

LIGHT AND ENVIRONMENTAL CHEMISTRY: Influence of Changing Solar UV Radiation on Aquatic Photoreactions

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ABSTRACT

Solar radiation provides the primary driving force for the biogeochemical cycles upon which life and climate depend. Recent studies have demonstrated that the absorption of solar radiation, especially in the ultraviolet spectral region, results in photochemical reactions that can have significant effects on the environmental cycling of carbon, oxygen, sulfur, and various trace metals in the environment. Other research has shown that photoreactions help cleanse the environment of the waste materials derived from human activities. Selected current research results on the photochemical reactions in aquatic environments are discussed here. Aquatic photoreactions considered include: photoinduced changes in the optical properties of dissolved organic matter; formation of greenhouse and chemically important trace gases; conversion of refractory organic matter, organic nitrogen and metals to biologically available compounds (and vice versa); and changes in the redox state of the upper ocean and freshwaters through formation of reactive oxygen species and changes in transition metal speciation.

Keywords: aquatic photochemistry, CDOM, carbon, nitrogen, metals, ROS

INTRODUCTION

The origins of the field of photochemistry date back to a period in which sunlight was the only available light source for photochemical studies. For example, pioneering research was conducted at the turn of the 20th century in a photochemical laboratory located on the rooftops of the University of Bologna (Heindel and Pfau 1965; Balzani and Moggi 1990). In sunlight experiments at the Bologna laboratory, Ciamician conducted photochemical studies that laid the groundwork for organic photochemistry. With the advent of artificial light sources, the great bulk of photochemical studies during the middle part of the 1900s no longer used sunlight due to its variable intensity and polychromatic nature.

Interest in sunlight-induced photoreactions in the environment has been rekindled since the 1960s through the emergence of various environmental problems. First, it was recognized that photoreactions play an important role in smog formation (Leighton 1961), stratospheric ozone depletion (Rowland and Molina 1975), acid rain (Calvert et al. 1985), and the cleansing of the aquatic and terrestrial environment of the waste materials derived from human activities (Zafiriou et al. 1984). Second, recent studies indicate that photoreactions in aquatic environments have significant effects on the cycling of carbon, oxygen, sulfur, and

various trace metals that are biologically important (Moran and Zepp 2000; Mopper and Kieber 2002; Zepp 2003).

Aquatic photoreactions that are strongly influenced by ultraviolet radiation include: formation of greenhouse and chemically important trace gases [carbon dioxide (CO₂), carbon monoxide (CO), nitric oxide (NO), dimethylsulfide (DMS), carbonyl sulfide (COS)] (Erickson et al. 2000); conversion of organically bound nitrogen to biologically available inorganic N (Bronk 2002); conversion of refractory organic matter to biologically available organic compounds (Moran and Zepp 1997; Mopper and Kieber 2002); photoinduced changes in the optical properties of dissolved organic matter (Frimmel 1998; Nelson et al. 1998; Blough and Del Vecchio 2002; Osburn and Morris 2003; Whitehead and de Mora 2004); and changes in the redox state of the upper ocean and freshwaters through formation of peroxides and changes in transition metal speciation (Sulzberger et al. 1990; Emmenegger et al. 2000; Kieber et al. 2003; Zepp 2003). Direct photoreactions of pollutants are also usually primarily initiated through absorption of UV radiation.

Interest in aquatic photochemistry has been stimulated in part by declines in stratospheric ozone over the past two decades that have resulted in increases in solar UV-B radiation (280–315 nm) reaching the Earth's surface

(Madronich et al. 1998). Current projections indicate that return of the ozone layer thickness to pre-1980s levels may not occur for another 50 years.

