

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

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LONG-TERM GOALS

Our long-term goal is to understand the factors affecting the optical characteristics of seawater. Of particular interest to us are the effects of sunlight-initiated physical/chemical processes on colored dissolved organic material (CDOM), and the resultant attenuation changes in ultraviolet and visible radiation in seawater and coastal environments.

OBJECTIVES

The chemical constituent of seawater that absorbs most of the incident solar radiation is collectively referred to as CDOM. CDOM is a complex aggregate of organic compounds derived from marine biota and terrestrial humic material introduced to the oceans by rivers. The photochemically active fraction initiates most of the photochemical reactions in seawater, altering CDOM itself and affecting the chemical speciation of oxygen, transition metals and various organic compounds. These reactions can have profound effects on the chemical characteristics of seawater and physical properties such as optical absorbance and luminescence. Our primary objective is to understand the differences and similarities between DOM of marine and terrestrial origin, the effects of photochemical processes on the structure and optical characteristics of CDOM and the impact these properties have on the optical characteristics of marine environments.

APPROACH

Our approach to CDOM characterization is to use Flow Field Flow Fractionation (FFFF) as the separation technique, together with optical characterization of fractionated CDOM by in-line absorbance and fluorescence and structural characterization by LC/MSⁿ. Ion trap mass spectrometry (LC/MSⁿ) is a powerful technique for the structural characterization of complex organic molecules. This is its first application to marine CDOM. Our principal focus over the last year was to complete the installation and testing of our newly purchased LC/MSⁿ system (some funds from ONR DURIP/1997: "Characterization of Coastal Optical Properties Through the Application of Flow Field Fractionation"). We used a series of riverine and marine DOM samples from South Florida waters for method development and evaluation. We also began photochemical studies using sunlight and UV-

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laser light sources to see if irradiation of fresh CDOM produces material with the same structural and optical characteristics as marine CDOM.

WORK COMPLETED

In the first year, we completed method development for the FFFF and LC/MSⁿ systems on schedule. During the upcoming year, we will examine a more extensive series of riverine, coastal and oceanic waters and participate in a cruise in the Mississippi River plume in June 2000 with other ONR investigators.

1. Samples:

As our primary goal is to understand the similarities and differences between DOM of marine and terrestrial origin and their impact on the optical characteristics of coastal environments, we used a series of samples for method development and instrument setup. These were taken from the Shark River plume in Florida Bay in 1996 and represent a time series. Two graduate students, a research technician and the PIs will participate in an upcoming 10-day cruise on the University of Miami's R/V Calanus in November to obtain samples from an extended set of river plumes on the southwest coast of Florida. We will also obtain Gulf of Mexico samples in preparation for the upcoming cruise in the Mississippi River plume in June 2000. Cruise planning and preparation have been completed.

2. FFFF:

FFFF has been used to characterize soil and riverine humic substances (Beckett et al., 1987). Separation relies on the molecular diffusion coefficient i.e. molecular size. FFFF thus has many advantages compared to other common techniques of DOM fractionation that suffer from charge adsorption and charge repulsive effects. Eliete Zanardi, a third-year PhD. graduate student, is working on the FFFF analysis of marine CDOM for her dissertation research. Over the last year, we showed FFFF could be applied to DOM samples from riverine, coastal and oceanic regions (Zanardi et al., 1999). The FFFF system was run under a wide variety of conditions, using both humic standard materials and natural samples, to derive optimal operating parameters for DOM fractionation. Adding a buffer solution to the carrier fluids had no effect on the separations (Beckett et al., 1989). Following separation, the absorbance and fluorescence of the size-fractionated components in the FFFF eluent are detected with in-line HP 1100 series diode array UV-VIS (200 – 700 nm) and fluorescence detectors. We are currently calibrating the FFFF system with commercial polystyrene standards of known molecular sizes. Early experiments without added detergent showed a significant effect of salinity on the shape of the fractograms (longer retention times at higher salinity). This appears to be due to an ionic strength effect on the membrane, rather than actual differences between fresh and marine source materials. Samples run with detergent in the carrier flow show a general trend of decreasing size for fresh to marine CDOM, as would be expected if photodegradation processes occurred.

