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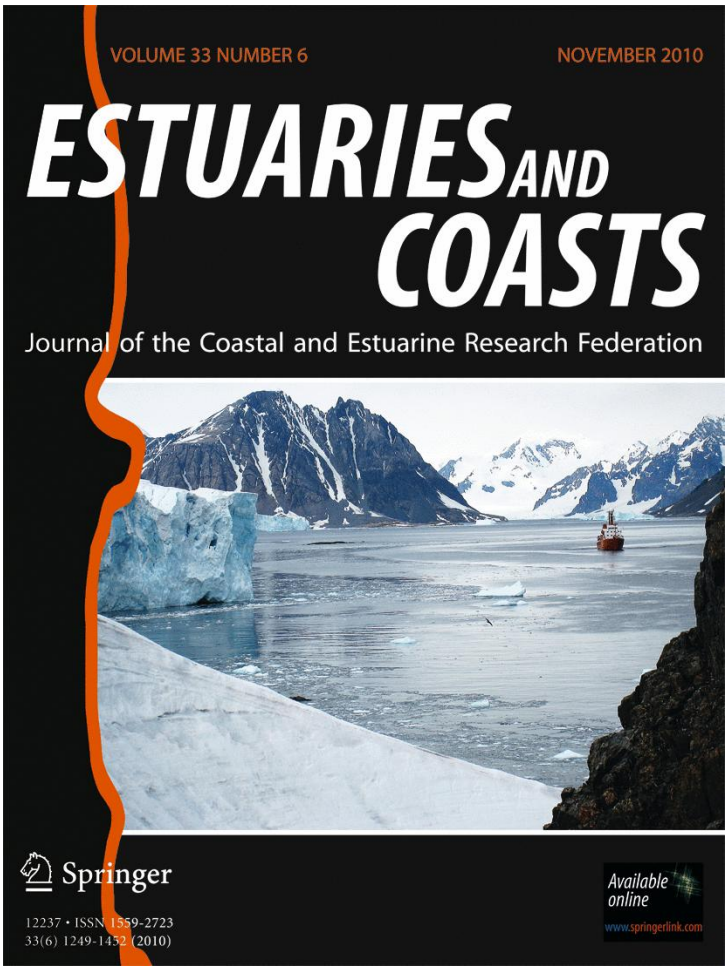

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Interannual Variation in Photosynthetically Significant Optical Properties and Water Quality in a Coastal Blackwater River Plume

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Abstract Surface water optical characteristics, nutrients, and planktonic chlorophyll *a* concentrations were analyzed in the Cape Fear River (CFR) plume over a 2-year period. CFR discharge during the dry year (109±105 m^3s^{-1}) was only 25% of the wet year discharge (429±337 m^3s^{-1}). Partitioning the contributions of phytoplankton pigments, non-pigmented particles, and colored dissolved organic matter (CDOM) to the absorption of photosynthetically active radiation (PAR) indicated that CDOM was the dominant contributor to PAR absorption. Particulate absorption was relatively greater during the dry year. Pigment absorption was minor and varied little among stations or between years. Chlorophyll *a* concentrations were reduced at the most plume-influenced stations during the wet year, despite lower turbidity and higher nitrate concentrations. Ammonium and orthophosphate concentrations were not different between years. CDOM absorption [$a_{CDOM}(412)$] ranged from 0.05 to 8.25 m^{-1} with highest values occurring near the CFR mouth. Our results suggest that for coastal ecosystems with significant blackwater river inputs, CDOM may exert a major limiting influence over near-shore primary production.

Keywords South Atlantic bight · River plumes · Optical properties · Water quality · Colored dissolved organic matter · Chlorophyll

Introduction

The Cape Fear River (CFR) is one of the largest blackwater (high-colored dissolved organic matter, CDOM, levels) riverine systems on the eastern coast of the USA. The CFR watershed encompasses 23,310 km^2, the largest river

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basin within North Carolina (Mallin et al. 1999a; Benedetti et al. 2006). The CFR is a Piedmont-derived sixth order river and, in conjunction with two Coastal Plain-derived fifth order black-water tributaries (Black and Northeast Cape Fear), discharges low-salinity water with high levels of suspended particles, nutrients, and CDOM to the coastal South Atlantic Bight (Mallin et al. 2002; Kowalczuk et al. 2003; Benedetti et al. 2006; Lin et al. 2008). Large quantities of suspended sediments and highly colored swamp water are forced into the CFR estuary and plume during high flow events, resulting in increased light attenuation and suppressed phytoplankton production (Mallin et al. 1999a, b, 2002; Mallin and Corbett 2006). Inherent and apparent optical properties (IOP and AOP, respectively) are very dynamic in the coastal waters adjacent to the CFR (Kowalczuk et al. 2006, 2009a). Changes in optical properties are linked to variation in CFR flow, the quantity and composition of transported materials, transformations within the system and differences in the relative contributions of dissolved and particulate material (Kowalczuk et al. 2003, 2009b; Shank et al. 2005).

The plume of the CFR is well defined because the river discharges directly into the coastal ocean, thus is not subject to dampening effects associated with intervening barrier islands, bays, or sounds (Lin et al. 2008). Under average river discharge conditions, the CFR plume is generally confined to the south-facing coastal shoreline in upper Long Bay and extends westward (Xia et al. 2007). Frying Pan Shoals inhibits the plume from spreading from Long Bay eastward to Onslow Bay (Fig. 1). Due to the effects of tidal and wind mixing, the water column in the plume area is well mixed, except in the deeper channels (Xia et al. 2007). The CFR also exhibits extreme variability in flow; the mean annual discharge of the CFR is usually less than the standard deviation (Carpenter and Yonts 1979). These variations in discharge may extend the CFR plume on the order of tens of kilometers into the coastal ocean (or 100 km or more along the shelf during extreme, high-flow events, e.g., Hurricane Floyd) or position it inside of the estuary, during periods of intense drought (Mallin et al. 2002), affecting the delivery of terrestrially derived particulates, CDOM, and nutrients to the coastal ocean.

The optical properties of water masses within river plumes are important in both biological (primary productivity) and chemical (photochemical) processes (Mopper and Kieber 2002; Mallin et al. 2005). The high turbidity and CDOM levels of the CFR plume limit phytoplankton production during periods of high river flow (Mallin et al. 1999a, b; Lin et al. 2008). These materials also provide optical tracers for delineating both water-mass sources and the plume spatial extent (Johnson et al. 2001). Optical properties of water masses may be informative about natural and anthropogenic influences on primary production within the plume, as affected by variable river discharge. The IOP, spectral absorption coefficient of seawater [$a_{\mathrm{tot}}(\lambda)$] is defined as a sum of four components:

$$a_{\mathrm{tot}}(\lambda) = a_w(\lambda) + a_{\Phi}(\lambda) + a_{\mathrm{detritus}}(\lambda) + a_{\mathrm{CDOM}}(\lambda) \quad (1)$$