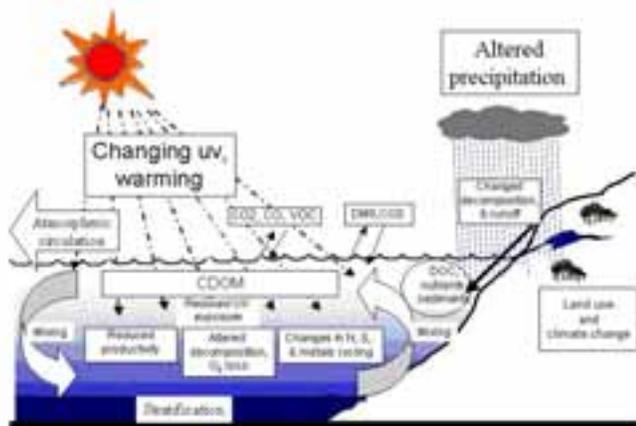


Figure 1. Interactions of aquatic photoreactions with changing UV and climate.

Aquatic photoreactions are sensitive to other factors that affect underwater UV exposure such as UV light attenuation in the water, mixing and stratification (Williamson et al. 1996; Vodacek et al. 1997; Nelson et al. 1998; Blough and Del Vecchio 2002; Del Vecchio and Blough 2002; Johannessen et al. 2003; Leavitt et al. 2003; Zepp 2003). Underwater UV exposure is thus sensitive to global changes in climate, land use and other human activities that affect aquatic transport, composition and optical properties. These effects are changing the UV-A (315-400 nm) as well as the UV-B (280-315 nm) spectral region so the discussions here include aquatic photochemical effects that are influenced by the entire solar UV spectrum (280-400 nm).

PHOTOREACTIONS OF ORGANIC MATTER

A significant portion of the photochemistry that occurs in aquatic environments is associated with the colored component of dissolved organic matter, referred to as CDOM (Williamson et al. 1996; Vodacek et al. 1997; Nelson et al. 1998; Blough and Del Vecchio 2002; Del Vecchio and Blough 2002; Johannessen et al. 2003; Leavitt et al. 2003; Zepp 2003). CDOM, which is a mixture of lignocellulose-derived polyelectrolytes that result mainly from the decay of terrestrial vegetation and aquatic detritus, constitutes the majority of the organic carbon in many lakes, rivers, and coastal waters. Humic substances make up an important part of CDOM. Photodegradation of CDOM results in loss of its UV and visible absorbance and fluorescence, a process referred to as “photobleaching,” changes in the biological availability of its carbon- and nitrogen-containing constituents, and production of carbon dioxide, carbon monoxide, volatile hydrocarbons, and sulfur-containing gases (Fig. 1).

The photobleaching of CDOM has been observed by many investigators (Stewart and Wetzel 1981; Kouassi and Zika 1992; Williamson et al. 1996; Vodacek et al. 1997; Frimmel 1998; Miller 1998; Zepp et al. 1998; Moran et al. 2000; Blough and Del Vecchio 2002; Vahatalo et al. 2002; Osburn and Morris 2003; Zepp 2003; Vahatalo and Wetzel 2004). The process is illustrated by photoinduced changes in the absorption spectrum of the CDOM in ocean water over coral reefs in the Florida Keys (Fig. 2). The photobleaching process is mainly induced by the UV part of solar radiation (Whitehead et al. 2000; Del Vecchio and Blough 2002). When the water in a lake or the ocean becomes stratified, photobleaching can result in increased UV penetration and exposure in the upper water column. Recent observations have shown that the warm upper layers of the stratified ocean and lakes are generally much more UV transparent than deeper, cooler waters (Williamson et al. 1996; Vodacek et al. 1997; Nelson et al. 1998). These observations suggest that global warming may lead to increased UV penetration into aquatic ecosystems.

Photochemical production rates of dissolved inorganic carbon (DIC) [and concurrent photochemical oxygen demand from CDOM (Andrews et al. 2000)] generally are at least an order of magnitude greater than those of other known photoproducts (Graneli et al. 1996; Moran and Zepp 1997; Miller et al. 2002; Johannessen et al. 2003; Anesio and Graneli 2004). However, a recent study has shown that therates and quantum efficiencies for formation of biologically-labile photoproducts (compounds that are readily assimilated by bacteria) from CDOM are about the same as those observed for DIC photoproduction (Miller et al. 2002). (Fig. 3).

