Characterization of Optical and Associated Properties of Marine Colored Dissolved Organic Material (CDOM)

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LONG-TERM GOALS

A long-term scientific goal of our research for ONR has been to develop an understanding of the physical and chemical processes affecting colored dissolved organic material (CDOM) and the resultant attenuation changes of ultraviolet and visible radiation in seawater, particularly in the coastal environment where complex variations of sources, sinks, and modification processes can result in dynamic and heterogeneous changes to the optical characteristics (attenuation, color) of the surface ocean . The goals of this work are to better characterize CDOM in seawater with respect to its molecular composition and to elucidate the effects of this composition on the optical properties of seawater.

OBJECTIVES

Our long-term objectives are to:

- develop an understanding of the photochemical processes affecting CDOM and the resultant changes in optical properties

- examine the differences and similarities between CDOM of marine vs. terrestrial origin, and the impact these properties have on the chemical and optical characteristics of coastal environments

- apply this new knowledge about CDOM characterization to the development of new autonomous real-time remote sensing capabilities that can be applied to global observation

APPROACH

During the past year of our ONR-funded research, we have been applying new technologies to the elucidation of the structural and associated optical properties of CDOM. Specifically, we are now using a FlFFF system to separate DOM by molecular size, rather than by chemical characteristics as HPLC does. In parallel with this, we have also developed an ion trap mass spectroscopy technique to directly measure the molecular size distribution of CDOM. These independent methods have shown

Report Documentation Page					*Form Approved* *OMB No. 0704-0188*	
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1. REPORT DATE **30 SEP 2002**		2. REPORT TYPE			3. DATES COVERED **00-00-2002 to 00-00-2002**	
4. TITLE AND SUBTITLE **Characterization of Optical and Associated Properties of Marine Colored Dissolved Organic Material (CDOM)**					5a. CONTRACT NUMBER	
					5b. GRANT NUMBER	
					5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)					5d. PROJECT NUMBER	
					5e. TASK NUMBER	
					5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Division of Marine and Atmospheric Chemistry,,Rosenstiel School of Marine and Atmospheric Science,,University of Miami,4600 Rickenbacker Causeway,,Miami,,FL,33149**					8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)					10. SPONSOR/MONITOR'S ACRONYM(S)	
					11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT **A long-term scientific goal of our research for ONR has been to develop an understanding of the physical and chemical processes affecting colored dissolved organic material (CDOM) and the resultant attenuation changes of ultraviolet and visible radiation in seawater, particularly in the coastal environment where complex variations of sources, sinks, and modification processes can result in dynamic and heterogeneous changes to the optical characteristics (attenuation, color) of the surface ocean . The goals of this work are to better characterize CDOM in seawater with respect to its molecular composition and to elucidate the effects of this composition on the optical properties of seawater.**						
15. SUBJECT TERMS						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**7**		

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

reasonably good agreement with each other and have provided evidence of a connection between the optical properties of coastal waters and the molecular mass of CDOM.

WORK COMPLETED

A series of 3 cruises in 2001 led to observations on the seasonal variation in the coastal waters of southwest Florida, examination of differences resulting from input sources such as mangrove regions (Everglades National Park) as compared to rivers draining more urban areas in Florida (Caloosahatchee River). Results from these studies were discussed in two presentations at the Ocean Sciences meeting (2002 AGU meeting, Hawaii)

FlFFF:

Flow field-flow fractionation (FlFFF) coupled with absorbance and fluorescence detectors was used to separate the CDOM molecules based on their diffusion coefficient (*D*), spectroscopy which is a function of molecular size and to characterize the different fractions based on their optical properties. During the last year we have improved the FlFFF operating protocols, which have increased the recovery rates of the analyte, and have led to a stable and highly reproductive system.

Ion trap mass spectroscopy:

Methods were developed and refined for using this instrumentation to study natural samples. The system produces a large volume of data which was difficult to visualize or evaluate in a meaningful quantitative or qualitative manner. Data routines were developed to elucidate the general characteristics of the sample, describe them in mathematical terms and relate them to their optical properties .

