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Multispectral in situ measurements of organic matter and chlorophyll fluorescence in seawater: Documenting the intrusion of the Mississippi River plume in the West Florida Shelf

Abstract—We performed multispectral, in situ fluorescence measurements of detrital colored organic matter (COM) and chlorophyll *a* (Chl *a*) in surface waters of the West Florida Shelf using the Wet Labs spectral absorption and fluorescence instrument (SAFIre). Continuous underway measurements allowed simultaneous mapping of the dispersal pattern of riverine organic material and Chl *a* on the shelf. We used two fluorescence emission ratios to differentiate between riverine and marine COM. The data showed unusually high concentrations of COM offshore. These were attributed to an offshore extension of the Mississippi River plume. Comparisons between in situ Chl *a* concentrations measured with the SAFIre and Chl *a* values obtained from the sea-viewing wide field-of-view sensor (SeaWiFS) satellite data using OC4 and MODIS algorithms showed that, although both algorithms overestimated Chl *a*, MODIS performed better than OC4, particularly in areas with high COM concentrations. Analysis of the relationship between Chl *a* and COM concentrations within the study area showed regional variability probably caused by differences in river source.

Accurate determinations of marine chlorophyll *a* (Chl *a*) and colored dissolved organic matter (CDOM) concentra-

tions using satellite color-sensor data are essential for our understanding of the global carbon cycle and its implications in modifying world climate. CDOM is a major impediment to accurately estimating Chl *a* concentrations in coastal regions from satellite ocean color sensors (Carder et al. 1989; Müller-Karger et al. 1989). The major source of CDOM in coastal waters is river runoff of terrigenous organic matter. Away from continental margins, the effect of rivers declines and CDOM is mostly composed of material produced in the oceans. Phytoplankton growth (Carder et al. 1989; Siegel and Michaels 1996) and zooplankton grazing (Momzikoff et al. 1994) produce new CDOM, whereas photodegradation is the major destructive pathway (Kouassi and Zika 1990; Kieber et al. 1989). These in situ processes result in changes in CDOM concentrations and could alter its optical properties. Understanding these changes has obvious implications in the study of the carbon cycle and in the determination of Chl *a* concentrations from satellite color sensors.

Several spectroscopic techniques can be used to study the optical properties of CDOM. Studies using high-resolution fluorescence spectroscopy demonstrate that CDOM fluorescence excitation and emission maxima (Ex_{max} - Em_{max}) are de-

pendent upon the source and history of the organic matter (Coble 1996). Marine CDOM generally shows $Ex_{max}-Em_{max}$ at shorter wavelengths than riverine CDOM, presumably due to lesser degree of aromaticity and complexity of the molecules. In regions influenced by riverine CDOM, such as the Orinoco River plume and the West Florida Shelf, fluorescence of CDOM decreases linearly with increasing salinity. However, the position of the $Ex_{max}-Em_{max}$ remains constant over a large salinity range (i.e., 0 to ~ 30) because the marine signal is masked by the larger riverine fluorescence signal. At higher salinities, the riverine end-member becomes more diluted and the marine signal becomes more preponderant, which results in a large shift in $Ex_{max}-Em_{max}$ toward shorter wavelengths (De Souza Sierra et al. 1997; Del Castillo et al. 1999). Likewise, differences have been observed in the shape of CDOM absorption spectra between riverine and open ocean environments (Blough et al. 1993; Del Castillo et al. 1999).

High-resolution fluorescence and absorption spectroscopy are labor-intensive techniques. This limits the number of samples that can be analyzed and the spatial resolution of the data. The development of new satellite sensors, such as Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and the Moderate-resolution Imaging Spectroradiometer (MODIS), and the promise of hyperspectral and high-spatial resolution sensors drive the development of new instruments capable of providing pigments, CDOM, and spectral data at fine spatial scales. Specifically, in situ instruments like the WetLabs ac-9 improved sampling resolution and enable researchers to simultaneously measure Chl *a* and CDOM absorbance. This helps to directly assess their individual contribution to light attenuation in the water column. However, absorbance measurements do not permit a detailed characterization of CDOM optical properties because CDOM absorption spectra are essentially featureless. In contrast, fluorescence spectroscopy provides greater spectral resolution.

We report herein multispectral, in situ measurements of Chl *a* and detrital organic matter fluorescence using the WetLabs spectral absorption and fluorescence instrument (SAFIre). Our purpose is to highlight the capabilities and interpretation of such data collected from 6 to 10 August 1998 in the West Florida Shelf (WFS) as part of the Ecology of Harmful Algal Blooms (ECO HAB) Program and to demonstrate its value in the interpretation of ocean color imagery. We further document an intrusion of the Mississippi River plume into the WFS.

