In Situ and Laboratory Measurements of the Optical and Photochemical Properties of Surface Marine Waters

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LONG-TERM GOALS

The principal long-term objective of this work is to determine what factors control the distribution and dynamics of the chromophore-containing constituents of dissolved organic matter (CDOM) in marine and estuarine waters. Two important secondary objectives are 1) to elucidate the photochemical properties of the CDOM and how photochemical reactions affect the optical properties and secondary reactivity of the CDOM, 2) to obtain a clearer understanding of the nature of the underlying light-absorbing constituents that produce the absorption spectrum of the CDOM. Field measurements are employed to determine the distribution of CDOM and its impact on the aquatic light field, whereas a combination of field and laboratory experiments are used to test mechanisms of its formation and loss.

OBJECTIVES

Over the last year, our principal near-term objectives were as follows:

1. Complete a comprehensive book chapter that reviews critically the optical properties of CDOM, its distribution and relationship to the dissolved organic carbon pool, and its sources and sinks (Blough and Del Vecchio, in press). A second review article provides a more general description of this topic (Del Vecchio and Blough, submitted). Finally, the results and analysis of a comprehensive photobleaching study was submitted for publication (Del Vecchio and Blough, submitted).

2. Convene a data workshop at the University of Maryland for investigators participating in a series of six cruises covering the Middle Atlantic Bight and the Delaware and Chesapeake Bays over the previous four years.

3. Complete the analysis and synthesis of field data collected over the last five years in preparation for publication.

4. Acquire and analyze data from a set of laser photobleaching experiments; initiate a new set of experiments to measure the low-temperature fluorescence and phosphorescence from CDOM. These experiments were performed to gain a better understanding of the molecular basis of CDOM absorption.

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14. ABSTRACT

The principal long-term objective of this work is to determine what factors control the distribution and dynamics of the chromophore-containing constituents of dissolved organic matter (CDOM) in marine and estuarine waters. Two important secondary objectives are 1) to elucidate the photochemical properties of the CDOM and how photochemical reactions affect the optical properties and secondary reactivity of the CDOM, 2) to obtain a clearer understanding of the nature of the underlying light-absorbing constituents that produce the absorption spectrum of the CDOM. Field measurements are employed to determine the distribution of CDOM and its impact on the aquatic light field, whereas a combination of field and laboratory experiments are used to test mechanisms of its formation and loss.

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APPROACH

Over the past 10 years, we have performed an extensive series of studies on the optical properties of CDOM and its distribution in a variety of geographical locales, including the outflow of the Orinoco and Amazon Rivers (Blough et al. 1993, Green and Blough, 1994), the Middle Atlantic Bight (Hoge et al., 1993; Green and Blough, 1994; Vodacek et al., 1995; DeGrandpre et al., 1996; Vodacek et al., 1997) and the Gulf of Mexico and the southwest Florida shelf (Green and Blough, 1994; Del Vecchio and Blough, in preparation). This work, along with the extensive work of others, has been collected and critically reviewed in a book chapter (Blough and Del Vecchio, in press) that we hope will provide researchers with a comprehensive view of the current state of the art in this field.

Both field and laboratory studies have been used to investigate the sources and sinks of CDOM in the marine environment. For example, field measurements first indicated that photochemistry could act as a significant sink of CDOM in stratified surface waters over the summer (Vodacek et al., 1997), with more recent studies supporting these conclusions (Del Vecchio and Blough, in preparation). Laboratory photobleaching studies have been employed to test whether the time scale of this process and the changes in CDOM spectral shape are compatible with the field observations (see below and Del Vecchio and Blough, submitted).

Because we know almost nothing about the structural nature of the underlying chromophores giving rise to the rather unique absorption spectrum of the CDOM, we have initiated a series of laboratory studies aimed at addressing this issue. Techniques that we are employing include laser photobleaching experiments of CDOM in high viscosity solvents, and the collection of low-temperature (77 K) 3-dimensional excitation, emission matrix spectra (EEMS) and phosphorescence spectra. Other approaches are also in development.

WORK COMPLETED

1. A major review article on the distribution and dynamics of CDOM in the coastal environment has been written and accepted for publication (Blough and Del Vecchio, in press). A second, more general review, developed from an invited NATO talk (Del Vecchio), has also been submitted.

