# Colored Dissolved Organic Matter in Sediments and Seagrass Beds and Its Impact on Shallow Water Benthic Optical Properties

David J. Burdige
Department of Ocean, Earth and Atmospheric Sciences
Old Dominion University
Norfolk, VA 23529
phone: 757 683-4930 fax: 757 683-5303 email: dburdige@odu.edu

Award No: N000149710005
http://courses.lib.odu.edu/ocen/dburdige/CoBOP.html

## LONG TERM GOALS

The optical properties of shallow water coastal environments are a complex function of physical and biogeochemical processes occurring both in sediments and in the water column. Developing models of the optical properties of these environments requires further knowledge of the processes affecting light alteration and modification by biogeochemical reactions in the surficial sediments and at the sediment-water interface. The goal of this proposal is to examine one aspect of this problem, namely the impact of dissolved organic matter (DOM) in sediment pore waters on benthic optical properties.

## OBJECTIVES

In this proposal I am examining the processes affecting the production of colored and fluorescent dissolved organic matter (CDOM) in sediment pore waters, the mechanism(s) by which this material may be transported out of the sediments, and the impact of pore water CDOM on the optical properties of the shallow water benthos (i.e., both the sediments, the sediment-water interface and the waters overlying the sediment, including the benthic boundary layer).

## APPROACH

To address these problems I am using a combination of field measurements and experiments, carried out in close cooperation and coordination with other funded CoBOP researchers. The bulk of our past field work was carried out in the carbonate sediments around Lee Stocking Island (LSI), Exuma, the Bahamas. A limited field study was also undertaken in seagrass sediments in Monterey Bay. Finally, in our first tear of CoBOP support we took advantage of funded ship-time through the ONR Harbor Processes Program to examine the role of sediments as sources of CDOM to more “turbid” coastal waters (Chesapeake Bay and the mid-Atlantic shelf/slope break; Burdige *et al.*, 2001).

CDOM from pore waters and bottom waters is being characterized both chemically and optically. Chemical analyses involve measuring total dissolved organic carbon and nitrogen, along with total dissolved carbohydrates. CDOM is characterized optically by UV/Vis absorption spectroscopy and fluorescence excitation-emission matrix spectroscopy (EEMS).

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14. ABSTRACT

**The optical properties of shallow water coastal environments are a complex function of physical and biogeochemical processes occurring both in sediments and in the water column. Developing models of the optical properties of these environments requires further knowledge of the processes affecting light alteration and modification by biogeochemical reactions in the surficial sediments and at the sediment-water interface. The goal of this proposal is to examine one aspect of this problem, namely the impact of dissolved organic matter (DOM) in sediment pore waters on benthic optical properties.**

15. SUBJECT TERMS

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Our work is carried out by myself (as PI of the project), Mr. Kip Gardner (a research technician in my lab) and Mr. Scott Kline (a Ph.D student working with me on this project who plans to use his work here as a part of his Ph.D. dissertation).

## WORK COMPLETED

No field work was undertaken this year. We have completed all analyses of samples collected at LSI in 2000 and are currently completing the analysis of the data.

## RESULTS

Specific results in FY01 include work in the following areas (see past ONR Annual Reports for results from previous years).

**Determination of DOM Sources Using Fluorescence Spectrospcopy.** One aspect of our work involves determining DOM and CDOM sources to the marine environment using spectroscopic techniques, an idea that has been discussed for some time in the literature (e.g., see discussions in Blough and Green, 1995; Coble, 1996; McKnight et al., 2001). In natural waters, peaks in fluorescence excitation/ emission spectra have been attributed to humic-like and protein-like materials. Humic-like peak M may have a marine source (Coble, 1996), while peaks A and C have been described in the literature as having terrestrial sources (Coble et al., 1993). It has also been suggested that peak M may simply be a blue-shifted version of peak C, implying that the fluorophore responsible for peak C is a diageneticaly-altered form of that responsible for peak M (Coble, 1996).