Methods—Collection of data: We made underway fluorescence measurements aboard the R/V *Suncoaster* from 6 to 10 August 1998 on the West Florida Shelf. The SAFIre was connected to the flow-through system of the vessel, which drew seawater from a depth of ~ 2 m. Seawater was not filtered to allow for simultaneous measurements of detrital colored organic matter and Chl *a* fluorescence, therefore the results indicated fluorescence of both dissolved and particulate organic materials. The sum of these materials will be referred to hereafter as colored organic matter (COM). Measurements were taken in two ways, underway and at each station, for a period of ~ 10 min. Discrete samples for the calibration of the SAFIre were collected at 22 stations.

Instrumentation: The SAFIre used has six excitation and 16 fluorescence emission channels. The instrument was configured for spectral CDOM fluorescence with simultaneous detection of chlorophyll fluorescence as follows: excitation filters with bandpass centered at 228, 265, 307, 375, 430, and 487 nm (± 20 nm), and emission filters with bandpass centered at 228, 265, 307, 340, 375, 400, 430, 470, 487, 510, 540, 590, 620, 685, 700, and 810 nm (± 20 nm).

Instrument calibration: Raw SAFIre data show a spectral bias. This is normal to all spectrofluorometers and is due to the characteristics of the light source, excitation and emission filters, and detectors. Therefore, raw data from different instruments with similar filter sets cannot be compared directly until appropriate correction factors are applied. A mismatch between the SAFIre response and the fluorescence spectrum of quinine sulfate precludes the use of this fluorescence standard for calibration of several emission wavelengths. For this reason, CDOM from seawater was used as a secondary standard (Conmy 1999). We collected water samples at 22 stations for the calibration of the SAFIre COM fluorescence channels. These were collected from the outlet of the instrument while station fluorescence data were being recorded. The samples were filtered through precombusted (12 hr at 450°C) GF/F filters mounted in a stainless steel in-line filter holder connected directly to the flow-through system. After filtration, the samples were store refrigerated ($\sim 3-4^\circ\text{C}$) until analysis. The samples were analyzed using a SPEX Fluorolog II spectrofluorometer (Coble et al. 1993). Both spectral and intensity data were calibrated against published data for quinine sulfate fluorescence in 0.1 N sulfuric acid (Velapoldi and Mielenz 1980). These corrected spectra were compared to data from the SAFIre obtained at the time of discrete sample collection to derive correction factors. These were applied to the remainder of the data. Fluorescence intensities were expressed in units equivalent to parts per billion of quinine sulfate (ppb QS). Details of the correction procedure for the SAFIre instrument data can be found in Conmy (1999).

It is pertinent that we comment briefly on the use of filtered samples to calibrate the fluorescence response obtained from unfiltered seawater, which contains particulate organic carbon (POC). The filtered seawater samples were used as a secondary standard to calibrate the fluorescence intensity and to correct the spectral response of the SAFIre. These calibration factors were valid for any substance fluorescing in the wavelength range of our secondary standard. Therefore, the results presented here adequately describe the fluorescence properties of the COM irrespective of its components (CDOM + POC). Nevertheless, the concentration of particles in our study site is usually low so we expect that the COM fluorescence data should be very similar to CDOM. For example, Gilbes (1996) reported that the concentrations of dissolved organic carbon in a station off Tampa Bay (within our study site) was ~ 18 times higher than that of particulate material (detritus + phytoplankton), and that the absorption coefficient of CDOM (at 400 nm) was seven times higher than that of the particulate fraction. The influence of POC in the offshore stations is even lower. Finally, qualitative analysis using fluorescence ratios was self-

consistent and was corroborated by using the CDOM fluorescence spectra from discrete samples (Conmy et al. pers. comm.). This agreement demonstrated the validity of the calibration method.

Chlorophyll fluorescence (Ex = 430 nm Em = 685 nm) was related to extracted chlorophyll (Holm-Hansen and Riemann 1978) using water samples collected at every other station (~10 nautical miles). Chlorophyll fluorescence and extracted Chl *a* showed an unusually strong positive correlation over the whole sampling region ($r^2 = 0.95$; $n = 22$). Microscopic observations in the field indicated that diatoms in near-shore areas dominated the algal population, whereas microflagellates dominated in offshore waters.

