



Roles of iron in light-induced transformations of dissolved organic matter

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Light-induced transformations of dissolved organic matter (DOM) play an important role with regard to DOM optical properties and bioavailability and thus carbon cycling. There exist several pathways of DOM photo-transformations, depending on DOM chemical composition and on environmental factors such as the presence of iron. In iron-abundant aquatic systems, light-induced transformations of DOM may proceed via photolysis of Fe(III)-DOM complexes and/or via attack by hydroxyl radicals (OH) that are formed in the Fenton reaction (oxidation of Fe(II) by hydrogen peroxide), in addition to direct phototransformation of colored dissolved organic matter (CDOM), which is part of DOM. This paper will present results from laboratory studies with model systems and natural water samples, combined with mathematical kinetic modeling, that demonstrate the importance of photolysis of Fe(III)-DOM complexes, both in solution and at the surface of Fe(III) (hydr)oxides, in overall DOM phototransformations in the presence of iron. Photochemical studies with high-molecular-weight (HMW) and low-molecular-weight (LMW) DOM fractions from both freshwater and marine systems further indicate that LMW compounds are more reactive towards light-induced Fe(II) formation than HMW compounds. This higher reactivity of LMW materials in photochemical reduction of Fe(III) may be rationalized by more efficient photolysis of Fe(III) complexes with LMW ligands, as compared to HMW ligands, possibly due to a higher content of carboxyl functional groups contained in aquatic LMW DOM. Results from a bioavailability study with various DOM fractions from the River Tagliamento, a semi-natural, iron-abundant river in Italy, revealed that photochemical transformations drastically decreased the bioavailability of initially bioreactive LMW compounds, while that of HMW compounds did not change. These findings may be due to the higher photoreactivity of LMW compounds in the presence of iron, as indicated by a higher net rate of hydrogen peroxide formation with LMW DOM than with HMW DOM from the River Tagliamento.

Iron also may play an important role in catalyzing photobleaching of CDOM. The extent of CDOM photobleaching generally increases with decreasing salinity, possibly reflecting the higher photochemical reactivity of terrestrial-derived CDOM and the importance of photo-Fenton reactions. Studies from the literature indicate that photobleaching via photo-Fenton reactions occurs most efficiently in acidic waters and under the influence of UV-B radiation. Since photolysis of Fe(III) complexes is the first process leading ultimately to OH formation via the Fenton reaction, the efficiency of photochemical Fe(II) formation in part determines the efficiency of photo-Fenton systems in producing OH. A wavelength-dependence study from our own laboratory showed that the apparent quantum yield of Fe(II) formation in irradiated lake water samples decreased with increasing wavelength between 300-450 nm. Another study from our laboratory found that formation of OH (as measured by degradation of atrazine via attack by OH) in homogeneous photo-Fenton systems occurred with highest rates between pH 4-5 (in the range $3 < \text{pH} < 8$) which was mainly due to different photolysis efficiencies of the pH-dependent Fe(III) species. Hence solar UV-B radiation may be particularly effective in CDOM photobleaching in acidic, iron-rich aquatic systems.