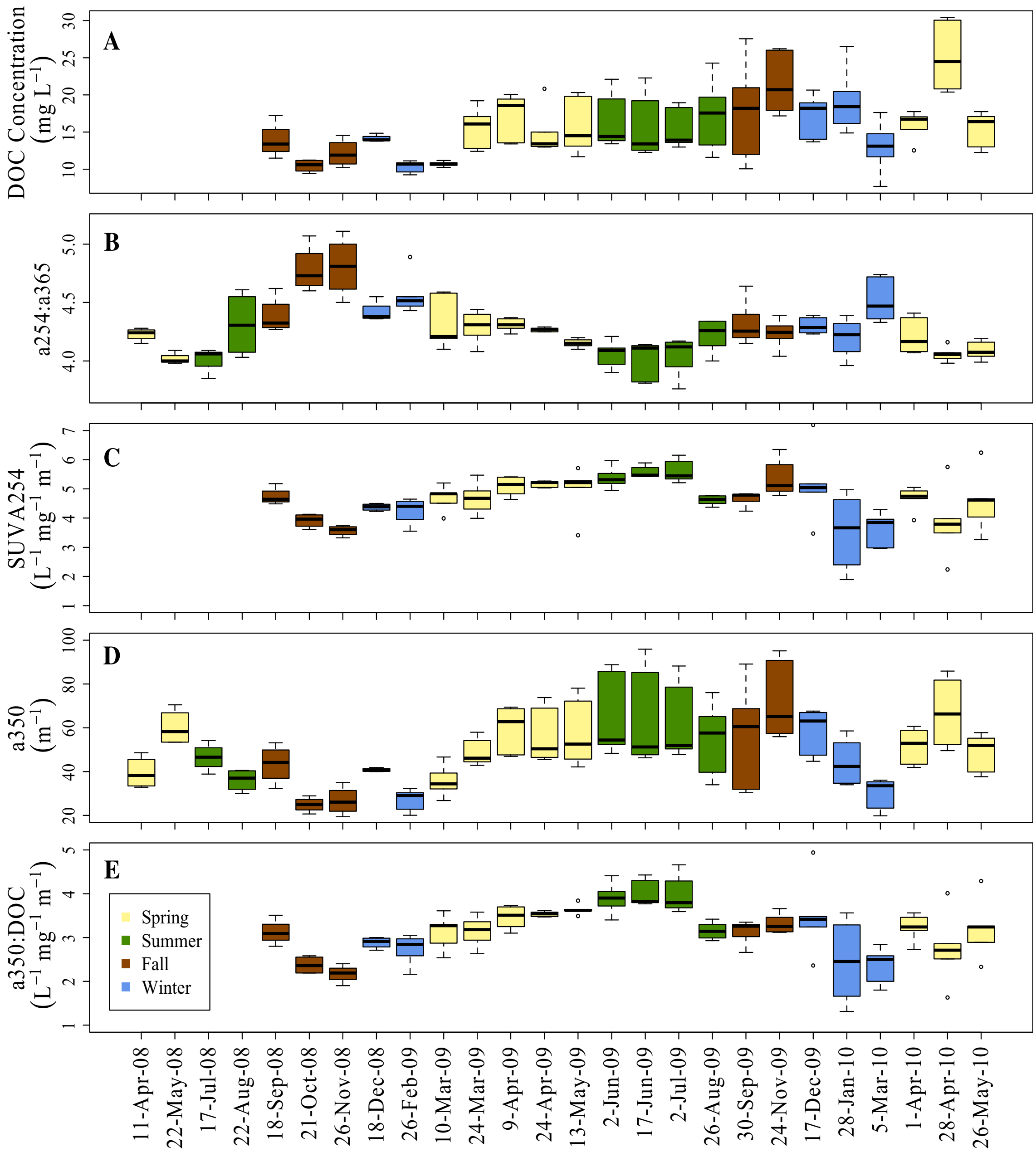

Fig. 4 Boxplots of **a** DOC concentration (mg L^{-1}) and **b** CDOM optical proxies *a*254:*a*365, **c** $SUVA_{254}$, **d** *a*350, **e** *a*350:DOC across time. From April 2008 through December 2008, data were compiled from the two sites on the mainstem and at the mouths of the two tributaries. Beginning 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

