Photochemical control of copper complexation by dissolved organic matte in Rocky Mountain streams, Colorado

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ABSTRACT: We investigated photochemical, seasonal, and source effects on copper (Cu) complexation by dissolved organic matter (DOM). Cu-DOM complexation regulates Cu toxicity by decreasing the activity of the cupric ion ($\{Cu^{2+}\}$), the most bioavailable Cu species. However, DO is photochemically unstable under solar insolation. We analyzed Cu-DOM complexation before ar after photooxidation of DOM collected from six rivers during spring runoff and late summer (n = DOM samples). After irradiation of DOM for 24 h in a solar simulator (~4 d of ambient insolation), we analyzed Cu-DOM complexation during potentiometric titrations of Cu into dissolved organic carbon concentrations of 5 mg L^{-1}. In 10 DOM samples across the range of titrations (Cu, 7.8 x 10 to 8.7 x 10^{-6} mol L^{-1}), photooxidation of DOM decreased Cu complexation, increasing $\{Cu^{2+}\}$ by an average of 156% $\pm$ 28% (mean $\pm$ SE). In one DOM sample, irradiation had no net effect on $\{Cu^{2+}\}$ (6% $\pm$ 12%), whereas in another Cu complexation was enhanced (30% $\pm$ 4%). Cu complexation th was indistinguishable before irradiation decreased significantly more during photooxidation of DOM in spring (185% $\pm$ 25%) than in summer (74% $\pm$ 14%). The specific ultraviolet absorption coefficient at 254 nm explained ~60% of the variation in conditional stability constants of Cu-DOM complexes regardless of DOM source, season, or extent of photooxidation. During a simulated contaminant event where 1.5 x 10^{-6} mol L^{-1} Cu was added to site waters, water chemistry reduce bioavailability in 6 of 12 cases to below the $\{Cu^{2+}\}$ expected to cause 50% mortality ($\{Cu^{2+}\}_{LC50}$) in larval fish. However, after 6 d of photooxidation, none of the site waters remained below $\{Cu^{2+}\}$ $_{LC50}$.