The Biogeochemistry of Chromophoric Dissolved Organic Matter in Coastal Waters

Robert F. Chen
Environmental, Coastal and Ocean Sciences
University of Massachusetts Boston
100 Morrissey Boulevard
Boston, MA 02125-3393
(617)287-7491; FAX: (617)287-7474 E-Mail: chenr@umbsky.cc.umb.edu
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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 anthropogenic dissolved organic matter in marine systems.

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.

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 ^{1}H 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?*

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Differentiation of sources with both optical and chemical characterization techniques will allow an estimate of DOC flux out of these four quite 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 (i.e. PCBs, PAHs, pesticides) as well as certain metals (Hg, Pb, Ag, etc) that are known to be associated with terrestrial, especially urban organic matter.

APPROACH

Development and deployment of a new undulating, towed sensor system (ECOShuttle) designed specifically for optical measurements of CDOM now allows high spatial resolution CDOM measurements and has been deployed in Boston Harbor, Delaware Bay/Chesapeake Bay, San Diego Bay, and San Francisco Bay. Discrete seawater samples have been taken 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, chlorophyll-a, and elemental analysis. CDOM characterization will rely on ^{1}H-NMR and direct temperature mass spectrometry of the high molecular weight fraction of DOM isolated and concentrated by ultrafiltration (>1000 NMW). Bernie Gardner (physical oceanographer-UMassBoston) is in charge of deployment of the CTD and towed vehicle as well as assisting in the overall design of the sensor system and sampling plan. Doctoral candidate Steve Rudnick has been assisting in deploying the time-resolved laser-induced fluorescence (TR-LIF) system [Chen, 1999]. Graduate Student, Julie Callahan, is in charge of large volume sampling and high molecular weight DOM characterization by ^{1}H-NMR and mass spectrometry. Discrete optical measurements and DOC analyses are handled by graduate students Penny Vlahos and Yixian Zhang. I am in charge of overseeing the project, organizing cruises, analyzing samples and data, and disseminating the results.

WORK COMPLETED

Five deployments of the ECOShuttle have been carried over the last year and a half. The ECOShuttle (based on the Chelsea Nu-Shuttle), winch, cable, and instruments including a pinger (for recovery), altimeter, CTD, CDOM fluorometer, Chl-a Fluorometer, backscatter sensor, and hydrocarbon fluorometer were all incorporated into a system that is deployable after a day or two of setup. To date, over 10 million data points in the 4 estuaries have been collected. Pictures of the ECOShuttle can be viewed at www.es.umb.edu/shuttle. A 4” stainless steel well pump has been attached to the top of the ECOShuttle in order to pump water from the Shuttle through the 1/2” teflon tube inside our tow cable to the shipboard lab. The current 130 m cable allows the shuttle to reach depths of 30 m at 8 knots. The 90 second delay required to pump water from the pump to the sampling manifold and in-line instrumentation allows us to observe small scale features in real-time and capture discrete samples. In-line instrumentation includes our time-resolved laser-induced fluorescence system for measuring CDOM emission spectra and pyrene as well as a Cary 50 spectrophotometer that measures the absorbance at 337 nm every second. Discrete samples (over 300 collected) are analyzed for total dissolved organic carbon (DOC), absorption, absorption slopes, fluorescence excitation-emission spectra, and fluorescence emission with excitation at 337 nm. Additionally, selected samples (~50) are analyzed for particulate organic carbon and nitrogen, chlorophyll a, total suspended matter, $DO^{13}C$, and fluorescence lifetime. These samples have all been collected and most have been analyzed. A subset of these results will be presented at the Ocean Sciences Meeting in San Antonio, January, 2000.

For large volume samples, two Amicon DC-10L cross-flow filtration systems were used on all cruises to recover 28 (50-200 l). Water was filtered with baked GFFs and cleaned 0.2 polycarbonate filters before ultrafiltration with 1 nm nominal pore size regenerated cellulose filters. More than half of the samples have been freeze-dried, and will be analyzed by direct-temperature mass spectrometry and ^{1}HNMR in December. DTMS runs at 25 eV are reproducible and show differences in TICs from sample to sample, but do not exhibit good recovery of higher mass fragments. We are working on lowering the electron impact voltage to below 20 eV to improve high mass resolution.

