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

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Abstract

We performed multispectral in-situ fluorescence measurements of colored dissolved organic matter and chlorophyll in surface waters of the West Florida Shelf using Wet Labs Spectral absorption and Fluorescence Instrument (SAFlRe). Continuous measurements underway allowed us to simultaneously map the dispersion of riverine organic material and chlorophyll on the shelf. By using two fluorescence emission ratios we were able to differentiate between riverine and marine CDOM. Our data also showed unusually high concentrations of CDOM offshore. These were attributed to an intrusion of the Mississippi River Plume. We performed limited comparisons between in-situ chlorophyll concentrations measured with SAFlRe and chlorophyll values obtained from SeaWiFS satellite data using OC4 and MODIS algorithms. Our results show that, although both algorithms overestimated chlorophyll, MODIS performed better than OC4, particularly in areas with high CDOM concentrations. Analysis of the relationship between chlorophyll and CDOM concentrations within the study area showed regional variability caused by differences in river source.

Introduction

Accurate determinations of chlorophyll and colored dissolved organic matter (CDOM) concentrations over large scales in the oceans using satellite color-sensor data are essential for our understanding of the global carbon cycle and its implications in modifying world climate. Large amounts of CDOM in coastal regions are a major impediment to accurately estimating chlorophyll concentrations from satellite ocean color sensors (Carder et al., 1989; Müller-Karger et al., 1989; Siegel and Michaels, 1996). The major source of CDOM in coastal waters is river runoff of terrigenous organic matter.
Away from continental margins, the input of rivers declines, and CDOM is mostly composed of material produced in seawater. Phytoplankton growth (Carder et al., 1989; Siegel and Michaels, 1996; Sieburth and Jensen, 1969) and zooplankton grazing (Momzikoff et al., 1994; Coble et al., 1998) produce new CDOM, whereas photodegradation is the major destructive pathway (Kouassi and Zika, 1990; Kieber et al., 1989). These in-situ processes result not only in changes in CDOM concentrations, but also alter its optical properties. Understanding these changes has obvious implications in the study of carbon biogeochemical cycle, and in the determination of chlorophyll concentrations from satellite color sensors.

Several spectroscopic techniques can be applied to the study of optical properties of CDOM. Studies using high-resolution fluorescence spectroscopy demonstrate that CDOM fluorescence excitation and emission maxima (Ex_max/Em_max) are dependent 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), and then shifts rapidly towards shorter wavelengths at higher salinities as the riverine end-member is diluted by the seawater (Coble, 1996; 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) and Del Castillo et al. (1999) observed that, similar to the Ex_max/Em_max, S remain constant over a
large salinity range (0 to ~30) along the Orinoco River plume, and then changes rapidly at higher salinities.

High-resolution fluorescence and absorption spectroscopy clearly provide detailed information of the concentration and optical properties of CDOM. However, these techniques are labor intensive and time consuming. This limits the number of samples that can be analyzed, affecting the spatial resolution of the data. The development of new satellite sensors with spatial resolutions better than 30 m created a need for new instruments capable of providing concentration and spectral data at a fine scale. The recent development of rapid multispectral in-situ absorption instruments, like the WetLabs AC-9, improved sampling resolution and enabled researchers to simultaneously measure chlorophyll (chl) and CDOM absorbance 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 and the technique lacks the spectral definition provided by fluorescence spectroscopy.

We report herein in-situ measurements of CDOM composition using the WetLabs SAFIre (Spectral Absorption and Fluorescence Instrument) in real-time mapping mode. Our purpose is to highlight the capabilities and interpretation of such data using information collected from August 6 through 10, 1998 in the West Florida Shelf as part of the Ecology of Harmful Algal Blooms (ECOHAB) Program and to demonstrate its value in interpretation of ocean color imagery. We further document an intrusion of the Mississippi River plume into the WFS.
Methods

*Instrumentation*-Continuous *in-situ* underway measurements of fluorescence were performed on surface waters of the WFS using a SAFIre. This instrument has six excitation and 16 fluorescence emission channels that are pre-selected by the customer at the time of manufacture. Our instrument was configured for spectral CDOM fluorescence with simultaneous detection of chlorophyll fluorescence as follows: excitation filters centered at 228, 265, 307, 375, 430, and 487 nm (+/- 20 nm) and emission filters centered at 228, 265, 307, 340, 375, 400, 430, 470, 487, 510, 540, 590, 620, 685, 700, and 810 nm (+/- 20 nm).