Where, $a_w(\lambda)$ is the absorption coefficient of pure water, $a_{\Phi}(\lambda)$ is the absorption coefficient of phytoplankton pigments, $a_{\mathrm{detritus}}(\lambda)$ is the absorption coefficient of non-pigmented particles and $a_{\mathrm{CDOM}}(\lambda)$ is the absorption coefficient of colored or chromophoric dissolved organic matter. The absorption of pure water measured by Pope and Fry (1997) is almost constant in natural waters and may be omitted in further analysis because it does not contribute to a variability of total absorption coefficient of seawater. Equation 1 may be simplified:

$$a_{t-w}(\lambda) = a_{\mathrm{detritus}}(\lambda) + a_{\mathrm{CDOM}}(\lambda) + a_{\Phi}(\lambda) \quad (2)$$

Where $a_{t\text{-}w}(\lambda)$ is total absorption coefficient of seawater less that due to water and is determined primarily by the additive spectral absorption contributions of three components: non-pigmented particles [$a_{\mathrm{detritus}}(\lambda)$], CDOM [$a_{\mathrm{CDOM}}(\lambda)$] and phytoplankton pigments [$a_{\Phi}(\lambda)$] (Gallegos and Jordan 2002; Babin et al. 2003). In oceanic case 1 waters, $a_{\mathrm{detritus}}(\lambda)$ and $a_{\mathrm{CDOM}}(\lambda)$ are low across the spectral range of photosynthetically active radiation (PAR, 400-700 nm) but often co-vary with phytoplankton chlorophyll *a* concentration, which dominates absorption and back scattering (Prieur and Sathyendranath 1981). The euphotic zone is often deeper than the mixed layer resulting in a high-light, nutrient-limited surface layer and a lower light, higher nutrient lower layer (Mallin et al. 2005). The shape and magnitude of the $a_{t\text{-}w}(\lambda)$ spectra in coastal case 2 waters are poorly documented, but contributions of the three components to $a_{t\text{-}w}(\lambda)$ across PAR are believed to exhibit independent variation (Babin et al. 2003). The higher spectral absorption in case 2 waters results in a mixed layer that is deeper than the euphotic zone leading to high-nutrient light-limited conditions.

As part of the Coastal Ocean Research and Monitoring Program (CORMP), we have been analyzing spatial and temporal variation in water quality, phytoplankton abundance, IOP, and AOP characteristics in the CFR's discharge plume and adjacent coastal waters (Kowalczuk et al. 2003, 2006, 2009a, b; Mallin et al. 2005). Here, we examined spatial and temporal variations in apparent and inherent optical properties across PAR in relation to planktonic chlorophyll *a* concentrations and possible forcing variables such as river discharge, salinity, and nutrient concentrations (which vary with river discharge). Determining the relative contributions by detritus, CDOM, and pigments to $a_{t\text{-}w}(\lambda)$ integrated across PAR is important in determining how

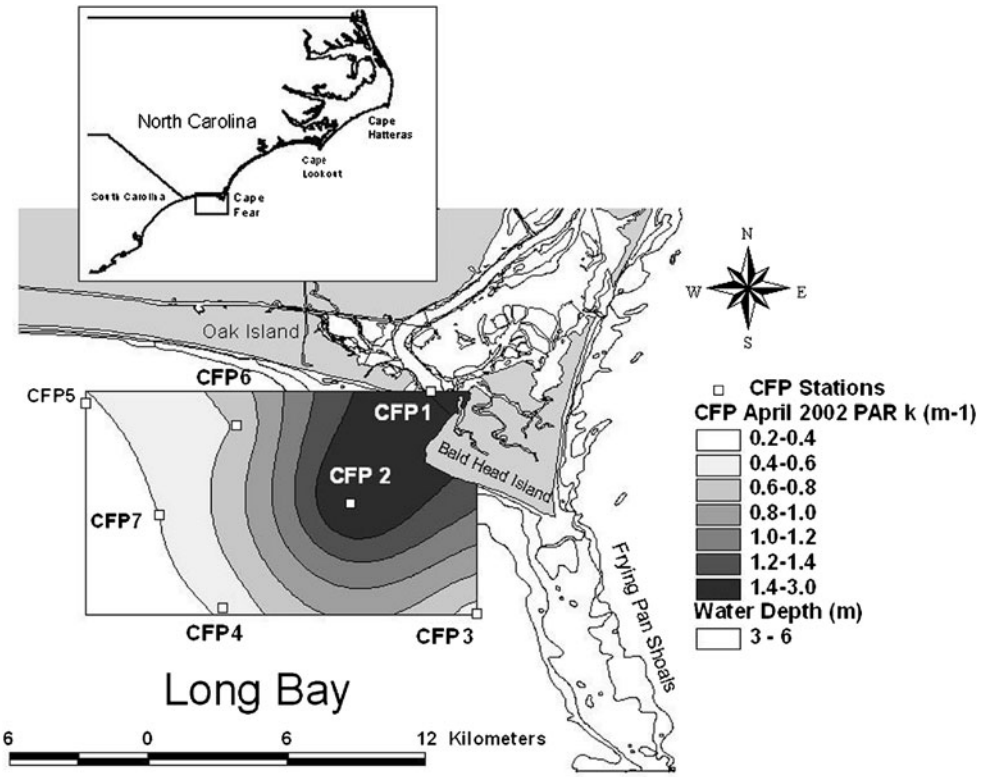

Fig. 1 Sample station locations and distribution of K_0(PAR) during 24 April 2002 sampling of the CORMP Cape Fear River (CFP) plume stations

these components control light availability to phytoplankton. The sampling period encompassed a year of below normal rainfall, from August 2001 to August 2002 (14.1 cm versus a 30-year average of 21.4 cm, National Oceanic and Atmospheric Administration (NOAA), National Climatic Data Center) and a year of above normal rainfall from August 2002 to August 2003 (23.6 cm). The dry period from 2001 to 2002 represented the end of a 4-year drought (1998-2002) spanning the USA, Southern Europe, and Southwest Asia (Hoerling and Kumar 2003).

Materials and Methods

Study Site

A grid of seven stations from the CFR mouth to approximately 13 km offshore (Fig. 1) was sampled during ebb tide at approximately monthly intervals between 15 August 2001 and 12 August 2003. Sampling was designed to study variation in the extent of the CFR plume during high and low discharge periods. Station CFP1 was located at the mouth of the CFR within the estuary proper; CFP2 was located approximately 5 km southwest of the CFR mouth in the direct influence of CFR discharge. Since the CFR plume is known to flow to the west of the estuary mouth (Xia et al. 2007), station CFP3, located east of the CFR mouth on Frying Pan shoals, served as a control station (Mallin et al. 2005). The remaining stations (CFP4-7) were distributed 7–12 km to the west and southwest of the CFR mouth. All seven stations had approximately 10 m water depths. Discharge at the Cape Fear River mouth (Fig. 2) was calculated according to Carpenter and Yonts (1979) using daily average river flow data from three US Geological Survey gaging stations (Black River at Tomahawk, Chinquapin, and Cape Fear River Lock and Dam #1).

Optical Water Sampling

Optical data were collected using methods consistent with standard published measurement protocols (Mueller and G. S. Fargion, 2002). At each station, simultaneous scalar irradiances were measured in the air and in the water using scalar quantum PAR (400-700 nm, photosynthetically active radiation) sensors (LiCor LI-193SA) connected to a LiCor LI-1000 data logger. The air scalar quantum sensor was mounted above deck on a 2-m pole 5 cm above a 0.6-m diameter black disk to reduce surface reflection; the water sensor was mounted to a weighted LiCor-lowering frame attached to a metered cable. The air sensor setup minimizes the effect of vessel roll for surface irradiance measurements and approximates 2π steradians of exposure (Miller and McPherson 1995). Vertical attenuation coefficients for scalar irradiance [K_0(PAR)] were calculated by regressing percentages of surface irradiance (SI) against depth at discrete 1 m depth intervals averaging both the downcast and upcast measurements (Mallin et al. 2005).

