Predicting Chromophoric Dissolved Organic Matter Distributions in Coastal Waters

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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.

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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 are refining 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 are developing a GIS-based hydrological model to predict freshwater CDOM source strengths. Second, because the opportunity exists to couple our observations with existing physical models in the Hudson Estuary system, we are attempting to link freshwater source strengths into an existing 4-dimensional New York Harbor model and to compare our high resolution observations with its output. Third, we will add chemical and biological production and degradation rates (some from the literature, some derived as part of this study) to the models. Finally, we will extend the GIS model with available Satellite products to a wide variety of estuaries (that we have already surveyed; e.g. San Francisco Bay, Chesapeake Bay, San Diego Bay) to test the general applicability of this approach. We have also added a remote sensing component to our approach by comparing *in situ* CDOM measurements, ship-based hyperspectral radiometer measurements, and multi-spectral/hyperspectral satellite measurements.

WORK COMPLETED

There were three major field efforts in Year 2. First, we revisited the Hudson River Estuary and tributaries (Raritan, Passaic, Hackensack, and Hudson) towing the Mini-Shuttle instrument package that includes temperature, salinity, CDOM, chlorophyll fluorescence, optical backscatter, dissolved oxygen, and an all Teflon pumping system. These week-long studies occurred in October (23-27), 2006 (low flow, fall dump) and April (16-20), 2007 (high flow-100 year flood). 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. We also purchased satellite overpass data from QuickBird for the closest cloud-free period to our sampling dates. In April, we added a UV (412 nm) sensor to the top of the Mini-Shuttle. Finally, we completed a cruise in the northern Gulf of Mexico (August 23-28, 2007) to map the Mississippi River Plume as well as study the behavior of subsurface CDOM production. In addition to field hyperspectral radiometer measurements, EO-1 Hyperion and ALI satellite images were purchased that correspond to cruise tracks for the Mississippi and Atchafalaya Rivers and MODIS images were downloaded for the entire Gulf of Mexico. Following the installation of a new tow cable, termination of the cable, and servicing of a leaky shuttle controller housing, the ICOS van and ECOShuttle performed admirably with only a loss of 1.5 hours during the entire 6-day cruise. Temperature, salinity, CDOM fluorescence, chlorophyll fluorescence, UV radiance, dissolved oxygen, optical backscatter, AC-9, LISST-100, and pyrene concentration data were all collected continuously. Discrete uncontaminated seaswater samples were collected for CDOM fluorescence and absorbance as well as TOC, TN and TSM measurements. In all, over 2000 individual samples were collected from the ECOShuttle and incubation experiments.

During all three field efforts samples of multiple endmember and estuarine water samples were incubated under dark/filtered, dark/unfiltered, sunlight/filtered, sunlight/unfiltered conditions (and in April at 3 different temperatures) and sampled over time to determine photochemical and bacterial degradation rates over 5 days. Additionally, Hudson watershed samples (n=12 for Oct, 20 for April) were collected from various pour points (waterways in the watershed) determined from GIS land use maps to calibrate the land use endmember prediction model. Finally, "mooring" boxes measuring temperature and CDOM were deployed on the Raritan and Hackensack endmembers before, during and after the April 2007 cruise to monitor changes in endmember CDOM. The Raritan mooring recorded data continuously until 9'-above-flood level waters immersed the control box under water. The data was retrieved after drying out the data logger. Hackensack mooring performed throughout the storm.

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.

A SWAT (soil and water assessment tool) model of the Neponset Watershed that determines stream flows in all rivers and tributaries has been calibrated and will soon be combined with the CDOM land-use/landcover model so that CDOM loading can be calculated throughout the watershed, throughout the year.

RESULTS

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

1.) CDOM fluorescence from forest endmembers are about 30% higher than from residential endmembers, while wetland and industrial endmembers were 2-3 times higher than forest endmembers in the Neponset River Watershed. Seasonal variations, rainfall events, and land use patterns allow the prediction of endmember CDOM and DOC concentrations throughout the Neponset Watershed and Estuary (see Figure 1). There is good agreement between predicted values and measured values for residential areas, while differences between predicted and measured values for forested areas suggest CDOM degradation during transport in forested areas. This is confirmed by a loss of up to 50% of CDOM in 5 day incubations of forest endmember samples and a significant variation in the excitation/emission matrix of the forest endmember to the subwatershed sample.