*Collection of data*-Fluorescence measurements were made along the cruise track of the *R/V Suncoaster* during the first week of August 1998 within the study area of the Florida ECOHAB Program. The SAFIre was connected to the vessels flow-through system drawing seawater from a depth of approximately 2 m. Seawater was not filtered prior to the measurements, therefore, the results reflect fluorescence of both dissolved and particulate organic materials, and are referred to hereafter as colored organic matter (COM). Measurements were taken in two modalities: continuous measurements underway between stations and continuous measurements made at the station for a period of ~10 min. Discrete samples collected at selected stations for SAFIre calibration were filtered through pre-combusted (12 hr at 450°C) GF/F filters mounted in a stainless steel in-line filter holder connected directly to the flow-through system and stored refrigerated (~3-4°C) until analysis.
*Instrument calibration*-Raw SAFIre data show a spectral bias normal to all spectrofluorometers due to the characteristics of the instrumental optical components, which include light source, excitation and emission filters, and detectors. Therefore, raw data from different instruments, even those with identical filter sets, cannot be compared directly until appropriate correction factors are applied. A mismatch between SAFIre response and quinine sulfate fluorescence spectrum 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 (Conny, 1999). Discrete water samples collected while the ship was on station were analyzed and spectrally corrected using a SPEX Fluorolog II spectrofluorometer (Coble et al., 1993). Both spectral and intensity data were calibrated versus published data for quinine sulfate fluorescence in 0.1 M sulfuric acid (Velapoldi and Mielenz., 1980). These corrected spectra were then compared to data from the SAFIre obtained at the time of discrete sample collection, and the correction factors generated were applied to the remainder of the underway data. Fluorescence intensities were expressed in units of parts per billion of quinine sulfate (ppb QS). Details of the correction procedure for SAFIre can be found elsewhere (Conny, 1999).

Chlorophyll fluorescence at excitation 430 nm emission 685 nm was calibrated using measurements of extracted chl-a from samples taken at every other station (10 nautical miles) using the method described by Holm-Hansen and Reimann (1978). Chlorophyll fluorescence and extracted chl-a showed a strong correlation over the whole sampling region ($r^2 = 0.95; n = 22$). However, correlations along individual transects showed

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better fits \((r^2 > 0.97)\) so these regressions were used to calibrate the SAFIre chl-a data collected at along each transect.

*Emission ratios-* Ratios of fluorescence emission at several wavelengths were used 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). In this work we used two emission ratios: fluorescence at 375 nm and 400 nm excited at 265 nm \((F_{375/400nm})\), and fluorescence at 430 nm and 540 nm excited at 307 nm \((F_{430/540nm})\). The selected ratios reflect changes in the emission maxima of humic substances found in CDOM from different sources (Coble, 1996; Del Castillo et al., 1999; De Souza-Sierra et al., 1997) and, therefore, provide 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, since there is an intervening high-salinity, low-COMET water mass present. Salinity values offshore fell below 31, indicating of a major freshwater influence.

Fluorescence emission ratios showed clear differences in the optical characteristics of COM in the region (Figure 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 indicate 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 $F_{375/400\text{nm}}$ values lower than 1 (Figure 2A), indicating 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 waters. The offshore, low-salinity waters showed low values 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 $Em_{430/540}$ (Figure 2B). Values for this 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, highest ratios occurred where COM concentration was highest, i.e., in waters influenced by rivers.

SeaWiFS satellite imagery showed a similar pattern for surface distributions of COM and chl-a (Fig. 3) in the study region, but concentrations of chl-a were high in surface waters along the entire offshore edge of the WFS. This offshore water mass 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 was the Mississippi River plume, which flowed south-eastward 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 to 86°W and southward from the coast to 27°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° W.

The Mississippi River water outflow is generally carried westward, hugging the coasts of Louisiana and Texas (Muller-Karger et al., 1991; Walker et al., 1994). Preliminary analyses of monthly composites of chl-a concentrations from Coastal Zone Color Scanner satellite sensor (CZCS) imagery showed easterly flow of the Mississippi River Plume in the April to July period between 1979-1982, with variable duration and extent, suggesting that conditions are favorable during spring-summer. 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 years resulted in a 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 time of occurrence of fall plumes, and the eastward dispersion of the Mississippi River waters.