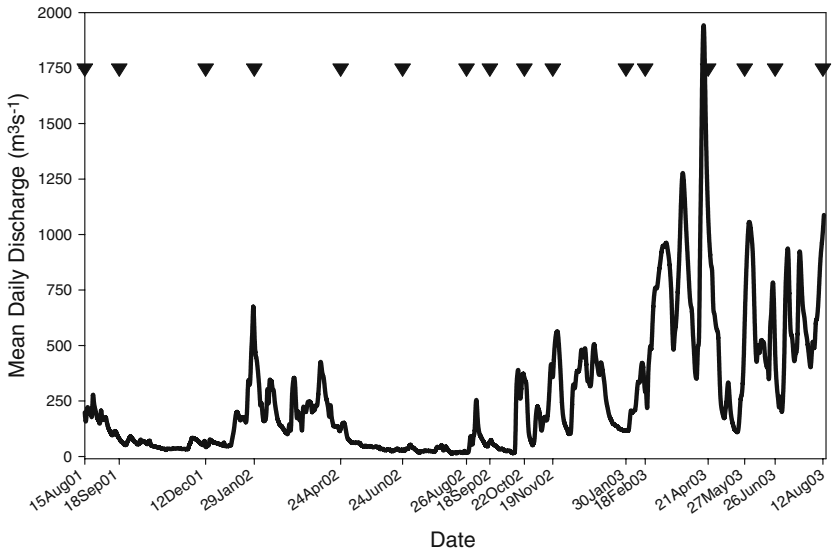

Fig. 2 Mean daily discharge at the Cape Fear River mouth during CORMP sampling (*triangles*) from 15 August 2001 to 12 August 2003

Salinity and turbidity (NTU) were measured in situ using an YSI 6920 Water Quality Monitoring system linked to an YSI 610D display unit. The YSI 6136 nephelometric turbidity sensor was two-point calibrated (0 and 100 NTU) using a formazin standard.

Surface water samples (4 l) were collected at each station and analyzed for nutrients and the contributions of non-pigmented detrital particles, methanol-soluble pigments (primarily chlorophyll *a*), and absorption by CDOM to the IOPs of the water ($a_{\text{detritus}}(\lambda)$, $a_{\Phi}(\lambda)$, and $a_{\text{CDOM}}(\lambda)$, m^{-1}). Water samples were collected using a pre-rinsed bucket, stored in HPDE bottles in the dark on ice in coolers, and processed in the laboratory the following morning. Spectral absorbance [$a(\lambda)$] of particulate fractions was determined from 350 to 800 nm at 2-nm resolution using a fiber optic spectrometer (Ocean Optics USB2000) by the quantitative filter technique (47 mm Whatman GF/F glass fiber filters) using water volumes ranging from 500 ml to 2 l, depending on particle load (Roesler 1998). Filters were mounted in plastic slide mounts and inserted into an inline filter holder. A collimated beam of light from a halogen light source was projected through the filters. Path-length amplification of the GF/F filters was corrected as described by Roesler (1998). Absorbance was converted to absorption coefficients (m^{-1}) by multiplying the absorbance by 2.303 [i.e., ln(10)] and multiplying by A/V, where A is the area of the filter and V is the volume of seawater filtered (m^3). The spectral absorption coefficients of non-pigmented particles, [$a_{\text{detritus}}(\lambda)$], were determined after pigments were extracted from the filters for 2 h in the dark with methanol; absorption coefficients for phytoplankton pigments, [$a_{\Phi}(\lambda)$], were calculated from the difference between the raw and methanol-extracted filter spectra normalized to a Milli-Q wetted blank filter. Final estimates of $a_{\text{detritus}}(\lambda)$ and $a_{\Phi}(\lambda)$ were baseline corrected by subtracting measured spectral values of $a_{\text{detritus}}(750)$ and $a_{\Phi}(750)$ from all measured values of $a_{\text{detritus}}(\lambda)$ and $a_{\Phi}(\lambda)$, respectively. It is important to note that $a_{\Phi}(\lambda)$, as described here, includes absorption by all pigments extracted in the methanol, which may include pigments other than solely chlorophyll *a* (Babin et al. 2003).

Absorption by CDOM [$a_{\text{CDOM}}(\lambda)$], the CDOM absorption coefficient at λ=412 [$a_{\text{CDOM}}(412)$] and spectral slope (S) were measured from spectrophotometric scans (300-800 nm) in 10 cm quartz cuvettes on water samples filtered through a 0.2 µm Nucleopore filter. Milli-Q water was used as a reference. CDOM spectra were baseline corrected by subtracting the absorbance at 750 nm from each spectral value (λ). Absorbance values were converted into absorption coefficients [m^{-1}] by multiplying by 2.303 and dividing by the path length (0.1 m; Kirk 1994). The spectral slope (S), which describes the exponential decrease in CDOM absorption with increasing wavelengths $\left[a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0)e^{-S\,(\lambda-\lambda)}_{0}\right]$, was determined from 300-500 nm using non-linear regression (Kowalczuk et al. 2005). We were primarily interested in how non-pigmented particles, CDOM, and phytoplankton pigments affected the availability of PAR and phytoplankton photosynthesis, thus, we calculated a(PAR) values by integrating $a(\lambda)$ for each of the three fractions from 400 to 700 nm.

Nutrient and Chlorophyll Analyses

Water samples for nutrient analysis were split with half of the volume filtered through 25 mm Gelman A/E glass fiber filters (nominal pore size 1.0 µm). The filtrate was stored frozen until used for inorganic nutrient analysis. Unfiltered

(total N and total P) and filtered (nitrate, nitrite and orthophosphate) samples were analyzed using a Bran & Luebbe Auto Analyzer 3. Samples for ammonium were field-preserved with phenol, stored on ice, and analyzed in the laboratory according to the methods of Parsons et al. (1984). Chlorophyll *a* concentrations were determined from the glass-fiber filters used for filtering samples for nitrate + nitrite ions and orthophosphate ion analyses. All filters were wrapped individually in aluminum foil, placed in an airtight container with desiccant, and stored in a freezer until processed. To extract pigments, the filters were immersed in 10 ml of 90% acetone solution and allowed to extract for 18–24 h. Acetone extracts were analyzed for chlorophyll *a* using a Turner 10-AU fluorometer (Welschmeyer 1994).

Statistical Analyses

Data were tested for normality using the Kolmorogov-Smirnov test and were log transformed, if necessary, before statistical analyses. Among-station variation within years and between year within-station differences among annual station means of physical, nutrient, and optical data were tested for significance ($p<0.05$) using one-way ANOVA in SAS (PROC GLM); means were then ranked using Fisher's LSD test (Mallin et al. 2005). Pooled station data were used to compare overall sample region differences between the dry and wet years. Regression was used to compare relationships between the IOP $a_{t\text{-}w}$(PAR) and the AOP K_0(PAR) for both the dry and wet years. All data are reported as means ± standard deviation.

