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ABSTRACT TITLE: Role of Sulfhydryl Sites on Bacterial Cell Walls in the Biosorption, Mobility and the Bioavailability of Mercury

ABSTRACT: Bacteria are ubiquitous in a wide-range of low temperature aqueous systems, and can strongly affect the distribution and transport of metals and radionuclides in the environment. However, the role of metal adsorption onto bacteria, via the reactive cell wall functional groups, has been largely overlooked. Previous macroscale metal sorption, and XAS studies have shown carboxyl and phosphoryl functional groups to be the important metal binding groups on bacterial cell envelops. However, our XAS studies have indicated that Hg^{2+} binds to sulfhydryl groups in preference to the more abundant carboxyl and phosphoryl groups on cell envelops when Hg concentration is submicromolar. The stoichiometry of these Hg-cysteine complexes on bacterial cell envelope changes as a function of the ratio of aqueous Hg concentration to bacterial cell density which has a significant impact on the solubility and bioavailability of Hg. The overall goal of our study is to provide a quantitative and mechanistic understanding of the impact of bacterial sulfhydryl groups on the uptake, speciation, transport and bioavailability of Hg in the environment.

We examined the speciation and stability of Hg complexes on the cell envelops of *Bacillus subtilis*, *Shewanella oneidensis* MR-1, and *Geobacter sulfurreducens* as a function of pH and aqueous Hg, in the presence and absence of organic (DOM) and inorganic (Cl^-) ligands. A novel technique using a fluophore was developed to characterize the concentration of reactive thiols on bacterial cell envelops. To complement fluorophore method, potentiometric titrations were performed after blocking the thiol sites. The estimated thiol density on the cell membranes of *B. subtilis* and *S. oneidensis* MR-1 obtained from these two different methods agrees well.

Hg XAS and UV-VIS luminescence spectroscopy studies indicate that Hg speciation is significantly different on methylating and non-methylating species. While the non-methylatig species (*S. oneidensis* MR-1 and *B. subtilis*) form the biologically unavailable HgS_3 (S= organic thiol) complex at low nanomolar Hg concentration, the methylating species *G. sulfurreducens* forms the bioavailable complexes HgS_2 (S = cysteine) at nanomolar Hg concentrations. Hg speciation on *G. sulfurreducens* was counter-intuitive because it exhibited HgS_2 complexes although it has far more reactive thiols on its cell envelope when compared to *S. oneidensis* MR-1. Transition from thiol to carboxyl binding occurred in the concentration range when all thiol sites on cell envelope were saturated.

We are currently exploring whether the presence of Hg induces thiol release onto the cell membranes or modify the redox behavior of reduced S-groups in the cell envelope, and the role of DOM on Hg interactions with different bacteria under different pH and DOM concentrations. We are also interested in understanding the ultimate fate of Hg complexed with cell envelope after cell turnover. Mercury is a common contaminant at several DOE sites, and our study provides important insights on the understanding of the bioavailaibilty, fate and transport of Hg at these sites.