RESULTS

FlFFF:

A series of samples was collected on the three cruises to map the area in terms of CDOM MM distribution, and two transects were sampled in the river plumes of Caloosahatchee (CR) and Shark (SR) Rivers to evaluate the changes in MM and optical properties due to seasonal variation. Figure 1 shows the MM distribution. The June 2001 cruise was during the dry season, with a low input of freshwater and terrestrial material. No significant variation in terms of MM distribution was observed in the river transects. During the September and November cruises, in the rainy season, compounds with higher MM were detected in the river and coastal samples. The chromophores' MM distribution for all end members samples of the two transects and other marine samples for all months were in the range of 1.43 – 1.49 ± 0.06 kDa, regardless the initial mass. This suggests that even with the introduction of new organic material, the higher compounds are removed or broken down to a certain point and then become resistant to further degradation processes or degrade so slowly that it was not possible to observe changes with the methodology used. This result was not observed for fluorophores, which had different MM distributions during the same periods, with higher MM during the wet season. However, during each cruise the MM's distribution for fluorophores in offshore samples were the same. This suggests that fluorophores are more resistant to the degrading/removal processes while chromophores are transformed faster reaching refractory status sooner. Correlation of optical properties and TOC vs. salinity (not shown) indicates that mixing is an important factor in the area, and the salinity data also indicates a local influence of rivers over adjacent areas during a wet season.

This work is the *first* measurement of changes on MM distribution due to seasonal variations for bulk CDOM in lower to more saline waters. Results indicate that using FlFFF coupled to optical detectors is a useful probe for measuring the changes in chromophores and fluorophores' MM distribution (and hence optical properties) of CDOM in coastal zones due to photochemistry, dilution, different sources and/or processes.

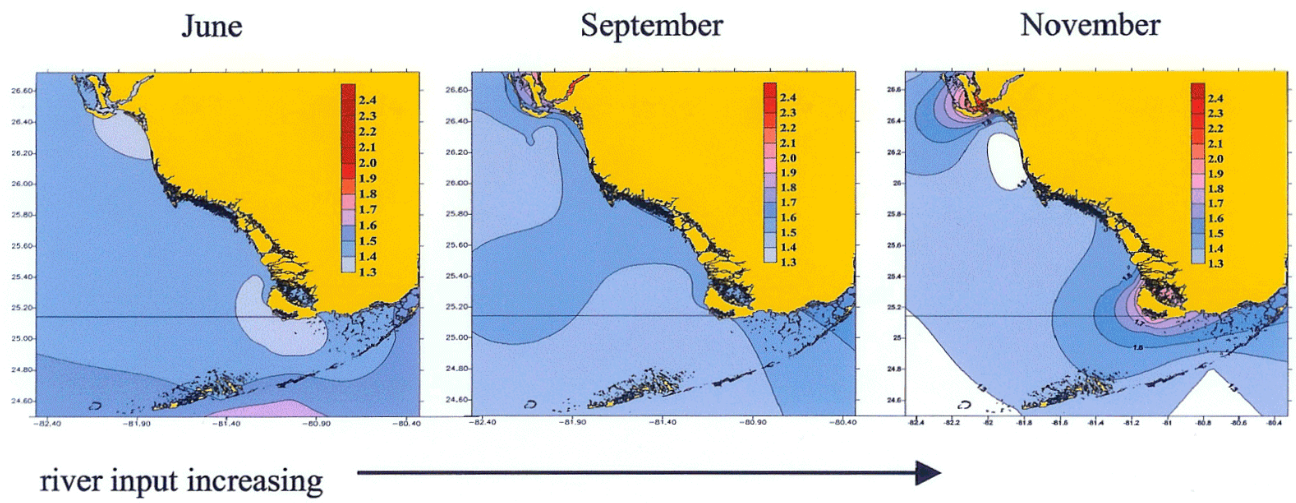
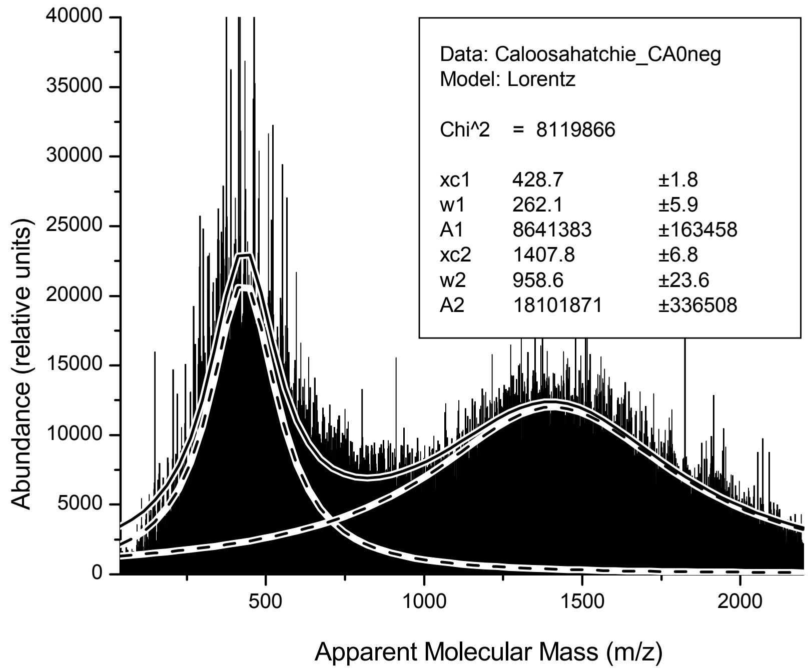


