Research and Technology Development Activities to Address the DOE-EM Environmental Mercury Challenge – 17497

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ABSTRACT

Human activities have altered trace metal distributions globally. This is especially true for the trace metal mercury (Hg), a pervasive global pollutant that can be methylated to form highly toxic methylmercury (MeHg), which bioaccumulates in aquatic food webs, endangering humans and other biota. Currently there are more than 3,000 mercury-contaminated sites identified worldwide and the United Nations Environment Programme has recently highlighted the risk of this contamination to human health [1, 2]. The Oak Ridge Reservation (ORR) represents an example of one of these mercury-contaminated sites.

Unlike other contaminants—metals, radionuclides, and organic solvents—that impact the Department of Energy Office of Environmental Management (DOE-EM) cleanup program at the ORR and other DOE sites, mercury has several unique characteristics that make environmental remediation of the Y-12 National Security Complex one of the most formidable challenges ever encountered. These distinctive physicochemical properties for mercury include the following: it is a liquid at ambient temperature and pressure; it is the only metal that biomagnifies; and it is the only contaminant transported as a cation, as a dissolved or gaseous elemental metal (similar to an organic solvent), or as both a cation and a dissolved or gaseous elemental metal under environmental conditions. Because of these complexities, implementing cost effective and sustainable solutions that reduce mercury flux from various primary and secondary contamination sources will require linking basic science understanding and applied research advancements into Oak Ridge Office of Environmental Management's (OREM) cleanup process. Currently, DOE is investing in mercury-related research through a variety of programs, including the Office of Science–sponsored Critical Interfaces Science Focus Area, EM headquarters–sponsored Applied Field Research Initiative, OREM-sponsored Lower East Fork Poplar Creek (LEFPC) Mercury Technology Development Program, Small Business Innovative Research (SBIR), and EM's Minority Serving Institutions Partnership Program. Collectively, these multi-institutional and multidisciplinary programs are generating new tools, knowledge, and remediation approaches that will enable efficient cleanup of mercury contaminated systems locally and globally. In this talk we will highlight the progress made to date in addressing key knowledge gaps required to solve this watershed-scale conundrum.

INTRODUCTION

Over the next three decades, the Department of Energy Office of Environmental Management (DOE-EM) will focus on reducing the flux of mercury contamination that exits the Y-12 National Security Complex (Y-12 NSC). The DOE-EM, Tennessee Department of Environment and Conservation, and US Environmental Protection Agency (EPA) have identified mercury contamination within and released from the Y-12 NSC as the highest priority cleanup risk on the Oak Ridge Reservation (ORR) [3–5]. Unlike other contaminants—metals, radionuclides, and organic solvents—that impact the DOE-EM cleanup program at the ORR and other DOE sites, mercury has several unique characteristics that make environmental remediation of the Y-12 NSC one of the most complex efforts ever encountered. These distinctive physicochemical properties for mercury include: it is a liquid at ambient temperature and pressure; it is the only metal that biomagnifies; and it is the only contaminant that is transported as a cation, as a dissolved or gaseous elemental metal (similar to an organic solvent), or as both a cation and a dissolved or gaseous elemental metal under environmental conditions. Most importantly, mercury also undergoes biogeochemical transformation processes, which include aqueous and surface complexation, redox reactions, and atypical methylation reactions, producing the potent neurotoxin methylmercury (MeHg) [6, 7]. Each of the aforementioned distinctive characteristics for mercury are observed within this complex and dynamic watershed-scale system, which includes the Y-12 NSC plant boundary and 23 km of contaminated creek and floodplain downstream.

Releases of mercury at the Y-12 NSC during the 1950s and early 1960s contaminated four former mercury use facilities—representing 1.5 million square feet—as well as the soil, sediment, surface water, and groundwater within the plant boundary. Further, the subsequent migration of mercury contamination from the source areas via atmospheric deposition, sediment transport, surface water runoff, and groundwater transport contaminated the East Fork Poplar Creek (EFPC) ecosystem. Despite various on-site abatement and remedial actions to reduce mercury releases over the last 25 years, mercury concentrations in water at the Y-12 plant boundary continue to exceed both the regulatory limit (51 ng/L) and the remediation goal (200 µg/L) [8]. Although aqueous mercury concentrations and fluxes have been reduced over the past 25 years, commensurate reductions in fish tissue concentrations (to achieve the EPA criteria of 0.3 µg/g) have not been observed [9]. The current estimated mercury cleanup cost ranges from $1 billion to $3 billion.

Implementing cost effective and sustainable solutions that will reduce mercury flux from various primary and secondary contamination sources will require linking basic science understanding with applied research advancements in the DOE-EM cleanup process. Various DOE offices that span the innovation pipeline—from fundamental research to technology development—are currently making investments; this includes the Office of Science–sponsored Critical Interfaces Science Focus Area, EM headquarters–sponsored Mercury Applied Field Research Initiative, the Oak Ridge Office of Environmental Management's (OREM) LEFPC Technology Development Program, SBIR, and EM's Minority Serving Institution Partnership Program (MSIPP). Provided below is a brief synopsis of the activities being performed across each of the aforementioned programs and how these activities collectively seek to close key scientific and technical gaps.

