# Legacy Mercury: A Watershed Scale Cleanup Challenge – 15559

Eric Pierce, DB Watson, T Mathews, and MJ Peterson
Oak Ridge National Laboratory

## ABSTRACT

Over the next three decades, the US Department of Energy (DOE) Oak Ridge Office of Environmental Management (OREM) will focus on reducing the flux of mercury contamination that exits at the Y-12 National Security Complex (Y-12 NSC) [1, 2]. OREM, Tennessee Department of Environment and Conservation (TDEC), 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). Furthermore, mercury contamination is a worldwide issue with more than 3,000 mercury-contaminated sites currently identified [3], and the United Nations Environment Programme has recently highlighted the risk of this contamination to human health [4].

Unlike other contaminants—metals, radionuclides, and organic solvents—that impact the DOE 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 NSC one of the most complex efforts ever encountered. These distinctive physicochemical properties for mercury include the following: it is a dense non-aqueous liquid at ambient-temperature-pressure; it is the only metal that biomagnifies; and it is the only contaminant transported as both a cation and/or a dissolved or gaseous elemental metal (similar to an organic solvent) 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 [5, 6]. Each of the aforementioned distinctive characteristics for mercury is observed within this heterogeneous and dynamic watershed-scale system—which includes the Y-12 NSC boundary and 23 km of contaminated creek and floodplain downstream. Because of these complexities, implementing cost effective and sustainable solutions that reduce mercury flux from various primary and secondary contamination sources will require the linking of basic science understanding and applied research advancements into OREM’s cleanup process. In 2009, the DOE-EM Office of Site Restoration’s Soil and Groundwater Remediation Program and Oak Ridge National Laboratory (ORNL) initiated an applied field research initiative with the goal of developing a systems-based approach to control mercury flux in soil and water to protect surface water, groundwater, and ecological receptors. The Remediation of Mercury and Industrial Contaminants Applied Field Research Initiative (ROMIC-AFRI) represents the vehicle that enables the linking of science to remedial applications. Here we discuss the progress made to date in addressing key applied research and technology development needs to address this watershed scale conundrum.

## HISTORY OF MERCURY IN OAK RIDGE

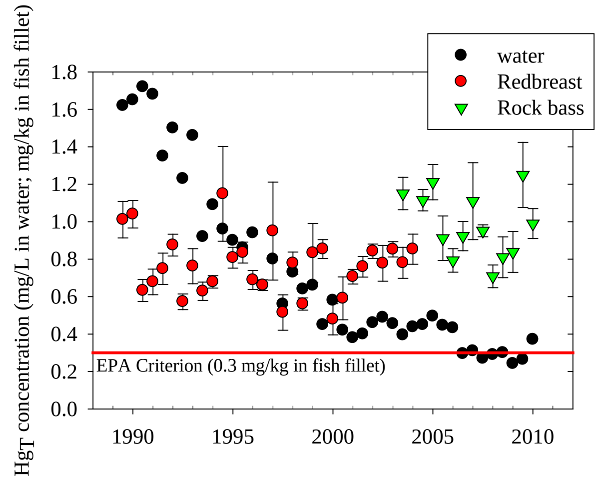


**Figure 1.** Historic mercury loading to Upper East Fork Poplar Creek.

Releases of mercury at the Y-12 NSC during the 1950s and early 1960s contaminated four large and multiple smaller former mercury use facilities—representing more than 1.5 million square feet—as well as the soil, sediment, surface water, and groundwater within the Y-12 NSC boundary. Furthermore, 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 remedial actions to reduce mercury releases over the last 25 years, mercury concentrations in water at the Y-12 NSC boundary continue to exceed both the regulatory limit (51 ng/L) and the remediation goal (200 µg/L) [7]. Although aqueous mercury concentrations and fluxes have been reduced over the past 25 years, commensurate reductions in fish tissue concentrations (to achieve the EPA criterion of 0.3 mg/kg) have not been observed (Figure 1) [8].