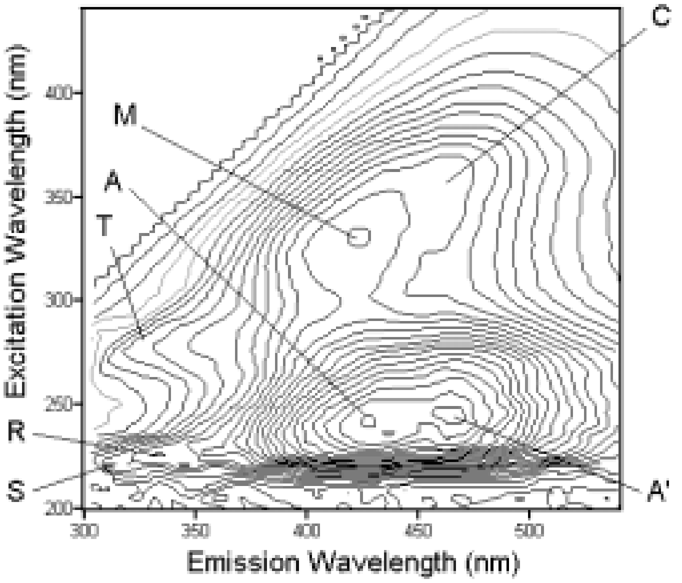

***Figure 1 Fluorescence excitation-emission matrix scan for a pore water sample (8.5 cm sediment depth) collected on 8/97 at station S3 in the Chesapeake Bay (see Burdige and Gardner, 1998) for a location map. The peak names shown here are based on the nomenclature used in Coble (1996), with the exception of the newly reported peak A' (see the text for further details). Prior to analyzing the sample it was diluted to avoid inner filter effects in the analysis of such strongly fluorescent samples. After correcting for dilution the maximum fluorescence observed here was 53 ppb QS for peak A.***

However, our CoBOP-funded work in sediments in the Chesapeake Bay and the mid-Atlantic shelf/slope break (see above) has demonstrated the occurrence of a previously unreported fourth humic like peak (peak A'; see Fig. 1). In conjunction with the other three humic-like fluorescence peaks (A, C, and M) we observed that these four humic-like peaks appear to exist in pairs (A and M, A' and C) in distinct emission bands. These bands are quite similar to those that have been observed in authentic amino acid and protein standards with the tryptophan fluorescence peaks T and R and the tyrosine peaks B and S (Blough and Green, 1995; Mayer et al., 1999). This could indicate that there is a distinct set of fluorophores for each of these pairs of humic-like peaks, although additional work will be required to examine this suggestion.

More importantly though, McKnight et al. (2001) have recently shown that the ratio of the fluorescence emission intensity at 450 nm to that at 500 nm (obtained with sample excitation at 370 nm) allows one to differentiate between microbially-derived (i.e., more autochthonous-like) and terrestrially-derived (i.e., allochthonous) fulvic acids in a wide range of fresh water systems. Our examination of this fluorescence ratio suggests that the ratio may actually be an indicator of the peak M to peak C ratio, since the emission wavelength (370 nm) used by McKnight et al. (2001) seems to run along the edge of these two humic-like peaks, below their maximum intensities. This then suggests the possibility that the occurrence of these peaks may provide us with general evidence for autochthonous versus allochthonous sources of CDOM in the marine environment. Again, additional work will be needed to examine this possibility.

**Studies of Carbonate Mineral Fluorescence.** Work carried out during CoBOP by myself, Charlie Mazel (PSI) and Mead Allison (Tulane) suggests important linkages between carbonate mineral fluorescence, the cycling of CDOM in shallow water marine systems, and the optical characteristics of such environments. Our work has determined that a large majority of the sand-sized sediment grains in the Lee Stocking Island (LSI), Bahamas field area fluoresce from an internal source that is independent of grain surface emitters such as biofilms, pore water CDOM, or chlorophyll-containing meiofauna. This fluorescence, determined by epi-fluorescence emission microscopy on individual sand grains, was observed to be broadband both in its excitation (UV to green) and emission (blue to orange) wavelengths. There is variation in both the intensity and emission wavelength of sediment grains from different origins (e.g., corals vs. ooids vs. mollusks, etc.), and even variations within phyla such as corals.

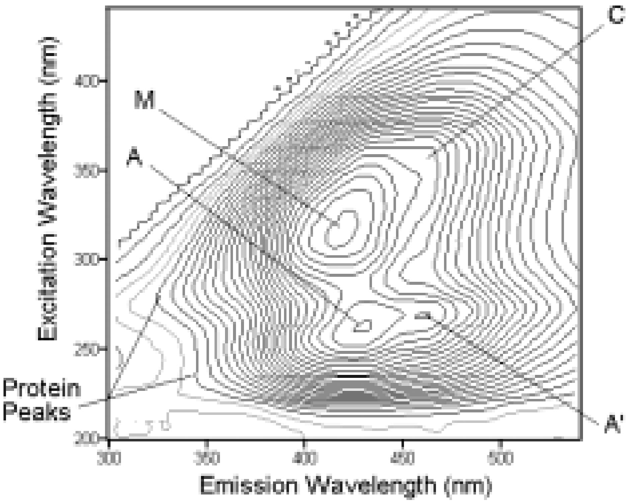

***Figure 2 Fluorescence excitation-emission matrix scan for a Pleistocene-age eolianite collected on LSI that was dissolved in a stoichiometric amount of HCl. The similarity of this spectrum with those for other natural waters (e.g., see Fig. 1) suggests that the observed fluorescence is due to organic matter intimately associated with the carbonate mineral matrix. This material appears to be strongly bound to the solids since simple seawater extractions do not separate this fluorescent material from this solid or other natural carbonates***

