

Colored Dissolved Organic Matter in Sediments and Seagrass Beds and its Impact on Benthic Optical Properties of Shallow Water Marine Environments - Data Analysis and Synthesis, and Student Support

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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 our work has been to examine one aspect of this problem, namely the impact of dissolved organic matter (DOM) in sediment pore waters on benthic optical properties.

OBJECTIVES

For the past six years we have been involved in studies of colored dissolved organic matter (CDOM) in sediment pore waters as a part of this award and the previous 5 year CoBOP DRI. We have examined the processes affecting the production of CDOM in sediment pore waters, the mechanism(s) by which this material is transported out of the sediments, and the impact of pore water CDOM on the optical properties of the shallow water benthos (i.e., the sediments, the sediment-water interface and the waters overlying the sediment).

In this project, our objectives are: to analyze, synthesize and write-up our CoBOP data; to continue to collaborate in similar efforts with other CoBOP researchers, in order to maximize our ability to use our combined CoBOP data sets in the examination of the problems outlined above. In the specific context of our work carried out during CoBOP, such efforts would greatly improve our ability to use these results to further understand the influence of the benthos on the optical properties of shallow water environments. In the larger context of the overall goals of the CoBOP project, these activities are important for improving the reliability of the interpretation of hyperspectral remote sensing reflectance data in optically shallow coastal waters.

APPROACH

Our approach involves the continued analysis of CoBOP data collected by my lab, as well several collaborative efforts involving other CoBOP PI's. Our work is carried out by myself (as PI of the project), Mr. Scott Kline (a Ph.D student working with me on this project who plans to use his work

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here as a the major part of his Ph.D. dissertation), Mr. Xinping Hu (a Ph.D student working with me on this project who plans to use his work here as a portion of his Ph.D. dissertation).

WORK COMPLETED

In the past year we submitted one manuscript for publication (to *Marine Chemistry*) on CoBOP-related work, and presented two talks at the 2002 AGU/ASLO Ocean Sciences Meeting in Honolulu. In addition, we plan to submit an abstract on CoBOP-related work to the 2003 ASLO Aquatic Sciences Meeting. We also submitted a manuscript that will be published in the November issue of *Limnology and Oceanography* based on ancillary data collected during CoBOP project.

Although not yet in finished form, work was carried out this year on Scott Kline's Ph.D. dissertation (which will result in at least two additional manuscripts for publication), and on at least two additional publications with other CoBOP PI's.

RESULTS

The results in the past year are best summarized by the abstracts for the manuscripts and talks discussed above.

1. Fluorescent Dissolved Organic Matter in Marine Sediment Pore Waters (David J. Burdige, Scott W. Kline and Wenhao Chen; manuscript submitted 7/3/02 to *Marine Chemistry*)

Fluorescent dissolved organic matter (FDOM) in sediment pore waters from contrasting sites in the Chesapeake Bay and along the mid-Atlantic shelf/slope break was studied using 3-dimensional fluorescence spectroscopy. Benthic fluxes of FDOM were also examined at the Chesapeake Bay sites. The major fluorescence peaks observed in these pore waters corresponded to those observed in the water column. These included peaks ascribed to the fluorescence of humic-like material (peaks A, C and M), as well as protein-like peaks that appear to result from the fluorescence of the aromatic amino acids tryptophan (peaks T and R) and tyrosine (peaks B and S). In these pore waters we also observed a fourth humic-like fluorescence peak (A'). These four humic-like peaks appeared to occur in two distinct fluorescence emission bands (peaks A and M in one band and peaks A' and C in another band), in a manner that was analogous to that observed for more simple chromophores. The emission band containing peaks A' and C was red shifted relative to the peak A and M emission band.

Humic-like fluorescence increased with sediment depth at almost all stations, and was closely correlated with total DOC. This fluorescence appeared to be a tracer for the refractory, relatively low molecular weight pore water DOM that accumulates with depth during sediment diagenesis. Fluorescence-DOC relationships indicated that larger relative amounts of humic-like FDOM were seen in anoxic sediments versus sub-oxic or mixed redox sediments. By extension, these observations suggest that refractory humic-like compounds (in general) are preferentially preserved in sediment pore waters under anoxic conditions. The sources of these humic-like fluorophores are not well understood although a simple model is presented here which proposes that different types of organic matter (e.g., marine vs. terrestrial) as well as internal transformations of DOM or FDOM may lead to the occurrence of these humic-like fluorophores. This model is consistent with a wide range of data on

