Effects of Biological and Photochemical Degradation on the Optical Properties of CDOM Exported to Coastal Marine Environments

Dissolved organic matter (DOM) exported from rivers and intertidal marshes to coastal oceans typically contains high concentrations of light-absorbing molecules that can interfere with remote sensing of ocean color. This project quantitatively assessed the ability of coastal ocean bacteria to degrade and produce CDOM and investigated the synergistic interactions between bacterial degradation and photochemical processes in transforming CDOM in seawater and altering its optical properties. Optical properties (absorption spectra, EEMs), photoreactivity and biological lability of CDOM formed during the bacterial degradation of selected vascular plants and algae was used to assess the relative importance of terrestrial and marine organic matter as sources of CDOM.

CDOM, photodegradation, marine bacteria, fluorescence, absorption, optical properties
FINAL REPORT

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PRINCIPAL INVESTIGATOR: Mary Ann Moran

GRANT TITLE: Effects of Biological and Photochemical Degradation on the Optical Properties of CDOM Exported to Coastal Marine Environments

AWARD PERIOD: 1 April, 1999 – 31 March 2003

OBJECTIVES: Dissolved organic matter (DOM) exported from rivers and intertidal marshes to coastal oceans typically contains high concentrations of light-absorbing molecules that can interfere with remote sensing of ocean color. The specific objectives of this project were to quantitatively assess the ability of coastal ocean bacteria to degrade and produce CDOM; to investigate the synergistic interactions between bacterial degradation and photochemical processes in transforming CDOM in seawater and altering its optical properties; to compare susceptibility of CDOM from different source materials to degradation processes; and to provide quantitative mass-balance comparisons of biological vs. photochemical processes in CDOM removal under realistic irradiation schemes.

APPROACH: Changes in the optical properties of CDOM due to biological and photochemical degradation were studied in laboratory and field experiments. For the laboratory studies, we investigated natural estuarine CDOM and model CDOM derived from degrading vascular plants and coastal phytoplankton (representing terrestrial and marine CDOM endmembers). Molecular biology techniques were employed to track microbial community composition during formation of CDOM from model terrestrial and marine source materials. Changes in CDOM concentrations and optical properties were quantified when the CDOM was subjected to both dark microbial degradation and irradiations with simulated sunlight. We investigated the potential influence of photocatalysis by iron as well as the role of particulates (through sorption processes) in modulating estuarine CDOM loss via photodegradation. In field studies of southeastern U.S. coastal areas (surface waters off Georgia and Florida), simultaneous measures of bacterial degradation, photochemical degradation, and optical properties of CDOM were carried out.

ACCOMPLISHMENTS:
Work during the first 12 months focused on assessing the variation in terrestrial CDOM end members with regard to biological and/or photochemical lability and optical properties. Research on an ONR-sponsored cruise on the Mississippi River plume in the Gulf of Mexico during June 2000 indicated the presence of two classes of CDOM in the Gulf of Mexico that exhibit distinct biological/photochemical lability: CDOM in the surface plume is susceptible to bleaching of color and photodegradation to biologically-labile photoproducits, while CDOM associated with the bottom of the chlorophyll maximum (i.e., produced in situ) is comparatively unreactive. Experiments in collaboration with Dr. Juanita Urban-Rich during the April 2001 (spring flood stage) ONR cruise demonstrated that bacterial/zooplankton interactions were important in the formation of CDOM. The first measurements of spectral quantum yields for photochemically-stimulated biological degradation of CDOM was accomplished during Year 1 for coastal Georgia locations. The spectral dependence for the quantum yields for combined photo- and biodegradation decrease exponentially in a remarkably similar fashion, suggesting that that common intermediates may be involved in both processes. Quantum yield spectra coupled with diffuse attenuation coefficients for downwelling irradiance were measured along a southeastern coastal U.S. transect from highly-productive to less-productive waters, to model the depth dependence and degradation fluxes of CDOM and examine the global significance of coastal DOM photodegradation.
Work during the second 12 months focused on assessing the optical properties of single-source CDOM produced during the degradation of vascular plants and algae; determining the biological availability and production of biologically labile photoproducts from single-source CDOM; characterizing the bacterial communities associated with the formation and degradation of CDOM from vascular plant and algal sources; and analyzing extensive field data sets of temporal and spatial variability of fluorescent DOM along the southeastern U.S. coast, including an analysis of variability in fluorescence quantum yield. Spectral and photochemical properties were also determined for water samples obtained at a series of depths during a June, 2001 cruise in the Florida Keys. Studies were initiated on sources and sinks of CDOM on particles.