3. LC/MSⁿ:

With LC/MSⁿ, complex molecules in the liquid FFFF or LC eluent can be fragmented in the mass spectrometer, with the resulting fragments repeatedly isolated and re-fragmented to yield compositional information difficult to obtain by other means. We took delivery of our new Esquire LC/MSⁿ system from Bruker/Hewlett Packard in May 1999. Erik Stabenau is a second year graduate student working with the LC/MSⁿ as part of his PhD. thesis dissertation. We have completed installation, testing and preliminary studies on Shark River and Florida Bay DOM extracts. Since humic materials are complex and difficult to characterize completely against model compounds, we looked for correlations between the structural features and optical characteristics for chromatographic

fractions of different CDOM samples. The MS and FFFF systems share a LC system with common pumps and detectors but interchangeable columns. This is causing some problems due to solvent incompatibilities between the two systems that result in reduced sensitivity and contamination. We are hoping to acquire funds for a second LC system so the two can run independently, with the MS as an interchangeable detector (pending ONR Durip/1999: "Application of Ion Trap Mass Spectrometry to the Characterization of Coastal Optical Properties"). We have also had some difficulties interfacing the FFFF with the MS due to solvent incompatibilities between the FFFF membrane (water only) and the ionization technique (requires methanol/acetonitrile). This will be addressed using a second LC pump to infuse the required MS solvent into the FFFF output.

RESULTS

Our novel experimental approach to DOM studies couples FFFF as the separation technique with structural characterization by LC/MSⁿ. Results to date show differences in both the structural and optical features of CDOM in fresh and coastal South Florida waters. Irradiating fresh water CDOM gives similar structural and optical features to the more marine CDOM in the river plume, suggesting that photochemical processes convert fresh CDOM to a major component of marine CDOM. Specifically, irradiating a sample from the head of the Shark River with sunlight for 8 hours ($\lambda > 290$ nm) significantly reduces the fluorescence and broadens the size distribution with FFFF (Figure 1). However, selective laser excitation at 308 nm (XeCl excimer, 15 minutes, 100 mJ/pulse, 2 Hz) does not have as dramatic an effect. For comparison, the marine sample taken in the river plume in Florida Bay (about a 3 day sunlight exposure) also shows reduced fluorescence and a broader size distribution. Similarly, a mass spectrum of a fresh water sample shows several peaks and associated fluorescence at both short and long retention times. These disappear on irradiation to give a total ion mass spectrum which is similar to that obtained for a more marine sample in the river plume (Figure 2). The results of this work will be presented at an upcoming meeting in a special session on "The Origin and Reactivity of Dissolved Organic Matter".

C. D. Clark, E. Stabenau, E. Zanardi, C. Moore, and R.G. Zika, "Photochemical Effects on the Structural Properties of DOM in Florida Coastal Waters: A FFFF/Ion Trap MS Study", Ocean Sciences, San Antonio, January 1999.

IMPACT/APPLICATIONS

The means by which we have studied CDOM is novel and appropriate for future investigations of the structural and associated optical features of this material. Our results suggest that the photochemical degradation of terrestrial DOM from rivers forms a significant fraction of marine CDOM in coastal zones. This has significant impacts for the cycling and sources of DOM in the ocean. Correlating changes in optical characteristics with associated changes in structural features under the action of sunlight will allow us to understand how changes in ultraviolet/visible radiation occur in seawater and coastal environments. Aside from developing an understanding of the factors affecting the chemistry and physics of light in the ocean, there are other more applied potential future impacts in the development of new analytical system approaches for examining complex organic substances in the environment.

TRANSITIONS

Our results suggest that coupling FFFF as the separation technique, with structural characterization by LC/MSⁿ, is a promising route to elucidating the behavior of CDOM and potentially other complex organic substances in marine systems. For example, the LC/MSⁿ system has been used in a study of marine coral proteins by members of the Marine Biology and Fisheries Division at RSMAS. In general, we see a strong future for the transition of the FFFF and LC/MSⁿ instrumentation/techniques to the study of other complex organic systems (eg. volatile organic carbons and polyaromatic hydrocarbons in aerosols), both in this laboratory and elsewhere.

