

# **Distribution and Cycling of Dissolved Organic Carbon and Colored Dissolved Organic Carbon on the West Florida Shelf**

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## **LONG-TERM GOALS**

The long-term goal of this project is to determine sources, sinks and dynamics of Colored Dissolved Organic Matter (CDOM) optical properties on spatial and temporal scales relevant to physical/ biogeochemical/ optical modeling efforts currently in progress for the West Florida Shelf HYCODE site. Predictive capability is needed for modeling in-water light attenuation and visibility in coastal regions. CDOM is one of the most significant and least understood light attenuating components, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone.

## **OBJECTIVES**

The short-term goals are to characterize spatial and temporal variability in optical properties by determining sources and sinks of CDOM and Dissolved Organic Carbon (DOC) for the West Florida Shelf. The loss of CDOM by dilution/physical mixing and photobleaching will also be investigated. Photodegradation rates and effects of sunlight on CDOM optical properties and CDOC/DOC relationship as a function of CDOM source will be determined. This information will be applied to bio-optical and predictive light field models.

## **APPROACH**

We propose to characterize spatial and temporal variability in optical properties and relative importance of the various sources and sinks of CDOM and Dissolved organic carbon (DOC) in the ECOHAB (Ecology of Harmful Algal Blooms)/HYCODE study area on the West Florida Shelf (between 27.5° - 26.0°N, 82.25° - 84.5° W, or roughly between Tampa Bay in the north to Charlotte Harbor in the south and 120 miles offshore). Sources to be studied include phytoplankton (diatoms, dinoflagellates, *Trichodesmium* spp.), rivers (Hillsborough, Manatee, Little Manatee, Alafia, Caloosahatchee and Peace Rivers), and sediments. We will also investigate loss of CDOM by dilution/physical mixing and photobleaching. Photodegradation rates and effects of sunlight on CDOM optical properties and CDOC/DOC relationship as a function of CDOM source will be determined. Analyses will include:

- Detailed surface mapping of CDOM and chlorophyll absorption, fluorescence and DOC concentration using AC-9 and SAFIRE.

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- Laboratory incubations of water samples using a solar simulator with subsequent measurement of DOC concentrations and CDOM fluorescence and absorption.

## WORK COMPLETED

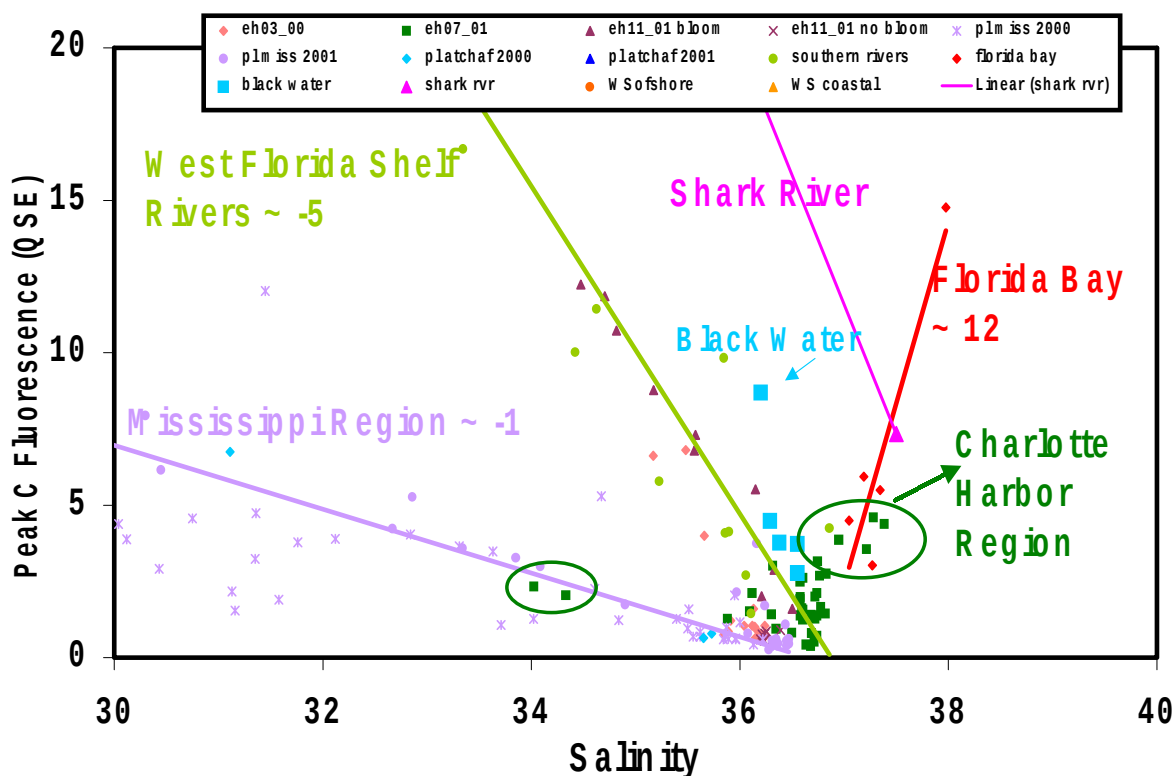
In the past 12 months, we have completed analysis of samples collected in the eight field experiments of the 2000-2001 project year and participated in the additional cruises listed in Table 1. EcoHAB (monthly survey cruise) experiments were conducted within the HYCODE study site. The Florida Bay experiments were conducted in the waters of south Florida influenced by Florida Bay and the Shark River. Surface mapping and discrete sampling activities took place on board, and samples for photochemistry experiments were returned to the laboratory. Table 1 also shows the status of sample analysis. Work is underway to complete data analysis, synthesis, and publication of results of these experiments.