Results

Sixteen sampling cruises were completed during the 2-year period of this study (Fig. 2). River discharge varied almost 150-fold over the sampling period (13-1,916 m^3s^{-1}); discharge rates during actual cruise sampling dates varied about 50-fold, from a low of 19 m^3s^{-1} on 26 August 2002 to a high of 980 m^3s^{-1} on 21 April 2003. For the 2-year sampling period, the standard deviation of mean daily discharge was 293 m^3s^{-1} compared with a mean discharge of 264 m^3s^{-1} reflecting the high temporal variability of CFR discharge. During the relatively dry period from August 2001 to August 2002, mean daily discharge was 109 m^3s^{-1} (±105 m^3s^{-1}), which was only 25% of the average flow (429±337 m^3s^{-1}) during the wet period from August 2002 to August 2003. All stations had average salinities below 35 and minimum values below 30, indicating that the CFR plume, at least occasionally, influenced the entire sample region (Fig. 3). The control station (CFP3) had the highest average salinity during both years, indicating that it was least affected by the CFR plume. However, although salinities increased from the CFR mouth to offshore, annual average values were not different statistically among stations during the dry year and only CFP1 and CFP2 were lower (least significant salinity difference=0.11, $p<0.05$) during the wet year (Fig. 3), again reflecting the high seasonal variability in CFR flow.

During the 2-year period of study, K_0(PAR) and turbidity varied by over an order of magnitude (Table 1, Fig. 3) and they were highest and most variable temporally at the stations located nearest to the CFR mouth (CFP1 & 2). Station CFP6, which usually lies within the plume (Mallin et al. 2005) was a transition station between the stations near the river mouth and the remaining sites (Fig. 3). There was a positive linear relationship between K_0(PAR) and $a_{t\text{-}w}$(PAR) during the dry year (Fig. 4), but more scatter was evident in this relationship during the wet year. In both

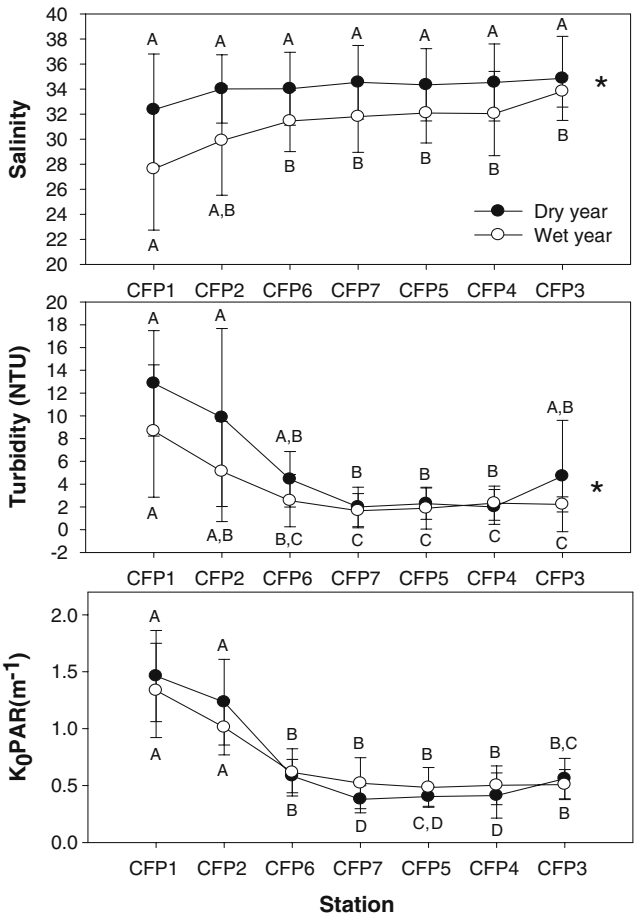

Fig. 3 Among-station and between-year variability in salinity, turbidity, and K_0(PAR) in the Cape Fear River plume from 15 August 2001 to 12 August 2003. *Similar letters* indicate no significant ($P<0.05$) among-station differences within each year. An *asterisk above a station* indicates significant between-year differences at that location; an *asterisk to the right of the lines* indicates an overall significant difference in that parameter between years

Table 1 Mean (±SD) of K_0(PAR), turbidity, chlorophyll *a* concentrations, and absorption coefficients of photosynthetically active radiation (PAR) contributed by detritus [$a_{detritus}$(PAR)], planktonic pigments [a_{Φ}(PAR)], and CDOM [a_{CDOM}(PAR)] for the Cape Fear River plume from August 2001 to August 2002 (dry year) and September 2002 to August 2003 (wet year)

Station	CFP1	CFP2	CFP3	CFP4	CFP5	CFP6	CFP7
Dry year							
K_0(PAR) (m^{-1})	1.46±0.40	1.23±0.38	0.56±0.18	0.41±0.20	0.40±0.09	0.58±0.15	0.38±0.12
Turbidity (NTU)	12.9±4.6	9.9±7.8	4.7±4.9	2.0±1.5	2.3±1.4	4.4±2.4	2.0±1.7
Chlorophyll *a* (μg l^{-1})	4.3±1.3	3.7±1.8	2.0±1.4	1.9±1.5	2.0±1.4	2.9±1.4	2.0±1.4
$a_{detritus}$(PAR) (m^{-1})	0.244±0.049	0.241±0.122	0.087±0.031	0.060±0.039	0.055±0.018	0.104±0.040	0.059±0.035
a_{Φ}(PAR) (m^{-1})	0.046±0.034	0.039±0.022	0.041±0.035	0.025±0.017	0.025±0.010	0.032±0.014	0.026±0.017
a_{CDOM}(PAR) (m^{-1})	0.255±0.132	0.176±0.075	0.119±0.076	0.142±0.077	0.133±0.046	0.149±0.066	0.132±0.062
Wet year							
K_0(PAR) (m^{-1})	1.34±0.41	1.01±0.24	0.51±0.13	0.50±0.17	0.48±0.17	0.62±0.21	0.52±0.22
Turbidity (NTU)	8.7±5.8	5.1±4.4	2.2±0.7	2.3±1.5	1.9±1.8	2.6±2.3	1.7±1.5
Chlorophyll *a* (μg l^{-1})	3.2±1.3	3.1±1.1	2.0±1.2	2.3±1.4	2.5±2.1	3.1±1.9	2.5±1.5
$a_{detritus}$(PAR) (m^{-1})	0.182±0.072	0.134±0.069	0.054±0.023	0.052±0.030	0.052±0.032	0.072±0.034	0.062±0.033
a_{Φ}(PAR) (m^{-1})	0.068±0.052	0.057±0.038	0.040±0.025	0.036±0.032	0.050±0.052	0.048±0.051	0.045±0.040
a_{CDOM}(PAR) (m^{-1})	0.757±0.650	0.633±0.605	0.184±0.166	0.400±0.392	0.348±0.236	0.430±0.343	0.411±0.315

