

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

Session: ORNL SFA (Laboratory Research Manager: Liyuan Liang)

Baohua Gu,¹ Wang Zheng,¹ Feng He,¹ Carrie Miller,¹ Bhoopesh Mishra,² Yongrong Bian,¹ Hao-Bo Guo,¹ Xiangping Yin,¹ Hong Zhang,³ Ken Kemner,² Jeffra Schaefer,⁴ François Morel,⁴ Liyuan Liang¹

¹Oak Ridge National Laboratory, ²Argonne National Laboratory, ³Tennessee Technological University, ⁴Princeton University

The oxidized mercuric ion, Hg^{2+} , has been generally considered as the species that forms complexes with dissolved organic matter (DOM). Although dissolved elemental mercury, $\text{Hg}(0)$, is also widely observed in sediments and water, reactions between $\text{Hg}(0)$ and DOM have rarely been studied in anoxic environments. In this study, DOM isolates of various origins were pre-reduced either chemically or biologically to simulate natural anoxic environments and subsequently studied for their reactions with either Hg^{2+} or $\text{Hg}(0)$. We found that DOM, particularly the reduced humic acid (HA), strongly interacts with dissolved $\text{Hg}(0)$ through thiolate-ligand induced reactions. The binding capacity between Hg and DOM complexation varied with different DOM isolates and diminished when DOM became oxidized. The reduced DOM isolates are also capable of rapidly reducing $\text{Hg}(\text{II})$ species to gaseous $\text{Hg}(0)$ under anaerobic conditions. The purgeable $\text{Hg}(0)$ was found to increase with increasing DOM initially, reach a peak value, and then to decrease at higher levels of DOM due to the formation of Hg-DOM complexes. This phenomenon is explained by the dual functional role of DOM in the reduction and complexation of Hg, since the reduced DOM usually contains a higher reducing than binding (thiol ligands) equivalent. This role played by DOM is likely important in influencing mercury species transformations and methylmercury formation, particularly in anoxic sediments and water where both microbial reduction of DOM and methylation occur.

Photochemical reduction of Hg^{2+} is also one of the most important pathways of elemental $\text{Hg}(0)$ production in natural and contaminated waters and plays a key role in Hg cycling. This redox transformation is affected by aqueous ionic species, among which the aromatic moieties of DOM are thought to be the most important because of their light-absorbing characteristics. However, the exact mechanism by which DOM mediates the photochemical reduction of $\text{Hg}(\text{II})$ is not clear owing to incomplete understanding of the structural arrangement and stoichiometry of reactive functional groups in DOM. Using DOM analogs of salicylic acid, 4-hydrobenzoic acid, anthranilic acid, 4-aminobenzoic acid, and phthalic acid, here we show that the photochemical reduction rates of $\text{Hg}(\text{II})$ are influenced not only by the neighboring functional groups but also their positioning on the aromatic benzene ring structure. The reduction rate increases in the order: anthranilic acid > salicylic acid > phthalic acid in response to changes in the neighboring functional groups from amine, hydroxyl, to carboxyl on benzoic acid. The substitution position of the functional groups affects reduction rates in the order: anthranilic acid > 4-aminobenzoic acid and salicylic acid > 4-hydroxybenzoic acid. These observations shed light on the role of DOM in Hg photoredox transformation and geochemical cycling.