Emission ratios: Ratios of fluorescence emission at several wavelengths were used as an index to differentiate between COM of marine and terrigenous origin. A similar method has been used to characterize discrete samples from black-water tributaries of the Orinoco River to discriminate between CDOM from aquatic and terrestrial sources (Battin 1998). We used two emission ratios: fluorescence at 375 and 400 nm from excitation at 265 nm ($F_{375/400nm}$), and fluorescence at 430 and 540 nm from excitation at 307 nm ($F_{430/540nm}$). These ratios indicated differences in the emission maxima of CDOM from different sources (Coble 1996; De Souza Sierra et al. 1997; Del Castillo et al. 1999), and therefore provided evidence of differing chemical composition of COM.

Results and discussion—Surface distributions of COM fluorescence, Chl *a*, and salinity showed typical coastal patterns in the nearshore region, with highest values of COM and Chl *a* associated with freshwater inputs from Tampa Bay and the Manatee, Peace, and Caloosahatchee rivers (Fig. 1). Elevated values of COM and Chl *a* observed 100 nautical miles offshore were not expected and did not appear to be derived from the adjacent coastal waters in the study area, since there is an intervening high-salinity, low-COM water mass separating these regions. Salinity values within the offshore COM patch fell below 31, indicating a major freshwater source.

Fluorescence emission ratios showed differences in the optical characteristics of COM in the region (Fig. 2). Values lower than 1.0 for $F_{375/400nm}$ indicated that maximum fluorescence is at, or above 400 nm, characteristic of terrestrial COM. Higher values indicated that maximum fluorescence is between 375 and 400 nm, characteristic of marine COM. Coastal waters influenced by freshwater discharge from the Tampa Bay Estuary and the Manatee, Peace, and Caloosahatchee Rivers showed $F_{375/400nm}$ values lower than 1 (Fig. 2A), which indicates red-shifted, riverine COM. High ratios from blue-shifted COM were detected in the high-salinity tongue between the offshore low-salinity water and coastal

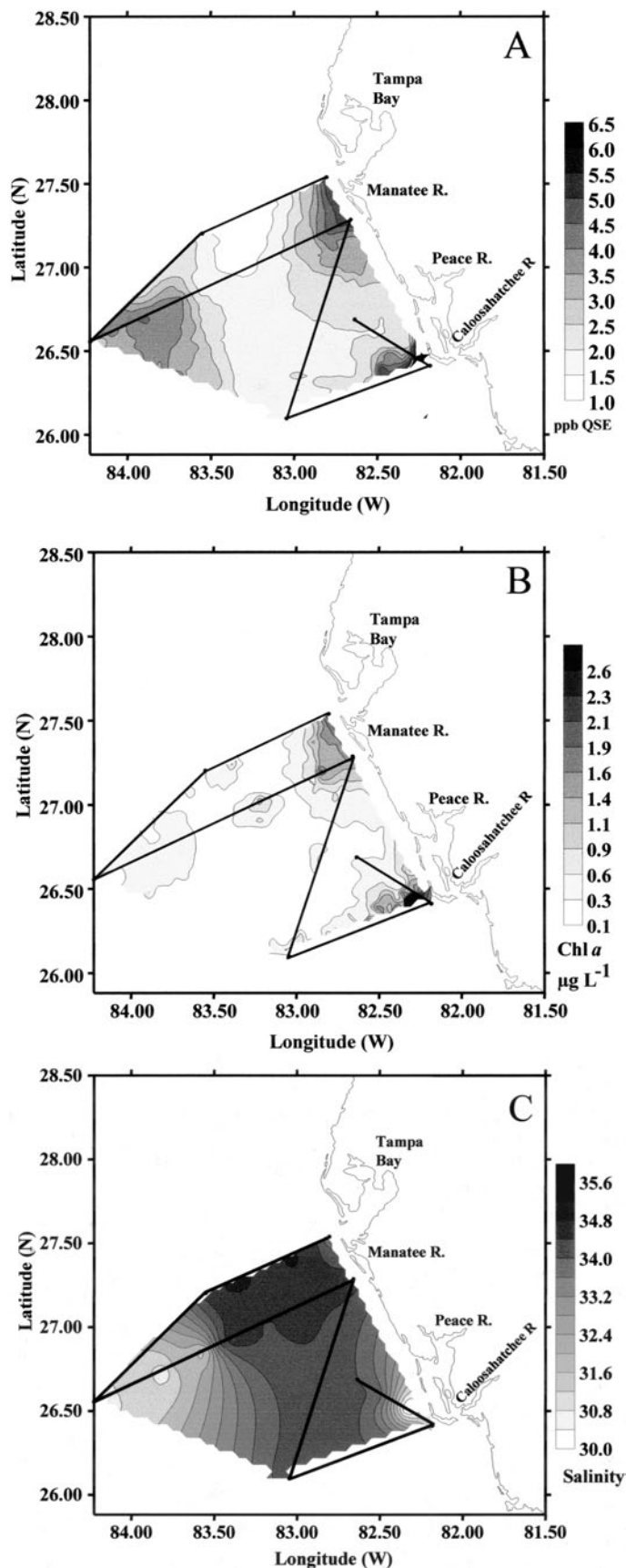


Fig. 1. Surface contour plots of (A) COM fluorescence, (B) Chl *a* ($\mu\text{g L}^{-1}$), and (C) salinity collected along the cruise track of the R/V *Suncoaster*. COM and Chl *a* data were collected underway whereas salinity data were collected at stations. Gridding of the data was done using inverse distance to a power on Surfer7 software.

