Microbe-Metal Interactions: Novel High Energy-Resolution XANES Spectroscopy of Zn and Hg Complexes and Nanoparticles at Bacteria-Water Interfaces

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Microbes are known to play an important role in the speciation of redox sensitive species, and initiate the formation of polymeric metal complexes and nanoparticles at bacteria-water interfaces. The major challenge in these studies is with the detection of different coordination environments of metal-ligand complexes. However, structures of such complexes are difficult to probe directly with commonly available imaging and spectroscopy techniques because of the inaccessibility of metals at environmentally relevant concentrations and insesnsitivity to distingish different metal-ligand complexes. As shown in our study, a novel high energy-resolution fluorescence detection XANES spectroscopy (HERFD XANES) technique can provide clues on the structures of such metal complexes and nanoclusters.

Using HERFD XANES spectroscopy we examined the interactions of Zn and Hg with different bacterial species. Our studies showed that Zn forms Zn-sulfhydryl, phosphoryl and cabroxylate complexes with different bacterial species, and the relative abundances of Zn-complexes varied with Zn concentration, bacterial type and growth stages of the organism. In the case of Hg reactions, our studies focused on a Hg-methylating organism, *Geobacter sulfurereducens*. Studies with this organism showed that Hg forms primarily sulfhydyl complexes in environmentally relevant Hg concentration. However, Hg coordination with sulfhydryl/S groups changed as a function of external additions of cysteine. In association with these speciation changes, we found a significant increase in the production of methyl Hg with increases in S coordination to Hg. During cell lysis these metal ligand complexes can transform to form nanoparticles.

A discussion on how different bacterial Zn and Hg complexes can be studied using this novel technqiue at environmentally relevant metal concentrations will be presented. This technique offers clues to the detection of polynuclear metal complexes, which are precursors of metal nanoparticles are harder to study with reguar XANES and EXAFS spectroscopy methods.