

The reduction of Hg(II) and complexation of Hg(0) with natural dissolved organic matter in aquatic environments

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The mercuric ion, Hg²⁺, has been generally considered as the species that form complexes with natural dissolved organic matter (DOM) such as humic acid (HA), a key component that affects mercury chemical and biological transformation and cycling in aquatic environments. Although the dissolved elemental mercury, Hg(0), is also widely observed in sediments and water, complexation reactions between Hg(0) and DOM have been largely overlooked and their effect on the biotic or abiotic transformation of mercury has never been examined. We report that DOM, especially the reduced HA, can strongly complex with dissolved Hg(0). The estimated binding capacity is about 3.5 $\mu\text{mol Hg(0)/g HA}$ and a partitioning coefficient is greater than 10^6 mL/g . However, the complexation capability is found to vary with different DOM isolates and diminishes when DOM becomes oxidized. Humic acids are also capable of reducing the ionic Hg²⁺ to Hg(0) under anaerobic conditions: the purgeable Hg(0) is found to increase with increasing HA initially, maximize at the addition of $\sim 50 \mu\text{mol Hg(II)/g HA}$, but decrease at higher levels of HA due to the formation of Hg(0)-HA complexes. These findings suggest that Hg(0)-DOM complexes likely constitute an important yet unexplored pool of Hg in anoxic sediments and water columns, and this pool of Hg could potentially impact on biological production of toxic methylmercury under such a reducing environment.