Description of Critical Interfaces Science Focus Area (CI-SFA)

Since its inception in 2010, the Critical Interfaces Science Focus Area (CI-SFA) led by Oak Ridge National Laboratory (ORNL) has made a number of groundbreaking insights and discoveries, including the discovery of the mercury methylation genes (*hgcAB*), their organismal and environmental distribution, and the development of molecular probes to determine methylation potential in environmental systems [10–12]. In parallel, field-relevant geochemical and microbial data established that dissolved organic matter dominates aqueous mercury speciation in East Fork Poplar Creek (EFPC) [13, 14], and that both iron- and sulfate-reducing bacteria are prevalent in the system [15–17].

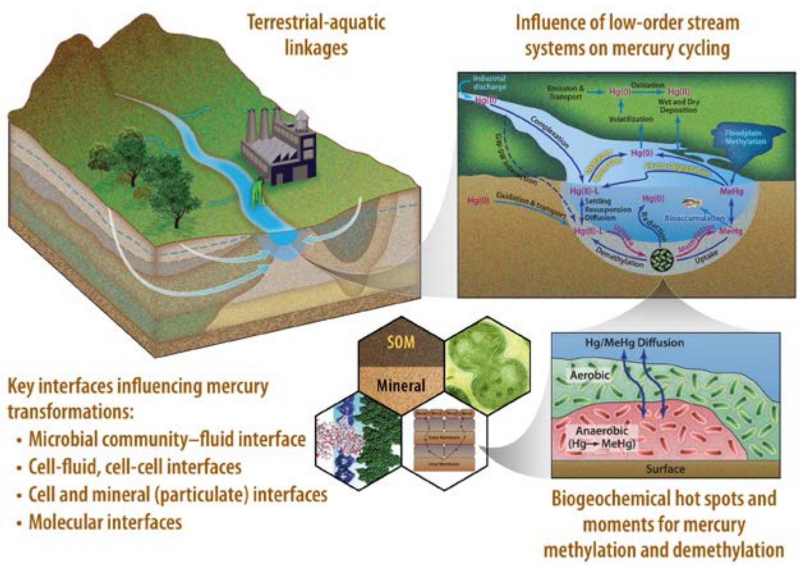

Fig. 1. Key biogeochemical interfaces.

The next phase of the program seeks to advance a predictive understanding of mercury transport and fate in streams, such as EFPC, by deciphering complex processes (i.e., physical, chemical, and biological), deconvoluting how these processes interact with one another, and understanding the factors that control system response over broad spatio-temporal scales.

Exchange and feedback processes at critical interfaces are central for determining fluxes, stocks, and transformation rates of key constituents, such as oxygen, nutrients, and dissolved organic matter that control mercury speciation, distribution, and bioavailability (Fig. 1). Therefore, over the next 3 years, the ORNL CI-SFA program will focus on determining the fundamental mechanisms and environmental factors that control mercury biogeochemical transformations at key interfaces in terrestrial and aquatic ecosystems.

The research outline in CI-SFA plan comprises collaborative and complementary research activities that support four research thrusts: (1) ecosystem features; (2) biogeochemical mechanisms; (3) microbial community functions and geochemical influences; and (4) molecular structure, dynamics, and mechanisms. For additional details visit the CI-SFA website at http://www.esd.ornl.gov/programs/rsfa/.

Remediation of Mercury and Industrial Contaminants Applied Field Research Initiative (ROMIC-AFRI)

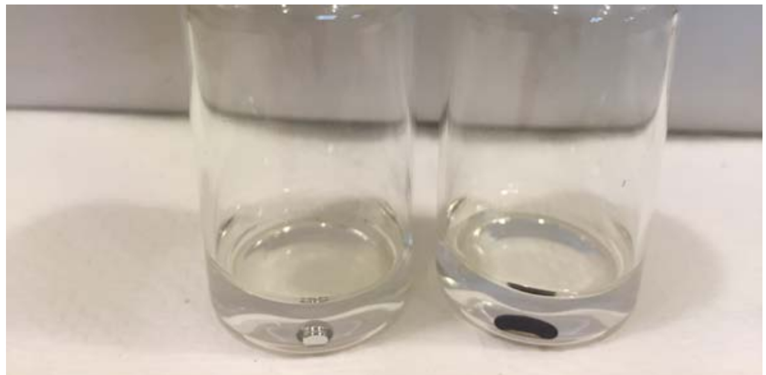

Fig. 2. Unreacted elemental mercury in deionized water (*left*) and elemental mercury reacted with a sulfide solution (*right*). Reacted sample shows evidence of a black coating of metacinnabar on the silver element mercury bead after 19 hours of reaction.

