OS22J HC: 319 B Tuesday 1330h

CDOM in the Coastal Ocean: Transformation Processes and Their Effects on Optical Properties I

Presiding: **D G Zika,** University of Miami**; D Coble,** University of South Florida

OS22J-01 1330h INVITED

CDOM Variability in the Coastal Zone From SeaWiFS

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SeaWiFS ocean color imagery in the northern Gulf of Mexico was used to determine the spatial and temporal variability of bio-optical properties of chlorophyll, backscattering, and CDOM absorption in the coastal zone. We have uncoupled the remote sensing reflectance signature to determine how CDOM is distributed in the coastal waters. Based on these optical properties, we present a new classification scheme to characterize coastal waters, which is closely coupled with processes influencing water masses. Ternary plots of these SeaWiFS-derived bio-optical products are presented to show the non-covarying response of these properties in the coastal waters.

Using SeaWIFS, the changes in CDOM absorption were determined for the northern Gulf of Mexico for a daily time sequence. We traced the time evolution of a river discharge plume and a shelf eddy, and determined the changes in CDOM absorption and chlorophyll during a one-month period. These daily and weekly changes in the CDOM concentration and distribution patterns observed in the SeaWIFS imagery are influenced by physical advection, river input, and photo-oxidation. Although we cant separate these processes, the new coastal CDOM images and water mass classification scheme provide new tools and challenges to aid interpretation of coastal biogeochemical processes.

OS22J-02 1400h

Forecasting the Colored Dissolved Organic Matter Dynamics on the West Florida Shelf

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The prediction of water-leaving radiance in coastal waters is strongly dependent on a quantitative prediction of the depth-dependent distribution of Colored Dissolved Organic Matter (CDOM) in the water column. In coastal waters, the CDOM distribution is a function of the supply of CDOM from allochthonous offshore and estuarine boundaries, and autochthonous production and removal processes. As part of a larger effort to forecast the Inherent and Apparent Optics Properties (IOPs and AOPs, respectively) of the coastal ocean, we have created a numerical solution of the sources and sinks of CDOM on the West Florida Shelf (WFS). This solution includes the autochthonous production via phytoplankton and bacterial grazing and lysis, as well as direct bacterial CDOM creation. The autochthonous sinks of CDOM are driven by photolysis of the colored matter to colorless organic and inorganic matter. These processes are embedded in a larger 2-dimensional ecological simulation (EcoSim 2.0) that resolves the time-dependent change of the phytoplankton and bacterial communities, as well as the in situ IOPs and AOPs.

An earlier numerical study of IOPs in the Sargasso Sea had difficulties resolving the seasonal cycles of CDOM. It was found in this study that contrary to the assumptions of the earlier work, the bacteria do not use CDOM as an energy or nutrient source. In addition, the rates of photolysis were far smaller than assume in the prior study. Lastly, the cross-shelf distribution of absorption on the West Florida Shelf is strongly dependent on the estuarine source of CDOM. Inclusions of these new estimates of autochthonous and allochthonous processes allowed us to simulate the depth-dependent distribution of CDOM during the fall of 1998 on the WFS.

URL: http://www.flenvironmental.org

OS22J-03 1415h

Evaluating the influence of CDOM on the remote sensing signal in the Mississippi River Bight

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A comprehensive set of vertical profiles of bio-optical variables such as particulate, and CDOM absorption, upwelling radiance and downwelling irradiance were acquired in coastal waters influenced by the Mississippi River in April of 2000. Apparent optical properties (AOPs) such as spectral diffuse attenuation coefficients for downward irradiance (kd) and for upward radiance (ku) along with the extrapolated values of above surface remote sensing reflectance (Rrs) are derived. These are examined in relation to the spatial and vertical CDOM absorption field especially at the 412, 443 and 490 nm spectral wavebands used to derive chlorophyll estimates from SeaWiFS satellite data. Preliminary analysis of the CDOM absorption data indicates considerable variability in spatial and vertical distribution with the magnitude varying by as much as 20 fold (0.4 to 0.02 m-1) at 443 nm at stations near to the Mississippi River and offshore. At many stations CDOM absorption were at a similar range to phytoplankton absorption. We examine this data in relation to the band ratio algorithms used for deriving phytoplankton biomass and CDOM from water leaving radiances.