RELATED PROJECTS

- In a pending-NSF proposal, we plan to examine the photoredox processes of CDOM in seawater.
- We will participate in an upcoming ONR-funded multi-investigator cruise in the Mississippi River plume in June 2000, taking water samples to investigate fresh to marine (and photochemically-aged) CDOM by FFFF and LC/MSⁿ.
- In collaboration with Gil Jones at Boston University, we continue to examine the fluorescence lifetimes of humic materials in natural waters as a probe of the nature and distribution of the fluorophore.

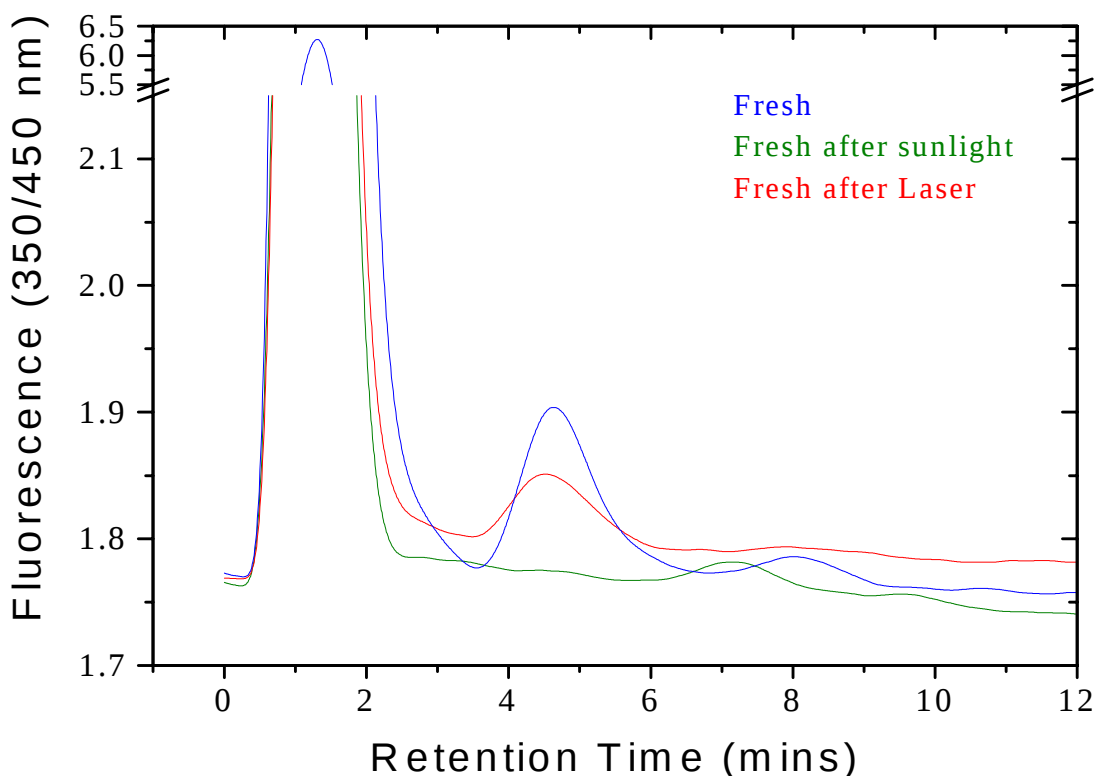


Figure 1. Fluorescence vs. retention time for irradiated South Florida water samples
(3000 Dalton regenerated cellulose membrane; 0.5 μ m filtered carrier flow: 0.1% (v/v) FL-70/0.0046M NaN₃/ ODW; flow rates: 0.3 mL/min sample inlet/outlet, 2.0 mL/min frit inlet/outlet, 1.0 mL/min crossflow)

