

## Fundamental Understanding of the Mechanisms and Geochemical Controls on the Speciation and Transformation of Mercury

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As part of the ORNL Science Focus Area (SFA), this research is aimed at fundamental understanding of the mechanisms and geochemical controls on the speciation and transformation of mercuric ion Hg(II), elemental Hg(0), and methylmercury (CH<sub>3</sub>Hg<sup>+</sup>) at the Upper East Fork Poplar Creek (UEFPC) site in Oak Ridge, Tennessee. Our initial focus is centered on the effects of particulates and dissolved organic matter (DOM), which have been shown to play a dominant role in the complexation, redox chemistry, reactivity, and transformation of mercury and CH<sub>3</sub>Hg<sup>+</sup> in aquatic systems.

Using a modified ion exchange technique and geochemical speciation modeling, we show that, even at relatively low concentrations (< 3 mg/L), DOM determines Hg(II) speciation at equilibrium by forming strong Hg-DOM or CH<sub>3</sub>Hg-DOM complexes through the reactive sulfur or thiol functional groups in DOM. Studies using reducible Hg(II) titration and C<sub>18</sub> solid-phase extractions on waters collected from UEFPC and simulated DOM solutions demonstrate that the interaction of Hg(II) with DOM is kinetically hindered. The strength and reactivity of the Hg(II)-DOM complex also change over time. The high fraction of reducible Hg(II) (Hg<sub>R</sub>) (>90%) at the headwaters of UEFPC and the persistence of Hg<sub>R</sub> in the upper 2.5 km of the creek suggest that the slow formation of Hg(II)-DOM complexes is important in the geochemical cycling of mercury, and that equilibrium models cannot be assumed in predicting the complexation and speciation of Hg(II) in this contaminated ecosystem. Furthermore, studies of the effect of DOM on the redox transformation of mercury reveal that reduced DOM, particularly the high molecular weight humic acid (HA), is capable of rapidly reducing the ionic Hg(II) to elemental Hg(0) under anaerobic conditions. More importantly, the reduced humics are found to form strong complexes with Hg(0), with an estimated partitioning coefficient up to 10<sup>6</sup> mL/g and a binding capacity up to 3.5 mmol Hg(0)/g HA. These findings suggest that, apart from strong complexation between Hg(II) and DOM, Hg(0)-DOM complexes are likely prevalent in anoxic sediments and water columns, and constitute an important yet unexplored pool of Hg, which could potentially impact biological production of toxic methylmercury and/or abiotic demethylation under such a reducing environment.

New findings of the nonequilibrium complexation between Hg(II) and DOM in the EFPC and the complexation between Hg(0) and DOM are significant, because both of these processes could greatly influence the net methylation or demethylation process, which will be the subject of our future studies. Our future work will also attempt to elucidate detailed mechanisms of the complexation through approaches such as competitive ligand interactions, molecular simulation, and detailed characterization of reduced sulfur functional groups in DOM. Furthermore, we will study the interactions between Hg and particulates, a process that could alter the partition and kinetics of Hg(II)-DOM complexation and dynamics in the EFPC ecosystem.