## DESCRIPTION OF ROMIC-AFRI

The objective of 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. Because OREM, TDEC, and EPA have identified mercury as a high-risk problem on the ORR, it has been the major focus of this project for the past several years. Remediation of mercury within the Y-12 NSC and the EFPC ecosystem poses a long-term cleanup challenge for DOE-EM. A number of previous efforts and reviews have identified applied research and technology development needs relevant to the mercury cleanup challenge. The focus areas of activity for ROMIC-AFRI are Nature and Extent, Remediation and Treatment, and Monitoring and Predictive Modeling. They are based on the needs identified in the document "*Conceptual Model of Primary Mercury Sources, Transport Pathways, and Flux at the Y-12 Complex and Upper East Fork Poplar Creek, Oak Ridge, Tennessee*" [8] and more recently on the OREM strategy for mercury remediation [1,2]. The ROMIC-AFRI activities are focused on addressing the watershed scale mercury challenge in two specific areas—West End Mercury Area (WEMA) and Upper East Fork Poplar Creek (UEFPC). An overview of the activities conducted by ROMIC-AFRI in support of enabling successful and efficient mercury remediation is provided below.

### Refining the Site Conceptual Model for WEMA Operable Units

The mercury use facilities located in WEMA contain unknown but significant quantities of elemental mercury that have soaked into concrete floor slabs and masonry walls and have leaked into the environmental media (i.e., water, soil, storm drains and sediment) surrounding these facilities. Reducing the volume of mercury contaminated media (e.g., rubble/debris and soil/sediment) represents a major challenge that affects the risk and cost of mercury cleanup at the Y-12 NSC. Another uncertainty affecting remediation of this region is mercury speciation and the flux of mercury that is transported via a combination of facility infrastructure (e.g., pipes) and shallow groundwater. ROMIC-AFRI activities focused on furthering WEMA area remediation include:

- **Accurately Quantifying Mercury Concentrations and Speciation in Contaminated Sediments:** A variety of field deployable analytical techniques have been tested and approved for use by the EPA to field screen soil samples for mercury contamination. The field-deployable x-ray fluorescence (XRF) instrument is one of the recommended techniques [9]. ROMIC-AFRI characterized hundreds of soil samples collected from various locations around mercury use facilities and compared XRF results to other, more laboratory-based measurement techniques, such as mercury vapor headspace analyses and acid digestion coupled with cold vapor atomic absorption. These results illustrate that sample heterogeneity has a significant influence on the XRF measured mercury concentration, suggesting this technique is not an accurate option for quickly screening mercury contaminated soils in the field. Additionally, sequential extractions and headspace analysis were performed on mercury-contaminated sediments to determine the dominant chemical form. Combining these results provides the technical basis for selecting the correct approach for mapping mercury contamination and selecting appropriate and effective remedial options.
- **Refining the Estimates of Contaminated Waste Volumes:** ROMIC-AFRI focused a portion of its efforts on using a novel soil gas measurement technique developed at ORNL to identify and map elemental mercury contamination surrounding the Alpha 2, mercury retort (81-10), Engineering (9733) and Alpha 4 buildings [10]. These results are being used to refine the estimates of the volume of contaminated soil that will require special handling and treatment. This quick screening information allows the application of an adaptive management approach when statistically designing data quality objectives, which require laboratory-based confirmatory measurements by providing information on the extent and magnitude of the areas with mercury contamination.
- **Speciation of Mercury in Contaminated Environmental Media:** Elemental mercury is present in soils and storm drains as well as under and within buildings at Y-12. The mobility of mercury from soils and buildings into surface water and groundwater is highly dependent on the speciation and reactivity of the mercury that has been released to the environment [11]. Additionally, the effectiveness of remedial treatment technologies will vary with the chemical form of mercury. To address this uncertainty and aid in the design of efficient remedial approaches, ROMIC-AFRI has been conducting first-of-a-kind studies by characterizing the speciation, chemical composition, and reactivity of elemental mercury that has been released to the environment and exposed to various media types. One significant finding is that elemental mercury beads exposed to Mn oxides were found to develop soluble mercury oxide coatings that may enhance the release and migration of mercury in the environment [11]. These results are supporting the lab-scale evaluations of chemical and thermal remedial treatment approaches and provide technical basis for the selection of a final remedy.
- **Refining the Estimates of Mercury Speciation, Flux, and Transport in Subsurface Infrastructure:** Determining the speciation, flux, and transport of mercury from WEMA storm drains and the associated outfalls is a key component for addressing the mercury flux to the headwaters of UEFPC. In conjunction with URS | CH2M Oak Ridge LLC, ROMIC-AFRI focused on integrating existing data contained in the Oak Ridge Environmental Information System database on the concentration of mercury in groundwater, surface water, and storm drains with

supplemental measurements to determine the speciation and flux of mercury from WEMA storm drains and four outfalls (Outfalls 150, 160, 163, and 169) under base flow and storm flow conditions. These results provide a portion of the data needed to model mercury flux under base flow and storm flow conditions, aid in sequencing WEMA deactivation and decommissioning activities by determining the area contributing the largest mercury flux, and assist in evaluating the impact of flow dynamics on mercury speciation and flux at the UEFPC headwaters.