Spatio-temporal patterns in the quality of CDOM exports

CDOM optical proxies displayed distinct variations across season but not sampling site. Hence, CDOM quality in the lower Chowan River watershed, including the mainstem, Bennetts Creek, and Wiccacon River, appears to vary in a similar manner over time. Values for the *a*254:*a*365 ratio, $SUVA_{254}$, $S_{275–295}$, $S_{350–400}$ 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. 2012; 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 (Jaffé et al. 2008; Shen et al. 2012). In the spring and early summer, increasing

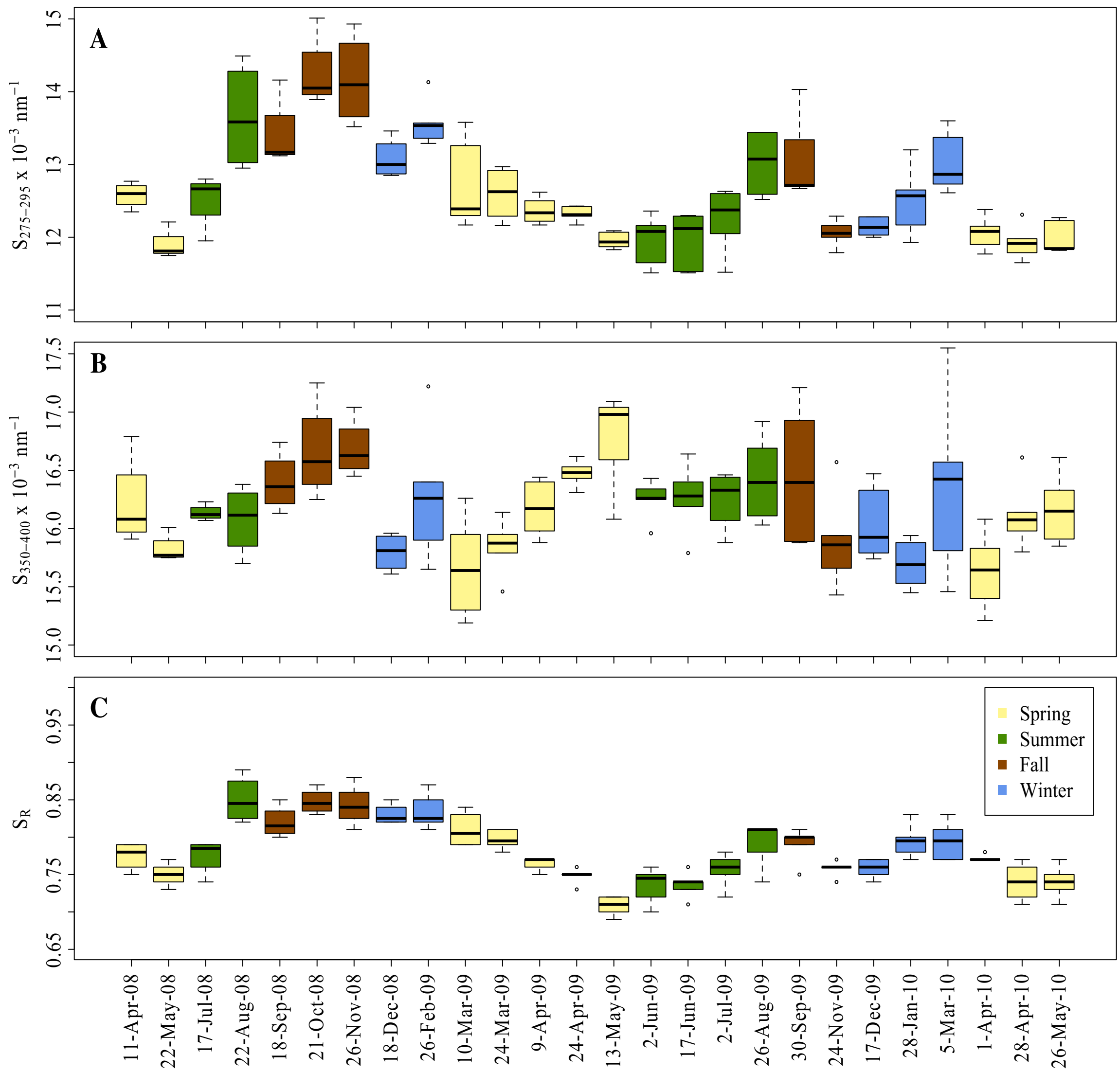

Fig. 5 Boxplots of the spectral slopes between **a** 275–295 nm and **b** 350–400 nm as well as **c** the spectral slope ratio (S_R). From April 2008 through December 2008, data were compiled from the two sites on the mainstem and at the mouths of the two tributaries. Beginning in February 2009, data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

