

Understanding Mercury Speciation, Reactivity and Binding Mechanisms with Dissolved Organic Matter

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This research is part of the ORNL Science Focus Area aimed at fundamental understanding of the mechanisms and geochemical controls on the speciation and transformation of mercury (Hg) at the Upper East Fork Poplar Creek (UEFPC) contamination site in Oak Ridge, TN. Our initial focus is on the effect of dissolved organic matter (DOM), which has been shown to play a dominant role in the complexation, reactivity and transformation of mercury in aquatic systems. To date, two reactive DOM components (hydrophobic and hydrophilic fractions) were isolated from UEFPC stream water and studied for their complexation with Hg(II) using a modified ion exchange technique. The rate of formation of Hg-DOM complexes was examined using stannous chloride reactive Hg measurements and C₁₈ solid phase extractions. Results indicate that ionic Hg(II) forms strong complexes with thiol functional groups in DOM. The Hg(II)-DOM complexes were predicted to be the dominant aqueous species in UEFPC, which agrees with most freshwater environments where equilibrium conditions are established. However, further studies indicate that equilibrium conditions at UEFPC cannot be assumed because of a constant input of inorganic Hg(II) to the creek. The complexation and the formation of Hg-DOM complexes appear to be kinetically limited, with a pseudo first-order rate constant on the order of 0.11-0.29 hr⁻¹ when the water collected from UEFPC is mixed with laboratory prepared solutions containing DOM isolates. The formation rate of Hg-DOM complexes was even slower ($k = 0.03$ hr⁻¹) when Outfall 200 water, the dominate source of Hg(II) in the UEFPC, was mixed with the creek water. These results suggest the presence of other reactive organic or inorganic ligands in Outfall 200 water, which is retarding the formation of the Hg-DOM complex. The slow formation kinetics of the Hg-DOM complex likely results in a reactive pool of Hg always present in the upper reaches of UEFPC which can not be described satisfactorily using equilibrium models. These reactive species need to be considered when the production of methylmercury and the particle reactivity of Hg(II) in this system are investigated. Continuing research is being conducted to understand the binding mechanism of Hg(II) with DOM and how interactions of mercury and DOM influences the reduction of inorganic Hg(II) and the abiotic demethylation of methylmercury.