OS22J-04 1430h

Chemical Characterization of Colored Dissolved Organic Matter in Seawater

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Spectral analysis of colored dissolved organic matter (CDOM) in seawater clearly shows the presence of several distinct chromophores. Spatial and temporal variations in the relative abundance of these chromophores further suggests they may arise from different CDOM sources. In the coastal zone, a large fraction of CDOM is supplied by freshwater, while in the open ocean, CDOM is principally supplied by upwelling of deepwater. Direct algal production of CDOM occurs in both environments, but may be most important in highly productive coastal waters lacking major river inputs, such as the US Pacific coast.

I have begun to characterize CDOM on a molecular level using a combination of high pressure liquid chromatography (HPLC) and mass spectrometry. My goal is to identify the components of CDOM and to investegate the potential for specific CDOM components to serve as source markers. CDOM is extracted from algal cultures, river water, coastal and open ocean seawater by adsorption onto octadcyl-bonded silica gel. CDOM components are removed with methanol and ammonium hydroxide, and separated into single compounds by HPLC. Compounds are characterized optically, and further characterized by mass spectrometry. We find CDOM in both algal cultures and seawater contain a suite of very distinct compounds with a range of optical properties that may be characteristic of CDOM sources.

OS22J-05 1445h

Application of LC/MSn to the Study of DOM Mediated Optical Properties: South Florida Coastal Zone 2001

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Presented are results from an investigation of optical and structural characteristics of dissolved organic matter collected from several cruises in a coastal environment covering Florida Bay, the Florida Keys, and Florida's western coast. River outflow provides a rich source of relatively new refractory organic material with fluorescence and absorbance properties that dominate those properties in coastal waters. A combination of solid phase extraction followed by continuous flow LC/MS provided a direct measure of molecular weight distribution and abundance. Meteorological conditions in June 2001 were extremely dry, with evaporation exceeding precipitation and river input, resulting in increasing salinity for shallow waters near shore. Average molecular weight of DOM for three western Florida rivers, the Shark River, Broad River, and Caloosahatchee River, during this time was 969 +- 44 m/z while the lowest observed mean mass offshore from each of these rivers averaged 848 +- 56 m/z (1 std.dev.). This observed decrease in mass indicates that some natural process preferentially removes the larger organic compounds and agrees with observations that photodegradation of large refractory compounds will produce increasingly smaller biologically labile compounds. For the Shark River a correlation between salinity and LC/MS determined mean molecular weight was observed (R2 = 0.72) while a higher correlation was observed between salinity and LC/MS determined concentration (R2 = 0.92). A unique correlation between LC/MS determined concentration or mean mass and CDOM fluorescence was observed for each river in the study region indicating differences in the source materials. Further, fluorescence values extrapolate to zero with approximately 1 mg/l TOC remaining in the sample indicating that this new technique for the direct analysis of DOM acquires information on both the fluorescing and non-fluorescing fractions of organic matter in coastal zones. Application of these findings in the investigation of the link between structure and optical properties of CDOM will be discussed.

OS22J-06 1500h

Molecular Mass Distribution and Optical Characterization of Colored Dissolved Organic Material in Coastal Waters of Southwest Florida

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Colored dissolved organic material (CDOM) is the most important sunlight absorbing substance affecting the optical properties of natural waters, and thus lies at the center of a photochemical cycle that impacts the marine environment. Although its role in these important processes is better understood today, fundamental questions about its structure and reactivity remain. In this study Frit inlet/frit outlet - Flow field-flow fractionation (FIFO-FlFFF) with absorbance and fluorescence detectors was applied to characterize CDOM from coastal waters in Southwest Florida in terms of molecular mass distribution (MM) during two consecutive years (June 2000 and 2001).

Preliminary results show that MM distribution determined in samples from June 2001 were smaller than those found in June 2000, for both chromophores and fluorophores. The very dry season in the summer of 2001 probably caused a low CDOM renewal from land run-off and river waters that generally have higher MM. In addition, CDOM had longer sun exposure, resulting in a lower MM distribution.

A shift of about 15% to lower MM distribution was seen in the fluorescent compounds from coastal to marine waters while chromophores remained the same. This would suggest that the fraction of CDOM containing the fluorophore moiety is undergoing degradation

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to lower MM material by photochemical processes, but that the fraction of CDOM containing the active chromophore is unaffected on this time-scale. The opposite behavior was observed in a fresh to marine transition zone in early studies, where chromophores shifted to lower MM but fluorophores were unaltered.