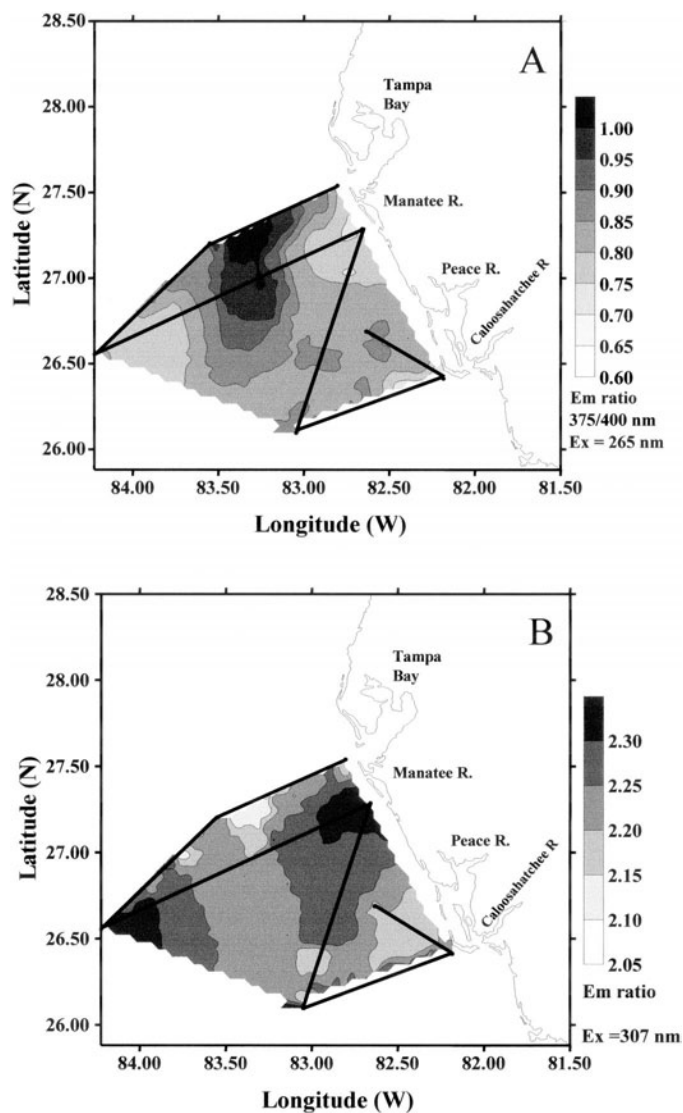


Fig. 2. Surface maps of emission ratios showing riverine and marine COM distribution in the study site. Ratios were calculated from corrected underway data. (A) Dark colors reflect blue shift in COM fluorescence emission maximum characteristic of marine organic matter. (B) Dark colors reflects a red shift in fluorescence emission maximum characteristic of riverine COM. In both panels, it is evident that riverine COM is present offshore. Gridding of the data was done using inverse distance to a power on Surfer7 software.

waters. The offshore, low-salinity waters showed low ratios (<1) similar to inshore waters indicative of riverine input. All possible ratios comparing emission at longer wavelengths ($Em_{400/470}$, $Em_{400/430}$, $Em_{400/540}$, and $Em_{430/470}$) yield results similar to those of $Em_{430/540}$ (Fig. 2B). Values for $Em_{430/470}$ ratio were greater than 2.0 for all samples due to a generally low fluorescence at 540 nm. Emission at 430 nm controlled the value of this ratio; thus, the highest ratios occurred where COM concentration was highest, i.e., in waters influenced by rivers.

