Biogeochemical controls on the molecular scale interactions of mercury with microbes

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Among the reactive functional groups within bacterial cell envelopes, carboxyl and phosphoryl groups are well established as important sites of metal binding under conditions resulting in high metal loadings. Complementary to previous studies, our studies have also shown the importance of thiol ligands (R-SH) as the primary bacterial cell envelope binding sites for Cd^{2+} and Hg^{2+} under conditions of low metal loading. Many metals are present in sub-micromolar concentrations in natural and contaminated systems, so bacterial cell envelope R-SH sites are likely to control the speciation, distribution, mobility, and bioavailability of chalcophile metals (e.g., Hg, Cd, Pb, and Zn) in aquatic systems by 1) providing high-affinity binding sites, 2) mediating redox transformations, and 3) controlling precipitation and mineralization of metals.

To test the redox immobilization of mercuric ions bound to bacterial cells, we determined the ability of magnetite, a mixed $Fe^{II/III}$ mineral phase, to reduce mercuric ions complexed with *Bacillus subtilis* cells. Our studies demonstrated that complexation of mercury by sulfhydryl groups on bacterial cells, typical at low Hg:biomass ratios, does not allow reduction of mercuric ions to elemental mercury by magnetite. While complexation of Hg^{2+} with sulfhydryl groups poses strong control on reduction of Hg^{2+} by magnetite, complexation of Hg^{2+} with carboxyl groups, commonly observed at high Hg:biomass ratios, have minimal (if any) effect on the rate and extent of the reduction of mercuric ions by magnetite.

In addition, we have examined the role of *Shewanella oneidensis* MR-1 cell envelopes in the nucleation and precipitation of colloidal phase mercuric-sulfide under sulfidogenic conditions. Similar to the role of thiols in natural organic matter, binding of Hg to the thiol groups on the cell envelope appears to act as a precursor to partitioning of mercuric ions between dissolved and particulate phase mercury, putting additional constrains on the size of the pool of bioavailable mercury.

Experimental details, specific results, as well as the environmental implications of the molecular scale processses described above will be discussed.