OPTICAL CHARACTERISTICS OF DISSOLVED ORGANIC MATTER DURING A BLOOM ON THE WEST FLORIDA SHELF.

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ABSTRACT

We investigated the changes in optical properties of riverine colored dissolved organic matter (CDOM) in the West Florida Shelf. We found a rapid decrease in riverine characteristics of the CDOM along river plumes. Mixing models based on riverine and marine end-members showed that the observed changes in optical properties can be explained by simple dilution of the riverine end-member with oligotrophic seawater.

INTRODUCTION

Remote-sensing studies of the Gulf of Mexico using historical data from the Coastal Zone Color Scanner (CZCS) show the existence of a chlorophyll bloom over the West Florida Shelf, occurring every year between the months of February and May (Gilbes et al., 1996). This bloom usually forms off Cape San Blas and can extend to the Florida Keys. Riverine discharge represents a significant source of nutrients, which are likely responsible for the phytoplankton bloom and also contributes with large amounts of colored dissolved organic mater (CDOM). In this work, we present results of dissolved organic matter spectroscopic analyses and discuss the influence of riverine discharge upon the optical characteristics of CDOM on the West Florida Shelf.

MATERIALS AND METHODS

Water samples were collected on board the *R/V Suncoaster* at selected stations in the area of the West Florida Shelf during March, 1995 (Fig. 1).

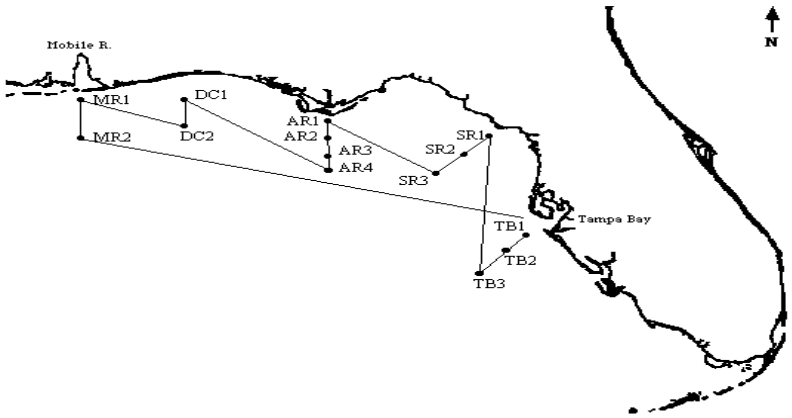

Figure 1. Station location and cruise track of the R/V Suncoaster.

All samples were collected at a depth of ≈1m using Teflon-coated Goflo bottles. The samples were filtered through pre-combusted (12 hr at 450°C) GF/F filters. Absorption spectra 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. The samples were scanned four times and the results were averaged. The absorption coefficient at 440 nm (a(440)) was used as an index of CDOM abundance. The spectral slopes (*S*) were calculated from the linear-least-square regressions of the plot of wavelength vs. ln $a(\lambda)$ for the interval between 400 and 500 nm.

High-resolution fluorescence spectroscopy was performed using a SPEX Fluorolog II fluorescence spectrophotometer running in ratio mode with a bandpass of 5 nm. Three-dimensional excitation-emission matrices (EEM) were created by measuring the emission spectra from 270 to 710 nm at forty separate excitation wavelengths ranging between 260 and 455 nm. Corrections for optical aberrations of the instrument were performed according to Coble et al. (1996). The fluorescence intensities were transformed to equivalents of quinine sulfate and expressed in parts per billion (ppb). The total fluorescence was determined by integrating the fluorescence emissions in a single scan from 360 to 700 nm at an excitation of 350 nm.

The EEMs were used to characterize the fluorescent organic matter using 3-D plots, contour plots, and the position of the wavelength-independent excitation emission maxima (EX/EM). Coble (1996) used water samples from different marine environments to determine their characteristic EX/EM, which can be used to identify the source of the fluorescent dissolved organic material.

