

- transport and quenching of chlorophyll fluorescence. *Biochim. Biophys. Acta* **990**: 87–92.
- HARTIG, P., K. WOLFSTEIN, S. LIPPEMEIER, AND F. COLIJN. 1998. Photosynthetic activity of natural microphytobenthos populations measured by fluorescence (PAM) and ^{14}C -tracer methods: A comparison. *Mar. Ecol. Prog. Ser.* **166**: 53–62.
- KOLBER, Z., AND P. G. FALKOWSKI. 1993. Use of active fluorescence to estimate phytoplankton photosynthesis in situ. *Limnol. Oceanogr.* **38**: 1646–1665.
- KRALL, J. P., AND G. E. EDWARDS. 1990. Quantum yields of photosystem II electron transport and carbon dioxide fixation in C_4 plants. *Aust. J. Plant Physiol.* **17**: 579–588.
- KROMKAMP, J., C. BARRANGUET, AND J. PEENE. 1998. Determination of microphytobenthos PS II quantum efficiency and photosynthetic activity by means of variable chlorophyll fluorescence. *Mar. Ecol. Prog. Ser.* **162**: 45–55.
- KROON, B. M. A. 1994. Variability of photosystem II quantum yield and related processes in *Chlorella pyrenoidosa* (Chlorophyta) acclimated to an oscillating light regime simulating a mixed photic zone. *J. Phycol.* **30**: 841–852.
- KUHL, M., AND B. B. JORGENSEN. 1992. Spectral light measurements in microbenthic phototrophic communities with a fiber-optic microprobe coupled to a sensitive diode-array detector. *Limnol. Oceanogr.* **37**: 1813–1823.
- , AND ———. 1994. The light-field of microbenthic communities—radiance distribution and microscale optics of sandy coastal sediments. *Limnol. Oceanogr.* **39**: 1368–1398.
- MACINTYRE, H. L., R. J. GEIDER, AND D. C. MILLER. 1996. Microphytobenthos: The ecological role of the “secret garden” of unvegetated, shallow-water marine habitats. I. Distribution, abundance and primary production. *Estuaries* **19**: 186–201.
- OLSON, R. J., A. M. CHEKALYUK, AND H. M. SOSIK. 1996. Phytoplankton photosynthetic characteristics from fluorescence induction assays of individual cells. *Limnol. Oceanogr.* **41**: 1253–1263.
- OXBOROUGH, K., AND N. R. BAKER. 1997a. An instrument capable of imaging chlorophyll *a* fluorescence from intact leaves at very low irradiance and at cellular and subcellular levels of organization. *Plant Cell Environ.* **20**: 1473–1483.
- , AND ———. 1997b. Resolving chlorophyll *a* fluorescence images of photosynthetic efficiency into photochemical and non-photochemical components—calculation of qP and Fv'/Fm' without measuring Fo' . *Photosynth. Res.* **54**: 135–142.
- PATERSON, D. M. 1989. Short-term changes in the erodibility of intertidal cohesive sediments related to the migratory behaviour or epipellic diatoms. *Limnol. Oceanogr.* **34**: 223–234.
- , AND OTHERS. 1998. Microbiological mediation of spectral reflectance from intertidal cohesive sediments. *Limnol. Oceanogr.* **43**: 1207–1221.
- PELETIER, H. 1996. Long-term changes in intertidal estuarine diatom assemblages related to reduced input of organic waste. *Mar. Ecol. Prog. Ser.* **137**: 265–271.
- PRAŠIL, O., Z. KOLBER, J. A. BERRY, AND P. G. FALKOWSKI. 1996. Cyclic electron flow around photosystem-II in vivo. *Photosynth. Res.* **48**: 395–410.
- SERÓDIO, J., J. M. DA SILVA, AND F. CATARINA. 1997. Non-destructive tracing of migratory rhythms of intertidal benthic microalgae using in vivo chlorophyll *a* fluorescence. *J. Phycol.* **33**: 542–553.
- SMITH, D. J., AND G. J. C. UNDERWOOD. 1998. Exopolymer production by intertidal epipellic diatoms. *Limnol. Oceanogr.* **43**: 1578–1591.
- UNDERWOOD, G. J. C. 1994. Seasonal and spatial variation in epipellic diatom assemblages in the Severn estuary. *Diatom Res.* **9**: 451–472.
- . 1997. Microalgal colonisation in a saltmarsh restoration scheme. *Estuarine Coastal Shelf Sci.* **44**: 471–481.
- , AND J. KROMKAMP. 1999. Primary production by phytoplankton and microphytobenthos in estuaries. *Adv. Ecol. Res.* **29**: 93–153.
- , C. NILSSON, K. SUNDBÄCK, AND A. WULFF. 1999. Short-term effects of UVB radiation on chlorophyll fluorescence, biomass, pigments and carbohydrate fractions in a benthic diatom mat. *J. Phycol.* **35**: 656–666.
- , M. PHILLIPS, AND K. SAUNDERS. 1998. Distribution of estuarine benthic diatom species along salinity and nutrient gradients. *Eur. J. Phycol.* **33**: 173–183.

Received: 14 October 1999

Accepted: 25 April 2000

Amended: 8 May 2000

On the dispersal of riverine colored dissolved organic matter over the West Florida Shelf

Abstract—We investigated the optical properties of surface water in areas of the West Florida Shelf influenced by riverine discharge and by the occurrence of a phytoplankton plume. Results of absorption and fluorescence spectroscopy analyses and determination of dissolved organic carbon (DOC) concentration showed that the injection of riverine colored dissolved organic matter (CDOM) strongly affected the optical properties and DOC concentrations over the shelf. Riverborne nutrients contributed to an increase in primary productivity. However, during the study period, the increase in primary productivity did not result in the production of significant amounts of CDOM.

Fluorescence spectroscopy results showed that optical prop-

erties of riverine CDOM were lost close to the mouth of the rivers. A simple mathematical model describing mixing between riverine and marine end-members demonstrated that most of the observed changes in optical properties of CDOM along salinity gradients can be explained by mixing. Laboratory mixing experiments between riverine water and seawater indicated that flocculation of organic matter during estuarine mixing did not affect the optical properties of CDOM.

