

# **Examining the Role of Quinone Moieties in the Photochemistry of Colored Dissolved Organic Matter in Coastal Waters**

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Grant Number: N000140110609

## **LONG-TERM GOALS**

My long term goals are to develop an understanding of the photochemical processes affecting CDOM, and the resultant changes in its optical properties and molecular composition, particularly in coastal environments.

## **OBJECTIVES**

CDOM is the most important sunlight-absorbing dissolved substance in the sea and a critical component of the global carbon cycle. Irradiated CDOM produces reactive species that interact in the ocean in a complex series of photochemical and electron transfer reactions that impact the color and oxidative capacity of surface waters, the growth of marine biota, and the production of volatile gases that impact climate. The identity of the key structural moiety in CDOM that absorbs sunlight and initiates this important cycling is unknown, but quinones have recently been hypothesized as likely candidates. The goal of this proposal is to investigate the structural features of CDOM associated with the photochemical formation of these reactive species, with the objectives of testing the quinone hypothesis and examining photochemical transformations of the optical and structural properties of CDOM in river and coastal waters.

## **APPROACH**

My approach is to combine NMR techniques for structural characterization, along with measurements of photochemical products, to correlate specific structural features with enhanced photochemical activity and determine if quinone functionalities are the key feature in CDOM that absorbs sunlight and produces transient products such as peroxide. Thus, the experimental approach combines photochemical experiments, separation of CDOM fractions by ultrafiltration and HPLC, and structural characterization by <sup>13</sup>C FT-NMR techniques. Dr Dan Wellman, an organic chemist at Chapman, is collaborating with me on the NMR studies. Making direct links between the structural features and photochemical reactivity of such a complex material as DOM will naturally be difficult. This approach is based on a combination of chromatographic size separations by ultrafiltration and HPLC/Size Exclusion Chromatography (HPSEC), and functional group investigation by FT-NMR. Hydrogen peroxide will be used as the "tracer" photochemical product for CDOM, since this compound is a direct photoproduct of irradiated quinones. One previous study examined the correlation of ketonic functionalities with CO production, an indirect photoproduct (Stubbins et al., 2000). Hydrogen peroxide will be measured by the newly developed method of Cooper et al. (2000), a

## Report Documentation Page

*Form Approved*  
*OMB No. 0704-0188*

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1. REPORT DATE <b>30 SEP 2001</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-2001 to 00-00-2001</b>			
4. TITLE AND SUBTITLE <b>Examining the Role of Quinone Moieties in the Photochemistry of Colored Dissolved Organic Matter in Coastal Waters</b>		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Dept. of Environmental and Chemical Sciences,,Chapman University, One University Drive,,Orange,,CA, 92866</b>		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <b>My long term goals are to develop an understanding of the photochemical processes affecting CDOM, and the resultant changes in its optical properties and molecular composition, particularly in coastal environments.</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a REPORT <b>unclassified</b>	b ABSTRACT <b>unclassified</b>	c THIS PAGE <b>unclassified</b>	<b>Same as Report (SAR)</b>	<b>5</b>	

chemiluminescent method that avoids some of the interference problems of earlier fluorescent enzyme-based methods (Moore et al., 1993).

Common structural features associated with high H<sub>2</sub>O<sub>2</sub> yields will be identified to test the quinone hypothesis. Relative absorbance, fluorescence and apparent quantum yields of photoredox products from different source materials (river vs. coastal) and sized fractions will be compared with relative functional group distributions from NMR studies to correlate particular structural features with photoredox production, and hence examine the chemical characteristics of the active redox site. Initial experiments will focus on the relative abundance of these photoredox active functionalities in the total CDOM mass. If different CDOM size fractions have similar H<sub>2</sub>O<sub>2</sub> yields, this would indicate that the active redox centers are evenly distributed throughout the humic material. By running the same size fractions by FT-NMR, we can estimate the relative number of quinone moieties associated with high photoproduct yields. Since studies with field flow fractionation and LC/MS<sup>n</sup> techniques have shown differences between marine and freshwater DOM due to structural changes associated with photodegradation reactions, I will also examine how these structural features change with photochemical transformation processes in model time-course photochemical experiments on seawater samples in the laboratory.

## **WORK COMPLETED**

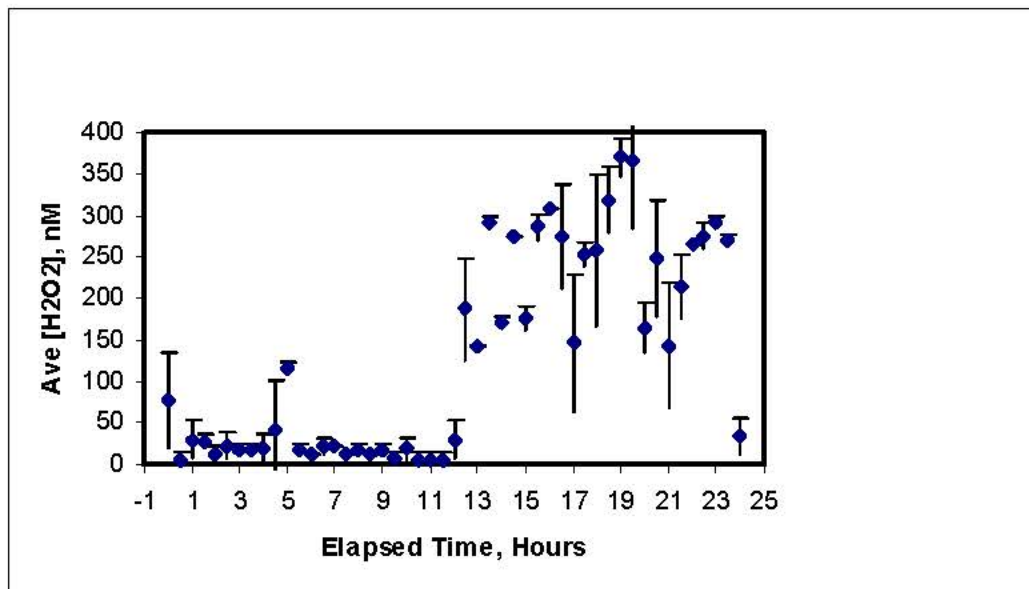
In this first short increment of the YIP grant (4 months), I have focused on ordering and installing the major capital equipment and other supplies for the research. The major instrument, the Bruker 300 MHz FT-NMR, has been installed and is operating to specifications. To develop methodology, preliminary experiments have been initiated with standard compounds (a series of quinones and an Aldrich humic acid). A student has begun work on this project. The Agilent UV-VIS spectrometer, Photon Technology 3-D fluorometer, Turner 10AU field fluorometer and Turner TDS 2020 luminometer have been installed and tested. The ultrafiltration system has been ordered and we are awaiting delivery from Separation Engineering.