The objective of Remediation of Mercury and Industrial Contaminants Applied Field Research Initiative (ROMIC-AFRI) is to develop a systems-based approach to control the flux of contaminants in soil and water to protect surface water, groundwater, and ecological receptors from extensive, recalcitrant, and decades-old contamination at Oak Ridge and other DOE sites. Over the past 3 years, ROMIC-AFRI accomplishments included:

- quantifying mercury concentrations and speciation in contaminated sediments [18];
- designing rapid, field-deployable tools for locating diffuse, shallow elemental mercury source zones [19];
- determining the speciation of aged elemental mercury in contaminated soil samples [20];
- refining the estimates of mercury speciation, flux, and transport from storm drains and four outfalls (Outfalls 150, 160, 163, and 169) under base flow and storm flow conditions; and
- evaluating commercially available and novel adsorbent media for water treatment [21–23].

Recent activities by ROMIC-AFRI are focused on designing new novel in situ chemical treatment approaches to remediate source zone mercury contamination within the Y-12 NSC. Because of the localized distribution of mercury contamination in the soil and sediment underneath Y-12 NSC, the traditional “dig and haul” approach to remediation will be extremely expensive. Additionally, access to contamination zones may be limited, and the cost of treatment and disposal of mercury wastes poses significant risk to DOE-EM. To address this risk, ROMIC-AFRI conducted a broad literature survey of promising mercury treatment technologies [24] and focused their efforts based on these results on chemical treatment using engineered polysulfide. This approach relies on the hydrolysis process of polysulfide to control sulfur release and react with mercury in the subsurface, which converts aged elemental mercury beads to a more stable form of mercury (e.g., cinnabar or metacinnabar) (Fig. 2). Laboratory-scale experiments were initiated on pure elemental mercury and aged mercury beads, and these tests will be scaled up in the coming years.

Lower East Fork Poplar Creek (LEFPC) Technology Development Program

The objective of the OREM-sponsored LEFPC Technology Development Program is to conduct targeted field and laboratory scale studies to identify promising approaches that decrease the primary regulatory concerns in the LEFPC: mercury flux, concentration, and bioaccumulation [25]. This project consists of three areas of thrust:

- **Soil and groundwater source control** seeks to reduce mercury flux by identifying and treating residual mercury sources to the EFPC (i.e., floodplain soils, bank soils, and groundwater).
- **Sediment and water chemistry manipulation** seeks to manipulate in-stream processes, including water and sediment chemistry, to reduce the dissolved mercury available for methylation.
- **Ecological manipulation** seeks to decrease the mercury concentration in fish through food chain manipulation at both the lower and higher trophic levels.

Although in its infancy, the LEFPC Technology Development Program has made significant progress in characterizing key legacy mercury sources and their influence on mercury flux in the downstream system. A key research finding is the importance of storm flow on mercury loading from mercury contaminated bank soils, especially in the upper end of the creek. Laboratory studies are underway to evaluate the potential for new sorbent technologies that might limit mercury flux from bank soils and sediments. New gauging studies have highlighted the importance of flow and instream chemistry on total mercury and MeHg concentrations. Finally, MeHg concentrations were measured for the first time in some trophic levels, providing insight about how changes in the food chain may reduce risks from fish ingestion. Understanding mercury transport, methylation, and bioaccumulation processes in the EFPC system is essential to the development of new cleanup technologies and ultimately to the development of remedial options and watershed management strategies.

DOE-EM's Minority Serving Institutions Partnership Program (MSIPP) and Small Business Innovation Research Program (SBIR)

Recent investments by DOE-EM in two programs, MSIPP and SBIR, have provided a unique opportunity to partner with outside institutions to develop technology. These institutions include Alabama State University in Montgomery, Alabama, the Army Corp of Engineers Environmental Research and Development Center (ERDC) in Vicksburg, Mississippi, InnoSense LLC, Jackson State University in Jackson, Mississippi, New Mexico State University in Las Cruces, New Mexico, and Troy University in Troy, Alabama. In collaboration with ORNL, each of the MSIPP and SBIR partner institutions continues to make targeted contributions to the development of sustainable remedial strategies for the Y-12 NSC and the 23-km downstream environment.

SUMMARY

DOE's successful implementation of sustainable cleanup solutions requires bridging the gap between basic science, "needs driven" applied research, and technology development. The need to bridge this gap has never been more evident than in the case of legacy mercury contamination at the Y-12 NSC. The chemical uniqueness, complexity, and dynamic environmental behavior of legacy mercury, as well as the watershed-scale hydro-geochemical processes that affect mercury fate and transport, are all factors affecting successful cleanup. Collectively, these multi-institutional and multidisiplinary programs are generating new tools, knowledge, and remediation approaches that will enable efficient cleanup of one of the most pressing environmental challenges facing the DOE, the United States, the state of Tennessee, and the city of Oak Ridge: remediating mercury contamination on the ORR.

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