The fluorescence of carbonate minerals has been well known for quite some time although its origins is not well understood (Machel et al., 1991; Matthews et al., 1996). Two possibilities discussed in the literature are trace element substitution in the calcite or aragonite crystal structure or organic matter strongly associated with the carbonate mineral matrix. We have examined this problem using both epi-fluorescence emission microscopy as well as 3-dimensional fluorescence EEMS. The latter has been undertaken with both solid materials as well as with aqueous samples obtained by dissolving the carbonate with stoichiometric amounts of HCl. The samples we have looked at range from fresh carbonate material obtained from living calcareous algae to Pleistocene-age eolianite dune deposits.

We have observed that carbonate mineral fluorescence is widespread, and is broadband in both excitation and emission. EEMS spectra also show peaks that have been ascribed to both humic-like and protein-like fluorescence (Fig. 2). These observations, and the fact that EEMS spectra for both solid carbonates as well as acid extracts are similar, suggest that the source of this fluorescence is organic matter trapped in (or intimately associated with) the carbonate mineral matrix. Finally, the fact that the Pleistocene-age eolianite has a measurable fluorescence signal further suggests that refractory humic materials are important here. We are further examining the sources of the organic matter responsible for this fluorescence using selected chemical analyses of these acid extracts. In addition to using these results to further examine the origin(s) of the fluorescence signal in carbonate minerals we will also examine the possible contribution of this sediment fluorescence signal to the upwelling light field.

**Studies of the Role of Seagrasses as Sources of CDOM to Coastal Waters**. This work involved using pore water and water column CDOM measurements made by our group and Emmanuel Boss and Ron Zanveld to further understand the role of seagrasses as sources of CDOM to shallow coastal waters. An examination of time series data collected during moored AC-9 deployments during the May 2000 closure experiment indicates that there were large changes in CDOM absorbance during tidal cycles (Fig. 3), with high dissolved CDOM absorbance being associated with high salinity waters that originate from the shallow banks (note that temperature, salinity and current data were obtained from Rob Wheatcroft who also had a mooring at the closure site with a CTD and current meter). When these results are combined with current measurements they indicate that there was a net flux of CDOM off the shallow banks to Exuma Sound. Both CDOM absorbance and total DOC show a positive relationship with salinity (Fig. 4), which is opposite from that seen in most coastal systems, in which high DOC and CDOM concentrations are generally associated with low salinity waters of terrestrial origin.

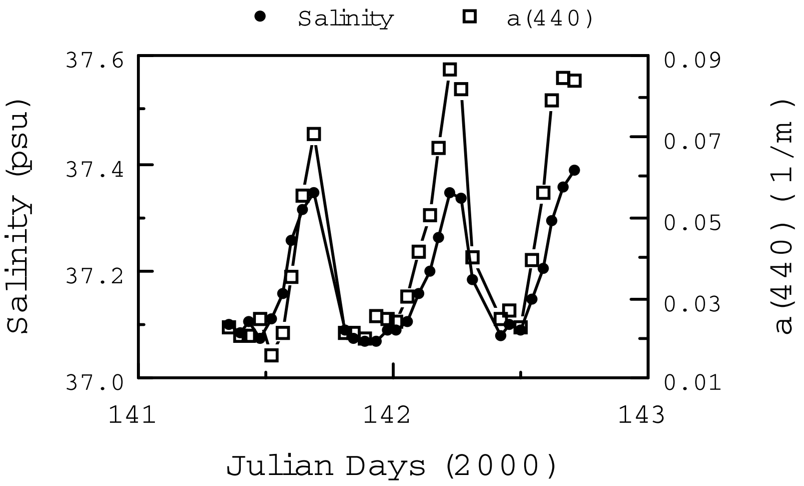

***Figure 3 A time series of salinity and CDOM absorbance at 440 nm [a(440)] at the Rainbow Gardens closure site (LSI 5, 5/00).***

