Predicting Chromophoric Dissolved Organic Matter Distributions in Coastal Waters

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Award #: N00014-06-10220
http://alpha.es.umb.edu/research/shuttle/index.html

LONG-TERM GOAL

It is the long-term goal of this work to evaluate our understanding of CDOM sources and distributions in coastal waters by comparing high-resolution observations with four-dimensional, physical, chemical and biological models of the CDOM fields.

OBJECTIVES

1.) Study freshwater CDOM endmember variability due to watershed and rainfall properties and seasonal cycling in detail in the Neponset sub-watersheds and by monitoring Hudson River (including several tributaries) and Neponset River endmembers.

2.) Use Geographical Information Systems (GIS) approaches to develop a predictive model of CDOM sources from terrestrial watersheds and groundtruth the predictive model in three watersheds of various sizes (Neponset River Watershed, Hudson River Watershed, Mississippi River Watershed).

3.) Compare our high resolution 4-dimensional measurements with the output of existing modeling efforts including Alan Blumberg's New York Harbor model.

4.) Incorporate biological and chemical processes into CDOM models including photochemical and biological modifications to CDOM distributions.

5.) Extend our predictive model to various estuaries to groundtruth the model and identify and quantify the key processes controlling CDOM distributions in coastal waters.

APPROACH

We have refined what we have learned about major processes that control CDOM distributions in coastal waters and continue to work with existing coastal models to attempt to predict coastal water CDOM distributions. Our approach is four-fold. First, we have developed a GIS-based hydrological model to predict freshwater CDOM source strengths and tested this model with an established 30 station monitoring program in the Neponset Watershed. Second, because the opportunity exists to couple our observations with existing physical models in the Hudson Estuary system, we have linked freshwater source strengths into an existing 4-dimensional New York Harbor model and compared our high resolution observations with its output. Third, we have added chemical and biological production and degradation rates (some from the literature, some derived as part of this study) to the models. Finally, we have used a hyperspectral radiometer mounted to a small boat to determine upwelling radiance and develop algorithms for high resolution satellite products in the Mississippi, Atchafalaya, and Hudson River Estuaries.

WORK COMPLETED

There were no major cruise efforts in Year 3 of this project. We continued to monitor 30 stations in the Neponset Watershed for flow and CDOM as well as develop a Soil Water Assessment Tool (SWAT) hydrological model for the Neponset. We can now predict CDOM at any time at any place within the watershed. We are in the process of calibrating the model to the Hudson Watershed as well. In addition, we have compared New York Harbor model CDOM distributions with Mini-Shuttle measurements for October, 2006 and April, 2007. For both field efforts, we mounted a hyperspectral (every nm from 350 to 2500 nm) radiometer on the bow of the ship and calibrated at least every 30 min with a Spectralon white reference disk and with satellite overpass data from QuickBird, we have developed algorithms for determining CDOM from remote sensing data. Finally, we have used EO-1 Hyperion and ALI satellite images purchased in conjunction with a cruise in the northern Gulf of Mexico (August 23-28, 2007) develop algorithms to map CDOM in the Atchafalaya River Estuary. purchased that correspond to cruise tracks for the Mississippi and Atchafalaya Rivers. Discrete uncontaminated seaswater samples collected for CDOM fluorescence and absorbance as well as total organic carbon (TOC), total nitrogen (TN) and total suspended matter (TSM) measurements have been mostly processed. In addition, Neponset watershed source waters have been collected monthly and incubated under light/dark and filtered/unfiltered conditions to determine the reactivity of these different quality CDOM sources. In all, over 2000 individual samples were collected and analyzed from the ECOShuttle, Mini-shuttle, and incubation experiments.

Monthly sampling of CDOM and DOC continued in the Neponset watershed. Samples were taken from 30 sites (15 sub-watershed outlets and 15 endmember samples) in the Neponset watershed and 9 stations along the Neponset estuary. GIS techniques were used to create a stream network such that 30 sites (pour points) could be chosen that represented sub-catchments and different land use types. Land use types included forest, industrial, wetland, residential, golf course, and other.

RESULTS

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

1.) Our GIS watershed model approach suggests that watershed properties (land cover/land use, soil type, temperature, rainfall, leaf litter, leaf area index, and hydrological characteristics) can be used to predict CDOM source concentrations. Combined with a Soil Water Assessment Tool (SWAT), the watershed model has been able to explain around 90% of CDOM loadings measured *monthly* over the last two years in the Neponset Watershed (Fig. 1). Our preliminary empirical model for predicting *daily* CDOM fluxes in corresponding sub-basins established a correlation coefficient of 0.75 (R^2 = 0.5625) with actual measurements using key parameters such as daily surface runoff and leaf area index.

