

## **Mechanisms and factors controlling photochemical transformation of mercury and net methylmercury formation in the aquatic environment**

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Atmospheric deposition of mercury (Hg) is the main source for methylmercury (MeHg) formation and bioaccumulation in fish in natural aquatic environments. Under natural sunlight, the net MeHg formation in water is strongly influenced by photochemical transformation of Hg and MeHg, in which Hg photoreduction, photooxidation, and MeHg photodegradation can occur simultaneously. However, the underlying mechanisms and factors that control these processes are not completely understood, especially the role of naturally dissolved organic matter (DOM) in freshwaters. It is also unclear whether the photo-redox transformation of Hg or Hg-DOM complexes may alter Hg reactivity and thus its bioavailability for microbial uptake and methylation. In this study, we show that Hg(II) photoreduction and Hg(0) photooxidation proceed concurrently in a Hg contaminated stream system—East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee. Carbonate ( $\text{CO}_3^{\cdot-}$ ) radicals primarily drive the Hg(0) photooxidation in EFPC. DOM and various organic ligands is found to increase MeHg photodegradation, but the first-order rate constants vary greatly depending on the oxidation state of DOM, and the type and concentrations of the complexing ligands, and the irradiation wavelength. Compounds containing both thiol and aromatic moieties within the same molecule (e.g., thiosalicylate and reduced DOM) increased MeHg photodegradation far greater than those containing only aromatics or thiols (e.g., salicylate or glutathione, or their combinations). The thiols and aromatics in DOM synergistically enhanced MeHg photodegradation. Importantly we also found that light exposure of Hg(II)-DOM solutions decreases MeHg production by *Geobacter sulfurreducens* PCA, particularly under the ultraviolet (UV) light. The decreased methylation upon light exposure coincided with decreased Hg(II) reactivity, measured by stannous-reducible Hg(II), and the UV is more effective than solar light in decreasing the reactivity. Collectively these studies identify previously unrecognized pathways for Hg(0) photooxidation, MeHg photodegradation, and the loss of Hg(II) reactivity and bioavailability upon light exposure. These findings are important to assess and predict Hg geochemical cycles and the net MeHg formation and bioaccumulation in natural aquatic environments.