RESULTS AND DISCUSSION

A detailed account of the position and displacement of the high productivity plume can be found in Gilbes, 1996J of the spectrum (400-500 nm) a decrease in value with increase salinity may be observed as a result of a loss in absorption at the blue end of the spectrum. In our data, this reduction can be observed in samples with salinities higher than 35 but we have observed similar reductions in slope under strong riverine frontal conditions in the Orinoco River plume (Del Castillo et al., 1998).

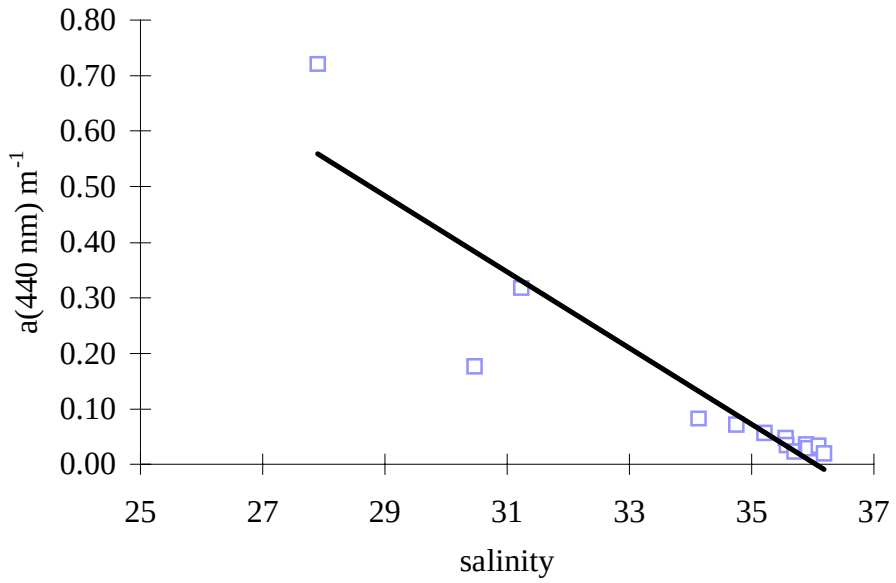

Figure 2. Salinity vs. a(440 nm) for samples collected in the West Florida Shelf ($P<0.001$; $r = 0.92$; $n = 14$).

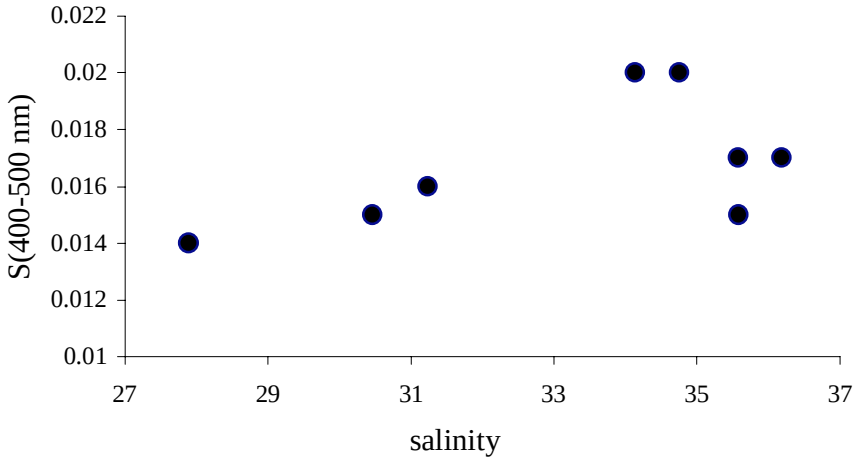

Figure 3. Salinity vs. spectral slope calculated between 400 and 500 nm.