A detailed comparison between modeled and measured chlorophyll was not possible for the entire study region due to cloudiness and temporal mismatches between satellite passes and data collection. These included offshore areas influenced by the Mississippi River plume. For areas where matches were possible (Peace/Caloosahatchee River and diagonal transects), we compared our in-situ chl-a concentrations measured with the SAFIre with modeled chl-a values (OC4 and Carder’s MODIS) obtained from a three-
pixel average composite of the study region taken at the time of the cruise (Fig 4). Carder’s MODIS performed better than the OC4 model inshore (< 25 nautical miles) were the concentrations of COM and chlorophyll were highest. Scatter plots of chlorophyll vs. COM obtained with the SAFire (Fig 5) showed differences in the COM-chlorophyll relationships between the Tampa Bay, Manatee, and Caloosahatchee-Peace River regions. High COM waters from 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 algorithms, even for those which, like MODIS, take into consideration CDOM. The potential for errors is higher within the aged waters of the Mississippi Plume, which reported high CDOM concentrations and very low chlorophyll values. In fact, values reported by bio-optical models 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 clearly affected the bio-optical properties of surface waters in the region and may have affected productivity and species composition in the normally oligotrophic waters of the Gulf. During an almost simultaneous cruise to the Gulf of Mexico (7/21-7/31/98) 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 chlorophyll (at 27.0°, -86.0°) were up to 1.5 µg/l, averaging ~0.5 µg/l, 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 pileatatus). Bathy- and mesopelagic species of fishes were also captured close to the surface and, for the first time in a 20-years record which includes over 1550 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 Gulf of Mexico. Long-term effects upon species composition 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 the carbon cycling in the region.

Conclusions

The use of the in-situ multi-spectral fluorescence instrument SAFIre provided identification of river plumes and chlorophyll concentrations on the West Florida Shelf. Fluorescence emission ratios provided additional information which was useful to validate the inference that river plumes are detectable by SeaWiFS imagery and demonstrates the usefulness of in-situ multispectral techniques for the study of optical properties of CDOM. SAFIre has the capability of simultaneously measuring chlorophyll and CDOM concentrations while at the same time provides information on the optical properties of CDOM. These capabilities could be used as tools to evaluate the effect of CDOM upon the performance of bio-optical models.

Presence of Mississippi River water in the Gulf of Mexico produced changes in species composition and bio-optical properties of the water column. The presence of riverine CDOM in offshore waters resulted in overestimates of pigment concentrations by the algorithms used for analysis of SeaWiFS data. This highlights the need to better
characterize the effect of CDOM upon global chlorophyll algorithms and to better
document the behavior of the Mississippi River plume. We have previously reported that
the influence of the river plumes draining into the Florida shelf was limited to coastal
regions (Del Castillo et al., 2000a). The data presented in this work as well as monthly
measurements made over a period of a year in the WFS (Del Castillo et al., 2000b)
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.

The property of red-shifted riverine COM fluorescence and blue-shifted marine COM
fluorescence has been reported elsewhere from high resolution spectroscopic analyses
(Coble, 1996, Del Castillo et al., 1999), but, to our knowledge, this is the first successful
report from a field study using in-situ continuous flow instrumentation. 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
adequate 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 produced by high-performance fluorescence spectroscopy.

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Figure captions

Figure 1. Surface contour plots of COM fluorescence (A), chlorophyll-a (B), and salinity (C) collected along the cruise track of the R/V Suncoaster. COM and chlorophyll data were collected underway whereas salinity data was collected at stations. Gridding of the data was done using inverse distance to a power on Surfer software.

Figure 2. Surface maps of emission ratios showing riverine and marine COM distribution in the study site. Ratios were calculated from corrected underway data. In plate A, dark colors reflect blue shift in COM fluorescence emission maximum characteristic of marine organic matter. In plate B dark colors reflects a red shift in fluorescence emission maximum characteristic of riverine COM. In both plates it is evident that the presence of riverine COM offshore, presumably originated from the Mississippi River plume. Gridding of the data was done using inverse distance to a power on Surfer software.

Figure 3. SeaWiFS satellite image of Gulf of Mexico. The image represents an averaged weekly composite (8/8/98-12/8/98) of chlorophyll concentration obtained during the time of the cruise. Chlorophyll values were obtained using OC2 default algorithm.

Figure 4. In-situ vs. chlorophyll (μg L⁻¹) modeled from SeaWiFS color data using OC4 and MODIS algorithms. Solid line represents the 1:1 fit for in-situ chlorophyll.

Figure 5. Chlorophyll vs. COM fluorescence. Line A, Tampa Bay transect ($r^2 = 0.95$). Line B, Manatee River transect ($r^2 = 0.83$). Line C, Peace-Caloosahatchee Rivers ($r^2 = 0.76$). Line D Mississippi River Plume waters ($r^2 = 0.46$).
Figure 1 (C). Del Castillo et al.
Figure 2. Del Castillo et al

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Figure 5. Del Castillo et al.
Fluorescence in Seawater: Documenting the Intrusion of the Mississippi River Plume in the West Florida Shelf

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CDOM, fluorescence, Mississippi River

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