

The Delivery of Chromophoric Dissolved Organic Matter to the Sea

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Grant #: N00014-00-1-0325

<http://alpha.es.umb.edu/shuttle/>

LONG-TERM GOAL

The long-term goal of this research is to better understand the biogeochemical cycling of dissolved organic matter (DOM) in coastal waters. Of particular interest is the fate of terrigenous and dissolved organic matter in coastal marine systems and its effects on ocean color.

OBJECTIVES

1.) *Determine high-resolution spatial and temporal variability of chromophoric dissolved organic matter (CDOM) in coastal regions.*

By applying recent advances in *in situ* measurement and real-time sampling, the differentiation of sources, synoptic mapping of distributions, and predictions of transformations of CDOM will become possible. An understanding of this natural variability is necessary for knowledgeable sampling strategies and relating chemical properties to governing physical processes in high energy environments such as coastal seas. In addition, large spatial coverage over a wide range of estuarine systems will provide valuable data in developing remote sensing algorithms.

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 The Delivery of Chromophoric Dissolved Organic Matter to the Sea				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) Environmental, Coastal and Ocean Sciences,,University of Massachusetts Boston,100 Morrissey Boulevard,,Boston,,MA, 02125				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 The long-term goal of this research is to better understand the biogeochemical cycling of dissolved organic matter (DOM) in coastal waters. Of particular interest is the fate of terrigenous and dissolved organic matter in coastal marine systems and its affects on ocean color.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

2.) *Determine the reactivity of DOM in estuaries*

By examining sources and sinks of colored and non-colored DOM along salinity gradients, estimates of water mass residence times can be converted to average reactivities for the various sources of DOM in coastal waters. Only through high resolution, highly sensitive measurements may the different reactivities of several sources of CDOM be determined simultaneously.

3.) *Relate the molecular level structure of DOM to the optical properties of CDOM.*

Detailed molecular level characterization of DOM isolates by ^1H NMR, Pyrolysis GCMS, and lignin analysis will supply valuable structural information to augment optical measurements of CDOM. In order to reliably predict the important photochemical, biological, and chemical processes governing CDOM, and hence its reactivity, the link between structure and optical properties must be defined.

4.) *To address the long-standing question: How much seawater DOM is derived from terrigenous sources?*

Differentiation of sources with both optical and chemical characterization techniques will allow an estimate of dissolved organic carbon (DOC) flux out of different estuaries into the open ocean [Meyers-Schulte and Hedges, 1986]. By understanding the processes governing this flux, an estimate for entire continental shelves can be made. Further, detailed understanding of the processes controlling the fate and distribution of DOM in coastal waters will allow detailed modeling of the fate of contaminants such as hydrophobic organic contaminants as well as certain metals (Hg, Pb, Ag, etc) that are known to be associated with terrestrial, especially anthropogenic organic matter.

APPROACH

Development and deployment of new undulating, towed sensor systems (undulating 3-50 m—ECOShuttle; tow-yo 0-3 m—MiniShuttle) designed specifically for optical measurements of CDOM now allows high spatial resolution CDOM measurements, and these sensor systems have been deployed in Boston Harbor, Delaware Bay/Chesapeake Bay, San Diego Bay, San Francisco Bay, Gulf of Mexico, and several northeast salt marsh estuaries. Discrete seawater samples have been taken (via submersible pump incorporated into the towed systems) in order to validate *in situ* measurements while large volume samples were taken to characterize the various sources of CDOM. Optical measurements include absorption spectra, fluorescence excitation-emission spectra, and time-resolved fluorescence spectra. Further analyses include high-temperature combustion dissolved organic carbon, ^{13}C and ^{14}C concentrations in various organic pools, chlorophyll-a, and elemental analysis. CDOM characterization will rely on ^1H -NMR and direct temperature mass spectrometry (DTMS) of the high molecular weight fraction of DOM isolated and concentrated by ultrafiltration (>1000 NMW). This project is an interdisciplinary effort combining physics (Gardner), organic geochemistry (Chen) and isotope geochemistry (Wang).