The lowest fluorescence intensity was found at stations SR2 and SR3 (0.50 ppb QSE). The highest intensity (11.3 ppb) was found in MR1. These values agreed with the results presented by Coble (1996) for waters with similar salinities elsewhere. Figure 4 shows the 3-D plots of two EMMs representative of the types of fluorescent organic matter 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 was at 315/428, intermediate between riverine and marine end-members. A salinity of 27.9 at this station indicates a large degree of dilution of the riverine end-member. Stations MR2, AR1, and AR2 also showed an average EX/EM maxima characteristic of marine transitional waters,

whereas AR3, SR2, SR3, DC1, and DC2 showed average maxima characteristic of marine shallow waters. These results indicate that the riverine signal, characterized by an average EX/EM at 340/448 nm, was lost at salinities as low as 27. The positions of the emission maxima showed a shift towards lower wavelengths (hypsochromic) with increasing salinity (Fig. 5) reflecting changes in chemical composition.

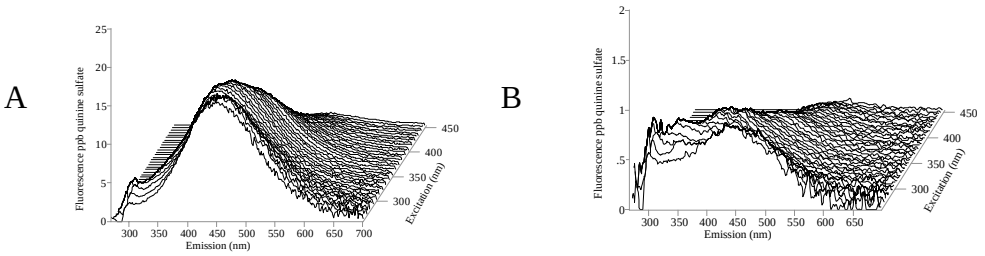

Figure 4. Three-dimensional and contour plots of EEMs from MR1(A) and SR2(B) showing riverine-marine transitional and marine fluorescence fingerprints.

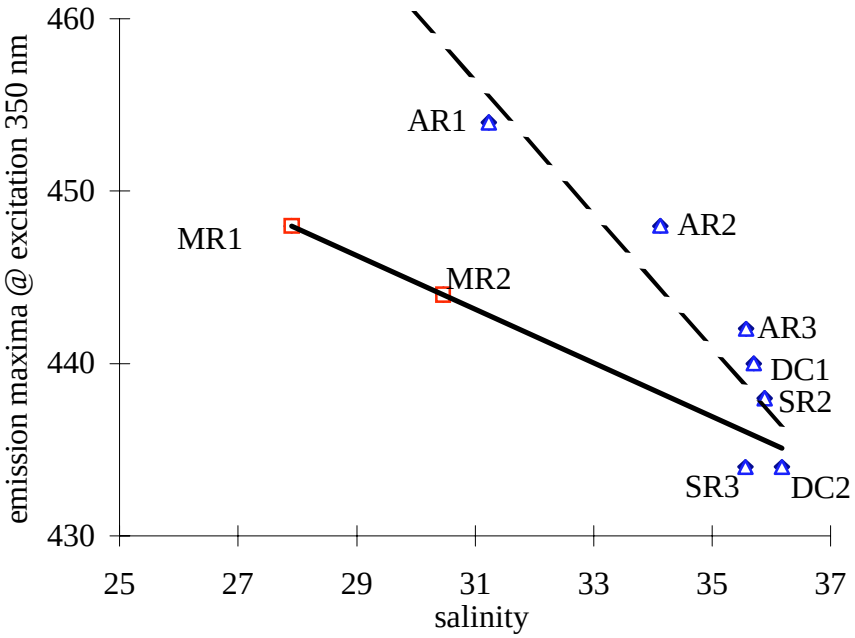

Figure 5. Salinity vs. emission maxima at excitation 350 nm. Deviations shown by MR1 and MR2 may be due to difference in the composition of CDOM in the source area.