2.) *In situ* hyperspectral reflectance data from the spectroradiometer were analyzed to predict CDOM measurements. Spectral reflectance as a function of wavelength can explain 86% of the variation of *in situ* and discrete CDOM measurements in the Hudson Estuary (see Figure 2).

3.) We extended our functional linear model to assess CDOM content from EO-1 satellite imagery in the Atchafalaya River in August, 2007. Our satellite approach also adapted a quasi-analytical algorithm (QAA) based on our *in situ* observation data using the ICOS van (ECOShuttle) and an Analytical Spectral Devices (ASD) spectroradiometer. EO-1 satellite imagery: Hyperion and ALI acquired for September and October were used for modifying the QAA algorithm. We weree able to map the CDOM concentrations from the Atchafalaya River offshore through the estuary (Figure 3).

4.) Model (Stevens Institute of Technology/Blumberg) outputs of CDOM match observations very well once endmember CDOM values for tributaries are used as boundary conditions for the model (see Blumberg Annual Report). A new source of CDOM, a sewage outfall not included in the model, was discovered near the head or the Hackensack River. With this new source added to the model, model CDOM outputs matched Mini-Shuttle CDOM measurements quite well. “Schmutz” from the Port Richmond sewage outfall behaves similarly in the model as has been observed on 5 Hudson River transects over the past 3 years. Physical mixing of a deep source of CDOM explains time-dependent behavior of this plume in the Upper New York Harbor.

5.) A new fluorometer designed to match a unique CDOM signature produced by zooplankton grazing (SeaPoint Sensors, Exeter, NH and J. Urban-Rich with SeaGrant funding) was deployed for the first time. Initial analysis of this data suggests a change in composition and potentially source of CDOM in some areas. The peak “Z” CDOM signature rides the edge of the “marine humic” peak and so is difficult to discern, but shows some unique characteristics compared to the marine humic CDOM fluorescence.

6.) A Boston Harbor physical model has been refined to produce 60 meter resolution and a 72 hour forecast in the Neponset Estuary and Boston Harbor. CDOM sources and reactivity can be easily added to this physical model once high resolution CDOM measurements become available.

IMPACT/APPLICATIONS

High resolution optical measurements along with auxiliary data allow a much better understanding of complex coastal processes. The ICOS van and Mini-Shuttle/winch system allows simultaneous collection of the necessary data to initiate existing models for the coastal environment. Our data shows processes in the Hudson and Neponset Estuaries are similar and CDOM endmembers vary both with land use and with season/flow conditions.

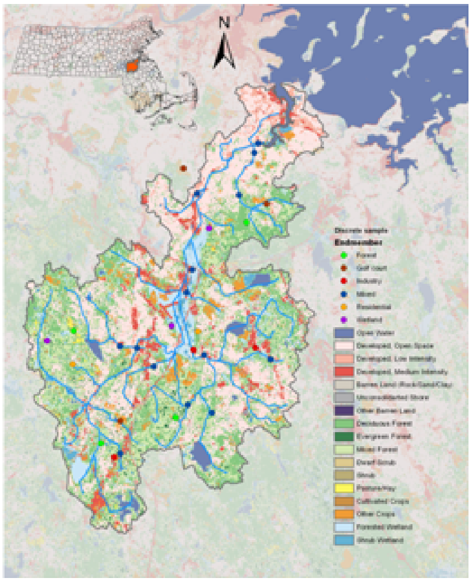
Our GIS watershed model approach suggests that watershed properties (land cover/land use, soil, temperature, rainfall, leaf area index) can be used to predict CDOM concentrations downstream. Combined with a SWAT model, are able to predict CDOM loadings in the Neponset Watershed. After initializing the models in the Hudson, we should be able to transfer our knowledge of coastal watersheds to the prediction of CDOM throughout the Hudson Watershed as well.