WORK COMPLETED

Samples have been processed from all cruises in the Mississippi River/northern Gulf of Mexico. In addition, most of the ECOShuttle data has been processed and analyzed. AC-9 data has been aligned (timing) with *in situ* ECOShuttle data. Julie Callahan has completed a 30 day cruise in the Pearl River Estuary, China and processed all DOC and fluorescence analyses. We have also completed 13 cruises

in the Neponset River estuary over a 48-hour time period to examine tidal, photochemical, precipitation, and salt marsh influences on CDOM distributions both vertically and horizontally.

High molecular weight DOM samples collected by ultrafiltration (1 nm) have been desalted and concentrated. They have all been analyzed by direct-temperature mass spectrometry (DTMS). DTMS is reproducible, and shows adequate sensitivity for HMW-DOM samples. While samples from different estuaries and at different salinities demonstrate clear differences in DTMS spectra, we are attempting to use principal component analysis to quantify these differences and relate observed DTMS differences to different compositions (C/N ratio, stable isotope ratio) or optical properties (Absorbance spectrum, fluorescence EEM, fluorescence/salinity ratio), in the water from which they were extracted.

RESULTS

Results so far from our field activities have yielded some important findings.

- 1.) CDOM fluorescence is not simply driven by conservative mixing of a freshwater endmember and seawater. In many cases, major sources of CDOM occur within estuaries, especially wetlands or salt marsh systems, and even on continental shelf systems. In fact, in the Parker River (Plum Island Ecosystems LTER), as much as 90% of the CDOM exported from the estuary is derived within the salt marsh estuary (in August). There is a clear seasonal trend with salt marsh estuaries with production peaking in late summer, early fall.
- 2.) Fluorescence-Salinity relationships change from estuary to estuary suggesting that watershed characteristics affect CDOM concentrations and distributions.
- 3.) Freshwater CDOM endmembers can change significantly (50%) in a few hours (Figure 2) in small estuaries making estuarine processes affecting CDOM difficult to decipher unless the endmember is continuously monitored.
- 4.) Fluorescence/Salinity relationships differ in different water masses/sources of CDOM within the northern Gulf of Mexico region. Optical properties in the Mississippi River plume are different from those in the nearshore waters (coastal current with CDOM from fringing wetlands).
- 5.) Fluorescence/absorbance ratios are relatively constant in all estuaries examined suggesting that CDOM fluorescence is a good proxy for CDOM absorption in estuaries.

IMPACT/APPLICATIONS

High resolution optical measurements allow a much better understanding of complex coastal processes. With a significant groundtruthing effort, this research has yielded a new, powerful technique for examining episodic and small-scale events and features in coastal waters. Our data shows that variations in intensity over very small scales (10s of meters horizontally, centimeters vertically) while CDOM composition shifts regionally (10s of kilometers or with watershed). Careful examination of the discrete samples is yielding valuable information on the reactivity of the CDOM in estuaries as well as the relationship between optical measurements and CDOM composition.