To determine if mixing between riverine and marine end-members can produce the observed changes in fluorescence properties of CDOM, we created a series of 5 mixing model based on end-members from the WFS. In these models, pairs of end-members were mathematically combined by adding their normalized EEMs to obtain a series of 12 mixtures with salinities between 28 and 37. The end-member pairs used were: MR1/DC2, MR1/AR3, AR1/AR3, and Manatee River/WFS water (26°.05', 83°.02'). From the resulting EEMs we obtained the emission maxima at excitation 310

nm. The results of the 4 models were averaged and plotted versus salinity in conjunction with results obtained from real samples from the WFS (Fig 6).

Comparison between mixing models and real data shows that conservative mixing alone can produce the observed shifts in emission maxima. A similar experiment was performed by De Souza Sierra et al (1997) with similar results, however, in their interpretation flocculation of CDOM was considered as an explanation for the hypsochromic shifts observed in natural samples.

The high concentration of fluorescent material associated with riverine discharge masked the signal from the marine end-members to salinities around 30. The salinity at which the hypsochromic shifts are observed depends on the concentration of fluorescent material in the riverine discharge, therefore, this inflection could be dependent on seasonal fluctuations in CDOM concentration in the rivers. As expected, the models followed a trend similar to that shown by real samples (Fig. 6) but they failed to accurately predict the observed shifts in emission maxima. A better fit would be obtained by a multiple riverine end-member model that takes into consideration the individual contribution of rivers along the WFS.

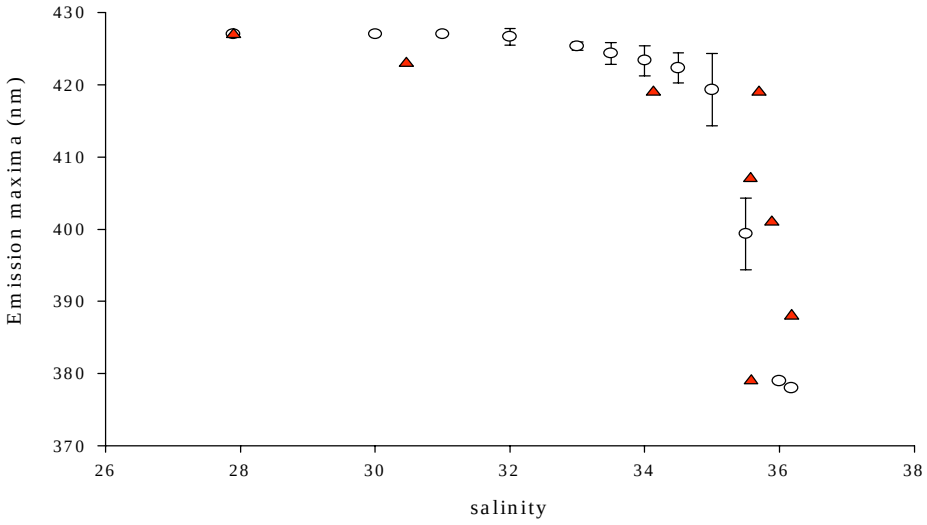

Figure 6. Salinity vs. emission maxima at 310 nm for stations in the WFS(▲) and average of mixing models(O). Error bars represent the standard deviation of the average.

CONCLUSIONS

Riverine CDOM signal, as shown by the absorbance and fluorescence data, was limited to the areas close to the mouth of the rivers where salinity values were below 30. This was particularly evident in the EEM data that showed fluorescence spectra

characteristic of marine transitional water found only at stations MR1, MR2, AR1, and AR2. The rest of the stations showed EEMs characteristic of marine waters.

The mixing experiment showed that dilution of the riverine waters with marine oligotrophic waters can account for the observed changes in fluorescence spectra. Photodegradation cannot be discounted as a possible contributor to optical changes in the region but we believe that dilution of riverine water was the primary mechanism in reducing the riverine signal. High concentrations of particulate material, phytoplankton, and terrestrial CDOM can reduce the penetration of light and photobleaching. 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.

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