SeaWiFS satellite imagery showed a spatial pattern similar to those observed in the COM and Chl *a* measured dur-

ing the cruise (Fig. 3). However, satellite-derived Chl *a* concentrations were higher than those observed in situ, particularly within the fresh water patches. The SeaWiFS data showed that the offshore patch was not contiguous to the region of high Chl *a* along the coast, except in the extreme northern Gulf of Mexico; therefore, it is not likely that it originated from local river inputs. The source of this water mass probably was the Mississippi River plume, which flowed southeast in the Gulf of Mexico at this time. The SeaWiFS image showed a region of high Chl *a* water to the east of the main channel of the Mississippi River, extending all the way to Cape San Blas and the Apalachicola River. The plume occupied the region between 84 and $86^{\circ}W$ and southward from the coast to $27^{\circ}N$. What appears to be a streamer from the main river plume, with slightly lower pigment concentrations, extended southward as far as the Florida Straits along $83.5^{\circ}W$.

The Mississippi River plume generally flows westward, hugging the coasts of Louisiana and Texas (Müller-Karger et al. 1991; Walker et al. 1994) but eastward movement of Mississippi River water has been detected in monthly composites of Chl *a* concentration derived from the coastal zone color scanner satellite sensor (CZCS) (see Müller-Karger et al. 1991). Eastward dispersal of the Mississippi plume was most frequent between April and July in 1979–1982, but both CZCS and more recent SeaWiFS data show that eastward dispersal may also be observed at other times of the year (Müller-Karger 2000). A large intrusion of the Mississippi River plume into the Florida Shelf was also observed during the summer of 1993 (Walker et al. 1994). During this period, westerly wind flow and the presence of an anticyclonic eddy in the northern Gulf of Mexico coupled with the highest river flow recorded in 63 yr resulted in this large intrusion event, which reached the Florida Keys (Walker et al. 1994). Observations of an offshore band of high chlorophyll that parallels the west Florida coast during spring have also been attributed to the inflow of rivers in the northwest coast of Florida, or to the Mississippi River (Gilbes 1996; Gilbes et al. 1996). However, we still lack rigorous documentation on the frequency and timing of occurrence of fresh water plumes, particularly during the fall season. Further, there is no systematic study of the frequency and magnitude of the eastward dispersion of the Mississippi River water.

It could be argued that other rivers in the Gulf Coast region may have contributed to the high-CDOM offshore patch described in this work. The following evidence is presented to strengthen our assertion that the source of the high CDOM patch was the Mississippi River. (1) TOPEX-Poseidon altimetry data collected prior to the cruise (May–July 1998) shows an anticyclonic eddy intruding into the North Eastern Gulf of Mexico (NEGOM). The eddy contributed to convergence near the Mississippi River Delta and resulted in an eastward flow of the plume along the coast (Müller-Karger 2000). (2) The anticyclone over NEGOM, and a second anticyclone over the outer shelf, west of Tampa Bay, were observed during the same period by shipboard acoustic Doppler current profiler (Nowlin et al. 2000). (3) Eastward winds ($>3 \text{ m s}^{-1}$) along the Alabama coast were reported by Müller-Karger (2000). (4) Data obtained from the United