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 are 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 μg 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 and photobleaching in rivers and streams are generally reduced with colder water

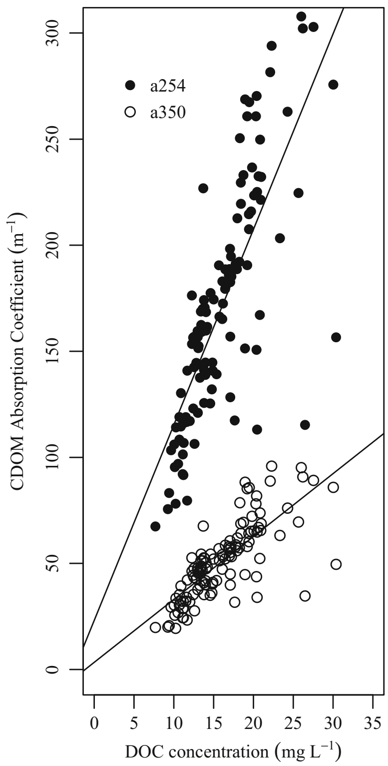

Fig. 6 Relationship between DOC concentrations and CDOM absorption coefficients (*a*254, *a*350, respectively) within the blackwater Chowan River watershed, North Carolina, United States. Because these two optical indices explained only 58 % of the variance in DOC concentration, the inverse slope (i.e., 0.34) was not used to calculate the mass of CDOM at 350 nm. Instead, we present CDOM load in Table 1 as the delivery of absorptive property at 350 nm, similar to Spencer et al. (2013), with the unit m^2 $year^{-1}$

temperatures and lower solar intensity, allowing labile compounds to persist and be transported downstream.

To our knowledge, the fate and influence of DOC/CDOM exports to the Albemarle Sound are currently unknown. 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). Further investigation is needed to test these hypotheses that are central to understanding carbon processing through the coastal ocean over several temporal scales.

Spatio-temporal patterns in the quantity of DOC and CDOM exports

Except for the two upstream sites on Bennetts Creek and the Wiccacon River, we observed no significant difference in DOC and CDOM concentration/absorbance over time or between sampling sites. Measured DOC (range 7.69–30.39 mg C L^{-1}) and CDOM (range 19.9–95.9 m^{-1}) concentrations/absorbances in the Chowan River and its tributaries were similar to other blackwater systems in the Southeastern US (Helms et al. 2008; Ensign et al. 2012; Avery et al. 2003; Hanley et al. 2013; Spencer et al. 2013) as well as tropical rivers that drain the rich organic soils of the Amazon Rainforest (Moreira-Turcq et al. 2003; Yamashita et al. 2010) and the Democratic Republic of the Congo (Spencer et al. 2010). DOC concentrations in the Chowan River were also higher than those reported for the nearby Roanoke River, NC (2.7–8.8 mg C L^{-1}; Hossler and Bauer 2013) whose watershed is approximately twice its size (25,294 km^2).

Riverine exports of DOC and CDOM are dependent on constituent concentration as well as discharge. While we did not observe significant temporal differences in DOC concentration and CDOM absorbance, discharge did vary with season and between the two study years. DOC and CDOM exports ranged from 2.63×10^{10} g $year^{-1}$ and 9.84×10^{10} m^2 $year^{-1}$, respectively, in a 'dry' year and 7.9×10^{10} g $year^{-1}$ and 2.22×10^{11} m^2 $year^{-1}$, respectively, in a 'wet' year. These loads are comparable to other blackwater rivers in the Southeastern US, such as the Edisto River (DOC load = 4.13×10^{10} g $year^{-1}$, CDOM absorption load = 8.93×10^{10} m^2 $year^{-1}$; Spencer et al. 2013), as well as non-blackwater 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) contribute disproportionately to the CDOM pool of the coastal ocean. Annual DOC and CDOM yields in the Chowan River ranged from 2.23 g m^{-2} $year^{-1}$ and 6.37 $year^{-1}$, respectively, in a dry year and 6.91 g m^{-2} $year^{-1}$ and 17.5 $year^{-1}$, 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} $year^{-1}$ and 1.25 $year^{-1}$, respectively; Spencer et al. 2013).