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.) Incubation experiments suggest that 30% of endmember CDOM from Hudson tributaries is photo/biodegradable in June (under ambient sunlight and temperature conditions), but there appears to be no significant photo/biodegradation in October (2006). This is likely due to temperature and sunlight variations as well as the varying composition of CDOM with season.

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). “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.) The Mississippi CDOM endmember is significantly lower than the Atchafalaya endmember as has been previously observed. 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. While this fluorometer (with lower excitation and emission wavelengths than the standard CDOM fluorometer) tracked the CDOM fluorometer for the most part, there are several areas where the Zooplankton/CDOM fluorescence was higher than other areas (see Figure 3). This suggests a change in composition and potentially source of CDOM in some places. We are still analyzing this recently obtained data.

6.) Sub-surface CDOM production (with and without high chlorophyll) was observed, and these layers appear to have some relationship with the Mississippi Canyon topography although they move quite rapidly (10’s of km in 12 hours).

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 litter) can be used to predict CDOM concentrations downstream. Combined with a SWAT model, we should be 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 will help refine these predictions.

With the combined watershed flow model (SWAT), the embedded seasonal vegetation growth model, and the physical estuarine model we are quite close to being 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 hope that developments in high resolution (spatial and spectral) remote sensing measurement capabilities (Quickbird, EO-1 Hyperion) in combination with *in situ* hyperspectral reflectance and CDOM measurements will yield better estimates of CDOM from space. This will allow more accurate synoptic coastal CDOM distributions and localized CDOM hotspots to be observed.