***Table 1: Participating cruises for October 2001 to September 2002***

| <u>Cruise</u> | <u>Date of Cruise</u> | <u>Status of sample analyses</u> |
|---------------|-----------------------|----------------------------------|
| Florida Bay   | September 2001        | analysis complete                |
| EcoHAB        | October 2001          | analysis complete                |
| EcoHAB        | November 2001         | analysis complete                |
| Florida Bay   | April 2002            | analysis underway                |
| EcoHAB        | April 2002            | stored frozen                    |
| Florida Bay   | June 2002             | analysis underway                |
| EcoHAB        | August 2002           | analysis complete                |

## RESULTS

One of the most unexpected results of our research to date is the marked difference in CDOM fluorescence-salinity relationships for the eastern and western regions of our study area. The freshwater endmember entering the Gulf of Mexico in the Mississippi Plume region has a much lower CDOM fluorescence than does the freshwater source in the HYCODE study area. Additional data collected during 2001 have allowed us to update our salinity to CDOM fluorescence relationships and allowed us to further characterize the high salinity, high CDOM water mass observed in the southern part of our study region (Figure 1). We have identified Florida Bay as the source of this water, and have observed it as far north as Charlotte Harbor during some seasons, especially during the summer months (see July 2001 data in Figure 1).

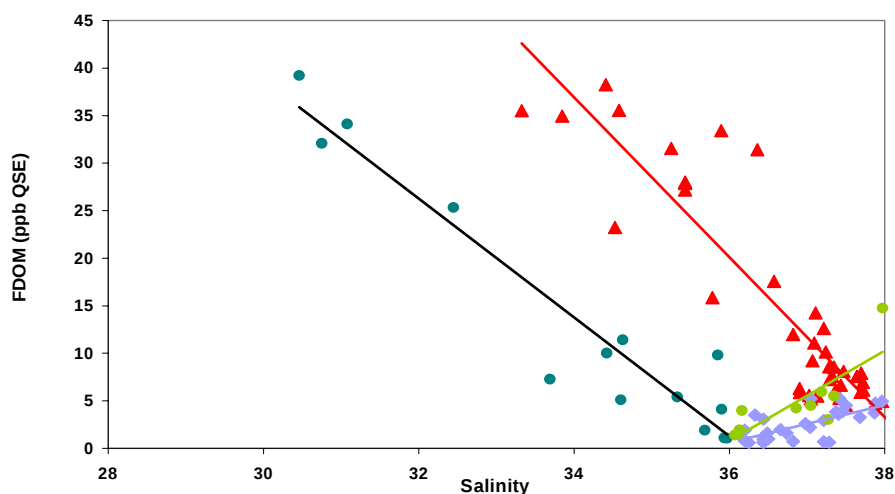


**Figure 1. Salinity-CDOM relationship showing the four important endmembers. River CDOM concentrations ranging from 50 to 450 ppb QSE, and concentrations decrease with increasing salinity, except in the Charlotte Harbor region, where input of Hypersaline, high CDOM water causes CDOM to increase with increasing salinity at salinities above 36.5. Miss. R. (lavender), WFS rivers (green), Shark River (magenta) and Florida Bay (red). Dark green symbols are from July 2001 ECOHAB cruise. Data from multiple cruises are grouped by region. Cruise designators as follow: eh – ECOHAB (month\_year), pl – Pelican (Mississippi or Atchafalaya, year), WS – R/V Walton Smith cruises to the SFS. Black water samples were collected in Mar.-Apr. 2002.**

