

GRADUATE TRAINING IN ENVIRONMENTAL PHOTOCHEMISTRY AND OPTICS

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LONG TERM GOALS

The long term goal of this grant is to produce high-quality Ph.D.'s who are capable of developing and implementing solutions to complex scientific and technical issues. Although this grant has supported graduate training in the broad disciplines of environmental photochemistry and optics, projects within the research group range from fundamental studies of the photophysics and photochemistry of well-characterized compounds to the detection of free radicals in biological and environmental systems, to the development of new approaches in analytical science, to field studies of biogeochemical processes. Students are thus subjected to a broad range of techniques, approaches and ideas cutting across a variety of disciplines. This type of training will hopefully produce a better equipped Ph.D. - one who is better able to confront complex scientific problems through inventive and flexible approaches.

OBJECTIVES

One of the main objectives was to develop a new method for determination of photochemically-generated OH radical by colored dissolved organic matter (CDOM) in natural waters under both aerobic and anaerobic conditions. This work, performed by Pamela Vaughan as one part of her Ph.D. thesis, indicates that OH is directly produced by the photolysis of CDOM via a dioxygen-independent pathway (see below). By augmenting the parent grant, this AASERT award has also allowed us to address indirectly three other major objectives: 1) the development of a spectral response function for the photobleaching of CDOM, a project initiated by Rossana Del Vecchio, a Fellowship student from the University of Pisa who will be returning to the University of Maryland in January 1998 to complete her Ph.D. studies; 2) the development of methods to assess the ability of CDOM to produce photochemically hydrated electrons as well as other strong photoreductants that can degrade halogenated compounds by reductive dehalogenation (the thesis work of Trudy Thomas-Smith); and 3) the completion of a series of field studies examining the spatial and temporal distribution of CDOM in marine waters and its impact on the aquatic light fields. Students involved in this latter effort

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have included Vaughan and Del Vecchio, as well as two other graduate students, Christopher Barringer and Yu Guo.

APPROACH

The detection and quantitation of OH employs the rapid reaction of OH with dimethylsulfoxide to produce quantitatively a methyl radical, which then reacts with an amino-nitroxide to produce a stable, O-methylhydroxylamine. Following derivatization with fluorescamine, this radical adduct is separated by reversed-phase HPLC and quantified fluorometrically. Unlike many previous OH detection methods, this method can be employed under both aerobic and anaerobic conditions and thus, can be used to test whether the presence of dioxygen is required for OH formation.

The detection and quantitation of photoreductants by CDOM employs the reaction of the photoreductants with an appropriate chlorinated hydrocarbon to produce carbon-centered radical (via reductive dechlorination) that is then trapped by an amino-nitroxide to form a stable O-alkylhydroxylamine. Following derivatization with fluorescamine, the radical adduct is then separated by reversed-phase HPLC and quantified fluorometrically. By examining the yield of adducts as a function of the one-electron reduction potentials of a series of halogenated compound, this approach should allow the photoreducing potential of the CDOM to be mapped.

The approach employed in the photobleaching experiments and the field studies are described in the report of the parent grant.

WORK COMPLETED

A new, highly sensitive method for the detection and quantification of photochemically-generated OH, produced either in the presence or absence of dioxygen, has been developed and applied to the formation of OH by isolated CDOM and in natural waters containing CDOM. This work is being prepared for publication.

We can now trap and identify (by mass spectrometry) the carbon-centered radicals produced by reaction of a series of halogenated compounds with the hydrated electron. We are now proceeding with the mapping of the photoreducing “power” of the CDOM.

Work completed on the photobleaching experiments and the field work is described in the report of the parent grant.

RESULTS

Both the aerobic and anaerobic production of hydroxyl radical by the photolysis of Suwannee River fulvic acid (SRFA) and CDOM in natural waters was determined using the new method of radical trapping. A linear relationship between SRFA concentration and OH production was observed under both aerobic and anaerobic conditions. The

wavelength of the quantum yields for hydroxyl radical formation above ~310 nm were similar to those found previously by Mopper and Zhou, whereas the yields below ~310 nm were significantly smaller. Further experiments indicate that Fenton chemistry can account for only 30-40% of the total OH signal under aerobic conditions. The results indicate the presence of a dioxygen-independent pathway of OH production which is not due to nitrate or nitrate photolysis or photo-Fenton chemistry.

The carbon-centered radicals produced by reaction of the hydrated electron (formed by photolysis of ferrocyanide) with a series of chlorinated compounds have been trapped, separated and identified by HPLC and mass spectrometry. The reaction of N₂O with the hydrated electron to form OH, followed by the reaction of OH with dimethylsulfoxide to form a methyl radical which is subsequently trapped with an amino-nitroxide, is currently being used to obtain the wavelength dependence of the quantum yields for hydrated electron production by CDOM. Once completed, the ability of CDOM to reductively dechlorinate a series of chlorinated compounds with differing one-electron reduction potentials will be examined.

The results of the photobleaching experiments and the field studies are described in the report of the parent grant.

IMPACT

Several novel and highly-sensitive methods to detect and quantify the production of transient photochemical intermediates have been developed.