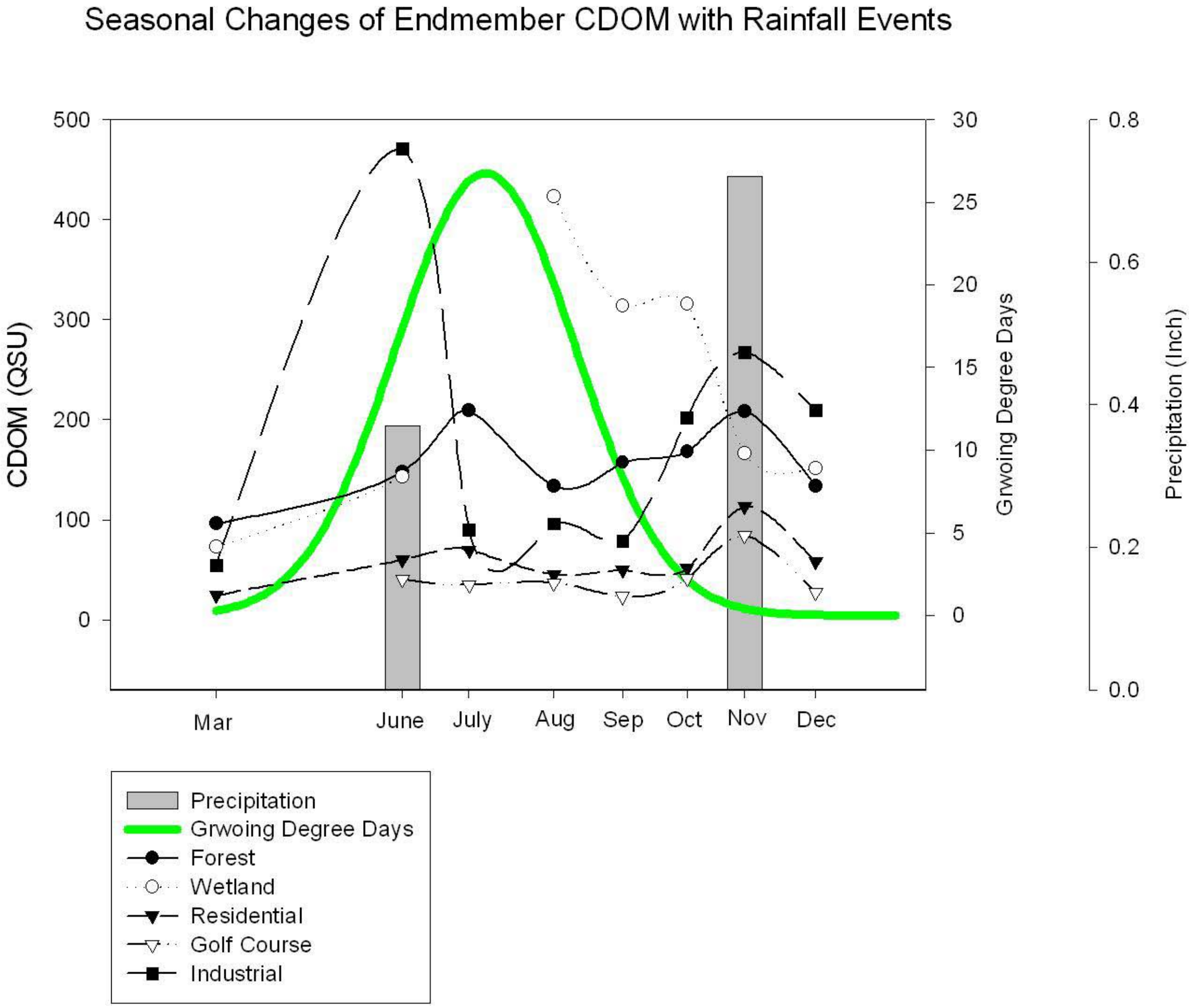

Figure 1: Neponset River CDOM measurements. Graph shows the CDOM from 5 different land use endmembers (forest, wetland, residential, golf course, industrial) varying with season. Wetland and forest samples correlate loosely with growing season, industrial samples are highly affected by rainfall events. Residential and golf courses have consistently lower CDOM values.

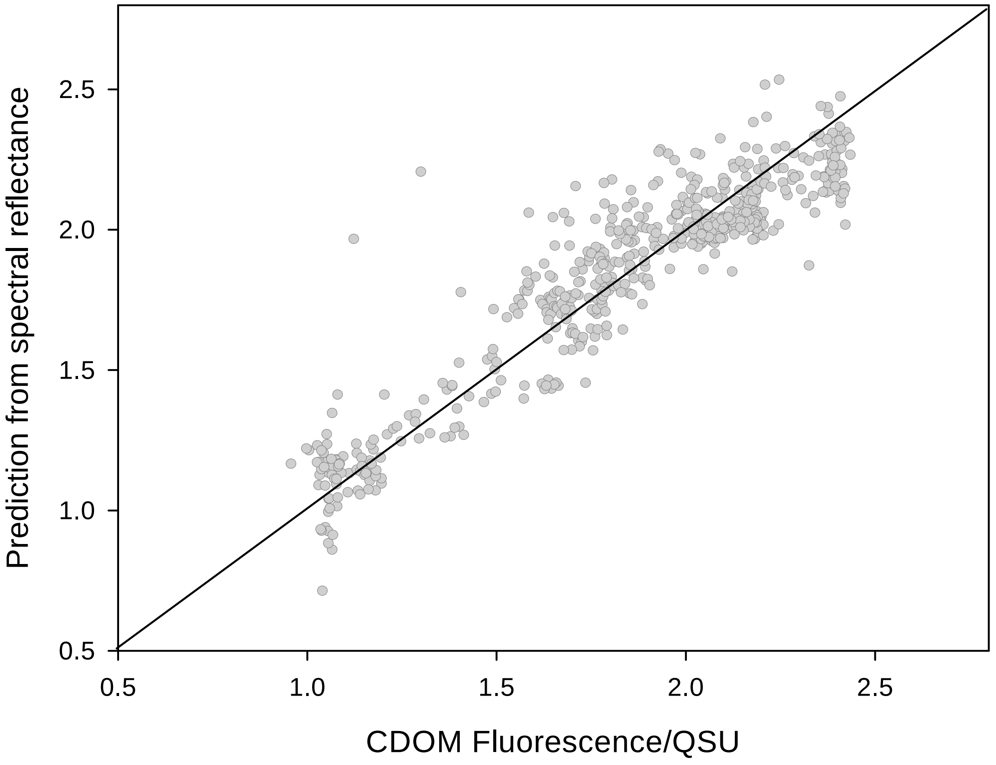

Figure 2: Hudson Estuary measurements. Discrete CDOM measurements vs. CDOM predicted from spectral reflectance measurements. R^2=0.86 for all data.