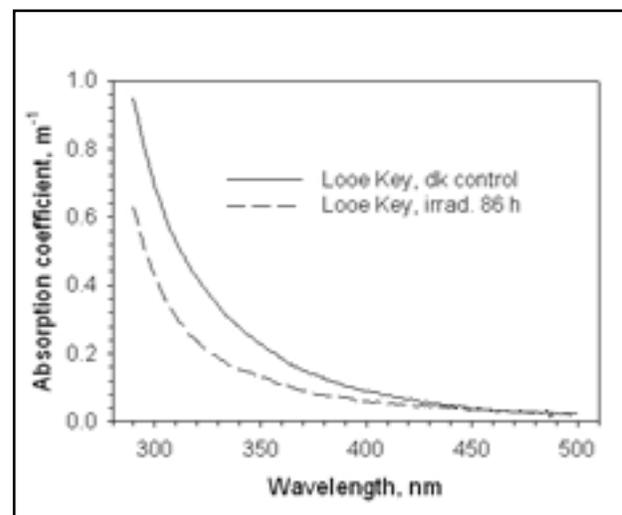


Figure 2. Photobleaching of CDOM in ocean water sample obtained from Looe Key Reef in Florida Keys on irradiation by simulated solar radiation.

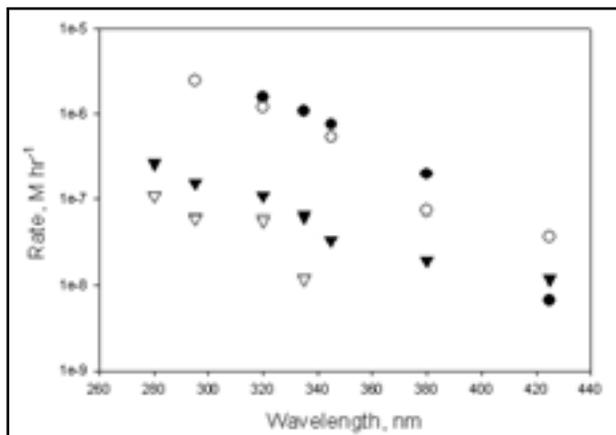


Figure 3. Comparison of the rates of photoproduction of biologically available photoproducts (circles) and carbon monoxide (triangles) in water samples from a saltmarsh and estuary on the coast of the Southeastern U.S.

The experiments shown in Fig. 3 were conducted by irradiating the samples using a xenon-arc lamp equipped with cut-off filters (cutoffs shown on X-axis) that blocked various parts of the UV spectrum. Rates of formation of BLPs were computed using cumulative bacterial oxygen consumption in inoculated samples during subsequent 2-week incubations (i.e., respiratory activity per absorbed photon) (Miller et al. 2002).

The effect of photoreactions on microbial interactions with DOM is dependent on the DOM source, however. The biological lability of refractory DOM (organic matter that is not readily assimilated by bacteria) is generally enhanced by exposure to sunlight (Wetzel et al. 1995; Moran and Zepp 1997; Osburn and Morris 2003; Vahatalo et al. 2003; Obernosterer and Benner 2004). However, the biological degradation of more reactive DOM may be little affected or, in some cases, can actually be decreased by exposure to UV (Benner and Biddanda 1998). The latter effect may be attributable in part to photoproduction of reactive oxygen species that inhibit biological activity or to UV-induced changes in DOM aggregates (Orellana and Verdugo 2003).