OS22J-07 1535h

Size Distributions of Colloidal CDOM in Coastal Waters as Determined by Flow Field-Flow Fractionation

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Although numerous studies have examined the size distribution of dissolved organic carbon in seawater, very little information exists on the size fractionation of marine chromophoric dissolved organic matter (CDOM). Detailed measurements of CDOM size distributions may contain useful information pertaining to the provenance, reaction-states, and removal pathways of the chromophoric material.Flow-Field Flow Fractionation (Flow FFF) has been shown to partition marine colloidal organic matter into a continuum of hydrodynamic sizes, providing a novel means for characterizing the molecular weight spectrum of marine CDOM.

In this study, Flow FFF molecular weight/colloid size spectra of CDOM measured from within and adjacent to the Mississippi River plume are compared under high (April) and low (June) flow conditions. While size spectra of riverine CDOM were similar under both flow regimes, there were marked differences in the CDOM size spectra in adjacent waters. Size distributions found to be associated with elevated chlorophyll concentrations during June were generally absent or minimal in April when chlorophyll concentrations were much lower. These results are contrasted with findings from the Damariscotta River estuary (Maine) and from laboratory estuarine mixing experiments designed to assess how abiotic factors may affect CDOM size distributions.

OS22J-08 1550h

What Factors Control the Distribution and Dynamics of Chromophoric Dissolved Organic Matter in the Middle Atlantic Bight and other Coastal Regions?

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Through its absorption of ultraviolet and visible light, chromophoric dissolved organic matter (CDOM) can play an important role in the aquatic environment by reducing the penetration depth of potentially damaging ultraviolet radiation and through photochemical reactions leading to its degradation and the formation of biologically-available forms of nitrogen, low molecular weight organic compounds, trace gases and altered metal speciation. Thus knowledge of the factors that control its distribution and magnitude is important for understanding its impact on aquatic systems. Using field data from the Middle Atlantic Bight as well as from other coastal regions, combined with laboratory data, we will attempt to synthesize the available information to address this question. Topics that will be examined include CDOM optical properties, the relationship of CDOM absorption to dissolved organic carbon, and controls on CDOM distribution (sources and sinks).

OS22J-09 1605h

Chromophoric Dissolved Organic Matter (CDOM) in the Mississippi River Plume

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Chromophoric dissolved organic matter (CDOM) is an important, easily measured fraction of dissolved organic matter in seawater and plays a critical role in determining the optical properties of seawater that may be measured remotely. Sources of CDOM in coastal waters include terrestrial runoff, estuarine production, and coastal plankton (phyto-, zoo-, and/or bacterio-) production while a major sink is photodegradation. Additionally, coastal waters are highly dynamic with vertical variability of less than 1 meter and horizontal variability over 10s of meters or less. In order to examine the temporal and spatial variability adequately, in situ, real-time measurements were carried out with the ECOShuttle, a towed-undulating vehicle designed to study surface waters (2-50 m) in high resolution. In situ measurements include CDOM fluorescence (lex=330 nm, lem=450 nm), "hydrocarbon fluorescence" (lex=239 nm, lem=360 nm), Chlorophyll fluorescence, optical backscatter, dissolved oxygen, temperature, salinity and depth.

Two studies of the Mississippi River Plume in the Gulf of Mexico in June, 2000 and April, 2001 were conducted. In June, 2000, a very low flow period, over 1000 miles were covered in the area both to the east and to the west of the Birdfoot Region of the Mississippi River Plume yielding over 10 million in situ measurements of CDOM along with other relevant oceanic parameters. In April, 2001, a high flow period, over 900 miles were covered mostly outside the southwest pass region to the west. While the Mississippi freshwater CDOM endmember was similar in Spring and Summer, the Atchafalaya River endmember was ~40 percent higher than the Mississippi in Summer and 100 percent higher in Spring. Since water for both rivers shares a common source, it appears that interactions with the undeveloped wetlands in the Atchafalaya River Watershed supplies a significant amount of CDOM to the "terrestrial" endmember and this source is magnified in the high flow period. Additionally, the effects of physical mixing, sunlight exposure, and subsurface phytoplankton production will be discussed.