In both years, DOC and CDOM exports were greatest in the winter and early spring when discharge was highest. Our optical data indicate CDOM quality varies greatly during this time period, with a general increase in molecular weight and aromaticity from winter to early spring. Again, the fate and influence of these varying organic matter inputs to the coastal ocean are currently unknown. 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). Consequently, a smaller proportion of the CDOM exports from the Chowan River and its other blackwater tributaries (i.e., the Alligator, Little, North, Pasquotank, and Perquimans Rivers) is likely to flocculate to the sediment due to increased salinity (Ertel et al. 1991). The probability of DOC becoming incorporated into the estuarine food web or photomineralized may therefore increase. Recent estimates of primary production, bacterial respiration, 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} $year^{-1}$ (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 (Secchi depth range = 0.15–1.25 m, North Carolina Department of Water Quality) likely shift primary production in the Albemarle Sound to the lower end of the 50–500 g C m^{-2} $year^{-1}$ range. Riverine organic carbon inputs from blackwater systems may therefore represent an important source of carbon to the estuarine food web, possibly increasing the amount of carbon respired to the atmosphere.

Relationship between DOC concentration and CDOM optical proxies

A potential problem with estimating carbon exports from blackwater rivers is that currently published models used to estimate DOC concentration 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 $S_{275–295}$ and $S_{350–400}$ only explained ~21–25 % of the variance in DOC concentration. For unknown reasons, CDOM was particularly poor at predicting the DOC concentration of the mainstem of the Chowan River compared to the two tributaries. This may be due to differences in connectivity to the terrestrial watershed. Upstream sites on the tributaries likely receive more inputs of 'fresh' CDOM while the mainsteam is primarily comprised of CDOM 'aged' by photobleaching and/or microbial degradation (Helms et al. 2014). Therefore, a larger proportion of the DOC pool of the mainstem may be less to non-chromophoric. This is generally supported by differences in the

