

Kinetic and thermodynamic controls on the speciation and reactivity of mercury with natural organic matter in a contaminated aquatic ecosystem in Oak Ridge, Tennessee

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Reactions between mercuric ion (Hg^{2+}) and naturally dissolved organic matter (DOM) are known to play a critical role in controlling the transformation, transport and bioavailability of mercury in the environment. This work reports the analysis of the complexation, speciation, and reactivity of Hg^{2+} under both equilibrium and non-equilibrium conditions in a contaminated East Fork Poplar Creek (EFPC) water in Oak Ridge, Tennessee, USA. We show that, under equilibrium conditions, DOM in EFPC dominates the $\text{Hg}(\text{II})$ speciation by forming strong Hg^{2+} -DOM complexes through reduced sulfur or thiol-like functional ligand (L) groups in DOM at pH about 7.8. The measured conditional stability constants ($\log K$) between EFPC-DOM and Hg^{2+} vary from about 23 for the monodentate HgL complex and about 31 for the bidentate HgL_2 complexes. However, further field investigations indicate that reactions between Hg^{2+} and DOM in EFPC are not at equilibrium. From the head water 0 to 2.5 km of EFPC, reducible Hg is progressively decreased over the distance, while the non-reducible Hg, i.e., the fraction tightly bound as Hg^{2+} -DOM complex, is increased and approaching the equilibrium values. By measuring reducible Hg in the creek water and in solutions containing DOM isolates, we confirm that formation of Hg^{2+} -DOM complexes is not instantaneous but kinetically limited. These observations likely result from the competitive interactions among DOM moieties or the transfer of Hg^{2+} from weaker to strong binding sites within the DOM macromolecules. This research indicates the importance of both kinetic and thermodynamic controls on the Hg^{2+} -DOM complexation, which can potentially lead to changes in the aqueous speciation, biological uptake/transformation, and cycling of Hg in the aquatic environment.