Also shown in Figure 1 are data from samples taken during a “black water” in March 2002, when large areas of discolored water were observed between Sanibel Island and the Florida Keys. This patch of water persisted for several months and was the cause of much local concern from the general public. Our analyses did not indicate an unusual or harmful chemical composition, and CDOM concentrations were only slightly elevated over what we would have predicted from CDOM-salinity mixing lines in Figure 1. However, this event may have been partially caused by new production of CDOM by algae and zooplankton. If so, it was a rare event and we are still analyzing results to determine what, if any, additional information can be obtained from these samples. Additional observations were made during August 2002, but sample analysis is incomplete at this time.

Unlike the unusually low rainfall conditions which persisted during 2000, rainfall has been at or above normal during the past 12 months. Figure 2 shows data collected from the same region of the South Florida Shelf (SFS; Marco Island to Key West) during June 2000 and June 2001. CDOM decreased

with increasing salinity and slopes were similar during both periods, however the line for 2000 has a higher y-intercept value. The reversal of the CDOM salinity relationship (from negative to positive) at salinities greater than 36 is indicative of input of high salinity, high CDOM water from Florida Bay. Maximum value observed was 12 ppb QSE at a salinity of 38. Mixing lines in this region of the plot are identical during both study periods. One possible interpretation of this plot is that during the dry summer of 2000, the influence of Florida Bay water was more extensive, causing elevated CDOM concentrations throughout the region. In contrast, during the rainy summer of 2001, riverine inputs were higher and had more influence on CDOM concentrations on the shelf. Several additional data sets have been collected from this region, and should allow us to further refine our understanding of CDOM dynamics.



**Figure 2. Salinity versus CDOM (FDOM) for two cruises to the SFS showing the periods of low rainfall during 2000 (red and lavender points) versus high rainfall during 2001 (blue points). High salinity high CDOM from Florida Bay results in a positive relationship between salinity 36 and 38.**

Continuous underway fluorescence data collected using the WetLabs, Inc SAFire are partially analyzed and will be used to expand spatial coverage of the discrete data.

## IMPACT/APPLICATIONS

CDOM is one of the most significant and least understood light attenuating components, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone. A major objective of this study is provide data for development and validation of coupled physical/ecological/bio-optical models which will incorporate phytoplankton, CDOM, suspended sediment distributions into models to account for hyperspectral water-leaving radiance  $L_w(\lambda)$  and inherent optical properties (IOPs) fields.

## TRANSITIONS AND RELATED PROJECTS

Our data will be integrated with data from several collaborative programs including:

- 1) an array of sixteen current meter (ADCP and ADV) moorings with meteorological instrumentation supported by multi-agency funding from State of Florida COMPS (Coastal Ocean Monitoring and PORTS Prediction System), NOAA/EPA-ECOHAB:Florida, and ONR-AUV programs,
- 2) bio-optical sensor packages on some of these moorings for continuous measurement of incoming irradiance, water-leaving radiance, hyperspectral downwelling irradiance, backscatter, forward scatter, absorption, attenuation and fluorescence funded by HYCODE/ONR (Carder/Steward, USF),
- 3) an ongoing program for monthly collection of CTD, phytoplankton dominant species cell counts, chlorophyll, phaeopigments, tow counts of macrozooplankton species and nutrient data (ECOHAB: Vargo et al., USF),
- 4) physical circulation model of WFS currents (Bob Weisberg and Mark Luther, USF),
- 5) coupled physical/ecological/bio-optical models which will incorporate phytoplankton, CDOM, suspended sediment distributions models for to account for hyperspectral water-leaving radiance  $L_w(\lambda)$  and inherent optical properties (IOPs) fields (HYCODE – Walsh/Weisberg/Bissett) and
- 6) on-going SeaWiFS and MODIS ocean color studies on the West Florida Shelf (Frank Muller-Karger, USF).