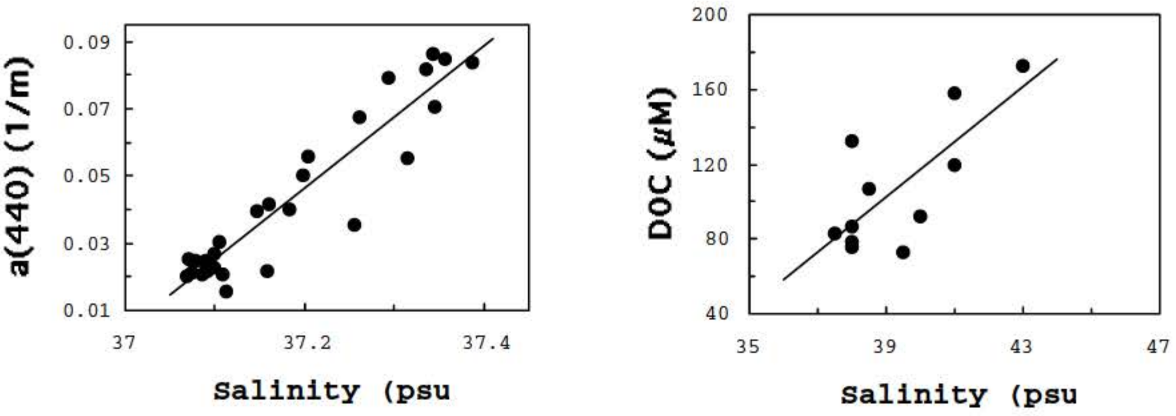

***Figure 4 (left) CDOM absorbance at 440 nm [a(440)] versus salinity from the Rainbow Gardens closure experiment time series (see Fig. 3). (right) Dissolved organic carbon (DOC) versus salinity in bottom water samples collected during LSI 5 at various sites around LSI. Although the time and space scales of the two data sets differ (e.g., compare the two salinity axes) the general trends are the same.***

The CDOM spectral slope also varies with the tidal cycle (data not shown here), implying that there are differences in the type of CDOM (as well as the absolute amount) that is being exchanged between the deep waters and the shallow banks over tidal cycles. Evidence for these differences in CDOM characteristics can also be seen in the observed hysteresis in plots of S versus salinity from this time series (data not shown here).

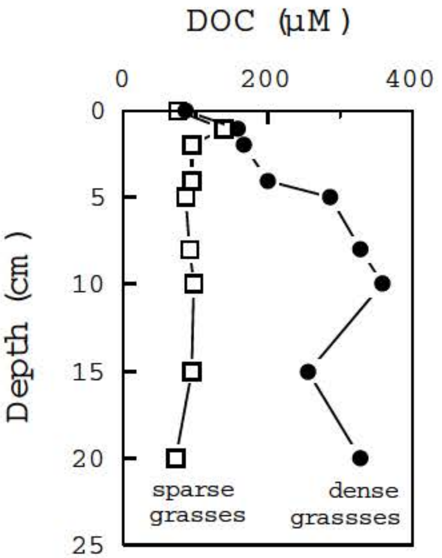

***Figure 5 Pore water DOC depth profiles in dense and sparse seagrass sediments, collected during LSI 5 (5/00) in the Channel Marker region.***

Our current working explanation for these results is that seagrasses and seagrass sediments represent the most likley sources of this CDOM. Seagrasses are important primary producers in oligotrophic coastal waters and generate much of the particulate organic material (POC) that settles into the sediments. Seagrass roots also inject photosynthetically-derived $O_2$ into the sediments, which promotes the production of CDOM during the oxidation of sediment POC. Thus, seagrasses are a major source of CDOM to oligotrophic coastal areas that experience little or no terrestrial freshwater input. Therefore, we believe that processes associated with seagrass biogeochemistry and decomposition likely represent the predominant mechanisms by which CDOM is input to oligotrophic coastal waters. Consistent with this suggestion, our CoBOP studies at LSI show that DOC and CDOM levels are dramatically higher in the sediment pore waters of vegetated areas than they are in adjacent bare (ooid) sands (e.g., Fig. 5).

## IMPACT

The fluorescence data collected so far have been useful in terms understanding the controls on DOM cycling in marine sediment pore waters (e.g., Burdige and Gardner, 1998; Burdige, 2001), and in examining the extent to which coastal sediments are sources of CDOM to coastal waters (Burdige et al 2000). Understanding these (and other) sources of CDOM to the water column and their rates of delivery is clearly important in the development of reliable algorithms for the interpretation of hyperspectral remote sensing reflectance in coastal waters.

## TRANSITIONS

Based on numerous discussions, our results appear to be of interest to many of the other CoBOP investigators. As can be seen above this has resulted in several collaborative projects at LSI with other CoBOP-funded researchers.

## RELATED PROJECTS

The efforts are closely related to several other CoBOP projects, including those of M. Allison, R. Wheatcroft, A. Decho, F. Dobbs/L. Drake, R. Zimmerman, P. Reid, C. Mazel and R. Zanfeld/E. Boss. We have explored these areas of common interest in past CoBOP field efforts and will continue to do so as we analyze our data in the up-coming year.

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## PATENTS

None applied for