Preface

Impact of photochemical processes in the hydrosphere

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The importance of solar-driven processes in the hydrosphere has become increasingly evident over the past decade. The absorption of sunlight by both natural and anthropogenic chromophores within natural waters can initiate a variety of environmentally important photochemical processes. These processes can include: 1) the direct and sensitized phototransformation of anthropogenic organic, organometallic and inorganic compounds; 2) the light-induced weathering of minerals and the light-induced redox cycling of dissolved metals, thereby influencing metal speciation; 3) photobleaching of the chromophore containing constituents of natural dissolved organic matter, thus altering the aquatic light field and the remote sensing of ocean color. Solar-driven processes also greatly affect the biogeochemical cycles of carbon, nitrogen, phosphorus, and sulfur. Photochemistry can be strongly linked to biological processes, most evident in biological photosynthesis, but also through the production and biological uptake of available forms of nutrients and of trace metals that are essential and/or toxic. Furthermore, many photochemical reactions occur at interfaces, e.g., at the particle-water interface or at the air-water interface, and can affect the production and consumption of atmospherically important trace gases. This special issue of *Aquatic Sciences* is based largely on contributions to the Symposium “Impact of Photochemical Processes in the Hydrosphere” that was co-organized by Neil V. Blough and Richard G. Zepp at the 225th American Chemical Society Meeting (New Orleans, March 23–27, 2003). The ten articles published in this special issue

either review or provide original research on many of the topics outlined above.

The release of pharmaceuticals into aquatic environments is of increasing concern, since these anthropogenic chemicals may have toxic effects on aquatic organisms. There are a myriad of different compounds entering aquatic ecosystems, and hence the elucidation of the fate of every single compound is an unrealistic task. It is, therefore, important to develop predictive tools or relationships. The review by Boreen and co-authors (Boreen et al., 2003) summarizes the current knowledge of the photochemical behavior of pharmaceuticals and highlights the application of the fundamental photochemistry and phototoxicity literature to help understand and predict the aquatic fate of pharmaceuticals. The research article by Packer and co-workers (Packer et al., 2003) presents a study of the photochemical fate of four distinct pharmaceutical compounds: naproxen, diclofenac, clofibric acid, and ibuprofen. This study illustrates that light-induced transformation of these compounds can occur through direct phototransformations, i.e., photolysis (naproxen and diclofenac) and/or via indirect, i.e., sensitized phototransformations, mainly involving the hydroxyl radical ($\cdot\text{OH}$) (clofibric acid and ibuprofen).

Another class of ubiquitous environmental pollutants are polycyclic aromatic hydrocarbons (PAH's). The article by Fasnacht and Blough (Fasnacht and Blough, 2003) provides a mechanistic analysis of the photodegradation of PAH's in aqueous solutions. Employing measured photochemical and photophysical parameters, these authors developed a kinetic model that allowed a quantitative evaluation of the fraction of PAH photodegradation that proceeds via the excited singlet ($^1\text{P}^*$) or triplet state ($^3\text{P}^*$), as well as the relative contribution of electron transfer to O_2 versus the direct reaction with O_2 from each excited

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state. From their results, they conclude that under aerobic conditions, photodegradation of PAH's may be controlled largely by $^1P^*$ lifetime and reactivity.

Yet another class of anthropogenic compounds that may enter aquatic systems is pesticides. Ultraviolet radiation (UV) is increasingly being used to treat such chemical contaminants in waste and drinking water. Sharpless and collaborators (Sharpless et al., 2003) investigated the effect of nitrate on UV treatment of atrazine in phosphate buffer and solutions containing Suwannee River natural organic matter. This paper provides the first report of the quantum yield of $^{\bullet}OH$ production from nitrate photolysis at wavelengths used in UV treatment (below 250 nm), and this information allows photodegradation rates upon UV treatment to be modeled as a function of nitrate concentration and water quality.

Two research papers in this special issue deal with the effects of sunlight on the chemical speciation of iron in coastal and offshore seawaters. Iron is an essential micronutrient for phytoplankton and has been proposed to limit or co-limit phytoplankton growth in several marine environments including coastal waters. The biological availability of iron depends on its chemical speciation. Light-induced redox cycling of iron is a key process for the formation of biologically available iron and is linked to the photooxidation of dissolved organic matter (DOM), including specific Fe(III) ligands. The study by Powell and Wilson-Finelli (Powell and Wilson-Finelli, 2003) with water samples from various sites in the Gulf of Mexico suggests that low-molecular weight compounds (< 1 kDa) are subject to photodegradation through photolysis of corresponding Fe(III) complexes in these marine environments.