## PAPERS & PUBLICATIONS

Jolliff, J.K., J. J. Walsh, R. He, R. Weisberg, A. Stovall-Leonard, R. Conmy, P. G. Coble, B. Nababan, F. Muller-Karger, J. Patch, and K. Carder. 2002. On the Dispersal of Terrestrial Organic Matter over the West Florida Shelf: A simulation of river discharge and photolysis of colored dissolved organic matter. Xth Annual International Conference on Harmful Algae.

Stovall-Leonard, A., and P.G. Coble. 2002. Optical Characterization of Coastal Waters In The Gulf Of Mexico As A Function of Multiple River Inputs. Ocean Sciences 2002 Meeting, Feb. 11-15, 2002. Honolulu, HI.

Conmy, R.N., and P.G. Coble. 2002. Changes in the Optical Properties of CDOM in Coastal Regions of the Gulf of Mexico (Mississippi River to Florida Bay). Ocean Sciences 2002 Meeting, Feb. 11-15, 2002. Honolulu, HI.

Del Castillo, C.E., P.G. Coble, R.N. Conmy, F.E. Muller-Karger, L. Vanderbloomen, and G.A. Vargo. 2001. Multispectral In-situ Measurements of Organic Matter and Chlorophyll Fluorescence in Seawater: Documenting the Intrusion of the Mississippi River Plume in the West Florida Shelf. Limnol. Oceanogr. 46: 1836-43.

Coble, P.G., A. Stovall-Leonard, R.N. Conmy, J.R. Boehme, and C.E. Del Castillo. 2001. Seasonal and spatial variability of CDOM in the Gulf of Mexico. Poster presented at the Gordon Research Conference on Chemical Oceanography, Tilton School, Tilton, NH. Aug. 12-17, 2001.

Boehme, J. R., and P. G. Coble. 2001. Seasonal- and Source-related Variability in Fluorescence of Colored Dissolved Organic Matter the Tampa Bay Estuary System. ASLO Winter Meeting, Feb. 12-16, 2001. Albuquerque, NM.

Coble, P.G., J. Boehme, C.E. Del Castillo, R.N. Conmy, and A. Stovall-Leonard. 2001. Using Physical and Optical Properties to Understand Cycling of Colored Dissolved Organic Matter Applied in a River-Dominated Margin: I. River Endmembers in the Gulf of Mexico. ASLO Winter Meeting, Feb. 12-16, 2001. Albuquerque, NM.

Conmy, R.N., P.G. Coble, J.R. Boehme, and J.E. Ivey. 2001. Changes in the Optical Properties of CDOM During a Lagrangian Experiment on the West Florida Shelf. ASLO Winter Meeting, Feb. 12-16, 2001. Albuquerque, NM.

Stovall-Leonard, A., P.G. Coble, C.E. Del Castillo, R. Conmy. 2001. Using Physical and Optical Properties to Understand the Cycling of Colored Dissolved Organic Matter (CDOM) in a River Dominated Margin: II. Gulf of Mexico. ASLO Winter Meeting, Feb. 12-16, 2001. Albuquerque, NM.

Coble, P.G., J. Boehme, C.E. Del Castillo, R.N. Conmy, and A. Stovall-Leonard. 2001. Optical Properties of Colored Dissolved Organic Matter in the Gulf of Mexico: Results from Recent Cruises on the R/V Pelican and R/V Walton Smith. ONR Workshop on CDOM, Feb. 10-11, 2001. Albuquerque, NM.

Coble, P.G., C.E. Del Castillo, R.N. Conmy, A. Stovall-Leonard, and J. Boehme. 2001. Optical Properties of Colored Dissolved Organic Matter on the West Florida Shelf: Results from Recent Cruises during FSLE 3 & 4 Experiments. ONR HYCODE Workshop, Jan. 8-10, 2001. St. Petersburg Beach, FL.

Coble, P.G., Effects of photo-oxidation, mixing, and biological activity on the optical properties of CDOM. Oceans from Space 2000, Oct. 9-13, 2000. Venice, Italy.

Coble, P.G., C.E. Del Castillo, and R.N. Conmy. 2000. Distribution and Cycling of CDOM in the Eastern Gulf of Mexico Using Multispectral In-situ Fluorometry. Ocean Optics XV, Monaco, October 2000.