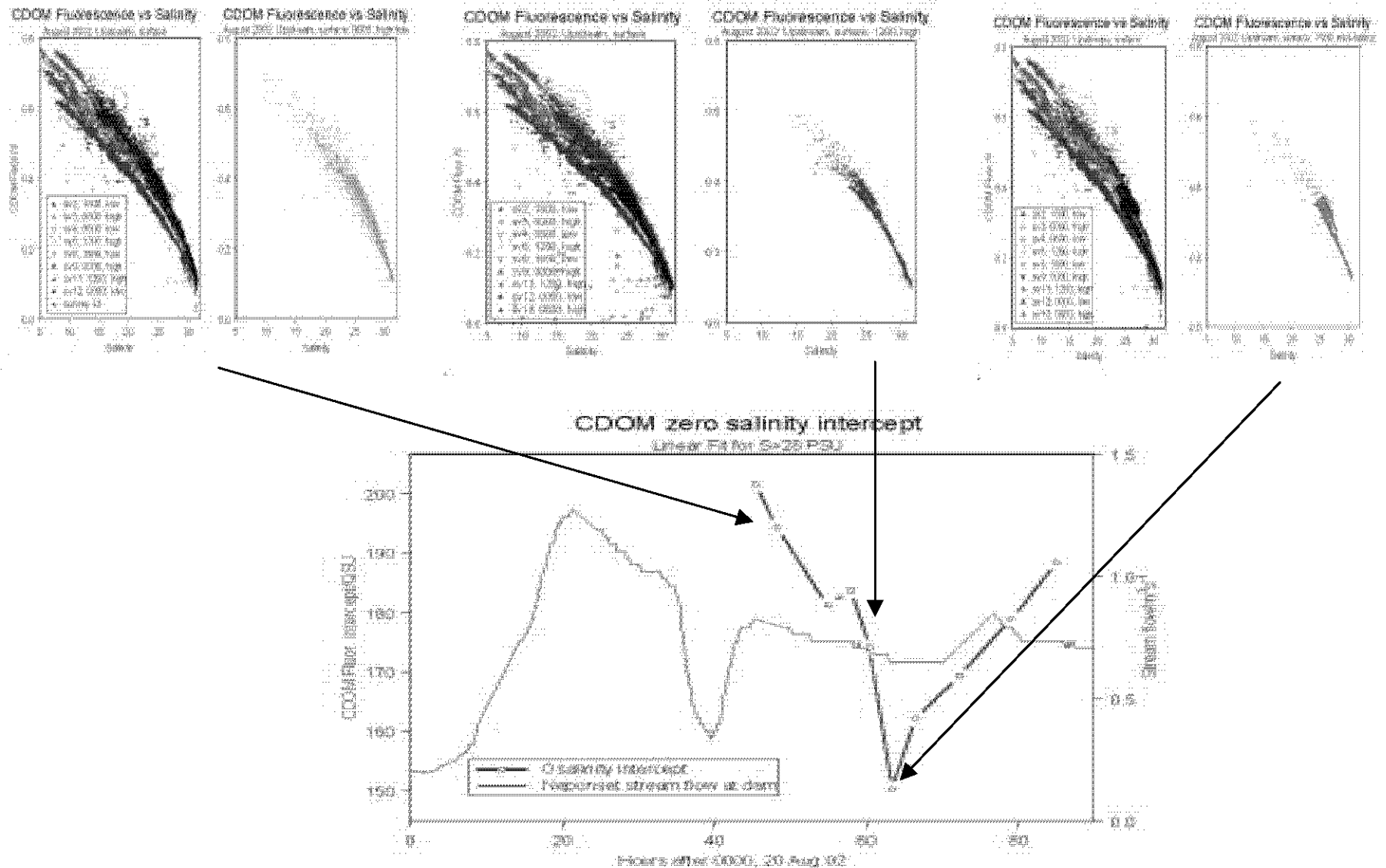


Figure 1. Three consecutive surveys showing salinity vs. CDOM in the Neponset River Estuary spanning 15 hours. Apparent freshwater endmembers vary by over 25% during the course of less than one day.