Remote-sensing studies of the Gulf of Mexico using historical data from the Coastal Zone Color Scanner show a recurrent, seasonal chlorophyll bloom over the West Florida Shelf (WFS) every year between February and May (Gilbes

et al. 1996). This bloom, which is different from the Gulf of Mexico winter–spring bloom (Müller-Karger et al. 1991), usually forms off Cape San Blas and extends as far south as the Florida Keys. Local rivers have their maximum discharge during spring (Gilbes et al. 1996) and their waters are transported offshore, leading to the formation of low-salinity plumes over the middle and outer shelf region. Riverine discharge represents a significant source of nutrients, which are likely responsible for the phytoplankton bloom. The presence of a high-productivity bloom in the WFS significantly affects the carbon budget in the region. A better understanding of the processes involved in the bloom dynamics will increase our knowledge about carbon cycling and improve our ability to interpret satellite ocean-color data.

Several studies recognize differences between the optical properties of organic matter from marine and riverine origin, as well as the complexity and importance of these compounds to the optical properties of the water column (Bricaud et al. 1981; Morel 1988; Carder et al. 1989). Remote sensing imagery has become an important tool in the study of the global carbon cycle; therefore, it is essential to understand how changes in concentration and optical properties of CDOM can affect the interpretation of remote sensing data. Several factors confound the study of CDOM in coastal regions affected by river discharge. First, river input can show strong seasonal changes introducing large variability in the CDOM concentration and optical properties. Second, several rivers may discharge into the same region, each contributing different amounts of CDOM with potentially different optical properties (Cabaniss and Shuman 1987; Coble 1996; Battin 1998). Third, river plumes also carry nutrients, which may stimulate the production of new CDOM formed as a result of biological activity.

The WFS is an excellent area to study the effects of river discharge in coastal regions. The shelf is wide, with the 30- and 100-fathom isobaths extending to ~60 and ~120 nautical miles offshore, respectively. Surface water from the Gulf of Mexico is high in salinity and low in CDOM, constituting a typical marine end-member. Important sources of fresh water are provided by several rivers such as the Mobile, Apalachicola, Suwannee, Manatee, Peace, and Caloosahatchee, as well as by other small rivers.

Two main processes are expected to produce changes in the optical properties of riverine CDOM along river plumes: mixing with seawater and photodegradation. In addition to decreasing CDOM fluorescence intensity, both processes also result in hypsochromic (blue) shifts in the excitation–emission maximum (Ex/Em_{max}). During mixing between river and seawater, the high concentration of fluorescent material associated with riverine discharge masks the optical signal from the marine end-member. As a result, changes in optical properties are usually negligible at salinities below ~30 (Coble 1996; Blough et al. 1993; De Souza Sierra et al. 1997; Del Castillo et al. 1999). When the relative proportions of riverine and marine CDOM become similar, the optical signature of the marine end-member begins to dom-

inate, and fast changes in optical properties along the salinity gradient are observed. The salinity at which the sudden hypsochromic shift is observed, the inflection point, will depend mostly on the concentration of fluorescent material in the riverine end-member. Consequently, it should be observed at higher salinities for rivers with the highest CDOM concentrations.

Several works present evidence showing that flocculation removes organic carbon during estuarine mixing (e.g., Eckert and Sholkovitz 1976; Sholkovitz 1976; Sholkovitz et al. 1978). De Souza Sierra et al. (1997) recently documented a slight hypsochromic shift in the fluorescence emission maximum in the Gironde Estuary along a salinity gradient between 0 and ~32 that was attributed to preferential flocculation of high-molecular-weight CDOM during estuarine mixing. Although other researchers have shown conservative behavior of organic carbon in estuaries (e.g., Laane 1981; Mantoura and Woodward 1983), the effect of flocculation upon the optical properties of CDOM has not been sufficiently investigated and remains unclear.

In this manuscript we address two questions: First, can we detect changes in concentration of CDOM associated with primary productivity (PP) induced by river plumes? Second, what is the geographical extension of the riverine optical signature and what are the processes controlling the changes in optical properties of CDOM along the river plumes? To answer these questions, we relied on DOC, PP, chlorophyll, and spectroscopic analyses coupled with laboratory experiments and models describing mixing between riverine and marine CDOM.

Methods—Water samples were collected on board the RV *Suncoaster* at selected stations in the WFS during March 1995 (Fig. 1). All discrete samples for DOC and optical analyses were collected at a depth of ~1 m using Teflon-coated Go-Flo bottles. Samples were filtered through precombusted (12 h at 450°C) GF/F filters mounted in a stainless steel in-line filtration system. This filtration apparatus was connected to the nipple of the Go-Flo bottles, and the filtrate drained by gravity directly into the sample bottles (amber-colored glass, precombusted at 500°C for 12 h), limiting the exposure of the sample to the atmosphere and light. Procedural blanks performed using Milli-Q water showed that this filtration method does not add detectable amounts of DOC. The samples were kept frozen until the time of analysis (within 3 months). Salinity and temperature were recorded underway using a thermosalinograph. Chlorophyll was continuously measured on a Turner model 10-AU fluorometer. Samples for the calibration of the chlorophyll fluorometer were collected at each station. Chlorophyll concentrations were obtained in the laboratory using the fluorometric method described by Yentsh and Menzel (1963). PP was calculated by ^{14}C -uptake experiments following the method described by Harding et al. (1986).

