

Kinetic Controls on the Interaction of Mercury with Dissolved Organic Matter

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Carrie L. Miller, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS6038, Oak Ridge, TN 37831-6038; (865) 241-2298; millercl@ornl.gov
Baohua Gu, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS6036, Oak Ridge, TN 37831-6036; (865) 574-7286; gub1@ornl.gov
Scott C. Brooks, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS6038, Oak Ridge, TN 37831-6038; (865) 574-6398; brookssc@ornl.gov
George R. Southworth, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS6036, Oak Ridge, TN 37831-6036; (865) 574-7240; southworthgr@ornl.gov
Liyuan Liang, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS6038, Oak Ridge, TN 37831-6038; (865) 241-3933; liangl@ornl.gov

Under equilibrium conditions, complexes between mercury (Hg) and dissolved organic matter (DOM) dominate the speciation of Hg in most oxygenated aquatic environments but the rate of formation of these complexes has not been extensively investigated. Reactive Hg(II) species (Hg_R), defined as the Hg(II) reducible by stannous chloride ($SnCl_2$), are introduced into aquatic systems through rainwater, industrial outfalls and oxidation reactions. The conversion of these reactive species to strongly bound DOM complexes may dictate the cycling and bioavailability of Hg in aquatic systems. This study was undertaken to determine the formation rates of strong Hg-DOM complexes, which are non-reducible by $SnCl_2$, in the Upper East Fork Poplar Creek (UEFPC) water in Oak Ridge, TN, USA, and to compare those with laboratory prepared solutions containing small organic ligands and natural organic matter isolates. Hydrophobic solid phase resins were also used to examine shifts in the complexation of Hg(II) to different fractions of DOM. In addition, experiments were conducted to determine how light, natural particles and inorganic and small organic ligands in solutions with the DOM influence the formation of strong Hg-DOM complexes. When an inorganic Hg complex was spiked into solutions containing DOM isolates, the formation of the strong Hg-DOM complexes took several hours to reach equilibrium. The formation rate of Hg-DOM complexes in solutions with DOM isolates were similar to the rates measured when Hg was spiked into UEFPC water. Under equilibrium conditions, Hg-DOM complexes should dominate the speciation of Hg in the UEFPC but the slow formation of these complexes results in a pool of reactive Hg in the system. The slow formation kinetics has important implications in systems such as the UEFPC which continually receive inputs of reactive Hg species from industrial outfalls and thus affect the partitioning of Hg between the dissolved and solid phases, the bioavailability and cycling of Hg in the system.