PHOTOREACTIONS AND INORGANIC NITROGEN PRODUCTION

UV radiation can affect nitrogen cycling through photoinhibition of nitrogen-related enzymatic activity. N cycling also is indirectly affected by enhanced decomposition of persistent dissolved organic nitrogen (DON) to biologically labile nitrogenous photoproducts (Bushaw et al. 1996; Bushaw-Newton and Moran 1999; Tarr et al. 2001; Bronk 2002; Koopmans and Bronk 2002; Mopper and Kieber 2002; Buffam and McGlathery 2003; Vahatalo and Zepp 2004). Biologically labile nitrogen compounds such as nitrate, ammonium and amino acids are rapidly recycled by the biota in aquatic systems, while N-containing substances whose structures are too complex or randomized to be readily assimilated accumulate in the water col-

umn. In aquatic environments with limited N fixation or low external inputs of labile N, the labile compounds drop almost to immeasurable levels in the photic zone where productivity occurs while the persistent dissolved organic nitrogen (DON) accumulates. Interactions of UV radiation and DON provide a pathway for the conversion of persistent DON to compounds that are more easily assimilated by aquatic microorganisms. A recent study has shown that the biologically-recalcitrant DON in the Baltic Sea can be decomposed to inorganic nitrogen, principally ammonium, by solar UV radiation (Vahatalo and Zepp 2004). This “photoammonification” process occurs most rapidly when UV radiation is absorbed by the DON (Fig. 4). The results of this study suggest that the rate of photoammonification equals the rate of atmospheric deposition of reactive inorganic nitrogen to northern Baltic Sea.

Two key inorganic species of nitrogen, nitrate and nitrite, photoreact when exposed to UV radiation to produce NO_x (nitric oxide plus nitrogen dioxide) plus reactive oxygen species, including hydroxyl radicals (Zafiriou and True 1979; Jankowski et al. 1999; Mopper and Kieber 2002; Zepp 2003). Free radicals produced by photoreactions of these species can have important effects on aquatic photochemistry (see Section 5 on reactive oxygen species in this paper). For example, the buildup of DMS in nitrate-rich Antarctic ocean waters is limited by its UV-induced photooxidation mediated by free radicals (Toole et al. 2004). Oceanic emissions of DMS produce particulates (i.e., sulfate aerosols) that directly and indirectly (via clouds) have a cooling effect on the marine atmosphere.

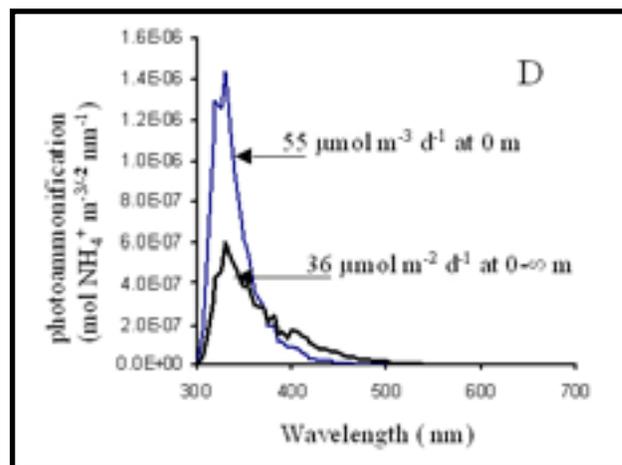


Figure 4. Computed wavelength dependence for the photochemical decomposition of biologically-recalcitrant dissolved organic nitrogen in the Baltic Sea to ammonium (Vahatalo and Zepp 2004).

PHOTOCHEMICAL METALS CYCLING

Photoreactions of metal oxides and organic complexes with metals (e.g. iron, copper, mercury) also are involved in environmental chemistry in aquatic environments, either via direct photoreactions of the complexes or reac-

tions of the complexes with reactive oxygen species that are produced photochemically. Iron and copper are essential trace nutrients that can limit productivity in aquatic environments. In the upper ocean, lakes and in clouds these metals usually exist in forms that are not biologically available. UV-induced photoreductions of these metals produce reactive forms that are readily used by aquatic organisms (Sulzberger et al. 1990; Voelker and Sedlak 1995; Emmenegger et al. 2000; Zepp 2003).

