Bacterial reduction of both mercuric Hg(II) species and natural organic matter (NOM) occur in anoxic environments, but the coupling of these reactions and the fate of elemental Hg(0) are poorly understood.

This research shows that NOM plays a dual role in mercury chemistry: readily reduces Hg(II) to Hg(0), and strongly complexes with Hg. This results in an optimal production of volatile Hg(0) with increasing NOM levels.

A new mechanism of ligand-induced oxidative complexation is found to be responsible for Hg(0) oxidation and sequestration by NOM.

We conclude that redox conditions, the redox state of sulfur in NOM, and the NOM:Hg ratios are linked critical factors influencing Hg transformation and toxic methylmercury (CH₃Hg⁺) production.
Mercuric Hg(II) species form complexes with natural dissolved organic matter (DOM) such as humic acid (HA), and this binding is known to affect the chemical and biological transformation and cycling of mercury in aquatic environments. Dissolved elemental mercury, Hg(0), is also widely observed in sediments and water. However, reactions between Hg(0) and DOM have rarely been studied in anoxic environments. Here, under anoxic dark conditions we show strong interactions between reduced HA and Hg(0) through thiolate-ligand induced oxidative complexation with an estimated binding capacity of about 3.5 μmol Hg/g-HA and a partitioning coefficient greater than 10⁶ mL/g. We further demonstrate that Hg(II) can be effectively reduced to Hg(0) in the presence of as little as 0.2 mg/L reduced HA, whereas production of Hg(0) is inhibited by complexation as HA concentration increases. This dual role played by DOM in the reduction and complexation of mercury is likely widespread in anoxic sediments and water and can be expected to significantly influence the mercury species transformations and biological uptake that leads to the formation of toxic methylmercury.