

Elucidating Biogeochemical Controls on Mercury Species Transformation in Reducing Environments

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DOE/Office of Science/Biological & Environmental Research

Objective

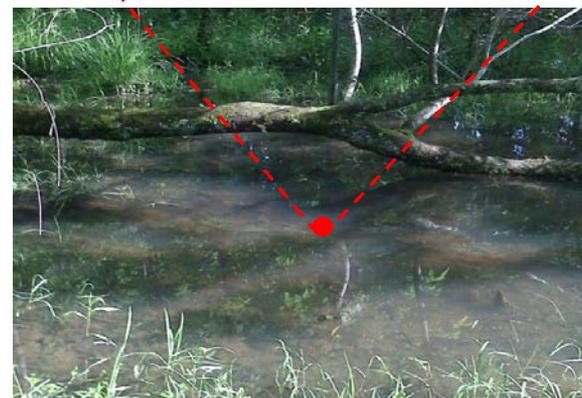
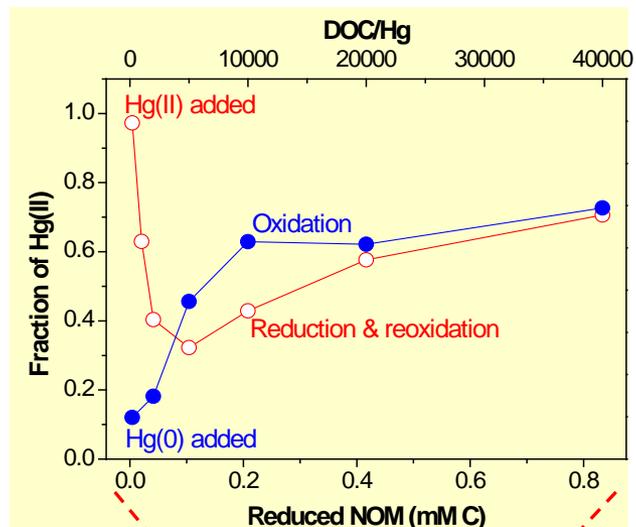
- Understand how natural organic matter in anoxic water and sediments mediates mercury reduction-oxidation cycling.

New Science

- Reduced quinones in natural organic matter are largely responsible for Hg(II) reduction, whereas Hg(0) oxidation is by thiol-ligand induced oxidative complexation.
- Natural organic matter mediates Hg(II) reduction at higher rates than that of photochemical reduction of Hg(II) in open surface water.

Significance

- We showed that the redox cycling of elemental mercury Hg(0) and mercuric Hg(II) is affected by natural organic matter. The process can affect inorganic mercury reactivity and availability to microorganisms for Hg methylation.



Zheng, W., L. Liang and B. Gu. 2011. Mercury reduction and oxidation by reduced natural organic matter in anoxic environments. *Environ. Sci. Technol.* 46:292-299 (doi:10.1021/es203402p).

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Natural organic matter (NOM)-mediated redox cycling of elemental mercury Hg(0) and mercuric Hg(II) is critically important in affecting inorganic mercury transformation and bioavailability. However, these processes are not well understood, particularly in anoxic water and sediments where NOM can be reduced and toxic methylmercury is formed. We show that under dark anoxic conditions reduced organic matter (NOM_{re}) simultaneously reduces and oxidizes Hg via different reaction mechanisms. Reduction of Hg(II) is primarily caused by reduced quinones. However, Hg(0) oxidation is controlled by thiol functional groups via oxidative complexation, which is demonstrated by the oxidation of Hg(0) by low-molecular-weight thiol compounds, including glutathione and mercaptoacetic acid under reducing conditions. Depending on the NOM source, oxidation state, and NOM:Hg ratio, NOM reduces Hg(II) at initial rates ranging from 0.4 to 5.5 h⁻¹, which are about 2 to 6 times higher than observed for photochemical reduction of Hg(II) in open surface waters. However, rapid reduction of Hg(II) by NOM_{re} can be offset by oxidation of Hg(0) with an estimated initial rate as high as 5.4 h⁻¹. This dual role of NOM_{re} is expected to strongly influence the availability of reactive Hg and thus to have important implications for microbial uptake and methylation in anoxic environments.

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