Work during the final 12 month period focused on molecular biology-based analyses of the bacterial communities responsible for formation and degradation of CDOM from vascular plant and algal sources; completing and submitting a manuscript describing an improved method for using excitation-emission matrices of fluorescence spectra (EEMs) to evaluate within-estuarine changes in CDOM optical properties; completing analysis of spectroscopic, biological and photochemical data obtained during an ONR-sponsored CDOM cruise and contributing to preparation of a joint manuscript; completing research on sources and sinks of CDOM on particles, including work on temperature and UV effects on CDOM released from degrading seagrass and mangrove detritus and the effects of sorption to suspended sediments on optical properties of riverine CDOM.

CONCLUSIONS:
We developed a new method for eliminating Rayleigh and Raman scatter peaks from CDOM fluorescence data that provides much improved results in the quantitative analysis of EEMs compared to the conventional blank subtraction procedure. Modeling results and observed EEM spectral changes indicate that photoreactions, interacting with microbial transformations, have an important effect on the FDOM optical properties in estuaries. EEM analysis with careful scatter correction can provide a powerful tool for evaluating pathways for carbon cycling in estuaries. Optical properties (absorption spectra, EEMs), photoreactivity and biological lability of CDOM formed during the bacterial degradation of selected vascular plants and algae can be used to assess the relative importance of terrestrial and marine organic matter as sources of CDOM. Woody vascular material (oak and pine) is more resistant to biological transformation into colored matter than are non-woody sources, although these form labile photoproducts upon irradiation. Molecular fingerprints of bacterial communities indicate that CDOM from various sources converges to a similar suite of organic compounds during bacterial decomposition. Iron catalysis and reactive oxygen species can also be causal mechanisms for photochemical CDOM loss in estuaries. Potent oxidants (OH radicals) are produced when CDOM from the Mississippi River plume and estuaries of the southeastern U.S. are irradiated by sunlight and monochromatic UV radiation, and these radicals contribute to the reactions that cause CDOM photobleaching. CDOM fluorescence in five Georgia estuaries show changes related to mixing of ocean water with riverine water; both a dilution effect as well as chemical reactions with the seawater salts that increased fluorescence quantum yields are involved. CDOM transformations can affect fluorophore concentrations and spectra within the estuaries, but the relative importance of such transformations depends on residence time in the estuary.

SIGNIFICANCE:
Robust algorithms are necessary for the retrieval of CDOM signals from satellite absorbance data. The information being obtained in this project will increase understanding of how rapidly terrestrially-derived CDOM is degraded in coastal seawater, which mechanisms are most important in bringing about its removal, how DCOM degradation rates vary over time and space scales, and whether the mechanisms by which CDOM is removed leaves a signature in its optical properties. This study will also provide information about the variability of CDOM originating from various terrestrial endmembers with regard to removal rates and changes in optical properties.
AWARD INFORMATION:
M. A. Moran: Promoted to full professor; Recipient of the National Oceanographic Partnership Program Award for Excellence, 2001; Selected as plenary lecturer, American Society for Limnology and Oceanography Annual Meeting, 2002

PUBLICATIONS AND PUBLISHED ABSTRACTS:

PRESENTATIONS