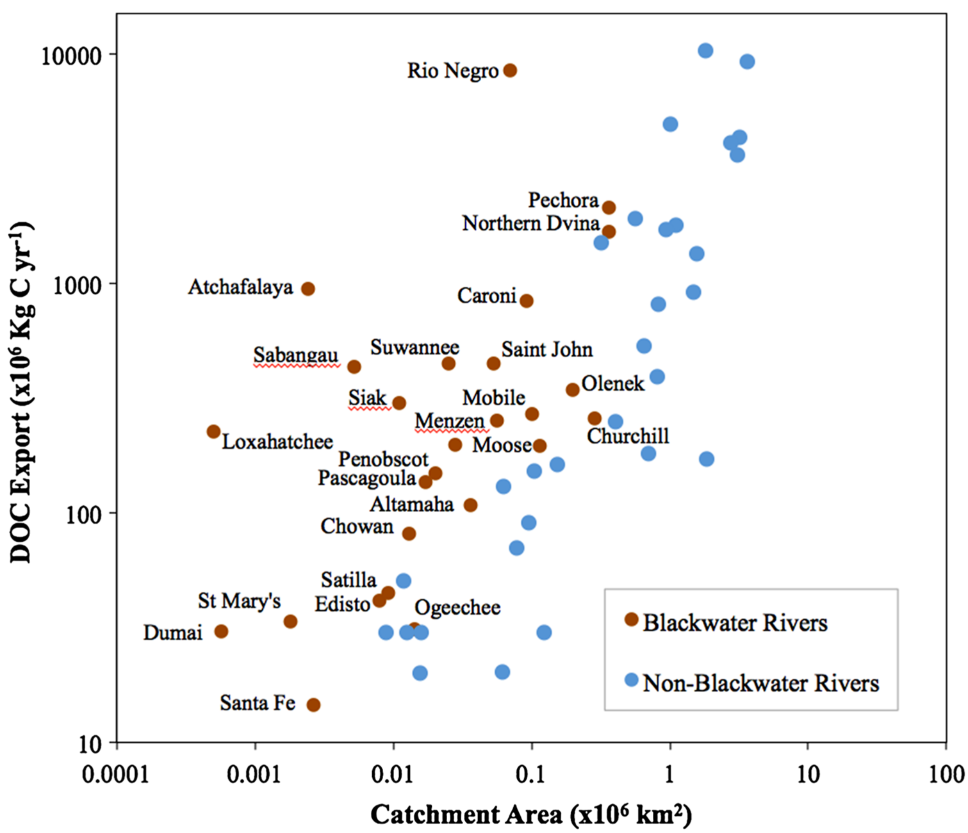

Fig. 7 DOC export vs. catchment area for several non-blackwater and blackwater rivers. Figure is modified from Alkhatib et al. (2007) and includes data from Baum et al. (2007), Dai et al. (2012), Hanley et al. (2013), Hopkinson et al. (1998), Moore et al. (2011), and Spencer et al. (2013). Blackwater rivers are labeled for reference. Non-blackwater rivers are representative of those commonly used in calculating estimates of global DOC export to the coastal ocean

a350:DOC ratio in the upstream tributary sites versus the mainstem (Fig. 4e).

Previous studies examining a variety of non-blackwater riverine systems have reported much stronger correlations between DOC and CDOM 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} (Fig. 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.

Global relevance of DOC and CDOM exports from blackwater rivers

Except for a few well-studied systems (e.g. the Suwannee River), blackwater rivers are generally underrepresented in calculations of global carbon budgets. The more recent estimation from Dai et al. (2012) appears to be the most inclusive, with 18 out of the 118 rivers possessing a DOC concentration consistent with blackwaters. 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 they are comparable to non-blackwater rivers with catchment areas several orders of magnitude larger (Fig. 7; Alkhatib et al. 2007).

Comparing the DOC export from several blackwaters worldwide, we found a large variation in export between rivers with similar catchment areas (Fig. 7). Unlike non-blackwater rivers, DOC export from blackwater rivers does not consistently increase with increasing catchment size. Discharge may be more critical than catchment size in determining total DOC export in coastal blackwater rivers (Fig. 8). Together, these 25 blackwater rivers alone represent approximately 7–9 % of the DOC exported to the coastal ocean. This is based on the assumption that current estimates of total riverine dissolved organic carbon exports are correct. However, our results suggest these estimates appear to underestimate the contributions of small blackwater rivers.

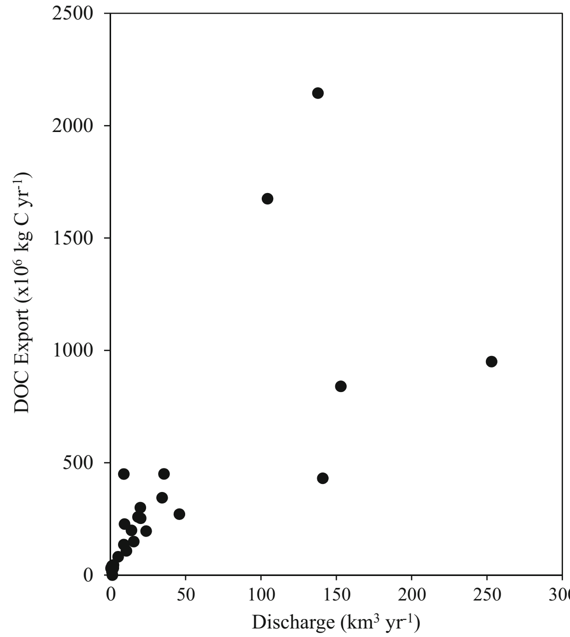

Fig. 8 DOC export vs. discharge for several blackwater rivers. DOC export data are from Alkhatib et al. (2007), Baum et al. (2007), Dai et al. (2012), Hanley et al. (2013), Hopkinson et al. (1998), Moore et al. (2011), and Spencer et al. (2013). Because the Rio Negro was a large outlier, it was omitted from the plot

Conclusions

Blackwater rivers, despite their low discharge, contribute substantial amounts of DOC and CDOM to the coastal ocean which affect the balance between primary production and bacterial respiration in receiving estuaries, and consequently, CO_2 evasion to the atmosphere. Our results from the Chowan River emphasize that both the quality and quantity of dissolved organic matter exported by coastal blackwater rivers is dynamic and may vary in predictable patterns with season that persist across years of varying precipitation. Understanding these patterns may increase our knowledge of temporal variation in carbon processing and transport through the coastal ocean and improve our estimates of global carbon fluxes between the land, ocean, and atmosphere. Moreover, we caution that commonly used CDOM optical indices may be less reliable when used to estimate the DOC concentration of blackwaters and encourage further method development.

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