**Biogeochemical and Molecular Mechanisms Controlling Contaminant Transformation in the Environment**

Oak Ridge National Laboratory Science Focus Area Program

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Mercury (Hg) is a pervasive and highly toxic global pollutant that, in the methylated monomethyl mercury (MeHg), bioaccumulates in the food web, endangering humans and other organisms. The biogeochemical mechanisms controlling MeHg production at contaminated sites present serious knowledge gaps globally, nationally and locally, as at the Oak Ridge Reservation (ORR). The SFA program aims to elucidate fundamental mechanisms governing mercury transformation and behavior in the environment. Its goal is to provide new understanding to facilitate long-term, targeted strategies to significantly mitigate the adverse impacts of mercury at ORR and around the world.

This SFA Program was initiated 3 years ago to provide focus to a diverse portfolio of environmental biogeochemical research. Since its inception in FY 2009, significant progress has been made in addressing the original knowledge gaps. A total of 42 peer-reviewed articles were published in the first phase of the SFA. Of these, 27 result from the new mercury research, and an additional 73 presentations and abstracts exclusively represent our Hg focused study. We presented 5 television, press, and radio interviews and releases, and participated in numerous national and international scientific conferences, often in leadership and planning roles. The SFA program website provides updated information on published work: http://www.esd.ornl.gov/programs/rsfa/index.shtml.

Key areas of progress include: 1. Establishing field research sites at ORR's East Fork Poplar Creek (EFPC) watershed and initiating collection of geochemical and microbial data. 2. Recognition that dissolved organic matter (DOM) dominates Hg speciation and redox/ photochemical reactions, and that DOM exhibits a dual concentration-dependent role in Hg redox chemistry. 3. Demonstrating differences in microbial community structure between Hg-impacted and unimpacted sites, and that *Desulfobulbus* and *Geobacter* spp. dominate at methylating sites. Genomic sequences have been obtained for known Hg-methylators. Hg uptake was shown to be an energy- and thiol-dependent process in *G. sulfurreducens*, but less so in *Dv. desulfuricans* sp. ND132. 4. Construction of a computational framework for understanding subcellular mercury processes. The roles of Hg-thiol interactions and protein dynamics were determined in Hg resistance proteins, including for MerB in demethylation by Hg-C cleavage, MerR in switching on Hg resistance, and MerA in $Hg^{2+}$ reduction. Structural characterization was accomplished for outer membrane proteins of potential importance in microbial Hg reduction.

In the coming summer this SFA will be under the DOE peer-review. In the Renewal Proposal we aim to resolve important new questions revealed by our research, concerning: (1) Exact sites of MeHg production in EFPC, (2) Mechanisms and geochemical controls on Hg and MeHg species transformation and Hg reactivity that lead to its uptake and methylation, (3) Microbial populations at EFPC that participate in Hg methylation and MeHg demethylation, (4) Microbial biochemical pathways, enzymatic mechanisms and genetic controls for Hg methylation and resistance. We therefore propose to continue to our goal of ***elucidating the mechanisms by which inorganic Hg is transformed into MeHg at the sediment-water interface, and in particular the processes that determine net MeHg production at contaminated sites,*** by accomplishing the following objectives: I: Examining site biogeochemical processes of the EFPC watershed and identifying key methylation source areas; II: Investigating key mechanisms and geochemical controls on Hg and MeHg species transformation and Hg reactivity leading to its uptake and methylation; III: Identifying microbial species and their biochemical pathways responsible for biological methylation and demethylation; IV: Understanding biogeochemical transformations within and outside microbial cells using structural biology and computational chemistry.

A multidisciplinary systems science approach will be employed to integrate geochemistry, microbiology, molecular biology and molecular simulations to elucidate mercury behavior over multiple scales. In collaboration with other SBR investigators, we are confident that the results of the SFA can make important fundamental progress toward essential goals of assessing and mitigating the effects of mercury at DOE complexes and other contaminated sites both nationally and globally.