years, the greatest variability in the K_0(PAR) versus $a_{t\text{-}w}$(PAR) relationship was evident in the most river-influenced stations (CFP1, 2, and 6). The 2.38±1.72 slope for the relationship between K_0(PAR) and $a_{t\text{-}w}$(PAR) during the dry year versus the 0.47±0.62slope during the wet year suggests greater contributions by diffuse and upwelling irradiance (i.e., backscatter from particles) to the light field within the plume during dry versus wet years. We also note that there was higher (p=0.021) average turbidity for all stations combined during the dry year (although no significant between year differences for individual stations) and higher $a_{detritus}$(PAR) (p=0.047) for the region during the dry year (Table 1, Figs. 3 and 5). In contrast, both a_{Φ}(PAR) (p=0.044) and a_{CDOM}(PAR) (p<0.001) were higher during the wet year (Fig. 5). What is also evident in Fig. 5 as well as in Table 1 is that the optical influence of detrital particles relative to CDOM and pigments is more restricted to stations near the CFR mouth; at CFP3 the elevated influence of particulates is due to sediment resuspension along Frying Pan Shoals (see also turbidity in Fig. 3). All other stations exhibited some degree of increased a_{CDOM}(PAR) relative to CFP3, again reflecting CFP3's non-plume location (Fig. 5). During the wet year, all stations except CFP3 exhibited increased a_{Φ}(PAR) (Table 1; Fig. 5). CDOM absorption [a_{CDOM}(412)] over the study period ranged from 0.05 to 8.25 m^{-1} and variation in a_{CDOM}(412) did not correlate very closely with salinity (linear regression r^2=0.13, data not shown). The average CDOM absorption coefficient over the entire study period was 1.11 m^{-1} (0.49 m^{-1}±0.33 dry year versus 1.60 m^{-1}± 1.65 wet year) reflecting the high quantities of CDOM in this blackwater river system.

During the dry year, detrital particulates were responsible for 36.0±15.4% of $a_{t\text{-}w}$(PAR) for the sample region, with pigments contributing 11.9±8.2% and CDOM contributing 52.0±18.2% (Table 1). Only at the two most river-influenced stations (CFP1 and 2) did $a_{detritus}$(PAR) equal or exceed a_{CDOM}(PAR) (Table 1). In contrast, during the wet season the regional contribution of $a_{detritus}$(PAR) to $a_{t\text{-}w}$(PAR) fell by almost half (19.2±12.2%); the contribution of a_{Φ}(PAR) dropped slightly (10.3±6.8%) and a_{CDOM}(PAR) increased by 35% (70.5±14.7%). The relative contributions of detritus, pigments and CDOM to $a_{t\text{-}w}$(PAR) also varied spatially as a function of river discharge (Fig. 6). In the most river-influenced stations (CFP1 and 2), as CFR discharge increased during the dry year the relative detritus and CDOM contributions to $a_{t\text{-}w}$(PAR) increased while pigment absorption decreased (Fig. 6). Following the peaks in CFR discharge, $a_{detritus}$(PAR) declined more rapidly than a_{CDOM}(PAR) and the relative contribution by pigments (i.e., phytoplankton) increased (Fig. 6). In contrast, during the wet year, as CFR discharge increased, the particulate load decreased and particulates seemed to be greatly diluted relative to CDOM, especially near the river mouth (Fig. 8).

The spectral slope coefficient of CDOM (*S*) may be considered a proxy for CDOM composition (Carder et al. 1989) and it may increase with decreasing CDOM absorption, as CDOM undergoes photobleaching (Vodacek et al. 1997; Shank et al. 2009), transformation of protein-like fluorophores (Kowalczuk et al. 2003), or sorption to particles (Shank et al. 2005). Although no significant among-station variation in *S* was observed here for either the dry or wet years (Fig. 5), *S* for the entire sample region

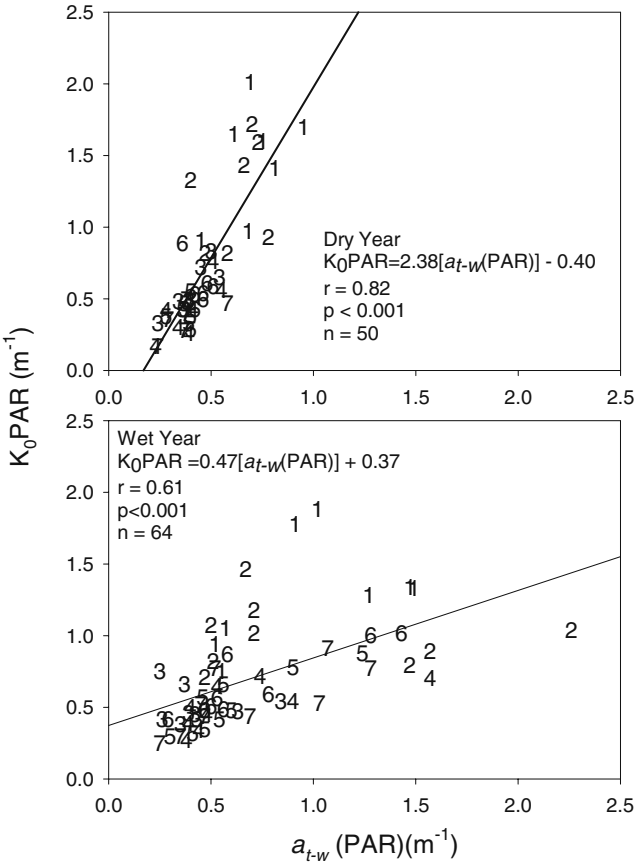

Fig. 4 Relationship between K_0(PAR) and calculated $a_{t\text{-}w}$(PAR) in the Cape Fear River plume during a dry year (15 August 2001 to 26 August 2002) and a wet year (26 August 2002 to 12 August 2003). Refer to Fig. 1 for station locations represented by the station number

was higher during the dry year ($p<0.001$) which also had lower a_{CDOM}(PAR) ($p<0.001$). Within-station comparisons between years indicated that S was higher at CFP1 ($p=0.015$), CFP2 ($p=0.046$), and CFP4 ($p=0.010$), during the dry year. Plotting the slope coefficient against salinity indicated little change in slope up to near-seawater salinities after which point S became highly variable with the greatest variability occurring at the least plume-influenced station (CFP3, Fig. 7).

Nutrient concentrations within the sampling grid were highest at the river mouth, decreasing offshore and at the control station, reflecting their riverine source (Fig. 8). Only the nitrate ion was significantly higher ($p=0.005$) overall in the region during the wet year compared to the dry year (2.86±1.65 μM versus 1.49±2.16 μM, respectively), being higher at both CFP1 ($p=0.037$) and CFP2 ($p=0.003$). Ammonium and phosphate ions exhibited very similar patterns of spatial variation during both years with a slightly greater magnitude of onshore-offshore decrease in ammonium during the wet year (Fig. 8). Chlorophyll *a* was higher at the plume-influenced stations (CFP1, 2 and 6, least significant chlorophyll difference=0.86 μg L^{-1}, $p<0.05$) during the dry year and decreased offshore (Table 1, Fig. 8). In contrast, there was no significant among-station variation in chlorophyll *a* concentrations during the wet year (Fig. 8). Due to high seasonal temporal variability, there were no significant wet versus dry year differences in average chlorophyll concentrations for any of the stations.