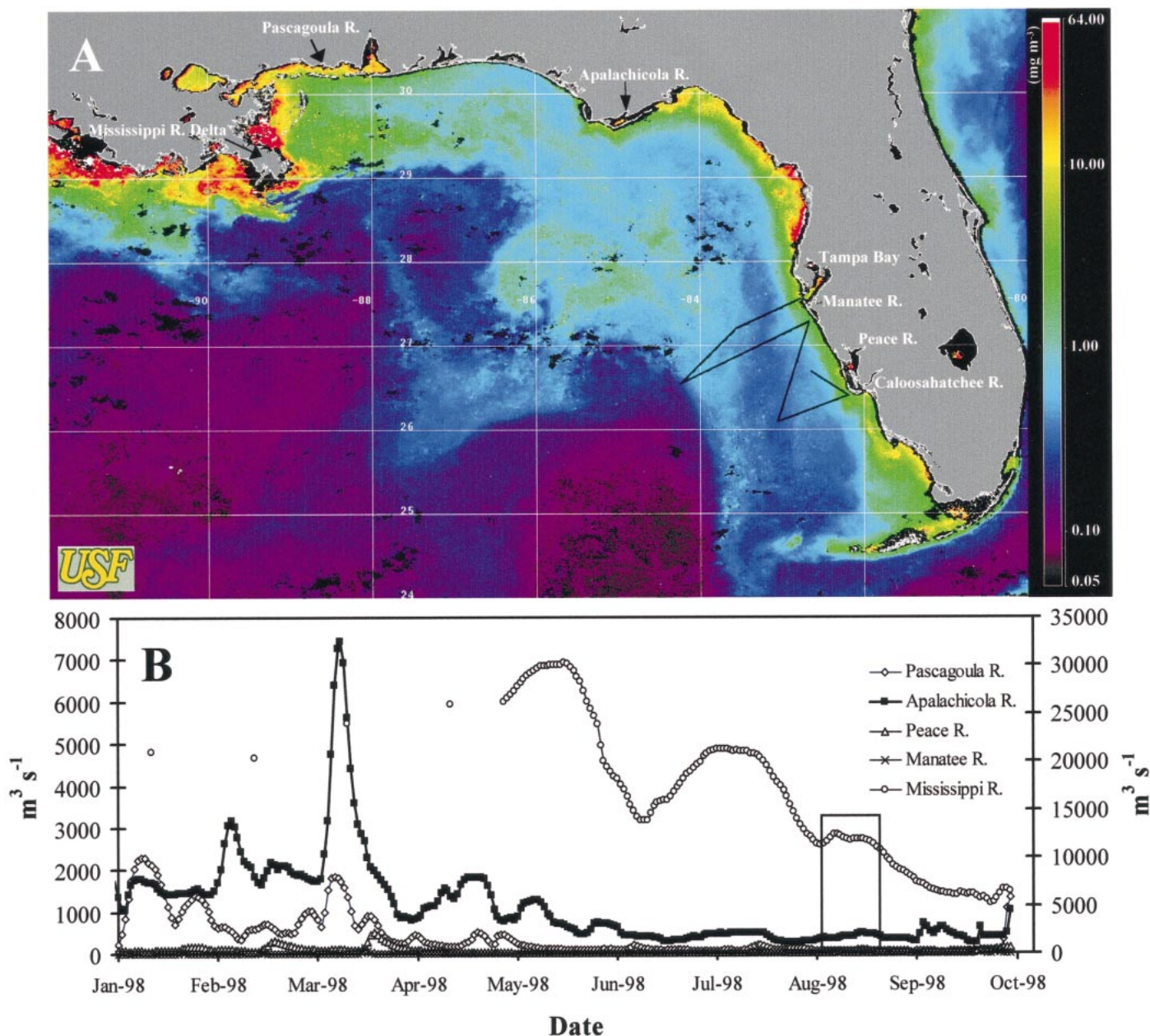


Fig. 3. (A) SeaWiFS satellite image of Gulf of Mexico. The image represents an averaged weekly composite of Chl *a* concentration obtained during the time of the cruise. Chlorophyll values were obtained using OC4 default algorithm. Cruise track is shown as a black line west of Tampa Bay. (B) Average daily flows for several rivers in the Gulf Coast. Data for the Mississippi River before May of 1998 are monthly averages. Scale for the Mississippi River data is on the right axis. The rectangle identifies the period sampled during the research cruise.

States Geological Survey (Fig. 3b) shows that the flow from rivers in the west coast of Florida during the months before the cruise was low. The same data set showed two strong pulses from the Mississippi River during the months before the cruise and a yearly river flow higher than the annual average (Fig. 3b). Two short pulses recorded during March 1998 from the Tombigbee River in Mobile Bay (Nowlin et al. 2000) and the Apalachicola River (Gilbes et al. 2001) contributed with significant amounts of fresh water during March 1998. During the first two weeks of March, a shelf

plume continuous with the Apalachicola River outflow extended to the Florida Keys. By late March, coinciding with the reduction in water flow from the Apalachicola, the shelf plume disappeared. The same image showed water from the Mississippi River moving southwest toward the West Florida Shelf (Gilbes et al. 2001).

We have previously reported that the influence of riverine CDOM draining into the Florida shelf was limited to coastal regions (Del Castillo et al. 2000b). The data presented in this work as well as monthly measurements made over a 1-