FDOM in marine as well as freshwater systems. Protein-like fluorescence showed no coherent depth trends in sediment pore waters, other than the fact that pore water fluorescence intensities were greater than bottom water values. Based on the results of benthic flux studies in Chesapeake Bay sediments, it appeared that protein-like fluorescence was associated with high molecular weight DOM intermediates of organic matter diagenesis (e.g., dissolved peptides and proteins) produced near the sediment-water interface. In contrast, this did not appear to be the case in sediment pore waters. Benthic flux studies at the Chesapeake Bay sites further indicated that sediments represent a source of chromophoric DOM to coastal waters, although further work will be needed to quantify their significance in terms of other known sources of this material (e.g., riverine input, phytoplankton degradation products).

2. The Role of Seagrasses as a Source of CDOM to Tropical Coastal Waters (D.J. Burdige, E. Boss [COAS, OSU], R. Zaneveld [COAS, OSU]; presented at the 2002 AGU/ASLO Ocean Sciences Meeting)

To examine CDOM sources to tropical oligotrophic coastal waters, we conducted a time series study using a moored AC-9, CTD and current meter placed at a site (7-8 m water depth) on the shallow water Bahama Banks. An examination of the data in this 30 hr time series indicated that there were large changes in CDOM absorbance over the tidal cycle, with high dissolved CDOM absorbance being associated with the high salinity waters that originate from the shallow banks. Combining these results with current measurements indicated that there was a net flux of CDOM off the shallow banks to the deeper waters of Exuma Sound. The CDOM spectral slope also varied with the tidal cycle implying that there were differences in the type of CDOM (as well as its absolute amount) being exchanged between deep waters and the shallow banks. Both CDOM absorbance and total DOC showed a positive relationship with salinity, which is opposite of that seen in most coastal systems, in which high DOC and CDOM concentrations are generally associated with low salinity waters of terrestrial origin. We believe that seagrasses and seagrass sediments represent the most likely sources of this CDOM. Seagrasses are important primary producers in oligotrophic tropical coastal waters and generate a significant amount of the particulate organic matter that settles into the sediments. They also promote the deposition of allochthonous organic matter to seagrass sediments as a result of the leaf canopy altering (dampening) water motion and tidal currents. Consistent with these suggestions, DOC and CDOM levels were significantly higher in the sediment pore waters of vegetated areas versus adjacent bare (ooid) sands. Therefore, we believe that processes associated with seagrass biogeochemistry and decomposition likely represent the predominant mechanisms by which CDOM is input to such oligotrophic tropical coastal waters that experience little or no terrestrial freshwater input.

3. Fluorescence of Pore Water Dissolved Organic Matter in Shallow Water Marine Carbonate Sediments as a Function of Seagrass Density (S W. Kline and D.J. Burdige; presented at the 2002 AGU/ASLO Ocean Sciences Meeting)

Pore waters from shallow water carbonate sediments in the Bahamas were collected over a period of three years on a seasonal basis (winter and early summer) to examine the factors controlling sediment organic matter remineralization. Sediments at these sites range from bare ooidic sands to sediments underlying dense seagrass meadows (*Thalassia testudinum*). In this study, pore water samples were analyzed for their fluorescence properties using EEMS (excitation - emission matrix spectroscopy)

focusing on humic-like and protein-like peaks observed in such fluorescence spectra. Dissolved organic matter (DOM) fluorescence in shallow water carbonate pore waters showed an overall increase with depth over the upper 20 cm of sediment. This is similar to that seen in siliciclastic estuarine and shelf/slope break sediments. However, in the interval from the sediment-water interface to approximately 2 cm depth, only minor depth changes were observed in the shallow water carbonate pore waters relative to gradients deeper in the sediment. This may indicate the possible occurrence of advective mixing of pore waters and bottom waters in these surface sediments. DOM fluorescence was observed to be a function of seagrass density at these sites. Sites with high seagrass density showed the largest fluorescence values, while sites with no seagrass (ooitic sands) showed the smallest fluorescence values. Furthermore, dense seagrass sites showed seasonal trends in DOM fluorescence, with winter samples having lower fluorescence values than summer samples. The fluorescence/DOC ratio was also lower in shallow water carbonate sediments as compared to siliciclastic estuarine and shelf/slope break sediments. Further examination of the data will involve using it in an attempt to differentiate between types of DOM present in the sediment pore waters (terrestrial versus marine) and examine the degradation and remineralization mechanisms affecting both DOM and total organic matter. We will also use the data to specifically examine the role of seagrasses in the cycling of DOM in these shallow water carbonate sediments.