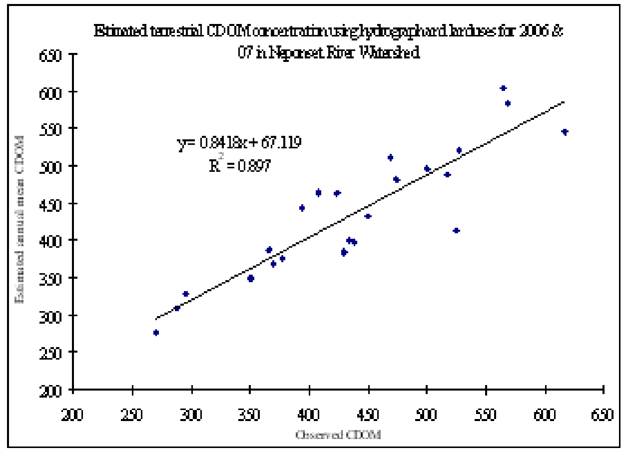
Seasonally- and flow-varying tributary CDOM contributions can be used to initiate model CDOM runs in the Hudson Estuary that can be tested by actual Mini-Shuttle observations. Observations in October, 2006 and April, 2007 suggest that physical mixing of CDOM endmembers with seawater explain the majority of the variability of CDOM in the Hudson Estuary. Biological and photochemical degradation rates obtained from incubation experiments under various sunlight, temperature, and seasonal conditions help refine these predictions, but are not dominant processes under normal conditions.

With the combined watershed flow model (SWAT), the embedded seasonal vegetation growth model, and the physical estuarine model we are able to predict CDOM concentrations in watershed, estuary, and coastal water knowing only season, land use type, rainfall, and physical mixing parameters. Only an interdisciplinary effort combining GIS, estuarine modeling, and high resolution measurements allows the development of this predictive capability.

In addition, we have developed high resolution (spatial and spectral) remote sensing measurement capabilities (Quickbird, EO-1 Hyperion) in combination with *in situ* hyperspectral reflectance and CDOM measurements that yield better estimates of CDOM from space. This allows more accurate synoptic coastal CDOM distributions and localized CDOM hotspots to be observed.

Estimating CDOM concentration with hydrograph and landuse variables at Neponset River Watershed





$$y = 0.306\ln(Q) - 0.226\ln(S) + 0.043w$$
$$+0.06d + 0.06f + 0.15a + 0.085wet + 0.725$$

Figure 1: CDOM predictions compared to measurements in the Neponset River Watershed. Sampling locations are shown in the watershed map. Correlation between model predicted CDOM and CDOM monthly measurements is r^2=0.90)