The reactive forms of iron and copper also can affect aquatic carbon cycling by catalyzing oxidations of organic matter (Zafiriou and True 1979; Sulzberger et al. 1990; Gao and Zepp 1998; Emmenegger et al. 2000; Kieber et al. 2003; White et al. 2003). Iron can play a role in the photochemical production of $\bullet\text{OH}$ radicals in natural waters through reactions between Fe(II) and hydrogen peroxide (H_2O_2), two reactive compounds that are produced by UV-induced photoreactions of CDOM and its iron complexes. Such iron-mediated photoreactions, sometimes referred to as Photo-Fenton reactions, are involved in the photooxidation of CDOM in some freshwater ecosystems, e.g. the rivers that drain into the Atlantic Ocean and the Gulf of Mexico in the coastal U.S.A. The addition of strong Fe(III) chelating ligands to such river waters can significantly reduce CDOM photodegradation rates, presumably by reducing concentrations of photoreactive Fe-CDOM complexes that participate in photoredox reactions or that catalyze free radical oxidation of the CDOM. For example, the photoproduction of hydroxyl radicals in an iron-rich water sample from a U.S. estuary was strongly inhibited by the addition of desferal, a potent Fe chelating ligand (White et al. 2003).

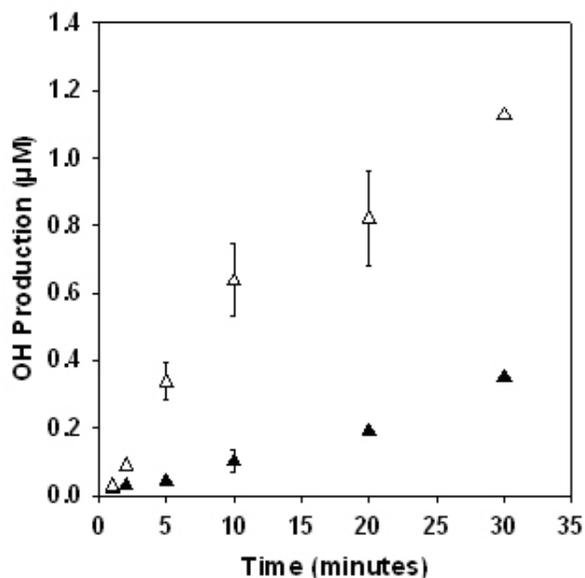


Figure 5. Photochemical production of hydroxyl radicals ($\bullet\text{OH}$) in a water sample from an iron-rich (5 to 15 mM Fe) estuarine water sample (A) and estuarine water containing 0.100 mM desferal (A), a strong Fe chelating

ligand. The samples were irradiated in an Atlas Suntest CPS tabletop solar simulator (White et al. 2003).

Mercury cycling also is affected by UV exposure in aquatic ecosystems. For example, elemental mercury in brackish water is oxidized by UV to form mercuric species (Lalonde et al. 2004) that are precursors to toxic methyl mercury that can adversely affect human health through biomagnification in aquatic food webs.

REACTIVE OXYGEN SPECIES IN AQUATIC PHOTOREACTIONS

The aquatic photoreactions discussed in this paper are mediated in part by a variety of reactive transients that are excited states, oxidants or reductants. The reactive transients are produced on absorption of sunlight by organic and inorganic chromophores in aquatic environments (Blough and Zepp 1995; Blough 1997; Kieber et al. 2003). The most important organic chromophore for ROS photoproduction is CDOM. Photoreactions of inorganic substances such as nitrite, nitrate, trace metals (iron and copper), and/or hydrogen peroxide also produce reactive transients. There is abundant evidence that solar UV drives the photoproduction of these transients. Certain reactive transients that include oxygen atoms are referred to as reactive oxygen species (ROS). ROS include hydroxyl radicals, alkoxy and peroxy radicals, singlet molecular oxygen, superoxide ions, and hydrogen peroxide. These ROS also can be produced within living systems by the action of UV radiation (as well as other mechanisms) where they cause various types of damage. The discussion of ROS in this paper focuses on exogenous photoreactions that produce ROS. The wavelength dependence for hydrogen peroxide production in ocean waters from the tropics and Antarctica illustrates the generality of the role of UV in initiating photoproduction of this widely distributed ROS (Fig. 6).