4. *Dissolved Carbohydrates and Organic Matter in Carbonate Sediments, Lee Stocking Island, Bahamas* (X. Hu and D.J. Burdige; abstract submitted to the 2003 ASLO Aquatic Sciences Meeting).

Total dissolved carbohydrates (DCHO) and total dissolved organic carbon (DOC) were examined in carbonate sediments with different seagrass densities. In dense seagrass sediments, DCHO concentrations generally increased with depth, while DOC profiles showed variable mid-depth maxima (≥ 5 cm). DCHO and DOC levels were also higher in summer than in winter. In sparse and no seagrass sediments, DOC showed little seasonal or depth variations. While DCHO had little seasonal variations, the concentrations reached maxima just below sediment-water interface. DCHO/DOC ratios showed distinct differences with regard to seagrass densities. The ratios reached maximum values at ~ 15 cm, ~ 5 cm and ~ 2 cm for dense, sparse and no seagrass sediments, respectively. All of the differences are likely related to sediment-seagrass interactions, since differences in seagrass densities lead to differences in both the organic matter input and the diagenetic environment in the sediments. Finally, larger calcium pore water gradients in dense seagrass sediments (indicative of carbonate dissolution) suggested that part of the DOC and DCHO may come from the release of organic matter either strongly adsorbed to, or integrally a part of, the carbonate mineral matrix.

5. *Impact of seagrass density on carbonate dissolution in Bahamian sediments* (D.J. Burdige and R.C. Zimmerman [MLML]; manuscript in press in *Limnology and Oceanography* [November issue]).

Carbonate dissolution has been widely observed in shallow water tropical sediments. However, sediment budgets have generally not been closed with respect to the amount of acid required to produce the observed carbonate dissolution. Recently it has been suggested that enhanced oxygen transport into sediments through the roots and rhizomes of seagrasses might play a role in resolving this mass balance problem. We conducted studies of seagrass-carbonate sediment interactions around Lee Stocking Island, Exuma Islands, Bahamas to further examine this problem. Our studies showed that alkalinity, total dissolved inorganic carbon (ΣCO_2) and Ca^{2+} increased with depth in the pore

waters, while pH and calculated carbonate ion concentration decreased with depth. These observations are consistent with the occurrence of carbonate dissolution in these sediments. The magnitude of pore water alkalinity, ΣCO_2 and Ca^{2+} changes were also related to seagrass density, with the largest gradients seen in the sediments of dense seagrass beds. Calculations suggested that less than ~50% of the O_2 needed to drive aerobic respiration (and ultimately carbonate dissolution via CO_2 production) could be supplied by transport processes such as diffusion, bioturbation and physical pore water advection. Furthermore, the O_2 needed to balance the carbonate dissolution budget could be provided by the transport of <15% of the photosynthetically derived O_2 to the sediments through seagrass roots and rhizomes without enhancing the removal of carbonate dissolution end-products. Thus seagrasses play an important role in controlling the rates of carbonate dissolution in shallow water tropical marine sediments.

IMPACT/APPLICATIONS

Work carried out during CoBOP and during this year of funding has been useful in terms understanding the controls on DOM cycling in marine sediment pore waters, and in examining the extent to which coastal sediments are sources of CDOM to coastal waters. Understanding these sediment 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. This has resulted in several collaborative projects at LSI with other CoBOP-funded researchers, as can be seen in part by the co-authorship above of manuscripts and abstracts.

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. Zarfeld/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.

PUBLICATIONS

Burdige D. J. (2002) Sediment pore waters. in *Biogeochemistry of Marine Dissolved Organic Matter* (D. A. Hansell and C. D. Carlson, eds.), pp. 611-663. Academic Press.

Burdige D. J. and Zimmerman R. C. (2002) The role of seagrasses in calcium carbonate dissolution in shallow water sub-tropical carbonate sediments. *Limnol. Oceanogr.* in press (Nov. issue).

Burdige D. J., Kline S. W., and Chen W. (2002) The cycling of fluorescent dissolved organic matter in contrasting marine sediments. ms. submitted to *Mar. Chem.*