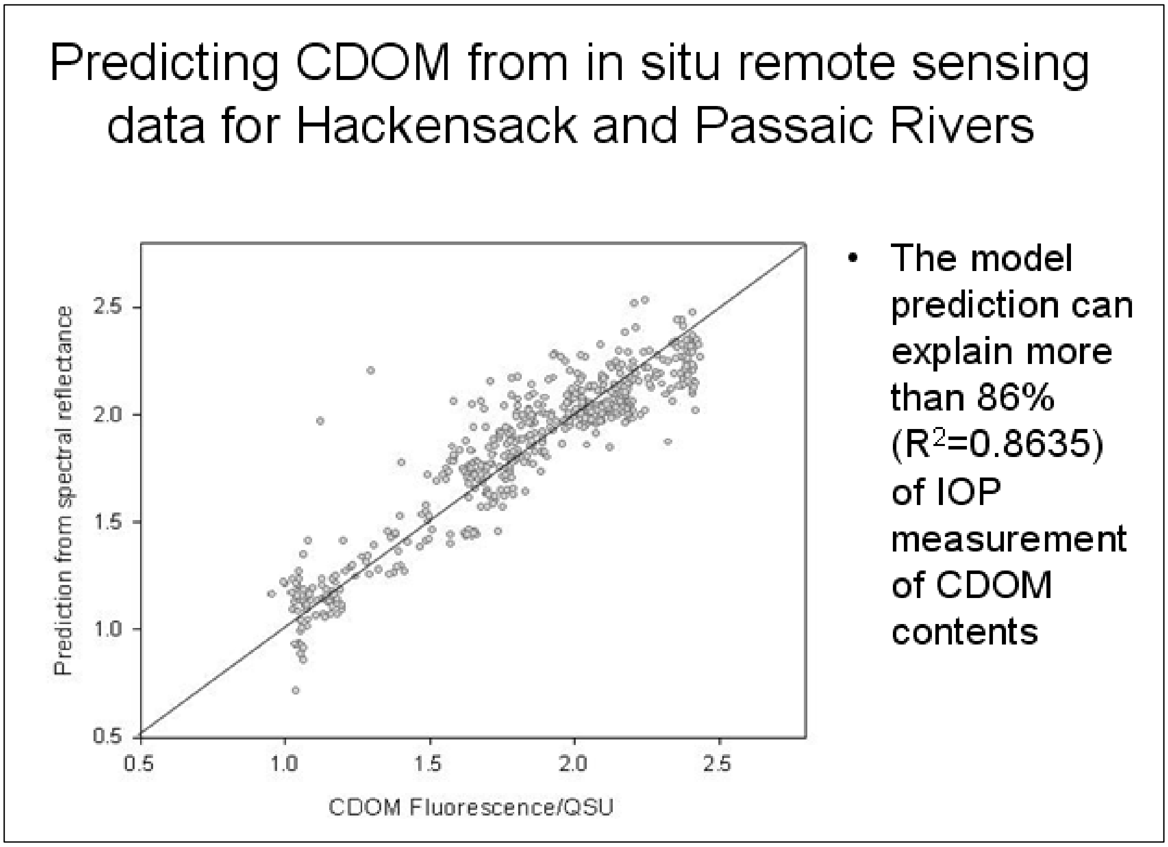


Figure 2: Hudson Estuary measurements. Discrete CDOM measurements vs. CDOM predicted from spectral reflectance measurements. R^2=0.86 for all data.

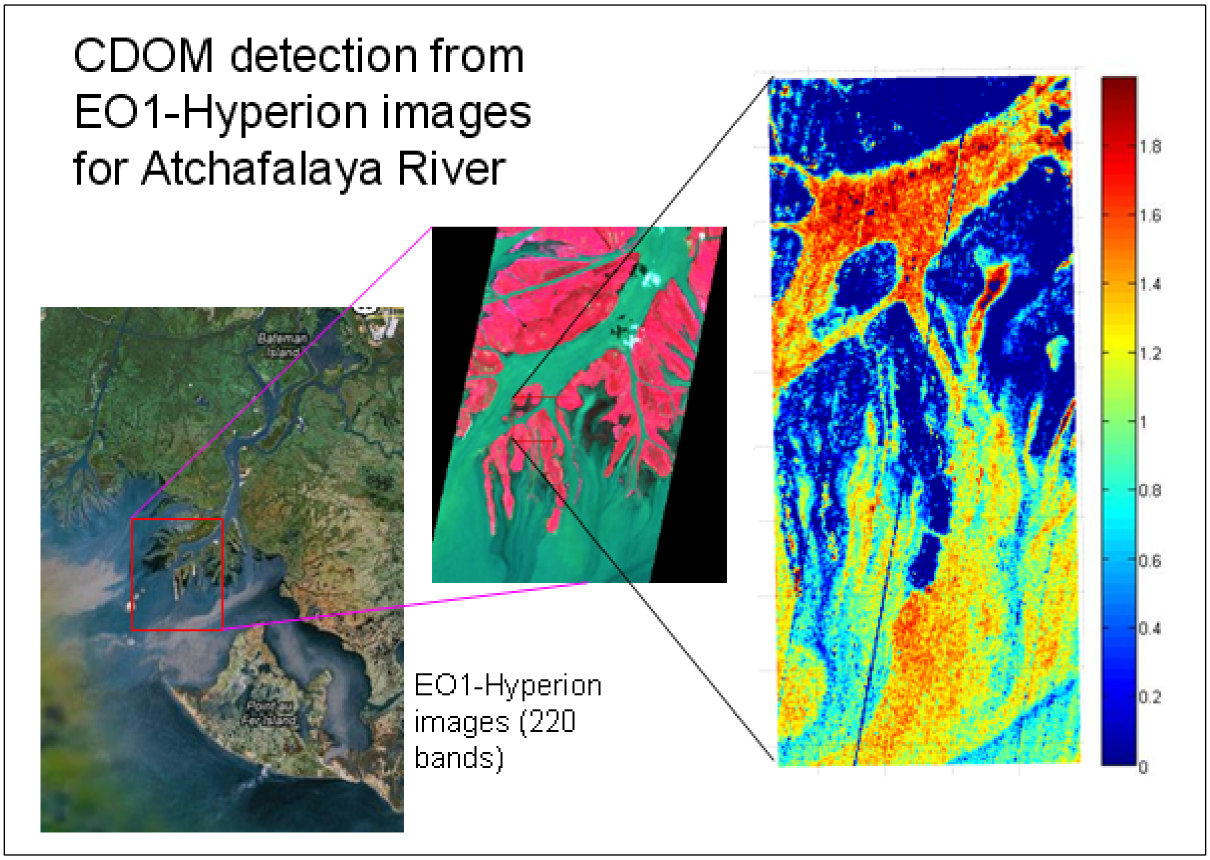


Figure 3: CDOM assessment from EO1-Hyperion images for Atchafalaya River Estuary. CDOM was calculated using a quasi-analytical algorithm (QAA) using an ASD spectral radiometer compared using a linear functionalized model to in situ CDOM data compared to satellite data. The figure shows high resolution (10s or meters) CDOM features within the estuary.

