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

University-Led Research

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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 that carboxyl and phosphoryl functional groups to be the important metal binding groups on bacterial cell walls. However, our preliminary XAS studies indicated that Hg^{2+} binds to sulfhydryl groups in preference to the more abundant carboxyl and phosphoryl groups on cell walls when Hg concentration is submicromolar. The stoichiometry of these Hg-cysteine bacterial cell wall complexes also change as a function of aqueous Hg concentration, and the structures of such complexes can have 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 sorption and structure of Hg complexes on the cell membranes of *Bacillus subtilis*, *Shewanella oneidensis*, and *Geobacter sulfurreducens* as a function of pH, and Hg and Cl^- concentration. The concentration of reactive thiols on cell membranes are also characterized using a newly developed fluorophore technique. Mercury adsorbs strongly, and exhibits similar sorption trends for all bacterial species; however, our XAS and fluorescence spectroscopy studies indicate that Hg speciation is significantly different on methylating and non-methylating organisms. In the case of *S. oneidensis*, Hg forms HgS_3 (S= organic thiol) complex at nanomolar Hg concentration, and HgS_2 and HgS (S = cysteine) with increasing Hg concentrations in the sub-micromolar range. Mercury binds to carboxyls with further increases in Hg concentration, and this transition occurred in the range of 20-25 □M of Hg per gram of cells. Our fluorescence spectroscopy studies indicate that the concentration of reactive thiols is also in the same range on cell membranes of *S. oneidensis*, indicating saturation of all available thiol sites by Hg before binding to carboxylates. Whereas *G. sulfurreducens* exhibit HgS_2 and HgS complexes although it has more reactive thiols on its cell envelope when compared to *S. oneidensis*. *G. sulfurreducens* may exhibit HgS_3 complexes at much lower Hg concentration range, which is difficult to access using XAS. The presence of Cl^- reduced Hg adsorption on cells significantly because of the formation of Hg-chloro aqueous complexes. The XAS studies indicate that the structure of the Hg surface complex on the cell membranes is not affected by the presence of Cl^-.

Our current studies are in progress- i) to evaluate the site density of thiols on cell envelope, and how they vary between different organisms under different environmental conditions, and ii) the role of DOM on Hg interactions with different bacteria under different pH and NOM concentrations. Mercury is a common contaminant at several DOE sites, and our study provides important clues on the understanding of the ultimate fate and biological toxicity of Hg at these sites.