Discussion

Previous studies have suggested that the principal factors attenuating light within the CFR estuary were turbidity, mainly due to fine silts and clays delivered by Piedmont runoff into the main stem CFR, and elevated water color, from dissolved organic materials (i.e., CDOM) leached from the riparian Coastal Plain swamps in the Black River and Northeast CFR basins (Mallin et al. 2002; Benedetti et al. 2006). However, only turbidity has been measured. Turbidity is well known to influence phytoplankton productivity in riverine estuaries (Cloern 1987; Mallin et al. 1999a) and phytoplankton blooms may themselves increase light attenuation through absorption by chlorophyll and later by their contribution to detritus and turbidity (Duarte et al. 1998; Gallegos and Jordan 2002). In the Cape Fear River, the turbidity maximum typically occurs in the upper estuary in oligohaline waters and at times is located in mid-estuary in mesohaline waters (Mallin et al. 1999a). Upstream of the turbidity maximum, turbidity is often two times greater than downstream of the maximum (Mallin et al. 1999a). While turbidity can be elevated (and highly variable) at the estuary mouth, turbidity concentrations reaching the plume down-current from CFP1 and CFP2 are usually low, averaging only 2-5 NTU, regardless of discharge (Table 1; see also Mallin et al. 2005). In this study, we measured the relative contributions of dissolved compounds in addition to particulates to the attenuation of PAR in water samples from the CFR plume during relatively dry and wet hurricane-free years. Our results indicated that CDOM, rather than particulate matter and turbidity, was the dominant contributor to the absorption of PAR, especially during periods of high discharge. Thus, light may become limiting to phytoplankton production in the CFR system when the water is nutrient rich, but highly colored (Lin et al. 2008).

The CFR estuary and plume have variations in CDOM absorption which cover nearly the whole known variability range reported in the literature (Kirk 1994; Blough and Del Vecchio 2002; Kowalczuk et al. 2003). Freshwater discharge is the primary source of CDOM to the CFR estuary and dissolved organic carbon concentrations can exceed 1,200 μM C (Avery et al. 2003). Thus, the CFR serves as a dominant point source of CDOM-rich water into the southeastern Atlantic bight (Kowalczuk et al. 2003) and

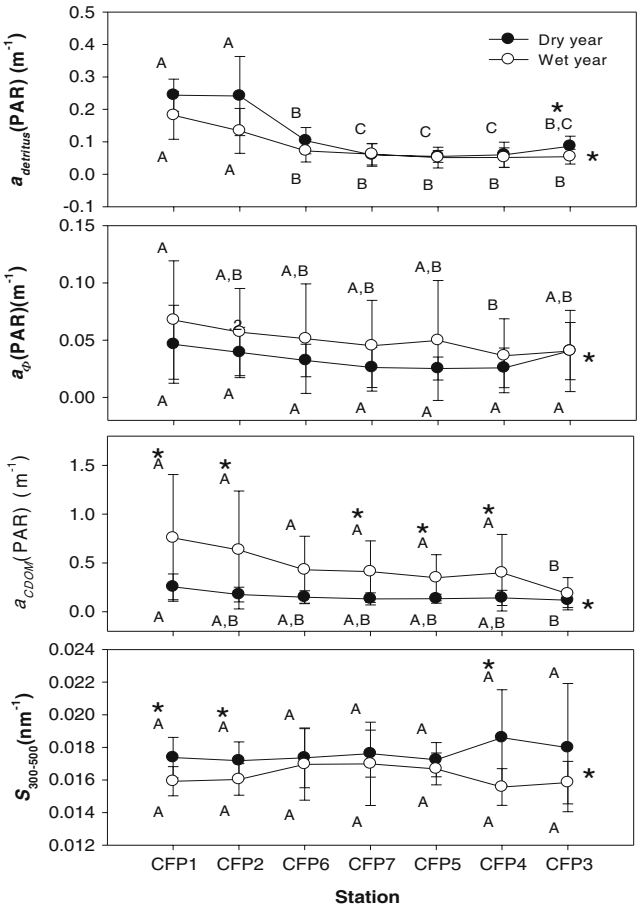

Fig. 5 Among-station and between year variability in $a_{detritus}$(PAR), a_{Φ}(PAR), a_{CDOM}(PAR) and spectral slope coefficient ($S_{300\text{-}500}$) in the Cape Fear River plume from 15 August 2001 to 12 August 2003. *Similar letters* indicate no significant ($P<0.05$) among-station differences within each year. An *asterisk above a station* indicates significant between-year differences at that location; an *asterisk* to the right of the lines indicates an overall significant difference in that parameter between years

its plume may extend from several kilometer (dry season) to >100 km (following hurricanes) offshore (Mallin et al. 1999b, 2002). Our results indicated that CFR discharge controlled not only the spatial extent of the CFR plume, but also the relative contributions of particulate matter, phytoplankton pigments and CDOM to the absorption of PAR in the CFR mouth and adjacent coastal waters. As discharge increased during the spring and summer of 2003, the relative contribution of particulates to PAR attenuation steadily declined. Following peaks of CFR discharge, elevated CDOM absorption of PAR was generally longer lasting and more widespread than absorption due to non-pigmented particulates. Shank et al. (2005) reported that under high particle loads in the CFR, ≈2.5% of the total CDOM pool was sorbed to particles. They suggested that the transfer of CDOM to particles may become more important than photobleaching in altering estuarine water optical properties in this system during high particle-load conditions. As particle loads are reduced (or diluted) their CDOM-sorption model predicted that >99% of CDOM would remain in the dissolved phase, which could explain its greater distribution and longer persistence in our sampling region during wet periods.

Decrease in the slope of K_0(PAR) versus $a_{t\text{-}w}$(PAR) during the wet year compared to the dry year also indicated a reduced contribution to light attenuation by particles during high discharge periods (Fig. 4). The only exception to this pattern occurred in water samples obtained during dry periods at the most river-influenced stations (CFP1 and 2, Fig. 6). High levels of CDOM are known to affect phytoplankton production by reducing the quantity and quality of available PAR (Bidigare et al. 1993; Keith et al. 2002). Similar to our observations, Gallegos (2005) observed that CDOM was the dominant contributor to absorption integrated over visible wavelengths (PAR) in all but a few samples from the mouth of the St Johns River, FL, USA during the dry season. In contrast, in the mid-Atlantic Chesapeake Bay and Hudson River outflows, detritus and CDOM contribute nearly equally to PAR absorption during high-flow plume states, but the CDOM contribution increases when upwelling disperses the plume (Johnson et al. 2001, 2003). Like the CFR plume, the magnitude of the phytoplankton contribution to absorption in the Hudson River plume was similar, at about 15%, for all dynamic states (Johnson et al. 2003).