Figure 1 shows the mapping of the southwestern coastal region of Florida for all three months sampled in terms of MM distribution for chromophores. The figure shows that in periods of low input of CDOM-containing freshwater (June), the MM distribution for chromophores was pretty much the same in the whole region. The fresh water introduction from the Caloosahatchee River observed in September generated a small gradient of MM in the area. In November, with a strong renewing of CDOM brought by rivers, the MM gradient was observed.

Ion trap mass spectroscopy:

This study focused on the changes in optical properties and mass distribution for CDOM as natural waters flow from rivers into the coastal ocean. Figure 2 shows the negative ionization mode mass spectral distribution of two samples collected in the Caloosahatchee River, Florida. The upper graph represents the mass distribution of CDOM extracts from water collected in the Caloosahatchee River at station CA0 with a salinity of 29.97. The lower sample was collected offshore outside the river mouth at station CA3 where the salinity was 35.23. Overlaid on this are the Lorentzian curves that were fit to each of the peaks in dashed lines and the summation of those two curves as a solid line. As can be seen, a bimodal mass spectral distribution adequately describes the mass spectra of these two samples. This was apparent in all samples for this study however, the exact location of the mean of the peaks and the total abundance of the masses varied with sample site. For convenience we have chosen to refer to these regions as the lower peak, lower mean or lower area for the region with masses near 400 m/z and upper peak, upper mean or upper area for masses observed in the 700 m/z and above mass region.

Trends observable in the data include a reduction of the relative abundance of all ions as the samples proceed from lower to higher salinity waters. This was not strictly a dilution effect but may be a combination of dilution and various losses or transformation processes including photodegradation, partitioning to sediments, or flocculation. In negative ionization mode, the center for the lower mass distribution stayed relatively constant, with its center (XC1, Figure 2 upper graph) of sample CA0 = 428.7 m/z and the center (XC1, Figure 2 lower graph) of sample CA3 = 423.3 m/z. In contrast the center of the upper mass distribution showed a reduction in average mass with increasing salinity, with the mean of sample CA0 = 1407.8 m/z and the mean of sample CA3 = 1233.4. This reduction in average mass of 174.4 m/z coincided with a reduction in salinity of 5.26 A similar trend was observed for the positive mode ions, however, the upper mass distribution in positive mode ranged from 990.9 to 734.2 m/z.



