Competitive Complexation of Mercury with Thiols from Natural Organic Matter and Bacterial Cell Envelopes

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Thiols are known to control the speciation and bioavailability of Hg by 1) providing high-affinity binding sites, 2) mediating redox transformations, and 3) controlling precipitation and colloidal formation. Natural organic matter (NOM) is considered the main sources of thiols in aquatic environments, and is believed to control the fate of Hg. Our studies have shown that bacterial cell envelopes are an additional source of thiols in aquatic and terrestrial systems. Complexation of Hg with thiols associated with NOM is similar to that of cell envelopes in many regards. The discovery of Hg-thiol binding on bacterial cell envelopes raises the question of the relative importance of NOM compared to cells in controlling the overall fate and transport of Hg. Using Suwanee River Fulvic acid (FA) as a proxy for NOM, we conducted Hg and S X-ray Absorption Spectroscopy (XAS) experiments to evaluate the chemical reactivity and stability of Hg complexed with NOM and bacterial cell envelopes.

Hg XANES and EXAFS spectroscopic results indicate that Hg binds predominantly to the high-affinity thiol groups on bacterial cell envelopes in the presence and absence of FA. Hg binding mechanisms with the bacterial biomass do not change in the presence of FA, ruling out the possibility of the formation of ternary complexes. Additionally, pH does not affect the binding mechanism of Hg onto biomass in the presence of FA. Hg XAS results suggest that thiols on *Shewanella oneidensis* MR-1 cell envelopes out-compete thiols in FA for Hg binding, and similarly S XANES results suggest that, on an average Hg binding to FA appears weaker than Hg binding to bacterial biomass. S XANES measurements of *S. oneidensis* MR-1 show that nearly the entire S budget of the biomass is present as reduced S groups, a fraction of which is known to form strong bonds with Hg. However, FA has a range of reduced and oxidized S species.

In summary, the speciation and distribution of Hg bound to NOM or bacteria is highly sensitive to their relative concentrations and to the specific make-up of thiol within each complexant. We have conducted further studies to understand the nature and behavior of Hg complexation with several NOM and DOM of varying age and composition. Our studies illustrate weakening of the binding strength of Hg complexation with DOM as a function of age, probably due to slow oxidation of thiols in DOM. Clearly, further studies are required to understand the reactivity and stability of Hg bound to NOM and bacterial thiol sites.