Concentrations of DOC were determined by thermal catalysis in a Shimadzu TOC-5000 instrument equipped with a platinumized quartz catalyst. The samples were acidified to

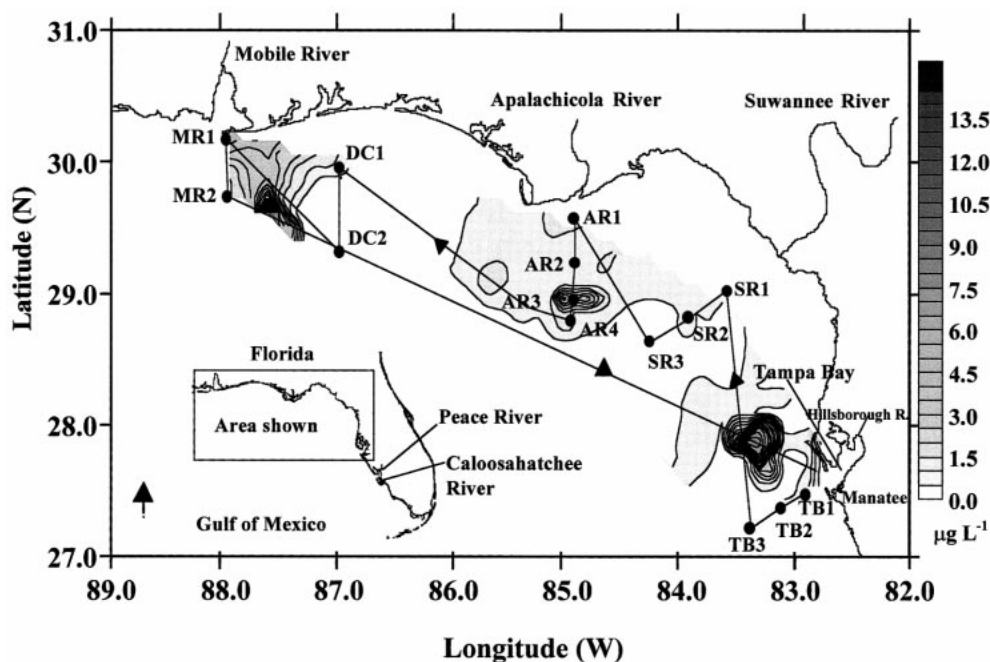


Fig. 1. Station position and cruise track of the RV *Suncoaster*. Contours of chlorophyll concentration were generated from fluorescence data collected underway and are presented to show areas of high-chlorophyll concentration.

pH <2 with 12 N HCl and sparged for 10 min with CO₂-free artificial air immediately before analysis. The concentrations of DOC were determined against a four-point standard dilution of glucose. The instrument blank was determined using proprietary methods for the Shimadzu TOC-5000. Its value was equivalent to ~7% of the signal produced by 80 µM standard, and it was subtracted from all samples. To ascertain the stability of the instrument, we performed one-point calibration checks randomly between the samples. Precision between replicates ($n = 3$) was better than 5%.

Absorption spectra of filtered samples were obtained between 250 and 700 nm at 1-nm intervals using a Hitachi U-3300 double-beam spectrophotometer equipped with matching 10-cm quartz cells. Milli-Q water was used in the reference cell. Data were corrected for scattering and baseline drift by subtracting from each spectrum the value of absorption at 700 nm (Bricaud et al. 1981). The accuracy and stability of the instrument were determined before each sample set using the instrument proprietary performance tests. The validity of these tests was later confirmed using National Institute of Standards and Technology-calibrated transmission filters. The absorption coefficients, a , were calculated using: $a(\lambda) = 2.303A(\lambda)/r$, where A is the absorbance ($\log_{10} I_0/I$) and r is the path length in meters. The value of a at 412 nm was used as an index of CDOM abundance, but values at other wavelengths (375, 412, and 440 nm) are also provided to ease comparison with other works.

Fluorescence spectroscopy was performed using a SPEX Fluorolog II fluorescence spectrophotometer running in ratio mode with a bandpass of 5 nm. Three-dimensional excita-

tion–emission matrices (EEMs) were created by measuring the emission spectra from 270 to 710 nm at 40 separate excitation wavelengths ranging between 260 and 455 nm (Coble et al. 1993; Coble 1996). Data processing and corrections for optical biases of the instrument were performed according to Coble et al. (1993). The fluorescence intensities at Ex/Em_{max} were transformed to equivalents of quinine sulfate and expressed in parts per billion (ppb QS). When the excitation maximum was not well defined, we used the emission maximum at excitation 310 nm. The EEMs were used to characterize the fluorescent organic matter using the position of the Ex/Em_{max} according to Coble (1996).

Modeling—Optical properties of CDOM were modeled in two ways: Model I: To better understand the effect of mixing between river and seawater upon the optical properties of CDOM, we created mixing models on the basis of four pairs of end-members from the WFS. Each model consisted of water mixtures with 12 representative salinities obtained by adding the weighted EEMs of the end-members using Galactic Grams software. The weighting factor was the proportion of each end-member needed to produce a mixture with a particular salinity. The end-member pairs used were: MR1 versus DC2, MR1 versus AR3, AR1 versus AR3, and Manatee River versus Gulf of Mexico water collected at 26°.05', 83°.02' (Fig. 1).

Model II: To ascertain if flocculation effects should be considered in our mixing models, we performed an experiment similar to that of De Souza Sierra et al. (1997), in which results from laboratory mixtures between river and seawater were compared with results from modeled mix-

tures. If the effects of flocculation were negligible, results between the laboratory and modeled mixtures should be similar. Two river-seawater pairs were used: Hillsborough River (Florida) versus seawater collected in the eastern Caribbean Sea (sal = 35), and Peace River (Florida) versus seawater from the Yucatán Strait (sal = 36). The river samples were first diluted with Milli-Q water to avoid self-shading during the fluorescence analysis and then mixed with seawater to obtain samples with different salinities. For the first pair, we created eight laboratory mixtures with salinities between 0 and 35. For the second one, we were interested in observing the effects of mixing river water with a high-salinity, low-CDOM end-member (fluorescence of Yucatán water in the visible is <1 ppb). We created 10 mixtures with salinities between 0 and 30, but in this case the increments in salinity between 0 and 6 were small to better observe possible changes in fluorescence at that early stage of mixing. All mixtures were stirred and allowed to stand in the dark for ~24 hours before analysis by fluorescence spectroscopy. The modeled mixtures equivalent to the laboratory mixtures were created as described above.