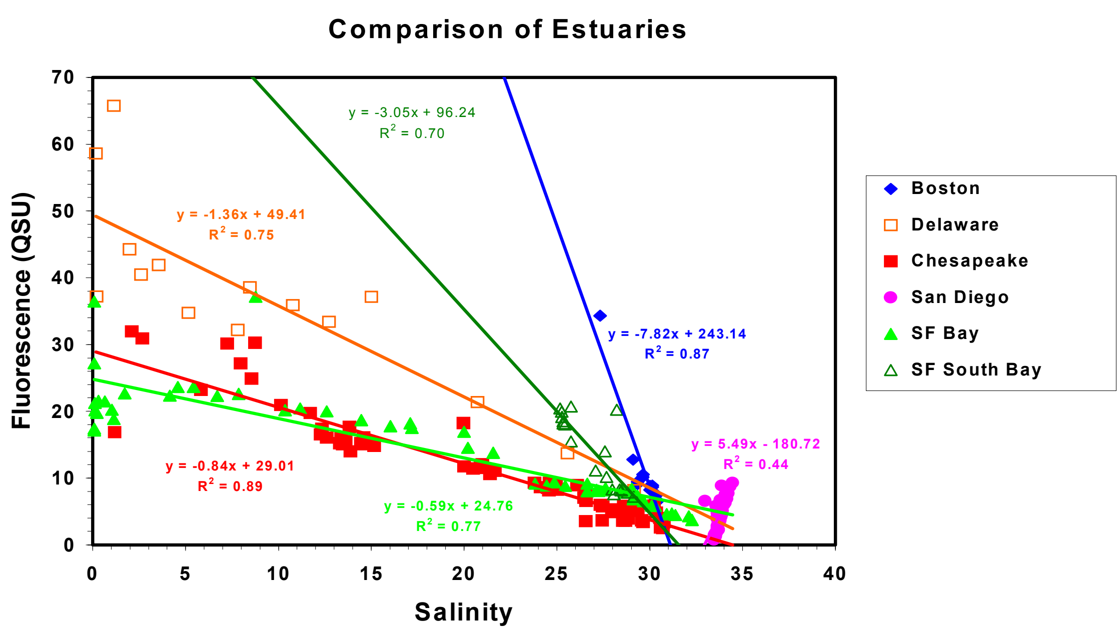
RESULTS

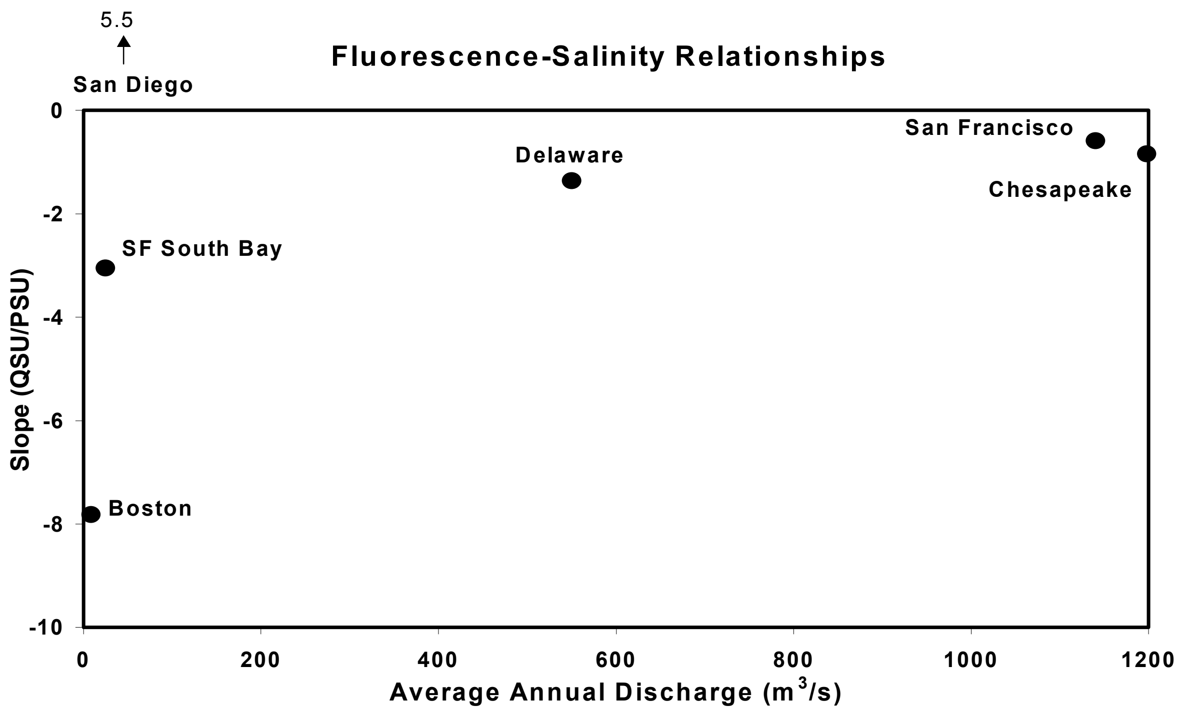
While data is still being reduced and large volume samples still need to analyzed, several general observations appear to be forthcoming.