The relatively higher pigment levels in the most river-influenced area of the CFR estuary during the low discharge period may have reflected increased light availability in response to significant decreases in CDOM, a nutrient "memory" effect due to remineralization of nutrients from river-deposited sediments (Mallin et al. 1999b), and the effect of increased residence time of the plume area water mass, which would allow phytoplankton time to increase their biomass in this nutrient-rich shallow area (Gallegos and Jordan 2002). Gallegos (2005) noted that during dry periods in the St. Johns River estuary, when estuarine CDOM levels were reduced and availability of PAR was increased, phytoplankton were able to utilize available nutrients and form blooms. Likewise, we observed the highest average phytoplankton chlorophyll levels in the CFR estuary during the dry year at stations near the river mouth where nutrient levels were highest (CFP1 and 2, Fig. 8). Salinity was not a good predictor of CDOM absorption in either the St. Johns River estuary (Gallegos 2005) or the CFR plume, during our study, indicating that linear relationships between inherent optical properties and routinely measured water quality parameters may break down at the high CDOM concentrations that typify these two blackwater systems. The non-conservative behavior of CDOM absorption and the spectral slope of absorption by

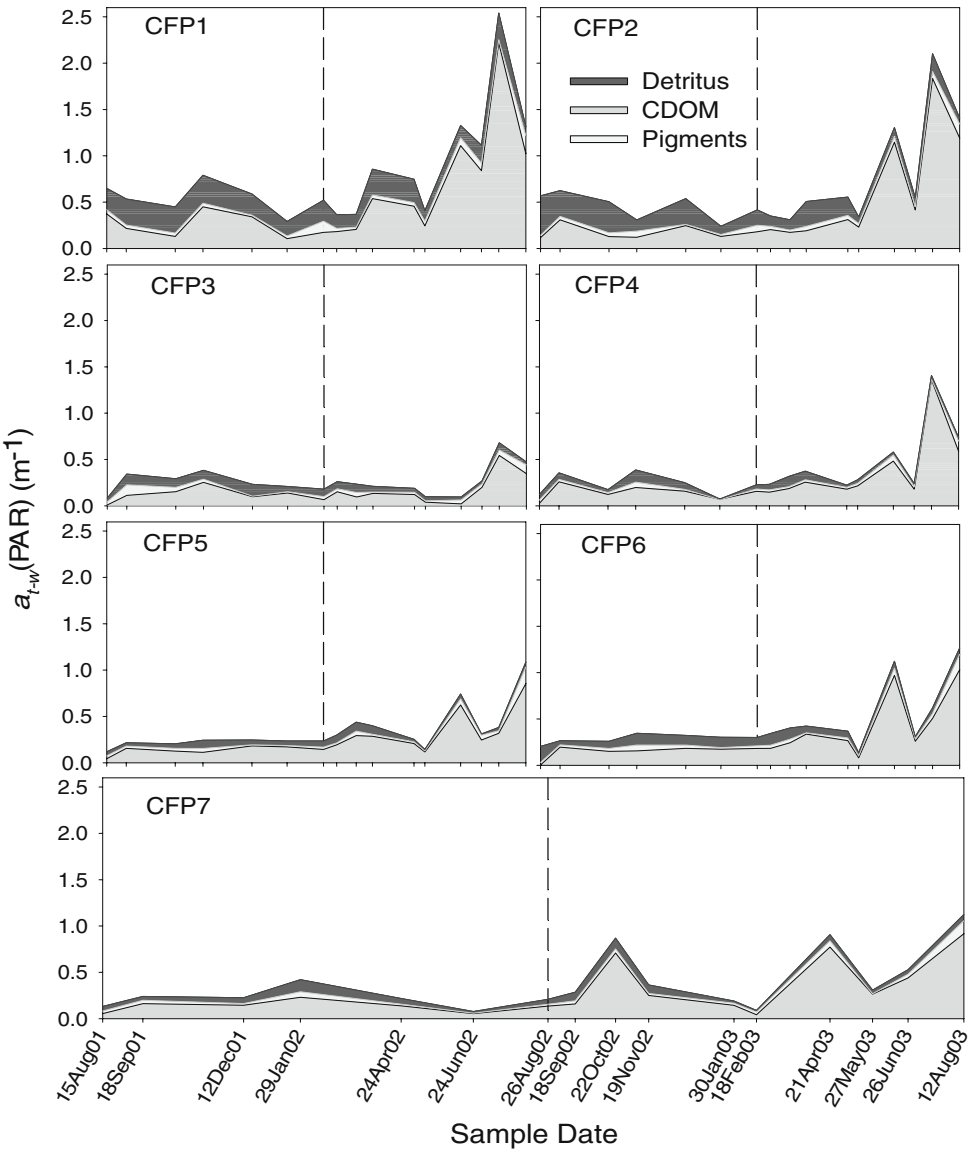

Fig. 6 Average absorption coefficients of detritus [a_{detritus}(PAR)], pigments [a_{Φ}(PAR)], and CDOM [a_{CDOM}(PAR)] at the seven Cape Fear River plume stations determined during cruise sampling from 15 August 2001 to 12 August 2003. *Vertical dashed line* separates dry year from wet year sample data. CFP7 graph has been widened to show cruise sampling dates more clearly

CDOM (*S*) versus salinity (Fig. 7), at higher salinities, may have reflected source variability (terrestrial vs. marine phytoplankton, Keith et al. 2002), photobleaching (Vodacek et al. 1997; Shank et al. 2009), preferential sorption of high molecular weight substance to particles (Shank et al. 2005), or an increase in proteinaceous matter (Kowalczuk et al. 2003, 2005) during the transit from river to ocean. All of these processes could have resulted in changes in absorbing efficiency of the CDOM within the outer edges of the CFR plume (Schwarz et al. 2002). Recent analyses of excitation emission matrix fluorescence data indicated that non-conservative behavior of CDOM at the zone of intensive mixing of fresh and oceanic waters (salinity range 30-35) in the CFR plume could be associated with changes in the dissolved organic matter composing the CDOM (Kowalczuk et al. 2009a). Variations in autochthonous production of protein-like components (tyrosine and tryptophan), microbial reworking of dissolved organic matter, and removal of the terrestrial humic fraction in the mixing zone all result in changes in the carbon-specific absorption coefficient, with higher contributions of protein-like components relative to terrestrial humic components decreasing this coefficient (Kowalczuk et al. 2009b). Some of these components are almost linearly correlated with salinity while others are weakly correlated or not correlated at all. Therefore, the relative contributions of different dissolved organic compounds composing CDOM will control its conservative or non-conservative optical behavior.

The importance of attenuation of PAR by CDOM in affecting phytoplankton production in the CFR plume during the wet year was indicated by the lack of increase in phytoplankton chlorophyll *a* levels, despite lower turbidity and higher nitrate levels than during the dry year. There was actually an indication of suppressed phytoplank-

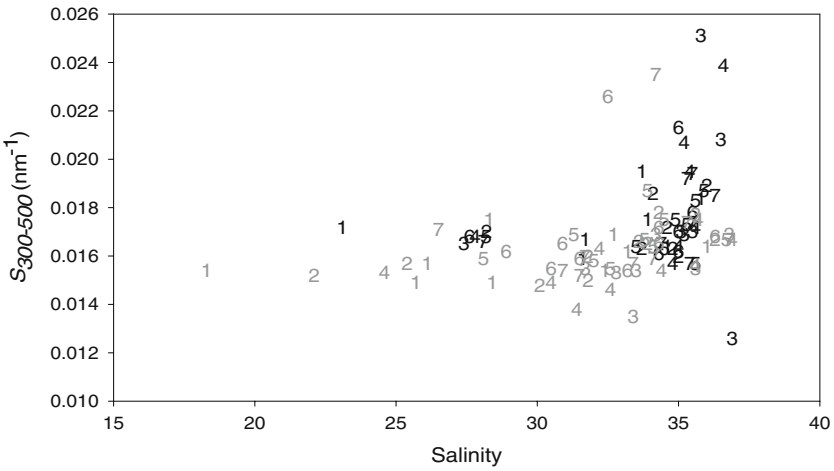

Fig. 7 Variability of spectral slope ($S_{300\text{-}500}$) with salinity in the Cape Fear River plume. *Black symbols* represent dry year samples, *gray symbols* represent wet year samples. Refer to Fig. 1 for station locations represented by the station numbers