Two main factors made the conditions in our laboratory mixing experiment different from real mixing in an estuary. First, as noted by De Souza Sierra et al. (1997), the experiments were done with filtered samples, removing sediments and suspended material that could be involved in the flocculation and adsorption process (Preston and Riley 1982). Second, the river end-members were diluted to avoid self-shading during the fluorescence analysis.

Filtering may introduce deviations from the natural mixing processes found in rivers with high-sediment loads (e.g., Mississippi, Mobile, Manatee, and Amazon rivers), but it should approximate conditions found in rivers with low sediment loads (e.g., Orinoco, Suwannee, Hillsborough, and Peace Rivers). Moreover, early experiments performed using filtered river water (Sholkovitz 1976; Sholkovitz et al. 1978) dismissed the importance of particulate material and showed that the flocculation observed in filtered samples was representative of in situ processes.

Predilution of a river end-member with Milli-Q water should not preclude flocculation because this phenomenon is caused by electrolytic interactions between negatively charged functionalities in humic acids and cations in seawater (Eckert and Sholkovitz 1976). Nevertheless, we performed a series of experiments in an attempt to circumvent this possible problem. We added $\text{NaCl}_{(s)}$ to undiluted Peace River water to create 16 solutions with salinities between 0 and 35 (sal = 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 31, 32, 33, 34, and 35). Second, we combined undiluted Peace River water with Yucatán Strait water (sal = 36) to produce mixtures with salinities 15, 20, 25, and 30. At this level of dilution self-shading is not a problem. All mixtures were stirred and allowed to stand for ~24 h before analysis. Undiluted samples were analyzed by fluorescence spectroscopy before and after filtration through 0.45- μm membrane filters. Samples with added $\text{NaCl}_{(s)}$ were then diluted 1/100 in pH 8 phosphate buffer and analyzed before and after filtration.

Finally, Eckert and Sholkovitz (1976) reported that diva-

Table 1. Temperature, salinity, [DOC], PP, and absorption coefficients of CDOM for samples collected in the WFS.

Sta.	Temp- erature (°C)	Salinity	[DOC] (μM)	PP*	a (375 nm)	a (412 nm)	a (440 nm)
AR1	18.09	31.23	289.2	14.96	0.938	0.506	0.318
AR2	17.77	34.13	206.6	2.97	0.312	0.141	0.083
AR3	19.42	35.58	89.1	na†	0.239	0.127	0.080
AR4	19.77	35.55	90.0	na	0.118	0.069	0.048
DC1	20.03	35.70	147.5	2.78	0.054	0.032‡	0.023‡
DC2	24.66	36.18	125.8	2.91	0.106	0.041	0.020‡
MR1	18.46	27.90	255.0	38.58	2.000	1.115	0.722
MR2	19.92	30.46	241.6	13.51	0.566	0.283	0.176
SR1	17.28	35.21	191.6	1.20	0.161	0.083	0.057
SR2	17.99	35.89	150.0	1.62	0.132	0.070	0.036‡
SR3	19.13	35.57	105.8	1.86	0.107	0.059	0.035‡
TB1	19.33	34.75	305.0	1.18	0.312	0.136	0.072
TB2§	18.29	35.92	158.3§	2.70	0.142	0.048	0.029‡
TB3§	19.04	36.09	156.6§	0.71	0.111	0.050	0.033‡

* PP $\text{mg C m}^{-3} \text{ h}^{-1}$.

† na, not available.

‡ Below the photometrical accuracy of the instrument.

§ Stations TB2 and TB3 showed contamination in the fluorescence signal.

lent cations are most effective flocculating dissolved organic matter. Trying to induce flocculation to study its effect upon Em_{max} , we added $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}_{(s)}$ to undiluted Peace River water (0.3 M added Ca) and after ~24 h performed the analyses as described above.

Results: On the formation of new CDOM—To determine if algal blooms produced new CDOM in the WFS, we used direct comparisons between PP, DOC, and CDOM concentration. Results from these analyses are shown in Table 1. Lacking ocean-color satellite imagery during the time of the cruise we relied on continuous in vivo fluorescence measurements of chlorophyll to detect the presence of the phytoplankton plume in the WFS. High values of chlorophyll were found in areas south of Cape San Blas (between stations AR3 and AR4), south of the Mobile River, and northwest of Tampa Bay. The position of the bloom is depicted in Figure 1 (details can be found in Gilbes 1996 and Gilbes et al. pers. comm.). Over the whole data range, PP correlated with CDOM ($r = 0.98$). However, this result was strongly skewed by stations AR1, MR1, and MR2 where coincident high values of PP and CDOM can be attributed to riverine discharge. The correlation disappears if these low-salinity stations are eliminated. Regression analyses also showed lack of correlation between chlorophyll and CDOM when the same low-salinity stations were ignored.

The concentrations of DOC ranged from 89 μM (AR3) to 305 μM (TB1). This last value was extremely high; thus we suspect contamination of the sample. Measurements of DOC fell within the range of values previously reported for coastal and shelf areas of the Gulf of Mexico (Fredericks and Sackett 1970; Eadie et al. 1978; Swaine 1996). Our observations from high-salinity waters over the shelf coincided with Swaine (1996) but were higher than the historical range reported for oceanic waters in the Gulf of Mexico (Fredericks and

Sackett 1970; Eadie et al. 1978). These higher values could result from high PP associated with a shallow shelf and to residual carbon from the rivers. As with PP, no correlation was found between DOC and CDOM when the three low-salinity high-CDOM stations were excluded.

Our results indicated that there was no increase in CDOM abundance associated with increases in chlorophyll concentration and PP. This lack of coherence between chlorophyll concentration and CDOM was observed in the Gulf of Mexico by Carder et al. (1989) and elsewhere by Bricaud et al. (1981). More interestingly, a lack of correlation has also been observed between DOC and CDOM (Stewart and Wetzel 1981; Siegel and Michaels 1996). Clearly, elevated PP did not result in immediate increases in CDOM concentration detectable by our instruments. The obvious consequence is that changes in optical properties of the water column during an algal bloom, away from riverine input, will be mostly controlled by the increase in chlorophyll concentration and not by production of new CDOM. Changes in CDOM concentration are ultimately tied to long-term cycles in primary production (Bricaud et al. 1981; Carder et al. 1989). In the WFS, these processes appear to be longer than the residence time of waters over the shelf.