2. A detailed study of the kinetics of absorption and fluorescence loss under both monochromatic and broad-band UV and visible radiation has been submitted for publication. The major conclusions of this study are provided below (abstract of the submitted paper).

3. A data workshop covering the results of cruises in the MAB was convened on the 2nd and 3rd of November, 2000, facilitating the sharing of data amongst cruise participants. The analysis and synthesis of data collected by our group in field studies over the last five years has been completed and this work is being prepared for publication.

4. A complete set of laser photobleaching experiments at wavelengths covering the visible and ultraviolet wavelengths has been collected and is currently being analyzed. For the first time, phosphorescence spectra and low-temperature fluorescence spectra of CDOM have been recorded. The results of these studies are outlined below.

RESULTS

The effects of monochromatic and broad-band UV and visible radiation on the optical properties (absorption and fluorescence) of chromophoric dissolved organic matter (CDOM) were examined for a Suwannee River fulvic acid standard and for water from the Delaware and Chesapeake Bays. The primary loss of absorption and fluorescence occurred at the irradiation wavelength(s), with smaller secondary losses occurring outside the irradiation wavelength(s). Exposure to broad-band light increased the CDOM absorption spectral slope (S), consistent with previous field measurements. An analysis of the monochromatic photobleaching kinetics argues strongly that a model based on a simple superposition of multiple chromophores undergoing independent photobleaching cannot apply; this conclusion further implies that the absorption spectrum of CDOM cannot arise solely from a simple superposition of numerous independent chromophores. The kinetics of CDOM absorption loss with the monochromatic irradiation were employed to create a simple, heuristic model of photobleaching. This model allowed us to examine the importance of the secondary photobleaching losses in determining the overall photobleaching rates and as well as to model the photobleaching of natural waters under broad-band light fields. Application of this model to natural waters closely predicted the change in the CDOM spectral shape caused by photodegradation. The time scale of this process was consistent with field observations acquired during the summertime for coastal waters in the Middle Atlantic Bight. The results indicate that the ratio of the photodegradation depth to the mixed layer depth is the key parameter controlling the rate of the photobleaching in surface waters.

Laser photobleaching experiments have provided evidence in support of that acquired under lower intensity (and wider bandpass) monochromatic experiments: namely that the observed behavior is inconsistent with a model based on a simple superposition of multiple discrete chromophores. Irradiation at short wavelengths (<300nm) appears to produce a direct loss of discrete short-wavelength chromophore(s), but a uniform loss of absorption at longer wavelengths. In contrast, irradiation at long wavelengths produces a primary loss of absorption near the irradiation wavelength, along with band(s) at short wavelength (<300 nm). This lack of reciprocity between the irradiation/observation wavelengths is inconsistent with a simple superposition of multiple discrete chromophores undergoing photobleaching independently (Del Vecchio and Blough, submitted).

Unequivocal evidence for discrete chromophores within CDOM with lowest energy absorption bands below 300 nm has been obtained from phosphorescence spectra for the first time. Two phosphorescing components have been observed: one with an excitation maximum at ~240 nm and emission maximum at 380 nm (lifetime of ~200 μs at 77 K) and one with an excitation maximum at ~260-270 nm and an emission maximum at ~480-500 nm (lifetime of ~150 ms at 77 K).

IMPACT APPLICATIONS

Because CDOM contributes significantly to the absorption of coastal waters, its presence substantially impacts underwater visibility and the aquatic light field. Thus an understanding of its sources and sinks, as well as the nature of the light-absorbing constituents contributing to its spectrum, are needed to predict its spatial and temporal variability in coastal (and open-ocean) waters.

TRANSITIONS

All of the CDOM absorption spectra and filter pad spectra (phytoplankton and detritus absorption spectra) collected by our group in the MAB and the Chesapeake and Delaware Bays from 1996 through 1999 have been supplied to NASA through Dr. Larry Harding.

RELATED PROJECTS

In other ONR-supported work, we are examining mechanistic aspects of the photochemistry of CDOM and how photochemistry affects the degradation of organic pollutants. This work entails the detection and quantification of reactive intermediates produced photochemically from the CDOM and their reactions with anthropogenic compounds, principally polycyclic aromatic hydrocarbons and halogenated organic compounds, in an effort to develop predictive models for the photochemical degradation of these materials.

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