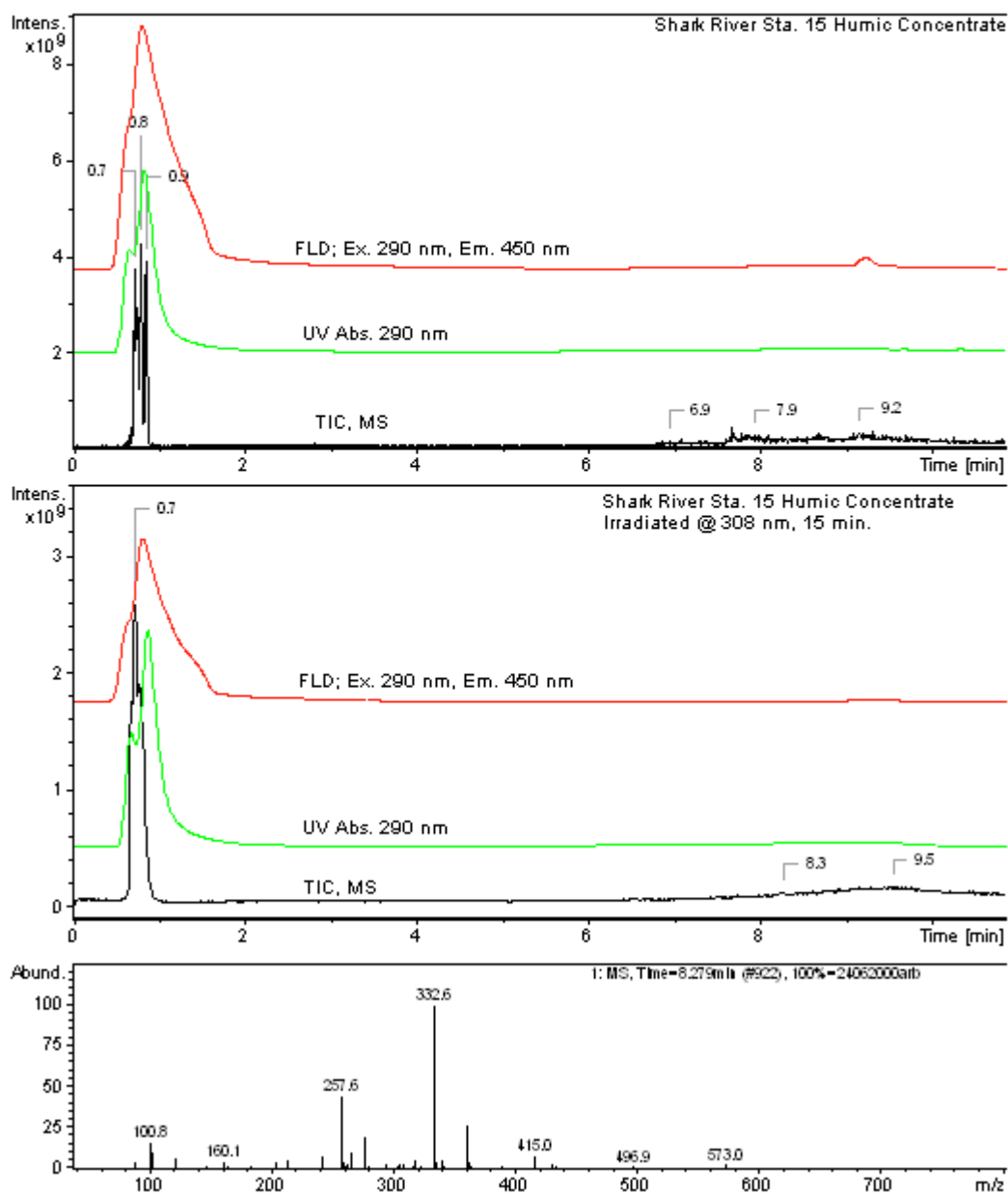


Figure 2. Fluorescence, absorbance and total ion count of irradiated South Florida water samples (C-18 column, methanol or acetonitrile, electrospray ionization 3500 V, positive mode, scan 40-800m/z)

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PUBLICATIONS

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