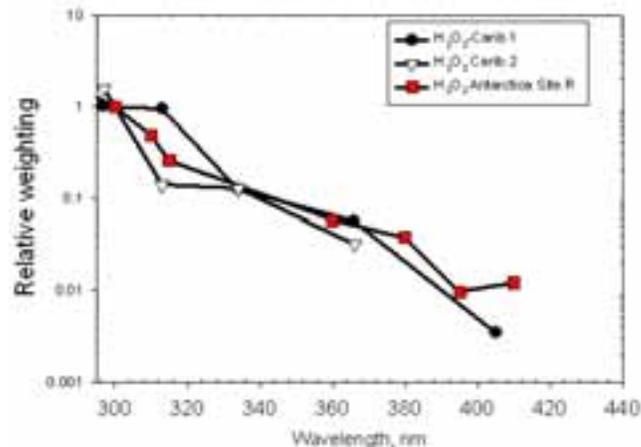


Figure 6. Action spectra (wavelength dependence) for photoproduction of hydrogen peroxide in water samples from the Caribbean Sea and from Antarctica (Kieber, Peake et al. 2003).

Secondary reactions between trace metals such as iron and copper and ROS can strongly influence the redox state and speciation of trace metals. Reactions between iron and hydrogen peroxide to enhance hydroxyl radical production have already been mentioned. More details about past research on metals, ROS and their interactions is available in several recent reviews (Kieber et al. 2003; Zepp 2003).

Reactive transients also play important roles in photoreactions of sulfur-containing compounds in marine environments (Erickson, Zepp et al. 2000; Mopper and Kieber 2002; Kieber et al. 2003). The sea is a major source of natural sulfur gases in the atmosphere. Of particular interest are DMS and carbonyl sulfide (COS). As noted earlier, oceanic emissions of DMS produce particulates (i.e., sulfate aerosols) may lead to a cooling effect on the marine atmosphere. Carbonyl sulfide is the most concentrated sulfur gas in the troposphere and it is believed to contribute to the formation of stratospheric aerosols. Both of these compounds are formed predominantly in aerobic marine environments, that is, the upper layers of the ocean, and their sources and sinks are affected by solar UV radiation. DMS does not absorb solar UV radiation and its major loss pathway involves indirect photoreactions in which photochemically-produced transients attack and oxidize the DMS (Mopper and Kieber 2002). Dimethylsulfoxide and carbonyl sulfide are two of the major products that are produced from indirect photoreactions of DMS in seawater. Although the nature of the transients involved in organosulfur photoreactions have not been defined, both CDOM and nitrate are involved in the photoreactions. COS photoproduction and DMS photooxidation may involve the intermediacy of dibromine radical ions and carbonate radicals, both of which can rapidly form via reactions of hydroxyl radicals with bromide or carbonate (Erickson et al. 2000; Mopper and Kieber 2002).

CONCLUSIONS

Aquatic photoreactions induced by solar UV radiation play an important role in carbon capture and storage, decomposition, and trace gas exchange. Photoreactions interact with microbial processes through effects on the biological availability of carbon and nitrogen substrates. One important aspect of UV interactions with carbon cycling involves the decomposition of UV-absorbing organic matter (photobleaching), principally chromophoric dissolved organic matter (CDOM). CDOM controls UV exposure in the sea and in many freshwater environments. Global warming may enhance the extent of CDOM photobleaching in the upper layers of lakes and the ocean by increasing periods of stratification. CDOM can be directly photodecomposed to dissolved inorganic carbon, carbon monoxide, and various carbonyl-containing compounds. UV-initiated photoreactions can potentially affect nitrogen and sulfur cycling in a variety of ways such as effects on

the biological availability of dissolved organic nitrogen and on sources and sinks of dimethylsulfide and carbonyl sulfide. Metal cycling also interacts in many ways with UV radiation via direct photoreactions of dissolved metal complexes and metal oxides and indirect reactions that are mediated by photochemically-produced reactive oxygen species (ROS).

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