The speciation of iron in various sunlit aquatic systems may differ substantially because of such factors as different concentrations and types of DOM and the nature and amounts of reactive oxygen species generated. Hence, it is useful to predict iron speciation with help of kinetic modeling. These models are based on rate and equilibrium constants of the major chemical reactions and equilibria involved in light-induced redox cycling of iron. In their research paper, Rose and Waite (Rose and Waite, 2003) show that their model can predict quite well the spatial and temporal variations in ferrous iron and hydrogen peroxide that have been observed in field measurements of coastal waters. Their results indicate that modeling of fundamental chemical reactions involved in overall processes is an extremely useful approach for understanding and predicting iron speciation at an ecosystem scale.

The chromophore-containing constituents of dissolved organic matter (CDOM) dominate absorption of sunlight throughout the UV-B, UV-A and blue portion of the visible spectrum in most natural waters. CDOM is also the primary, abiotic photo-reactive species in natural waters.

Thus, an understanding of the nature, distribution and fate of this material is essential for quantifying its impacts on the optical and photochemical properties of natural waters over local, regional and global scales. Kowalczyk and co-workers (Kowalczyk et al., 2003) characterized the nature and distribution of CDOM in and around the Cape Fear River and Onslow Bay (North Carolina, USA) employing excitation emission matrix (EEM) fluorescence and UV/VIS spectroscopy. These EEM spectra indicate that a radical change in composition of CDOM occurs along the river-to-ocean salinity gradient.

Photochemical degradation of CDOM also affects the penetration of sunlight into the water column owing to the loss of CDOM absorption (called photobleaching). Photobleaching of CDOM can occur through both direct and sensitized photochemical processes; one possible sensitized route is through reaction with $^{\bullet}OH$ produced through a number of possible pathways. White and co-workers (White et al., 2003) compared changes in the light absorption and fluorescence properties of water samples from the Satilla River (southeastern United States) to the $^{\bullet}OH$ production rate. The results of this study indicate that photo-Fenton reactions (light-induced reduction of Fe(III) and subsequent oxidation of Fe(II) by H_2O_2) account for more than 70% of total $^{\bullet}OH$ production, and that $^{\bullet}OH$ possibly contributes to CDOM photobleaching in Satilla River water.

Photodegradation (and thus photobleaching) of CDOM is a consequence of the destruction of CDOM chromophores (as well as other moieties) into lower molecular weight compounds, which generally produces an increase in the bioavailability of the CDOM. Employing size-exclusion chromatography, Brinkmann and co-workers (Brinkmann et al., 2003) observed a decrease in the average hydrodynamic radii upon irradiation with simulated solar UV-light of CDOM from a bog lake in the northern Black Forest (Germany). Their results also suggest that hydrophilic CDOM moieties were preferentially photodegraded, while hydrophobic moieties remained relatively unaffected or were even formed. Brinkmann et al. (2003), similar to White et al. (2003), concluded that the high Fe concentrations in these samples were an important factor in CDOM photobleaching. In contrast, however, Cu was observed to inhibit photobleaching.

Employing a laser flash photolysis – long path UV-visible absorption – competitive kinetics technique, Zhu and co-workers (Zhu et al., 2003) investigated the kinetics of the aqueous phase reactions between $^{\bullet}OH$ and dimethylsulfoxide (DMSO), dimethylsulfone (DMSO₂), and methanesulfonate (MS). These organic sulfur species are produced from the free radical initiated oxidation of gas phase dimethyl sulfide (DMS). DMS is the primary reduced sulfur species emitted into the atmosphere from the ocean and accounts for about 15% of the global sulfur burden. The heterogeneous chemistry of these sulfur

species has been of great interest for atmospheric researchers, and both model studies and field observations have demonstrated that their condensed phase transformations are potentially important in the atmospheric sulfur cycle and in affecting the chemical/physical properties of aerosols and cloud/rain droplets. The results of this new kinetics study are discussed in terms of increasing our understanding of the atmospheric sulfur cycle.

As exemplified above, the ten articles of this special issue cover a broad range of sunlight-driven processes, spanning the range from light-induced transformations of pollutants to effects of sunlight on metal, carbon and sulfur cycling. We hope that this special issue will motivate environmental photochemists to submit their papers to *Aquatic Sciences*.

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