On the dispersal of riverine CDOM—Three main fluorescence peaks have been observed in marine samples: a humic peak with Ex_{max} below 260 nm and Em_{max} around 425 nm (fluorophore A), and two humic peaks (C and M) that are classified as terrestrial and marine, respectively (Coble 1996). On the basis of fluorescence analyses from several water types, Coble et al. (1996) found average values of $Ex/Em_{max} = 340/440$ nm for riverine waters, 310/412 nm for intermediate waters (a mixture between riverine and marine end-members), and 303/404 nm for marine surface waters. Similar Ex/Em_{max} values have been reported for the Arabian Sea (Coble et al. 1998), and the eastern Caribbean and Orinoco River plume (Del Castillo et al. 1999).

The positions and fluorescence intensities of Ex/Em_{max} for all stations are detailed in Table 2. Figure 2 shows the three-dimensional and contour plots of EEMs representative of low- and high-salinity end-members found in this study. MR1 was the only station with an EEM similar in shape to riverine EEMs reported elsewhere (Coble 1996). However, its Ex/Em_{max} was at 315/428 nm, suggesting that CDOM composition was intermediate between riverine and marine end-members. A salinity of 27.9 at this station indicated a large degree of dilution of the river water. Stations MR2, AR1, AR2, and TB1 also showed an average Ex/Em_{max} characteristic of marine transitional waters. Stations AR3, SR1, SR2, SR3, and SR4 showed Ex/Em_{max} characteristic of marine shallow waters. This particular water type has its Ex/Em_{max} at lower wavelengths than that of marine deep waters (Coble 1996). Stations TB2 and TB3 showed possible contamination in fluorescence and were not classified. Our results indicate that pure optical properties of riverine CDOM in the WFS were lost close to the coast. In the Mobile region, where the river influence was most evident, the riverine CDOM optical properties were already lost at station MR1

Table 2. Ex/Em_{max} , maximum fluorescence intensity, and salinity for samples collected in the WFS.

Station	Salinity	Ex/Em_{max} (nm)	QS (ppb)*
AR1	31.23	305/434	6.6
AR2	34.13	310/424	2.6
AR3	35.58	285/341	2.0
AR4	35.55	310/414†	1.5
DC1	35.70	300/422	1.9
DC2	36.18	300/382	0.2
MR1	27.90	315/428	14.2
MR2	30.46	305/422	5.7
SR1	35.21	285/344	5.4
SR2	35.89	305/394	0.8
SR3	35.57	305/402	0.8
TB1	34.75	310/420†	4.35
TB2	35.92	—‡	—‡
TB3	36.09	—‡	—‡

* Fluorescence intensity at the Ex/Em_{max} .

† Ex/Em_{max} is not well defined, so we report the emission maximum at excitation 310 nm.

‡ Stas. TB2 and TB3 showed contamination in the signal.

(salinity = 27.9) some 4 nautical miles from the mouth of Mobile Bay and restricted to the 10-fathom isobath. We did not detect riverine signals along the Suwannee River transect.

Changes in optical properties—We observed hypsochromic shifts in fluorescence Em_{max} of CDOM similar to those reported in previous works (Coble et al. 1996; De Souza Sierra et al. 1997; Del Castillo et al. 1999). To illustrate the relation between salinity at the Em_{max} inflection point and concentration of CDOM in river end-members, we plotted emission maximum versus salinity (Fig. 3) for samples collected in Puget Sound (Coble 1996), the Orinoco River plume (Del Castillo et al. 1999), and WFS (this work). The inflection points were approximately at salinities 26, 32.5, and 34.5 for Puget Sound, Orinoco, and WFS, respectively. Values for the 0-salinity end-members of Puget Sound (20 ppb) were measured from discrete samples (Coble 1996). Values from the Orinoco River plume (57 ppb) and WFS (63 ppb) were estimated from the regression equation of salinity versus fluorescence intensity at the emission maxima for each individual data set. The salinity at which the inflection points occurred correlated with fluorescence intensity for the 0 salinity end-members ($r = 0.99$, $n = 3$), that is, rivers with lowest CDOM concentration will have inflection points at lowest salinities. Although the WFS data fitted the trends well, we have recorded fluorescence values higher than 100 ppb for 0-salinity waters from the Apalachicola, Manatee, Peace, Hillsborough, and Caloosahatchee rivers (unpublished data); therefore the fluorescence value reported here should be considered as a low estimate.

Figure 4 shows the emission maximum at excitation 310 nm versus salinity for mixing model results and actual samples from the WFS (Model I). These results showed that conservative mixing alone could account for the majority of