We plan to measure hydrogen peroxide by Cooper's new chemiluminescence method (requiring lengthy synthesis of reagents), but had also planned to compare this to the existing peroxidase method (Moore et al., 1993). In a preliminary experiment, the peroxidase method and new field fluorometer were field tested in a 24-hour diurnal study of peroxide in the surf zone at Huntington Beach (Sept 14-15, 2001). This was carried out as part of a much larger on-going study of beach water quality organized by Dr. Stanley Grant (UCI) and Dr. Sam Mowbray and Dr. Charlie McGee (Orange County Sanitation District). Ten Chapman University undergraduate students took part in the sampling and analysis in this field study.

## **RESULTS**

The peroxidase method worked acceptably in these relatively low optical-density coastal waters. Samples had to be pre-filtered through GFF filters prior to analysis since the surf zone sampling protocol in ankle-deep water introduced large amounts of suspended particles. At least three measurements were made for each sample, and averaged. Sampling ran from 9 pm Friday September 14 to 9 pm Saturday September 15. Peroxide levels showed a clear diurnal cycle. During the night, peroxide levels were low, averaging 20-30 nM. About two hours after sunrise, levels rapidly rose an order of magnitude. During the day, peroxide oscillated between two zones of ~200 nM and ~300 nM. This effect appeared consistent and largely outside of the measurement error. It also seemed to be

correlated with the turbidity data collected by Grant/UCI, suggesting possible sampling of different zones in the highly variable surf zone. Once the sun set, peroxide levels stabilized at 300 nM until the last sample at 9 pm, which decreased again to 30 nM. These are typical peroxide levels and diurnal behavior expected for coastal waters, aside from the interesting variability introduced by the surf zone study site.



*Figure 1. Hydrogen peroxide concentrations (in nM) vs. time elapsed (in hours) at Huntington Beach, Sept 14-15, 2001. Error bars are the standard deviation. [Values are 20-30 nM during the night, rising to 200-350 nM after sunrise, and returning to ~30 nM two hours after sunset]*

## IMPACT/APPLICATIONS

Correlating photochemical activity with specific structural features in CDOM will allow us to develop better mathematical models for the attenuation of radiation in coastal environments. To really understand and model an optical process, we need to know the identity of the molecular chromophore, its concentration and its absorption coefficient. This proposed work will contribute to a fuller understanding of the nature of the active sites responsible for the redox cycling and photochemical transformation of CDOM in sunlit waters, and hence the pathways by which the reactive species that impact ocean color, marine life and atmospheric composition are produced in the ocean.

## TRANSITIONS

Peroxide measurements have been used by Dr. Sam Mowbray (Orange County Sanitation District) and Dr. Stanley Grant (UCI) in a study of diurnal variations in bacterial levels at Huntington Beach. They had hypothesized that unusually high levels of photochemically generated oxidants might account for the observed diurnal declines in bacterial levels. However, the measured peroxide levels of ~200 nM are within the normal range for coastal waters, and are several orders of magnitude too low to cause bacterial mortality.

## **RELATED PROJECTS**

A library of coastal water samples is been accumulated in this laboratory for the optical and structural studies. Samples were collected and exchanged on two recent cruises in the coastal waters of the Gulf of Mexico (April 2001, Bob Chen, Mississippi River; September 2001, RSMAS, west coast of Florida revisiting the sites from the June 2000 ONR-funded cruise). Local coastal water samples have also been taken. In June/July 2001, I participated in a large study of the waters of two local salt marsh systems in collaboration with Stan Grant (UCI), Jim Noblet (SCCWRP) and the OCSD. These will be resampled in January 2002. In a multi-investigator project recently funded by the NSF, I will be incorporating field studies of the Upper Newport Back Bay, an ecological reserve, into undergraduate geoscience courses. This will provide an additional opportunity for collecting different source waters.

On a related small ONR grant, initial FFFF studies on CDOM in two South Florida fresh to marine transition zones were completed in collaboration with Dr. Rod Zika at RSMAS over the last year. Optimal operating parameters for DOM fractionation were determined using humic standard materials and natural samples. One manuscript has been published on the methodology for CDOM in natural waters, and one has been submitted on the differences in CDOM between the two rivers and fresh to marine waters. As part of the same grant, a special session titled "CDOM in the Coastal Ocean: Transformation Processes and Their Effects on Optical Properties" was proposed and accepted for the upcoming National Ocean Sciences meeting (February 2002, Honolulu). My co-conveners are Dr. Paula Coble (USF) and Dr. Rod Zika (RSMAS). This session will serve as a focused venue for results from the many ONR-funded cruises and studies over the last few years that have addressed these questions.

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