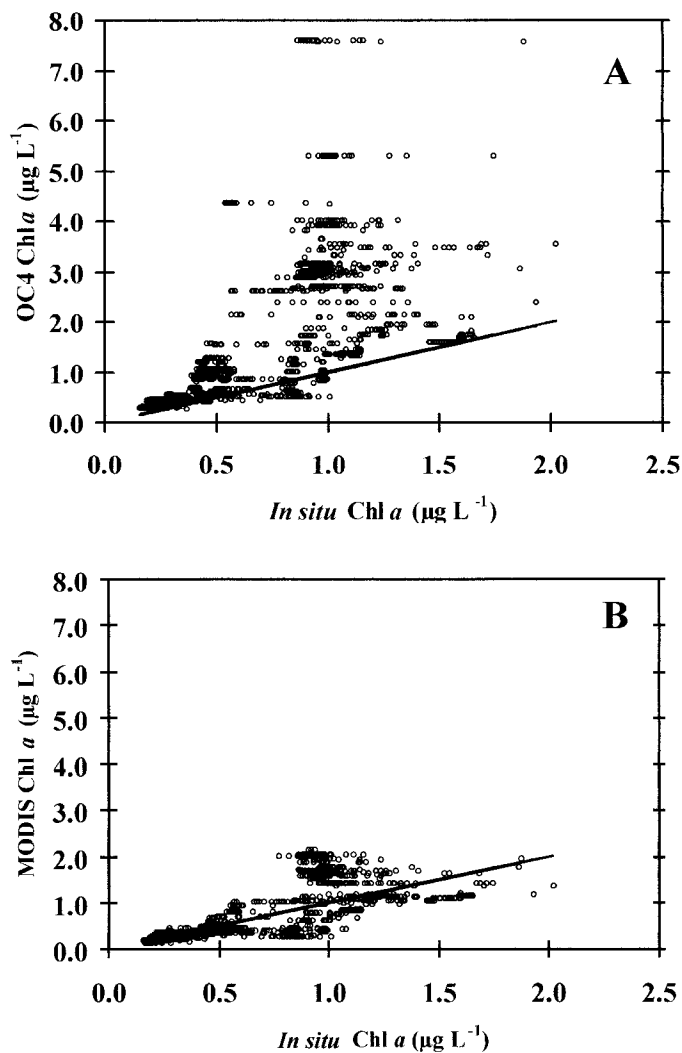


Fig. 4. In situ vs. chlorophyll ($\mu\text{g L}^{-1}$) modeled from SeaWiFS color data using (A) OC4 and (B) MODIS algorithms. Solid line represents the 1:1 fit for in situ Chl *a*.

yr period in the WFS (Del Castillo et al. 2000a) sustain this conclusion and underline the importance of the Mississippi River as the main source of terrigenous CDOM in offshore waters in the Gulf of Mexico.

A detailed comparison between in situ and satellite-derived chlorophyll was not possible for the entire study region due to clouds and temporal mismatches between satellite passes and the in situ data collection. These included offshore areas influenced by the Mississippi River plume. For areas where close comparisons were possible (<24 hr; Peace-Caloosahatchee River and diagonal transects), we compared our in situ Chl *a* concentrations measured with the SAFire with Chl *a* values derived from the SeaWiFS data. Two different biooptical algorithms were used on the satellite data, OC4 (O'Reilly et al. 1998) and MODIS (Carder et al. 1999). Values were obtained from 3×3 pixel average composite of the study region taken at the time of the cruise (Fig. 4). Carder's MODIS algorithm performed better than the OC4 model in inshore areas (<25