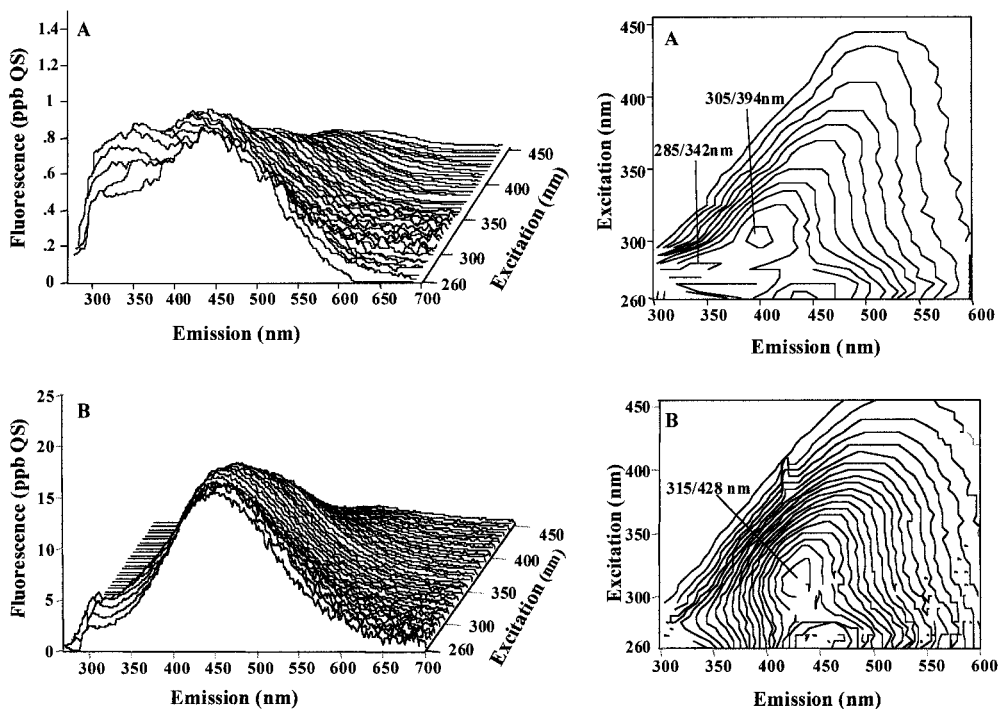


Fig. 2. Three-dimensional and contour plots of EEMs from (A) SR2 and (B) MR1, showing examples of high- and low-salinity end-members found in the WFS.

the observed changes in emission maximum among our sampling stations. Slight deviations from the model may be explained by procedural problems (e.g., use of incorrect end-members) or photodegradation. Possible effects of flocculation are discussed in the following section.

Flocculation experiments—The results of the mixing experiment (Model II) performed to determine possible effects of flocculation (Fig. 5) showed nearly identical behavior of the optical properties for laboratory and modeled mixtures although the two river systems behave differently. The variability in Em_{max} between modeled and laboratory mixtures for both experiments was ± 1 nm, and there were no signif-

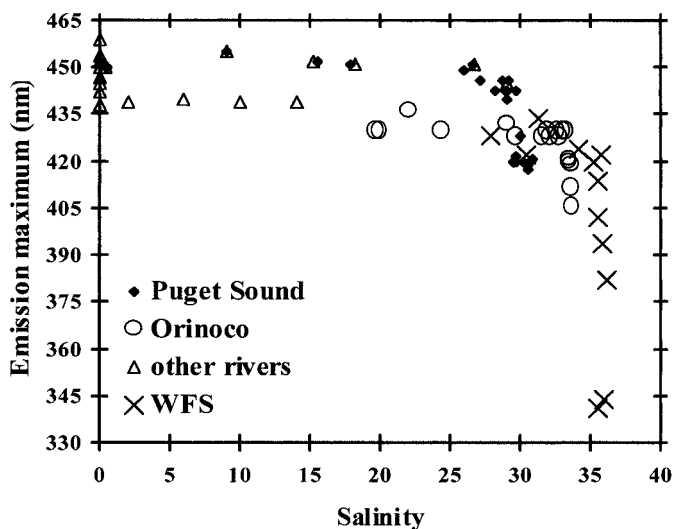


Fig. 3. Emission maxima (nm) at the excitation maxima versus salinity for samples collected in Puget Sound (Coble 1996), Orinoco River plume (Del Castillo et al. 1999), and WFS (this work). Data from other rivers (Coble 1996) include the Mississippi, Amazon, Negro, and Columbia rivers.

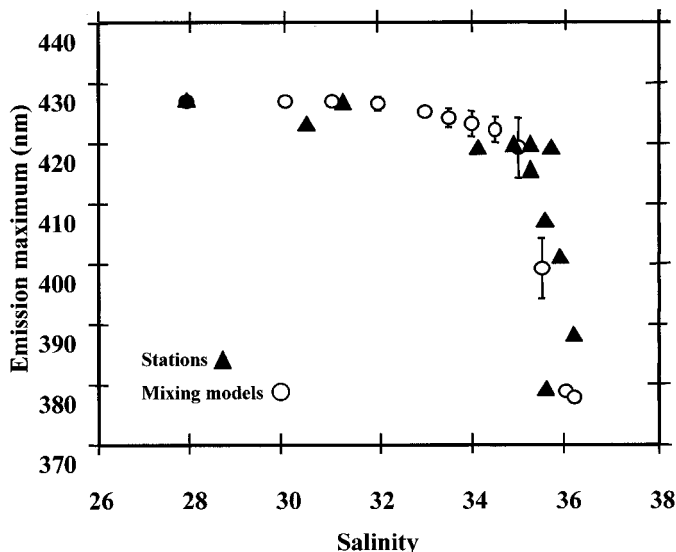


Fig. 4. Emission maximum at the excitation 310 nm versus salinity. Stations in the WFS and average of mixing models. Error bars represent the standard deviation for the average of the models.

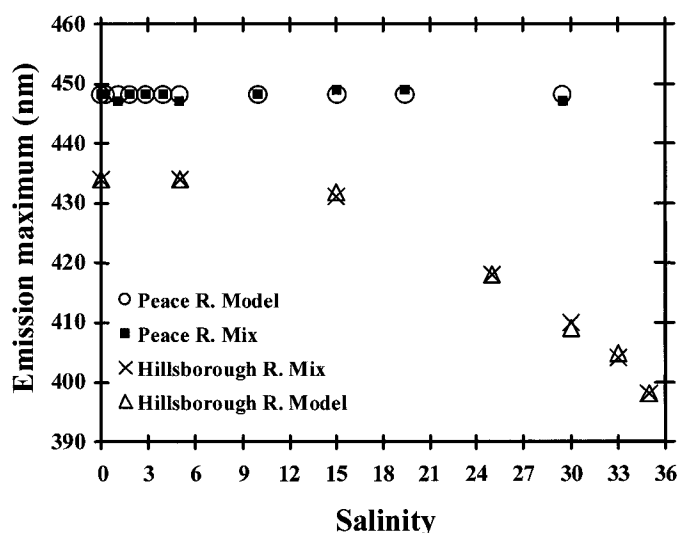


Fig. 5. Comparison between modeled and mixing experiments. Hillsborough and Peace River samples were collected upriver away from the estuary. Yucatán Strait and eastern Caribbean were collected during two separate cruises. Emission maximum is at excitation 310 nm. The inflection point at salinity ~ 15 in the Hillsborough River experiment was caused by dilution (1/100) of the 0 salinity end-member.