TRANSITIONS

The Hudson tributary surveys serves to link with estuary/plume surveys taken for the NSF sponsored Coastal Ocean Processes project entitled LATTE (Lagrangian Transport and Transformation Experiment). We are beginning to have a better understanding of this complex system and have been sharing our results with Alan Blumberg (Stevens Institute of Technology). The CDOM endmembers based on land use in the Neponset have been extended to the Hudson to initiate CDOM flowing in Blumberg's New York Harbor Observation and Prediction System (NYHOPS) model. So far, comparisons between predictions and observations have been very good suggesting we have a good understanding of watershed and estuarine processes affecting CDOM distributions.

The results obtained so far have led to discussions with scientists at Rutgers, University of Georgia, the Marine Biological Laboratory in Woods Hole, WHOI, Xiamen University and numerous others. The comparisons between diverse estuaries should yield far-reaching conclusions that can be used by these and other estuarine researchers. The ECOShuttle and ICOS van have been used for other projects including LATTE. Several proposals were developed with this capacity. The Mini-Shuttle/winch system has been used to study natural hydrocarbon seeps off Santa Barbara, California, as well as the Apalachicola estuary and the Hudson tributaries and is now fully operational on a variety of ships. A newly designed Surface Mapper on the RV Cape Hatteras replaces the Mini-Shuttle with a stable platform on larger ships. We have been asked to build a second winch with the same design for another proposal that is currently pending (Robert Chant, Rutgers University).

The need for high-resolution data in coastal systems has led to the creation (and initial funding) of the Center for Coastal Environmental Sensor Networks (CESN) at UMassBoston. This center is working with industry and other university partners to strengthen the high technology workforce in Massachusetts as well as university-industry partnerships and the transitioning of research products into the commercial sector. Our CDOM "moorings" with solar panel and batteries for power and dataloggers are being redesigned for use within a sensor network. A similar system designed for monitoring pond water quality has been designed, built, and deployed in local pond for educational purposes (sensor system is real-time and wireless, and is housed in a swan decoy; http://www.cesn.umb.edu/data/turnerspond.html).

Brian Gaas (student) and James Ammerman (PI) have participated on our Mississippi cruise and will use our ECOShuttle data to place their continuous bacterial enzyme activity sensor (measures phosphorus limitation in samples every 12 minutes) in an oceanographic context. Students Jun Zhu and Brittan Wilson (UMassBoston) have used Hudson Estuary surveys and Mini-Shuttle measurements to guide their water/sediment studies of organic carbon and triclosan (antibacterial compound).

RELATED PROJECTS

1.) Our DURIP project to increase observational capabilities with our Integrated Coastal Observation System (ICOS) has been completed and continues to be maintained and upgraded to meet the needs of this proposal.

2.) An NSF sponsored Coastal Ocean Processes project entitled LATTE (Lagrangian Transport and Transformation Experiment), Bob Chant, Rutgers, PI, has ended and has used this project's data to drive sampling and observation strategies. Data from both projects are being shared to meet common objectives including high resolution mapping, coastal transport and transformation processes in the Hudson River/New Jersey Shelf region.

3.) The Center for Coastal Environmental Sensor Networks (CESN; UMass President's Science and Technology Fund; $480,000) has been established to study coastal processes with high resolution, real-time smart sensor networks. A major thrust is the measurement of CDOM in the Neponset salt marsh estuary.

4.) CESN has just received Department of Energy funding ($479k) to establish the Boston Environmental Area Coastal Ocean Network (BEACON), a set of moorings providing real-time coastal ocean data including CDOM in a machine readable format. This effort will be folded into the GOMOOS data center.

5.) The Massachusetts Ocean Partnership (MOP) has been funded by the Moore foundation ($8.5M) to create a comprehensive management plan for coastal Massachusetts. Our team has been "pre-qualified" to carry out data management and data analysis tasks associated with this plan.

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