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The role of light-induced transformations of DOM for Fe(II) oxidation kinetics in aquatic systems

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Light-induced transformations of dissolved organic matter (DOM) alter its chemical composition. As a consequence, bioavailable or biorecalcitrant DOM compounds are formed. Furthermore, ligands may be produced that affect the oxidation kinetics of reduced metal species, e.g. Fe(II). In various laboratory studies we observed a decrease in the apparent rate constant of Fe(II) oxidation, k(ox), after irradiation of natural water samples with simulated sunlight, as compared to k(ox) of non-irradiated samples. We hypothesize that Fe(II)-stabilizing ligands are formed upon irradiation of these water samples. This hypothesis is, in part, based on an excellent agreement between experimental data and mathematical kinetic modeling of the Fe(II) concentration course in a low-molecular-weight freshwater sample during irradiation and after the light source was turned off, where the modeling included light-induced formation of Fe(II)-stabilizing ligands. To assess the question whether Fe(II)-stabilizing ligands are initially present in natural water samples, we measured k(ox) in water samples from Lake Greifensee (Switzerland) that were collected during the summer in 2005 and 2006 and compared it to that of corresponding samples without DOM. DOM elimination was done by irradiating water samples for 24 h with a Hg lamp at pH 2. The apparent rate constant of Fe(II) oxidation, k(ox), was consistently lower in the water samples (pH 8.3) with ambient DOM concentrations as compared to the samples in which DOM was eliminated and the pH readjusted to 8.3. Upon addition of Fe(II) (up to 10 nM) to the water samples with ambient DOM concentrations, k(ox) remained approximately constant. We conclude from these results that Fe(II)-stabilizing ligands are already present in these water samples before irradiation with simulated sunlight - although at much lower concentrations than after irradiation - and that the concentration of these ligands equals or exceeds 10 nM.