icant differences in fluorescence intensity. Addition of $\text{NaCl}_{(s)}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}_{(s)}$, and mixing with high-salinity seawater (Yucatán Strait) did not produce changes in the position of the Em_{max} . A slight decrease in fluorescence intensity ($\sim 2\%$) was observed after filtration but it was almost identical to changes observed in the procedural blanks and, therefore, was attributed to absorption of CDOM onto the membrane filter. We conclude that flocculation is not an important factor in the changes in optical properties of CDOM from the WFS.

Even if flocculation occurs in rivers draining into the WFS, its importance might be overshadowed by large concentrations of CDOM in the river end-member. To illustrate this, we modeled the possible effects of flocculation during mixing between Peace River and Gulf of Mexico waters (Fig. 6). In this simple model, we simulated losses of 5, 10, 20, and 80% of the riverine end-member CDOM in early stages of mixing ($\text{sal} = 0$ to 1). The model showed that even after losing 20% of the initial riverine fluorescence, mixing continues to be the prevalent process controlling changes in CDOM Em_{max} . This modeled loss was equivalent to 11% DOM and 20% color removal reported by Sholkovitz et al. (1976). However, this model did not take into account the possibility of preferential flocculation of the largest-molecular-weight CDOM fraction that might result in hypsochromic shift of the Em_{max} . This effect, however, was not observed in our laboratory mixing experiments.

Conclusions—From our results we reached the following conclusions: (1) The injection of riverine organic matter into the WFS largely affected the abundance of CDOM and DOC

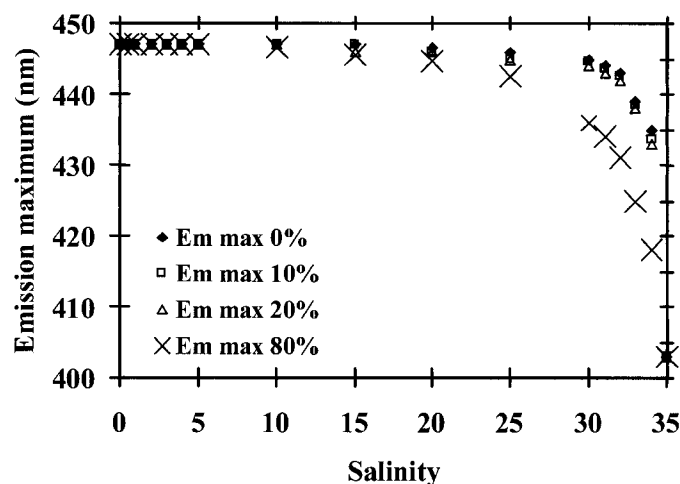


Fig. 6. Models showing the effect of reduction of CDOM fluorescence in the position of the $\text{Em}_{(\text{max})}$ at excitation 310 nm. Percentages represent modeled loss of riverine end-member fluorescence at salinity < 1 .

in the stations close to the rivers. The large input of nutrients also had a significant impact upon primary productivity, but our data suggested that PP did not produce significant changes in the concentration of CDOM. (2) The optical signature of riverine CDOM was limited to areas close to the mouths of the rivers. This was evident in the EEMs data, which showed fluorescence spectra characteristic of marine transitional waters only at stations MR1, MR2, AR1, and AR2. The remaining stations showed EEMs characteristic of marine waters. (3) Results from the mixing experiment indicated that dilution of the riverine waters with marine oligotrophic waters could account for the observed changes in optical properties. Changes due to flocculation appeared to be negligible, but more studies are necessary in rivers with high loads of sediments. Photodegradation was not studied in this work and cannot be discounted as a possible contributor to optical changes in the region. However, we believe that mixing of river and marine waters is the primary mechanism in reducing the riverine signal and controlling optical properties, particularly at low salinities. High concentrations of particulate material, phytoplankton, and terrestrial CDOM can reduce the penetration of light and photobleaching. We have observed this phenomenon in the Orinoco River plume where CDOM is abundant (Del Castillo et al. 1999). Moreover, photodegradation processes are limited to periods in which the solar irradiance is sufficient to initiate photoreactions, whereas mixing between riverine and seawater is a continuous process. Photodegradation could play a major role in the modification of CDOM in clear oligotrophic waters. (4) Studies on the basis of remote-sensing measurements of pigments need to consider the large differences in concentration and nature of the CDOM between low- and high-salinity regions in the shelf, and the periodic changes in riverine input. However, the limited geographic dispersal of riverine CDOM, the apparent decoupling between PP and production of CDOM, and the predictable behavior of its

optical properties should simplify the interpretation of remote-sensing measurements in most regions of the WFS.

Carlos E. Del Castillo¹

Department of Marine Science
University of South Florida
140 7th Avenue South
St. Petersburg, Florida 33701

Fernando Gilbes

Departamento de Ciencias Marinas
Universidad de Puerto Rico
Recinto Universitario de Mayagüez
Mayagüez, Puerto Rico 00680

*Paula G. Coble
Frank E. Müller-Karger*

Department of Marine Science
University of South Florida
140 7th Avenue South
St. Petersburg, Florida 33701