OS22J-10 1620h

Optical Characterization Of Coastal Waters In The Gulf Of Mexico As A Function Of Multiple River Inputs

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A portion of dissolved organic matter consists of colored constituents known as colored dissolved organic matter (CDOM) or "gelbstoff". The unique chromophoric nature of dissolved organic matter allows us to use optical techniques to investigate the chemical composition of carbon and its cycling process. Much of CDOM in coastal environments is of terrigenous origin entering via run off from river sources. CDOM differs spatially and seasonally as a consequence of river discharge and mixing. However little has been done to elucidate optical properties of individual riverine endmembers. This presentation will characterize 10 riverine endmembers that flow into the Gulf of Mexico based on hyperspectral fluorescence, absorption, salinity, total organic carbon and seasonal variability. This presentation will also discuss how these properties alter as a consequence of mixing, photobleaching and biological activities

OS22J-11 1635h

Changes in the Optical Properties of Colored Dissolved Organic Matter in Coastal Regions of the Gulf of Mexico Between the Mississippi River and Florida Bay.

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Variations in concentration and optical properties of colored dissolved organic matter (CDOM) in river-dominated margins provide information on the chemical composition and cycling of carbon. Based on results from cruises during 2000 and 2001, we have observed large scale seasonal and spatial variability in CDOM optical properties (absorption coefficients, spectral slopes, position of the fluorescence maxima, fluorescence intensities, and fluorescence ratios) in the Gulf of Mexico. Although the primary forcing is due to quantity of freshwater runoff, strong regional variability in freshwater sources also plays a major role. We have observed a 5-fold variability in the concentration of CDOM observed in the rivers entering this part of the Gulf of Mexico, with lowest values in the Mississippi River endmember.

The enormity of mixing effects across the region makes observation of biological and photochemical effects challenging. We have used two approaches to distinguish between source and transformation effects: mixing models which include not only concentration but also optical properties of CDOM, and high resolution surface mapping of multispectral fluorescence properties. Results from the Mississippi plume, the Atchafalia plume, the West Florida Shelf, South Florida Rivers and Florida Bay will be presented.

OS22J-12 1650h

Dynamics of Chromophoric Dissolved Organic Matter (CDOM) in a Microestuary

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Characterization of chromophoric dissolved organic matter (CDOM) dynamics within an estuary requires identification of multiple sources, including terrestrial input from rivers, production in fringing marshes and in situ biological production. The required measurements in a large estuary present a daunting challenge due to temporal (tidal) variations over the time required for an adequate survey to be completed. However, in small estuarine systems, detailed surveys can be adequately completed by a miniature towed vehicle that has been developed at UMass Boston. This towed vehicle (Mini-Shuttle) is composed of an Endeco-YSI 2 foot V-Fin Hydrodynamic Depressor with a Falmouth Scientific 2 Micro CTD as the primary data acquisition system. CDOM is characterized by fluorescence at 370/440 nm excitation/emission provided by a Sea Point Electronics ultraviolet fluorometer.

The Mini-Shuttle has been deployed in several surveys of the 6 km long tidal portion of the Neponset River (~45 minute transects) a small estuary entering the Dorchester Bay region of Boston Harbor. The width of the Neponset River varies from 50 to 200m wide depending on tidal stage, and is less than 5m deep at high water through most of length. Extensive salt marshes adjacent to much of river have been protected from urbanization and significantly influence the dynamics of the estuary. In addition broad mud-flats exist between the narrow channel and the fringing marsh. The tide range is approximately 3 m, resulting in large exchanges between the estuary and Spartina marshes.

We will present results from two surveys, one conducted at high tide in the afternoon and the other at low tide on the following morning of July 19 and 20, 2001. We were able to resolve a strong vertical salinity/density gradient in the top meter of the water column. The CDOM approximately followed the expected pattern of higher values at lower salinity, but the dense data coverage provided by the Mini-Shuttle showed significant departures from a simple conservative relationship. There was an indication of mid-estuary sources of CDOM in concave-up CDOM-salinity curves for both days. However, at the same salinity, CDOM fluorescence was lower in the afternoon than in the morning. This pattern was mirrored by higher temperatures (relative to salinity) during the afternoon survey. We propose that these observations indicate a source of CDOM from the fringing marshes, with a reduction of fluorescence and increase in temperature during the afternoon due to solar radiation. Since the afternoon survey was conducted around low water, much of the water in the channel would have flowed off the mud flats and salt marshes, and been subject to intense sunlight in relatively shallow water, enhancing both solar heating and photobleaching of CDOM.

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Application and Assessment of Coastal Sediment Transport Models III

Presiding: **C Sherwood,** USGS MS-999**; R P Signell,** NATO/SACLANTCEN

OS22K-01 1330h

Buoyant Plume Lift-off Zones as a Test of Coastal Sediment Transport Models

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