

# Organic Thiols Play an Important Role in Mercury Redox Cycling in the Environment

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DOE/Office of Science/Biological & Environmental Research

## Objective

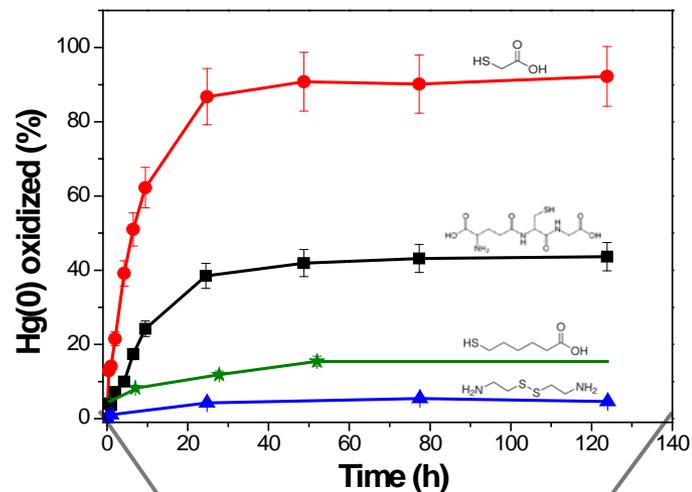
- Determine how organic ligands with varying molecular structures and oxidation states affect oxidation of dissolved elemental mercury [Hg(0)] in dark, anoxic environments.

## New Science

- Hg(0) oxidation observed with all thiols but not with ligands containing no S or compounds with oxidized S (e.g., disulfide).
- The rate and extent of Hg(0) oxidation varies depending on structural properties of thiols, thiol/Hg ratio, and the presence or absence of electron acceptors.
- Validated the mechanism of thiol-induced oxidation of Hg(0).

## Significance

- The environmental fate of Hg appears more complicated than previously recognized – organic thiols may play a key role in the redox cycling of Hg in dark, anoxic sediments and can thus affect Hg speciation and bioavailability for microbial methylation.



Zheng, W., H. Lin, B. F. Mann, L. Liang, and B. Gu. 2013. Oxidation of dissolved elemental mercury by thiol compounds under anoxic conditions. *Environ. Sci. Technol.* 47:12827-12834 (doi: 10.1021/es402697u).

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Mercuric ion,  $\text{Hg}^{2+}$ , forms strong complexes with thiolate compounds that commonly dominate Hg(II) speciation in natural freshwater. However, reactions between dissolved aqueous elemental mercury ( $\text{Hg}(0)_{\text{aq}}$ ) and organic ligands in general, and thiol compounds in particular, are not well studied although these reactions likely affect Hg speciation and cycling in the environment. In this study, we compared the reaction rates between  $\text{Hg}(0)_{\text{aq}}$  and a number of selected organic ligands with varying molecular structures and sulfur (S) oxidation states in dark, anoxic conditions to assess the role of these ligands in  $\text{Hg}(0)_{\text{aq}}$  oxidation. Significant  $\text{Hg}(0)_{\text{aq}}$  oxidation was observed with all thiols but not with ligands containing no S. Compounds with oxidized S (e.g., disulfide) exhibited little or no reactivity towards  $\text{Hg}(0)_{\text{aq}}$  either at pH 7. The rate and extent of  $\text{Hg}(0)_{\text{aq}}$  oxidation varied greatly depending on the chemical and structural properties of thiols, thiol/Hg ratios, and the presence or absence of electron acceptors. Smaller aliphatic thiols and higher thiol/Hg ratios resulted in higher  $\text{Hg}(0)_{\text{aq}}$  oxidation rates than larger aromatic thiols at lower thiol/Hg ratios. The addition of electron acceptors (e.g., humic acid) also led to substantially increased  $\text{Hg}(0)_{\text{aq}}$  oxidation. Our results suggest that thiol-induced oxidation of  $\text{Hg}(0)_{\text{aq}}$  is important under anoxic conditions and can affect Hg redox transformation and bioavailability for microbial methylation.

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