ORNL SFA: Biogeochemical and Molecular Mechanisms Controlling Mercury Transformation in Contaminated Environments

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The ORNL Science Focus Area program aims at understanding coupled biogeochemical processes that affect net methylmercury (MeHg), because it is toxic and bio-accumulates in the food-web in ecosystems globally. In the last 12 months, we made significant progress in (1) setting up field sampling sites, (2) understanding role of natural dissolve organic matter (DOM) on mercury (Hg) complexation and redox transformation, (3) surveys of both bacteria and archaeal communities at sites and (4) determination of molecular mechanisms of Hg-ligand interaction and intra-molecular Hg handoff within enzymatic proteins. The SFA takes a systems approach, examining processes from the molecular scale to field scale to obtain a comprehensive understanding of key controls on Hg cycling in contaminated environments.

Field studies provide key information on major chemical species and processes involved in Hg biogeochemical transformations in water and sediment along a longitudinal transect of East Fork Poplar Creek (EFPC). We found that dissolved methylmercury concentration is positively correlated with the aromaticity and molecular weight of DOM. Preliminary results of vertical profiling of creek sediments and interstitial porewater may give the impression that the creek margin is the primary source of MeHg to the surface water of EFPC, other observations make this interpretation unclear (See accompanying poster by Brooks et al.).

Studies of the biogeochemical controls on rates and mechanisms of Hg speciation and bioavailability have revealed key roles played by DOM, including recent findings that DOM plays a dual role facilitating concentration dependent Hg(II) reduction and Hg(0) oxidation (Gu et al., 2011). We show that the redox states of sulfur in DOM and the DOM:Hg ratio critically influence the transformation of Hg, and thereby the potential microbial production of toxic MeHg. In addition, small ligands, functional groups and their steric arrangements on aromatic compounds are found to be important factors influencing not only mercury microbial uptake (see accompany poster by Schaefer et al.), but also photo-chemical redox transformation (see accompany poster by Gu et al.).

Using 454 16S rDNA pyrosequencing, we found that archaeal communities have a significant increase in community diversity in MeHg vs Hg(II) at contaminated areas (Porat et al., 2010). The bacterial community structure and diversity were strongly influenced by Hg(II), MeHg, and U(VI) (Vishnivetskaya et al., 2011) with *deltaproteobacteria* and sulfate-reducers strong trending towards Hg(II) and MeHg, particularly for those closely related to *Desulfobulbus propionicus* (See accompany poster by Moberly et al.). In pure culture studies, the genome of the known methylating bacteria, *Desulfovibrio desulfuricans* ND132 was sequenced (Brown et al., 2011), and is being used to elucidate the genes responsible for Hg methylation (See accompany poster by Hurt et al.). We have created a random Tn5 transposon mutant library with established assays. So far we obtained 3070 constructs, of which 905 have been assayed, with 45 possibly decreased in methylation. A second generation FGA is being tested for quantification of all *mer* genes. Duplicate meta -genomes, -transcriptomes, and -proteomes from the field are being done to

examine the structural and functional differences of these sites and comprehensively understand methylation and demethylation at this site.

Studies at the molecular level aim to unravel mechanisms of bacterial mercury resistance and interactions of Hg with organic ligands in the environment. Combining small-angle X-ray scattering (SAXS), and molecular dynamics (MD) simulations we found that a single Hg ion can trigger a structural change in MerR. This change is propagated to its operator DNA, causing an underwinding of the double helix which leads to transcription of mer genes by RNA polymerase (Guo et al., 2010). The multiheme protein OmcA is known to be involved in dissimilatory electron transfer to mineral surfaces. Results from neutron reflectometry studies suggest that OmcA attaches to hematite with a preferred orientation that maximizes interaction with the mineral. In addition, SAXS data show that the molecular shape of OmcA changes in the conformation depending on the redox states of OmcA (Johs et al., 2010). SAXS and MD are also used to study the handover of Hg(II) from the N-terminal domain to the catalytic domain of the mercuric reductase, MerA (See accompanying poster by Johs et al). Progress on Hg-ligand complexation calculations and protein solubility optimization for x-ray crystallization of MerR are described in the accompanying poster by Parks et al.

The SFA program as a whole has produced 23 peer reviewed journal publications, of which 15 are on Hg biogeochemistry. There are ~50 conference abstracts, presentations, and invited talks. The SFA team organized two special sessions on “Biogeochemical Controls on Mercury Transformation and Global Cycling” at the Goldschmidt Conference in June 2010, Knoxville TN. The SFA will be hosting a special session on “Mechanisms of microbial mercury methylation and resistance” the ICMGP 2011, which will be held July 24-29, 2011 at Halifax, Nova Scotia, Canada.