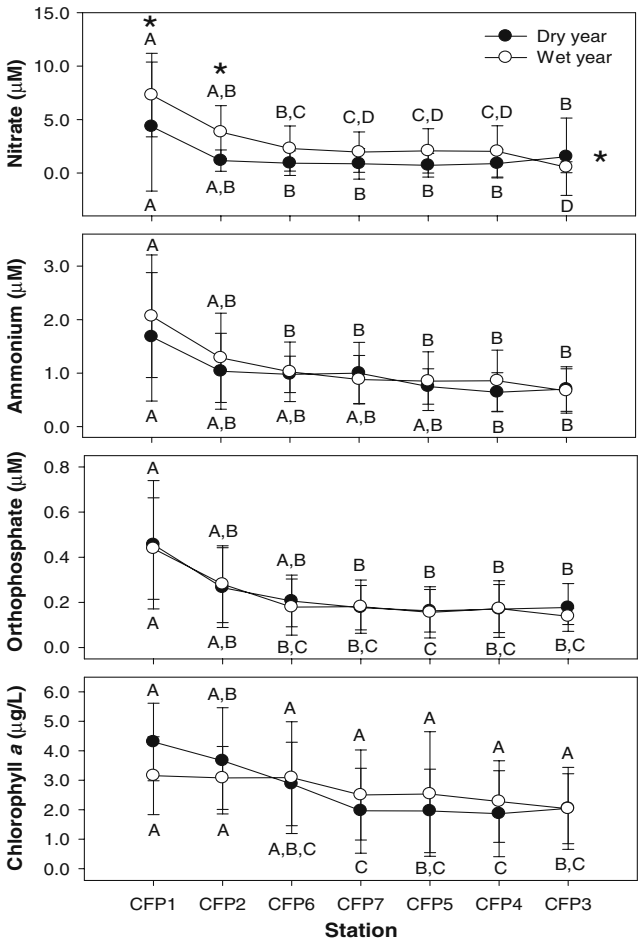

Fig. 8 Among-station and between-year variability in nitrate, ammonium, orthophosphate, and chlorophyll *a* concentrations in the Cape Fear River plume from 15 August 2001 to 12 August 2003. *Similar letters* indicate no significant ($P<0.05$) among-station differences within each year. An *asterisk above a station* indicates significant between-year differences at that location; an *asterisk to the right of the lines* indicates an overall significant difference in that parameter between years

ton production during the wet year at the two most river-influenced stations (CFP1 and 2, Table 1, Fig. 8), a response consistent with recent model predictions, which account for the high CDOM levels in this system (Lin et al. 2008). The lack of an increase in chlorophyll *a* towards the river mouth during the wet year corresponded to higher a_{CDOM}(PAR) and lower spectral slope coefficients (Fig. 5). Higher CDOM influence during the wet year in the Cape Fear system is similar to observations in other southeastern United States blackwater rivers. For instance, in the Ogeechee River dissolved organic carbon concentrations increased with stream discharge, as the river received increasing drainage from riparian swamp forests, the ultimate sources of CDOM to the system (Meyer 1992). Both the Cape Fear River and its two major tributaries, the Black and Northeast Cape Fear Rivers, have abundant riparian swamp forests that drain in rainy conditions. Thus, CDOM is not diluted by rainfall/runoff, but increases in concentration. The lack of significant changes in K_0(PAR) among CFP stations between the wet and dry years (Fig. 3) may reflect similar optical outcomes from two very different processes. Absorption from CDOM strongly contributed to K_0(PAR) during the low-turbidity wet year. Although CDOM absorption decreased during the dry year (Fig. 5), the relative increases in suspended load (Fig. 3) increased photon scattering, path length and the probability of absorption, thus K_0(PAR) was unchanged. This process has been called radiant energy trapping (Stavn 1987).

That light, rather than nutrients, limits phytoplankton production in the CFR during periods of high flow has been established by empirical data (Mallin et al. 1999b) and water-quality modeling (Lin et al. 2008), but previously only K_d(PAR) and turbidity from upstream runoff and estuarine dredging was directly measured (Mallin et al. 1999b). Increased attenuation of light by CDOM in the CFR estuary has been suggested as an important natural effect limiting phytoplankton productivity (Lin et al. 2008), particularly following stochastic high-rainfall

events such as the passage of hurricanes (Mallin et al. 1999b, 2002; Mallin and Corbett 2006). Mallin et al. (1999b, 2002) indicated that relative contributions of darkly stained swamp water to light attenuation in the CFR estuary were higher following hurricanes that primarily affected the coastal plain and the heavily forested Black and Northeast Cape Fear River watersheds (e.g., Hurricanes Bertha and Bonnie), whereas storms delivering most of their precipitation to the Piedmont and the mainstem CFR watershed increased both turbidity and water color (e.g., Hurricanes Fran and Floyd). During the period of this study, no hurricanes made landfall in the CFR region. The relative contributions of the Black River and the Northeast CFR tributaries to total CFR discharge decreased slightly from 20% to 15% between the dry year (15 August, 2001-26 August 2002) and the wet year (26 August 2002-12 August 2003) while the Piedmont-derived input from the mainstem CFR, as estimated from gaging station data from Lock and Dam #1 north of Wilmington, increased from 50% to 66% of total CFR discharge. Thus, over longer periods of elevated precipitation particulate loads may become reduced over time by dilution with the increasing proportion of freshwater in the runoff and increasing retention of materials in the floodplain (Mallin and Corbett 2006).

Bio-optical and water quality data collected over the 2-year period from August 2001 to August 2003 indicated that partitioning absorption of PAR by dissolved (CDOM and pigments) and particulate (non-pigmented detritus) materials may provide a means of describing how river discharge affects carbon sources and transformations in the near-shore waters of the Cape Fear River plume during dry versus wet years. These data also indicated that within the CFR plume, AOPs and IOPs reflected changes in sources, distribution, and transformations of dissolved and particulate constituents within the plume. During periods of high flow, the spatial distribution and abundance of CDOM, detritus, and nutrients in the plume clearly reflected riverine inputs, while phytoplankton pigment concentrations suggested light limitation in the CFR plume induced primarily by high CDOM. High CDOM may also have resulted in a shift towards heterotrophy because of limited light availability and an increase in labile DOM, resulting from CDOM photolysis, which may promote heterotrophic bacterial growth (Zafiriou 2002; Shank et al. 2009). During periods of low flow, the contribution of detrital particles to light attenuation equaled or exceeded that due to CDOM, but was much more restricted spatially. The Cape Fear River system, with its substantial contribution of riparian forest-derived blackwater typifies many river systems from North Carolina through Florida (Dame et al. 2000). Bio-optical data, in conjunction with other water-quality measurements, can provide a powerful tool to quantify the relative contributions of terrestrial dissolved and particulate inputs versus coastal marine processes in regulating nearshore productivity in the South Atlantic Bight.

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