The Biogeochemistry of Chromophoric Dissolved Organic Matter in Coastal Waters

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LONG-TERM GOALS

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.

SCIENTIFIC 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.

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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 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 measurements and has been deployed in Boston Harbor and Delaware Bay/Chesapeake 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, direct temperature mass spectrometry, and pyrolysis 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, 1998]. 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

Three deployments of the ECOShuttle have been carried out last summer. 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. Pictures of the ECOShuttle can be viewed at www.es.umb.edu/shuttle. Unfortunately, the 2” diameter pump that we purchased to pump water from the Shuttle through the 1/2” teflon tube inside our tow cable is driven by an inverter that creates an interference with data transmission to the CTD and the Chelsea controller. Therefore, for the two deployments in Boston Harbor and the cruise in Delaware Bay/Chesapeake Bay we used a surface pumping system for both discrete water sampling (DOC, ABS, Fluorescence spectra) as well as real-time measurements of time-resolved fluorescence and absorption at 337 nm. In addition, three dimensional fluorescence excitation/emission matrix scans were taken in stopped flow mode on a Hitachi F-4500. This data is all being reduced and analyzed.

For large volume samples, two Amicon DC-10L cross-flow filtration systems were used on both cruises to recover 6 (50-200 l) samples in Boston Harbor and 8 samples in Delaware and Chesapeake Bays. Water was filtered with baked GFFs and cleaned 0.2 polycarbonate filters before ultrafiltration with 1 nm nominal pore size regenerated cellulose filters. Retentates are currently being freeze-dried so that they may be analyzed by direct-temperature mass spectrometry.

RESULTS

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

1.) Salinity/Fluorescence relationships of the Delaware and Chesapeake Bays are distinctly different suggesting that the different watersheds have different CDOM compositions.
2.) The mouth of the Chesapeake Bay is a complex mixing regime with tidal and wind driven circulation creating strong gradients across as well as longitudinally down the center of the Mouth.
3.) High fluorescence is consistent with high absorbance and high DOC, and these features can shift over 10s of meters.
4.) Pyrene can be detected at levels greater than 5 parts per trillion in Boston Harbor suggesting localized sources of pollution [Rudnick and Chen, 1998].
5.) 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.

IMPACT/APPLICATION

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 should yield valuable information on the reactivity of the CDOM in estuaries as well as the relationship between optical measurements and CDOM composition.

TRANSITIONS

New instrumentation and the ECOShuttle will allow us to further examine coastal waters in other areas. An understanding that terrestrial systems do not have a large effect on offshore waters and that estuaries are great reactors for DOM is emerging. This project should support these new ideas with data from four major estuaries. While we have not done so yet, we plan to compare data from our cruise to data obtained by Neil Blough on several ONR funded cruises in Chesapeake/Delaware Bay and offshore across the shelf. Our January cruise will augment efforts by Bart Chadwick and Chuck Katz (NRaD) in San Diego Bay. The Boston Harbor data should be of use to the Massachusetts Water Resources Authority as well as a number of researchers in the area.

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 an upcoming Special Session (with

Bernie Gardner) on Recent Advances in Underwater Vehicle Technology at the 1999 Spring AGU Meeting.

RELATED PROJECTS

1.) Bernie Gardner, doctoral candidate Steve Rudnick (UMassBoston) and I have completed an MIT SeaGrant funded study of Boston Harbor. We developed and deployed the LIF system in Boston Harbor on 10 cruises and are studying the spatial and temporal trends of DOM and polycyclic aromatic hydrocarbons (PAH) in an urban estuary.

2.) Steve Lieberman, Bart Chadwick, Jim Leather (NRaD, San Diego) and I are studying PAH in contaminated sediments of Boston Harbor and San Diego Bay using a time-resolved fluorescence probe (Doctoral Dissertation, Yixian Zhang). We are also interested on the effects of contaminated sediments on water quality due to benthic fluxes (Masters Thesis, Gongmin Lei). This project is funded by the DOE Measurement Sciences Program.

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

4.) Dan Repeta, Tim Eglinton, doctoral candidate Lihini Aluwihare (all at WHOI), Doctoral candidate Penny Vlahos (UMassBoston)and I completing a DOE Ocean Margins Program project involving characterizing DOM on the Mid-Atlantic Bight and determining the fluxes of DOC across the continental shelf of the northeast United States.

5.) Jean Whelan (WHOI), Xuchen Wang (UMB) and I have been collaborating in an effort to quantify seeps in hydrothermal and gas producing regions. Seeps could be a source of hydrocarbons as well as porewater DOM to the deep ocean. This work is currentlynot funded.

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Pictures of the ECOShuttle are viewable at www.es.umb.edu/shuttle