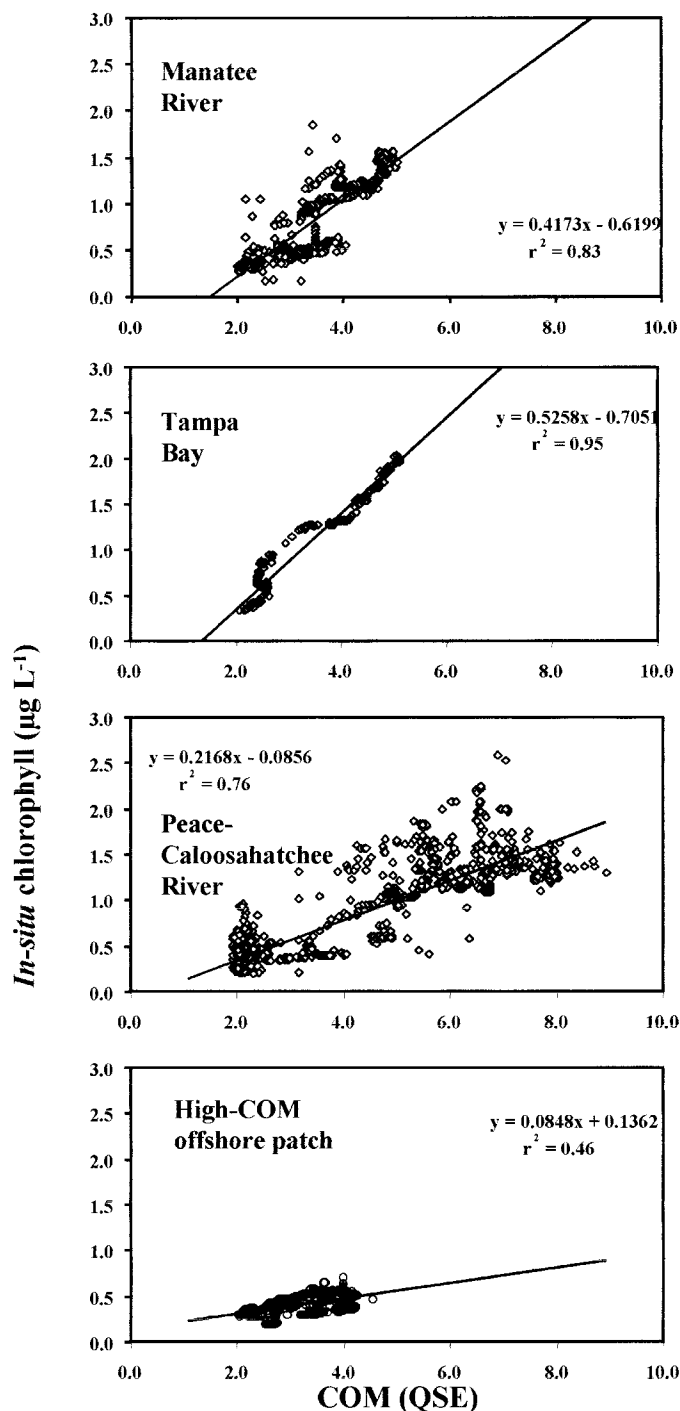


Fig. 5. Chlorophyll vs. COM fluorescence along several transects lines.

nautical miles from the coast) where the concentrations of COM and chlorophyll were highest.

SAFire data showed differences in the COM-chlorophyll relationships between the Tampa Bay, Manatee, and Caloosahatchee-Peace River regions (Fig. 5). The offshore waters influenced by the Mississippi River also showed a distinct chlorophyll/COM relationship with high COM and low chlorophyll fluorescence. This variability can contribute to the

shortfalls of the ocean-color algorithms, even for the MODIS algorithm, which takes into consideration CDOM. The potential for errors may be higher within the waters of the Mississippi plume, in which the in situ data showed high COM concentrations and very low apparent freshwater end-member Chl *a* values. In fact, values reported by biooptical models applied to SeaWiFS data in offshore regions of this plume are consistently higher than those measured by Remsen and Hopkins (1999) or those reported here.

Intrusions of the Mississippi River plume into the Gulf of Mexico and the WFS affected the biooptical properties of surface waters in the region and may have influenced increases in productivity and changed species composition in the normally oligotrophic waters of the Gulf. During an almost simultaneous cruise to the Gulf of Mexico (21–31 July 1998), colleagues from the University of South Florida encountered the same low-salinity feature 85 nautical miles west of our most offshore station (Remsen and Hopkins 1999). Concentrations of Chl *a* (at 27.0°, –86.0°) were up to 1.5 $\mu\text{g L}^{-1}$ averaging $\sim 0.5 \mu\text{g L}^{-1}$, that is 10 times higher than normal values reported for the Gulf. The influence of the river plume was also observed over several trophic levels. Plankton assemblies were dominated by diatoms and zooplankters typical of coastal and estuarine environments (e.g., *Eucalanus pileatus*). Bathypelagic and mesopelagic species of fishes were also captured close to the surface and, for the first time in a 20-yr record, which includes over 1,550 net troll samples, they reported the capture of anchovies (Remsen and Hopkins 1999). Evidently, the Mississippi River plume had a strong short-term impact in the eastern Gulf of Mexico. Long-term effects upon species distribution and the carbon budget of the region will depend upon the periodicity of these intrusion events. More detailed analysis of frequency and source of these fresh water plumes is needed, particularly because of the significant impact of the phenomenon upon carbon cycling in the region.

Conclusions—The use of the in situ, multispectral fluorescence instrument SAFire provided identification of river plumes, COM, and Chl *a* concentrations on the West Florida Shelf. Fluorescence emission ratios provided additional information that was useful to validate the inference that river plumes are detectable by SeaWiFS imagery. It also demonstrated the usefulness of in situ multispectral techniques for the study of optical properties of COM. SAFire can measure simultaneously chlorophyll and COM concentrations and provide information on the optical properties of COM. These capabilities could be used to evaluate the effect of COM upon the performance of biooptical models.

The Mississippi River plume produced changes in biooptical properties in what otherwise would be an oligotrophic water column in the interior of the Gulf of Mexico. Riverine COM present in offshore waters probably led to overestimates of SeaWiFS-derived pigment concentrations in the river plume. This highlights the need to better characterize the effect of COM upon global chlorophyll algorithms and to better document the behavior of the Mississippi River plume.

We have not attempted to use SAFire data to distinguish between individual riverine sources. However, other studies using fluorescence have demonstrated that spectral data have ad-

equated specificity for this task (Ferrari and Mingazzini 1995). Extension of these analyses to additional excitation and emission channels and improvement of the throughput of emission filters at 375 and 400 nm will lead to further improvement in rapid determination of spectral differences in COM in a way analogous to the use of excitation-emission matrices.

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