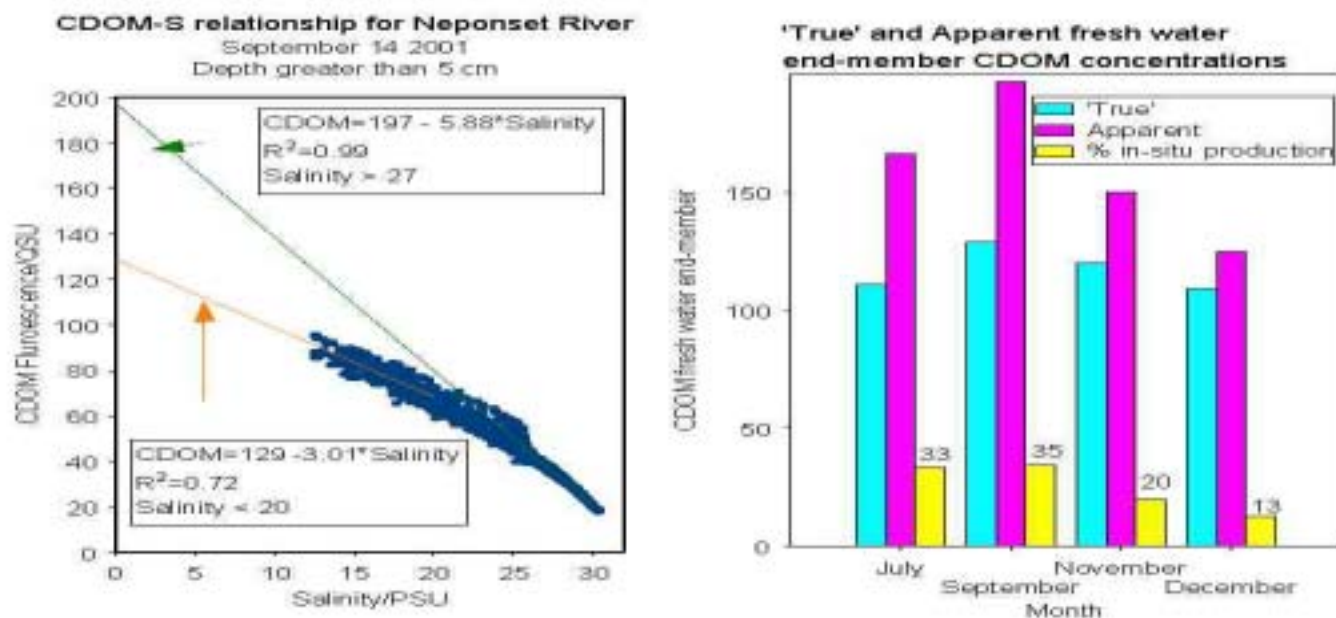


Figure 2. CDOM vs. salinity in September shows a significant production of CDOM in the estuary. By comparing actual freshwater endmembers and apparent freshwater endmembers from the high salinity regions, it is shown that significant amounts (up to 35% in this case) of the exported CDOM in produced within the estuary.

Further, it appears that freshwater discharge is a master variable controlling the concentration of terrestrial CDOM that enters and passes through estuaries before entering coastal waters. However, it appears that some systems have increasing CDOM in the freshwater with increasing discharge, and other systems have decreasing CDOM freshwater endmembers with increasing discharge (dilution). If a relationship can be established, it may be possible to predict the flux of CDOM into coastal regions worldwide.

TRANSITIONS

The results obtained so far have led to discussions with D. Bart Chadwick (SPAWAR) in San Diego, Jim Cloern (USGS) in San Francisco Bay, Jonathon Sharp (U. Delaware) in the Delaware Bay, and numerous others. The comparisons between these diverse estuaries should yield far-reaching conclusions that can be used by these and other estuarine researchers. The ECOShuttle has not yet been used for other projects, but proposals to use it for a dye study in the Hudson River and New Jersey Shelf region as well as to study krill overwintering in a Norwegian Fjord are pending. The Mini-Shuttle has been used to study natural hydrocarbon seeps off Santa Barbara, California, as well as the Apalachicola estuary. Juanita Urban-Rich, Diane McKnight and I have organized a Special Session at the ASLO meeting in Salt Lake City, February of 2003 on Discrete sources of DOM in the aquatic systems.

RELATED PROJECTS

- 1.) Our current DURIP funding to increase observational capabilities with our Integrated Coastal Observation System (ICOS) is reported on a separate report.
- 2.) Dan Repeta, is studying the production of discrete CDOM components by phytoplankton in culture (ONR funded). Phytoplankton produced DOM is extracted by solid phase extraction (C₁₈) and examined by ¹H NMR. Fluorescent EEMs are also measured of the several cultures at various growth phases to examine the production of CDOM components.

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