Mercury redox cycling and species transformation affected by complex interactions with natural organic and thiolate compounds

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Mercury (Hg) redox cycling in anoxic environments directly links to the bioavailability of Hg by limiting available Hg(II) species for microbial uptake and mehtylation. However, factors that affect this process are poorly understood. Here we demonstrate that natural organic matter (NOM) and thiolate compounds play critical roles in Hg redox reactions in anoxic environments. We studied the kinetics of reduction and oxidation of Hg by using chemically reduced NOM (NOM_{re}), as well as a range of selected thiolate compounds with varying functional groups and redox state under dark, anaerobic conditions. We show that NOM_{re} simultaneously reduces and oxidizes Hg via different reaction mechanisms. Reduction of Hg(II) is governed by reduced quinones in NOM_{re}, whereas Hg(0) oxidation is primarily controlled by thiol-induced oxidative complexation. This mechanism is supported by the observation that Hg(0) is oxidized by low-molecular-weight thiol compounds, such as cysteine, 2-mercaptopropionic acid, and thiosalicylic acid. The oxidation rate was also found to vary with S oxidation state, substitutional functional groups (e.g. amine), thiol/Hg ratio, and pH. Similarly, depending on NOM oxidation state, NOM:Hg ratio, and the type of NOM, the initial Hg(II) reduction rates vary greatly from 0.4 to 5.5 h^{-1}, which is about 2 to 6 times higher than that observed for photochemical reduction of Hg(II) in open surface waters. However, rapid reduction of Hg(II) by NOM_{re} is offset by oxidation of Hg(0) with an estimated initial rate as high as 5.4 h^{-1}. This dual role of NOM_{re} in Hg redox transformation and the effect of thiol compounds on Hg(0) oxidation are expected to strongly influence the availability of reactive Hg and thus to have important implications for microbial uptake and methylation in anoxic environments.