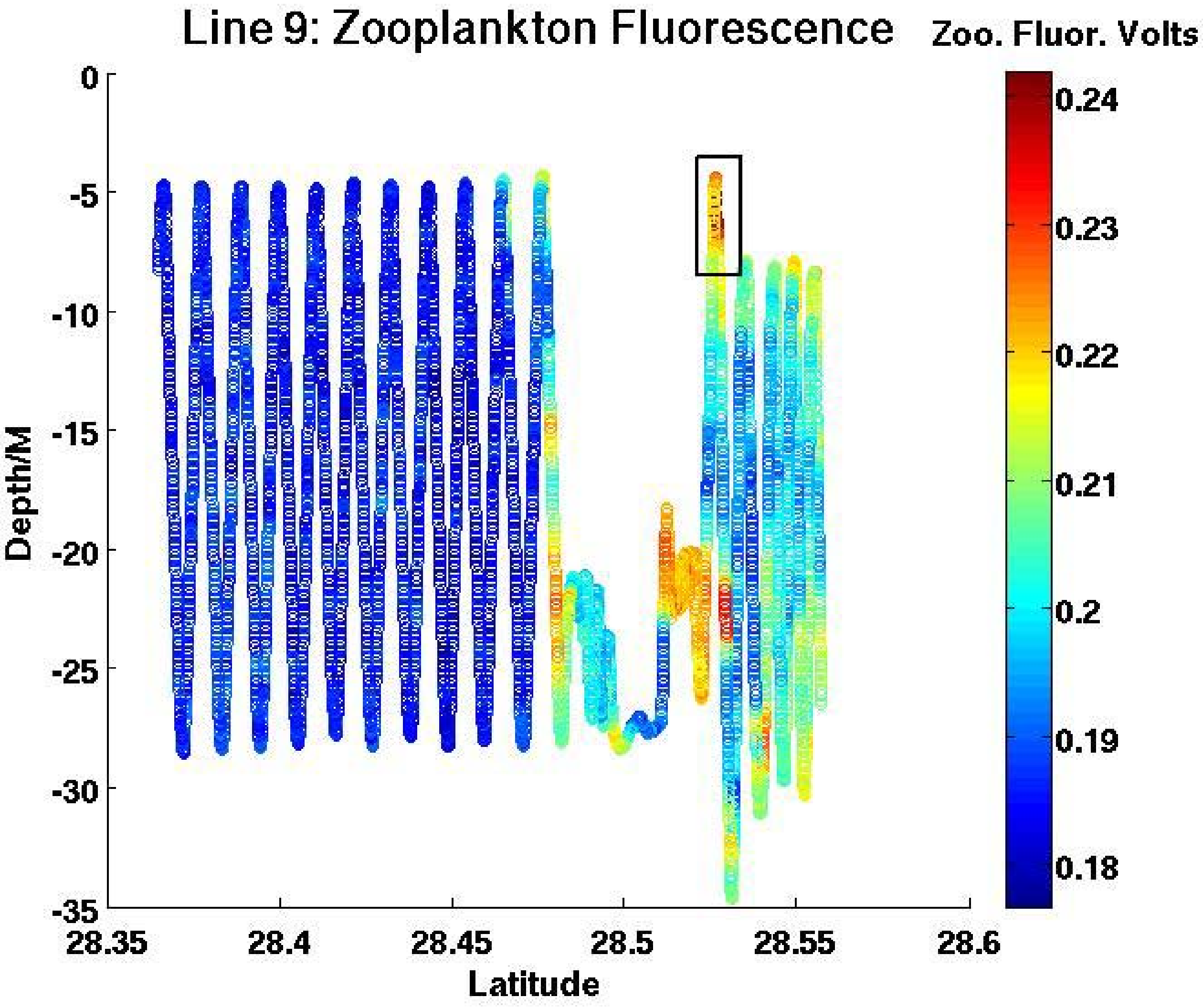

Figure 3: ECOShuttle measurements of "zooplankton" fluorescence in the northen Gulf of Mexico. Subsurface CDOM production shows similar distributions as measured by the standard fluorometer and the "zooplankton" fluorometer, but "zooplankton" fluorometer shows higher values in the Mississippi River Plume. The "zooplankton" fluorometer measures CDOM at lower excitation and emission wavelengths than the standard CDOM fluorometer.

TRANSITIONS

The Hudson tributary surveys servs 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, 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, is ending 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 (UMass President's Science and Technology Fund) 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.) Heather Saffert and David Smith (URI) are studying the distribution of bacterial indicators in the Hudson Estuary. We have provided both samples as well as hydrographic data to put their samples in context. We are also developing a rapid bacterial indicator system (MIT SeaGrant) so this data is helping to place that on in context.

5.) These observational capabilities are being proposed as essential components of any coastal ocean observational network. Proposals for ORION, environmental sensor networks, and coastal monitoring involving these systems and CDOM optical measurements have been and are being proposed and developed.

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