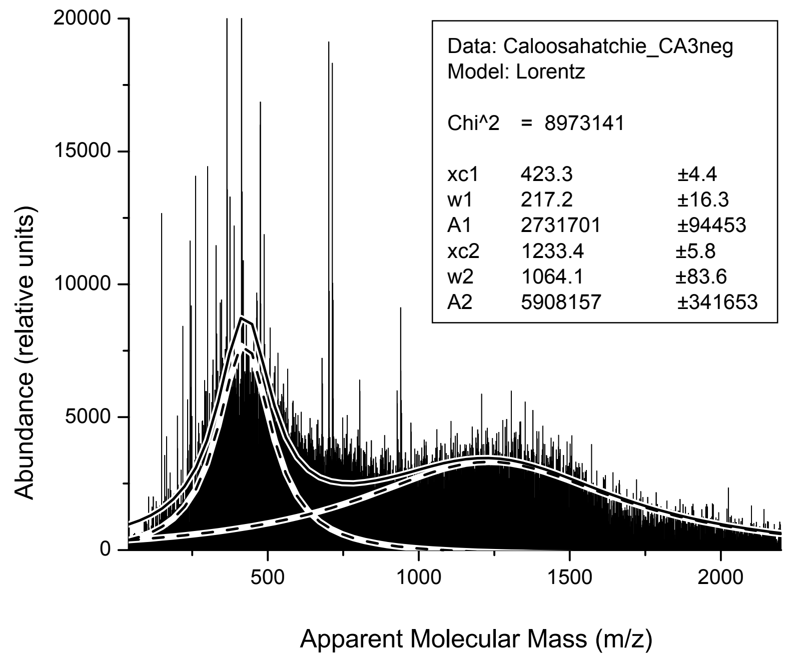


Figure 2. Mass spectrographs (negative ion mode) for 2 samples from a Caloosahatchee River transect. The upper plot (lower salinity) has higher total intensity and a higher mean molecular mass for the upper peak of the bimodal distribution of ions.

IMPACT/APPLICATIONS

The primary and immediate impact of this work is concerned with developing a more comprehensive and quantitative understanding of ocean optics, particularly as it relates to CDOM. The results of this study are providing valuable information on how the oceans optical characteristics vary on the molecular level and on how such quantitative assessments can be routinely made. This capability will lead to the development of predictive modeling tools for determining optical properties that will be useful in applications involving remote sensing and underwater light field characterization. The new tools developed in this work will be useful for other kinds of marine biological and chemical applications involving complex molecular species.

TRANSITIONS

The technologies used in this project have great potential for use in the study of complex macromolecular matrices and their use in this project is helping to expand applications in such studies. New and improved applications of these technologies will be an asset to environmental studies as well as in fields like medicine and chemistry. Also, refinements in these employed technologies should lead to more rugged and field applicable systems that can function in near real time.

RELATED PROJECTS

The study of ocean and coastal CDOM has become a major area of interest over the last ten years. This was evident from the attendance and number of papers submitted to a special session on CDOM at the 2002 Oceans Sciences Meeting in Hawaii. Many of the people working on CDOM are involved in cooperative meetings, joint research studies and field programs. This is true for all of the student and staff involved in the project discussed in this report.

PUBLICATIONS

Zanardi-Lamardo, E., Clark, C.D., Moore, C.A. and Zika, R.G. 2002. Comparison of the Molecular Mass and Optical Properties of Colored Dissolved Organic Material in Two Rivers and Coastal Waters by Flow Field-Flow Fractionation. Envir. Sci. Technol. 36 (13): 2806 - 2814.

Clark, C.D., Jimenez, J., Jones II, G., Zanardi-Lamardo, E., Moore, C.A.and Zika, R.G. 2002 A Time-Resolved Fluorescence Study of Dissolved Organic Matter in a Riverine to Marine Transition Zone. Mar. Chem. 78: 121-135.

PRESENTATIONS

Zanardi-Lamardo, E.; C.D. Clark and R. G. Zika "Molecular Mass Distribution and Optical Characterization of Colored Dissolved Organic Material in Coastal Waters of Southwest Florida". Eos. Trans. AGU, 83(4), Ocean Sciences Meet. Suppl., Abstract OS22J-05, 2002.

Stabenau, Erik R., Cynthia Moore, and Rod G. Zika, Application of LC/MSn to the Study of DOM Mediated Optical Properties: South Florida Coastal Zone 2001, Eos. Trans. AGU 83(4), Ocean Sciences Meet. Suppl., Abstract OS22J-05, 2002.