References

- BATTIN, T. J. 1998. Dissolved organic matter and its optical properties in a blackwater tributary of the upper Orinoco River, Venezuela. *Org. Geochem.* **28**: 561-569.
- BLOUGH, N. V., O. C. ZAFIRIOU, AND J. BONILLA. 1993. Optical absorption spectra of waters from the Orinoco River outflow: Terrestrial input of colored organic matter to the Caribbean. *J. Geophys. Res.* **98**: 2271-2278.
- BRICAUD, A., A. MOREL, AND L. PRIEUR. 1981. Absorption by dissolved organic matter of the sea (Yellow Substance) in the UV and visible domains. *Limnol. Oceanogr.* **26**: 43-53.
- CABANISS, S. E., AND M. S. SHUMAN. 1987. Synchronous fluorescence spectra of natural waters: Tracing sources of dissolved organic matter. *Mar. Chem.* **21**: 37-50.
- CARDER, K. L., R. G. STEWARD, G. R. HARVEY, AND P. B. OTNER. 1989. Marine humic and fulvic acids: Their effects on remote sensing of ocean chlorophyll. *Limnol. Oceanogr.* **34**: 68-81.
- COBLE, P. G., C. A. SCHULTZ, AND K. MOPPER. 1993. Fluorescence contouring analysis of DOC intercalibration experiment samples: A comparison of techniques. *Mar. Chem.* **41**: 173-178.
- . 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Mar. Chem.* **52**: 325-346.
- , C. E. DEL CASTILLO, AND B. AVRIL. 1998. Distribution of DOM in the Arabian Sea during the 1995 summer monsoon. *Deep-Sea Res.* In press.
- DEL CASTILLO, C. E., P. G. COBLE, J. M. MORELL, J. M. LÓPEZ, AND J. E. CORREDOR. 1999. Analysis of the optical properties of the Orinoco River Plume by absorption and fluorescence spectroscopy. *Mar. Chem.* **66**: 35-51.
- DE SOUZA SIERRA, M. M., O. F. X. DONARD, AND M. LAMOTE. 1997. Spectral identification and behavior of dissolved organic fluorescent material during estuarine mixing processes. *Mar. Chem.* **58**: 511-558.
- EADIE, B. J., L. M. JEFFREY, AND W. M. SACKETT. 1978. Some observations on the stable carbon isotope composition of dissolved and particulate organic carbon in the marine environment. *Geochim. Cosmochim. Acta.* **42**: 1265-1269.
- ECKERT, J. M., AND E. R. SHOLKOVITZ. 1976. The flocculation of iron, aluminium, and humates from river water by electrolytes. *Geochim. Cosmochim. Acta* **40**: 847-848.
- FREDERICKS, A. D., AND W. M. SACKETT. 1970. Organic carbon in the Gulf of Mexico. *J. Geophys. Res.* **75**: 2199-2206.
- GILBES, F., C. TOMAS, J. J. WALSH, AND F. MÜLLER-KARGER. 1996. An episodic chlorophyll plume on the West Florida Shelf. *Cont. Shelf Res.* **16**: 1201-1224.
- . 1996. Analysis of episodic phytoplankton blooming and associated oceanographic parameters on the West Florida Shelf using remote sensing and field data. Ph.D. thesis, Univ. of South Florida.
- HARDING, L. W., B. W. MEESON, AND T. R. FISHER. 1986. Phytoplankton production in two east coast estuaries: Photosynthesis-light functions and patterns of carbon assimilation in Chesapeake and Delaware bays. *Estuar. Coastal Shelf Sci.* **23**: 773-806.
- LAANE, R. W. P. M. 1981. Composition and distribution of dissolved fluorescent substances in the Ems-Dollart Estuary. *Neth. J. Sea Res.* **15**: 88-99.
- MANTOURA, R. F. C., AND M. S. WOODWARD. 1983. Conservative behavior of riverine dissolved organic carbon in the Severn Estuary: Chemical and geochemical implications. *Geochim. Cosmochim. Acta.* **47**: 1293-1309.
- MOREL, A. Y. 1988. Optical modeling of the upper ocean in relation to its biogenous matter content (Case I waters). *J. Geophys. Res.* **93**: 10749-10768.
- MÜLLER-KARGER, F., J. J. WALSH, R. H. EVANS, AND M. B. MEYERS. 1991. On the seasonal phytoplankton concentration and sea surface temperature cycles of the Gulf of Mexico as determined by satellites. *J. Geophys. Res.* **96**: 12645-12665.
- PRESTON, M. R., AND J. P. RYLEY. 1992. The interaction of humic compounds with electrolytes and three clay minerals under simulated estuarine conditions. *Estuar. Coastal Mar. Sci.* **14**: 567-576.
- SHOLKOVITZ, E. R. 1976. Flocculation of dissolved organic and inorganic matter during mixing of river water and seawater. *Geochim. Cosmochim. Acta* **40**: 831-845.
- , E. A. BOYLE, AND N. B. PRICE. 1978. The removal of dissolved humic acids and iron during estuarine mixing. *Earth Planet. Sci. Lett.* **40**: 130-134.
- SIEGEL, D. A., AND A. F. MICHAELS. 1996. Quantification of non-algal attenuation in the Sargasso Sea: Implications for biogeochemistry and remote sensing. *Deep-Sea Res. II.* **43**: 321-345.
- STEWART, A. J., AND R. G. WETZEL. 1981. Asymmetrical relationship between absorbance, fluorescence, and dissolved organic matter. *Limnol. Oceanogr.* **26**: 590-597.
- SWAINE, R. M. 1996. Characterization of marine humic material by high-performance liquid chromatography. M.S. thesis, Univ. of South Florida.
- YENTSCH, C., AND D. MENZEL. 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. *Deep-Sea Res.* **10**: 221-231.

Received: 12 January 1999

Accepted: 27 April 2000

Amended: 10 May 2000

¹ Present address: National Aeronautics and Space Administration, Earth System Science Office, Building 100 Code #SA00, John Stennis Space Center, Mississippi 39529.

Acknowledgments

Thanks are due to the crew of the RV *Suncoaster* and the personnel of the Florida Institute of Oceanography for their help. Our gratitude also goes to Juan G. González and José M. López from the Department of Marine Science, University of Puerto Rico at Mayagüez for providing the Go-Flo bottles, and to Larry Harding and Mike Maloney from the University of Maryland for providing the primary productivity data. Anonymous reviewers provided useful suggestions to this manuscript. The NASA grants NGT-30316, NGT-70375, and NAGW-3483 supported this research.