

The Influence of Kinetics on the Formation of Complexes Between Mercury and 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

Strong complexes between mercury (Hg) and dissolved organic matter (DOM) dominate the speciation of Hg(II) in most oxygenated aquatic systems but the rate of formation of these complexes has not been thoroughly investigated. Kinetic experiments were used to measure the formation rate of strong Hg(II)-DOM complexes in water collected from the Upper East Fork Poplar Creek (UEFPC) in Oak Ridge, TN and in solution prepared using various DOM isolates. The loss of reactive mercury (HgR), defined as the amount of Hg reducible by stannous chloride (SnCl_2), was used to examine the formation rates of strong Hg-DOM complexes which are nonreactive with SnCl_2 . We found that the formation of nonreactive Hg complexes followed first-order reaction kinetics, and the rate constant for the formation of these complexes is similar both in creek water and solutions containing unfractionated DOM isolates ($\sim 4.8 \text{ day}^{-1}$). C_{18} solid phase extractions were also used to examine the association of Hg(II) with different fractions of DOM as the mercury transformed from reactive, inorganic complexes to strong Hg-DOM complexes. In both the UEFPC and in laboratory solutions containing Hg and an unfractionated DOM isolate, the complexation of Hg shifted from hydrophilic to hydrophobic complexes as the strong Hg-DOM complexes were formed. This study concludes that, while equilibrium models suggest that strong Hg-DOM complexes dominate the speciation of Hg under equilibrium conditions, the formation of these complexes is kinetically limited. The slow formation of strong Hg-DOM complexes may have important implications in understanding the cycling, transport and bioavailability of Hg in systems such as the UEFPC with varying input sources of organic and inorganic Hg complexes.