1.) CDOM fluorescence acts conservatively even when DOC is clearly not conservative (e.g. Chesapeake Bay) and therefore may represent a refractory, terrestrial fraction of estuarine DOM.

2.) Fluorescence-Salinity relationships change from estuary to estuary (Figure 1) suggesting that estuarine characteristics affect CDOM concentrations and distributions.

3.) Fluorescence/salinity ratios appear to be related to the freshwater discharge of an estuary (Figure 2).





4.) Fluorescence/absorbance ratios are relatively constant in all estuaries examined suggesting that CDOM fluorescence is a good proxy for CDOM absorption in estuaries.

5.) Pyrene can be detected at levels greater than 5 parts per trillion in Boston Harbor suggesting localized sources of pollution [Rudnick and Chen, 1998] and shows levels from 5-100 ng/l in urban estuaries.

6.) The hydrocarbon fluorometer (240/360) and the CDOM fluorometer (320/450) while generally correlated (low salinity waters are higher in both CDOM and pollution), show different relationships in different regions suggesting that they are measuring two different chromophores in seawater.

7.) A hydrophobic CDOM fraction can be extracted from seawater in urban estuaries. This component may be responsible for as much as 25% of the CDOM fluorescence in some area. Its hydophobic nature suggests that it does not stay in the water column more than a few days.

IMPACT/APPLICATIONS

High resolution optical measurements allow a much better understanding of complex coastal processes. With a significant groundtruthing effort, this research should yield a new, powerful technique for examining episodic and small-scale events and features in coastal waters. Even without thorough analysis, our data shows that variations in intensity over very small scales (10s of meters) while CDOM composition shifts regionally (10s of kilometers or with watershed). Careful examination of the discrete samples should yield valuable information on the reactivity of the CDOM in estuaries as well as the relationship between optical measurements and CDOM composition.

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. If this relationship holds up, 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 locating sea scallop spat in Georges Bank for aquaculture (with Harlyn Halvorson) and for environmental monitoring of Boston Harbor have been developed. I (with Bernie Gardner and Judy Pederson) have organized a Special Session on Boston Harbor: The Experiment at the 1998 AGU Spring Meeting in Boston and a Special Session (with Bernie Gardner) on Recent Advances in Underwater Vehicle Technology at the 1999 Spring AGU Meeting.

RELATED PROJECTS

1.) Jim Bales (MIT), Bernadette Johnson (MIT Lincoln Labs), John Zayhowski (MIT Lincoln Labs), Bernie Gardner, Carl Gruesz (Masters Thesis) and I are developing a low power, miniaturized fluorometer for use on autonomous underwater vehicles (MIT SeaGrant funded).

2.) Dan Repeta, Lihini Aluwihare and I are studying the production of CDOM by phytoplankton in culture (ONR funded). Phytoplankton produced DOM is extracted by cross-flow filtration (1000 NMW) or solid phase extraction (C_{18}) and examined by ^{1}H 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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