ORNL SFA Task 4:
Molecular Scale Interactions and Transformations of Mercury in the Environment

ORNL SFA (Laboratory Research Manager: Liyuan Liang)

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As an integral part of the ORNL SFA, this Task investigates subcellular processes, including mechanisms of mercury-ligand interactions, mercury trafficking, and enzyme-catalyzed reactions involved in bacterial mercury resistance, dissimilatory reduction, and methylation.

Our initial focus has been on the biomolecular structure and function of key proteins and enzymes that confer mercury resistance in bacteria and impact mercury speciation and bioavailability in the environment. Expression of mercury resistance genes in the *mer* operon is controlled by the metalloregulator MerR (see poster by Johs et al.). A key component of the *mer* operon, the mercuric reductase MerA, catalyzes the reduction of Hg(II) to Hg(0). Using Neutron Spin-Echo spectroscopy, we are characterizing the interdomain dynamics of MerA at multi-nanosecond time scales. We have also crystallized the N-terminal domain of MerA, NmerA, and obtained X-ray diffraction data to a resolution of 3.25 Å. Solution of the 3D structure using molecular replacement is currently underway.

Understanding the interactions of mercury with various ligands is essential not only for characterizing abiotic reactions but also for complex biological systems. These interactions determine the speciation, biological transport and transformation of mercury in the environment. We have used quantum chemical calculations to carry out quantitative studies of the molecular factors that determine condensed-phase Hg speciation (see poster by Smith et al.). Hg(II) in complex with DOM is known to undergo photoreduction. Using substituted benzoic acids as models of DOM, quantum chemical calculations are being carried out to study photoexcitation of benzoic acids and subsequent photoreduction of Hg(II) upon UV irradiation.

Hg(II) reduction also occurs at low levels as a side reaction of dissimilatory iron reduction in iron-reducing bacteria such as *Shewanella* and *Geobacter*. Many have hypothesized that this reduction is carried out by outer-membrane multiheme cytochromes whose natural role is to transfer electrons to external Fe(III). We purified the decaheme outer-membrane cytochrome OmcA from *Shewanella oneidensis* MR-1 and collected X-ray diffraction data. Solution of the structure of OmcA is currently underway.

Future efforts of this SFA Task will combine biophysical experiments, structural bioinformatics and computer simulations to determine mechanisms of mercury transformations in biotic and abiotic systems.