- **Evaluation of Commercially Available and Novel Adsorbent Media for Mercury Treatment.** One of the primary efforts in 2010–11 was the evaluation of both commercially available (i.e., Dow 43604, Forager M-TU, granular activated carbon (GAC), GT-74, Keyle:X, SAMMS, and SIR-200,) and novel (i.e., KMS-1 and Zn-doped biomagnetite) adsorbent media with the ability to remove mercury from short sections of storm drains in the WEMA (Table 1) [12, 13]. Based on a 2009 survey, sections of the storm drain system that appear to contribute the most significant fluxes of mercury to Outfall 200 were identified. Therefore, equipping each of these sections with a mercury removal system containing adsorbent media could reduce the overall concentration of mercury being released at Outfall 200. These results were incorporated into the planning for the proposed Outfall 200 mercury treatment system.

**Table 1.** Properties of Selected Mercury Sorbents

| Sorbent name | Manufacturer | Nominal Particle Size | Matrix | Active sites |
|---|---|---|---|---|
| GT-74 | Rohm and Haas | 0.45–0.70 mm | Styrene-DVB Macroporous | Thiol |
| SIR-200 | ResinTech | 0.3–1.0 mm | Styrene-DVB Macroporous | Thiol |
| Dow 43604 | Dow | 0.4–0.72 mm | Styrene-DVB Macroporous | Thiol |
| Keyle:X | SolmeteX | 0.6–0.8 mm | Polyacrylate | Thiol |
| Forager M-TU | Dynaphore | 12.7 mm | Polymer | Dithiocarbamate |
| SAMMS | Steward | - | Silica | Thiol |
| Zn-Doped Biomagnetite | Oak Ridge National Laboratory | 17 nm | Iron Oxide | Thiol |
| KMS-1 | Northwestern University | 0.005 mm | K2xMnxSn3-xS6 | Sulfide |
| GAC | Calgon | 0.8–1.0 mm | Carbon | Activated Carbon |

### Refining the Site Conceptual Model for UEFPC Operable Units

Although a series of interim cleanup actions from 1985 to present resulted in improvements to EFPC water quality—specifically decreasing aqueous mercury concentrations—the concentration of mercury in fish tissue has not decreased proportionally to meet the EPA regulatory endpoint and, in some cases, has increased over time. Terrestrial ecosystems such as EFPC are typically slow to respond to changes in mercury loading rates. For example, in a forested catchment site 10 years after a manipulation that limited atmospheric mercury and methylmercury deposition onto a watershed, there was no decrease in mercury or methylmercury export from the watershed and no indication that the soil mercury pool was being depleted [14]. At a boreal forest ecosystem, it took several years of elevated mercury applications to uplands and wetlands before the applied mercury was observed in runoff [15]. Mercury that accumulates in floodplain soils and creek banks constitutes a large pool of residual contamination that may be released gradually over long periods. The newly released mercury may be more readily available for microbial-mediated methylation (the bioaccumulated form of mercury) in soils or transported to methylation sites in the creek. These processes can maintain elevated fish mercury levels masking water quality improvements; therefore, increasing the understanding of these processes and the effect of specific sources on mercury transformation will allow for upstream cleanup activities to be realized in fish tissue. ROMIC-AFRI activities focused on furthering UEFPC area remediation include:

- **Conduct Controlled Laboratory Studies to Evaluate the Relative Importance of Mercury Sources to UEFPC and lower EFPC:** Fiscal year (FY) 2013 efforts continued a series of batch tests examining mercury leachability, methylation, and bioaccumulation characteristics of mercury sources, including floodplain soil, stream sediments, and bank soils. Future experiments will use stream mesocosms to examine the relative importance of legacy (sediment-bound) vs. "new" (aqueous) mercury sources in contributing to methylmercury production are being planned. Results have implications for the development of effective technologies and site remediation prioritization.

- **Evaluating the Importance of Water Chemistry in Controlling Mercury Bioaccumulation:** In many ORR streams, fish tissue mercury concentrations are elevated despite a wide range in aqueous water concentrations. Previous work completed for this task has shown that the relationship between aqueous total mercury and mercury concentrations in fish is not linear [16]. Subsequent controlled laboratory experiments will examine inorganic mercury and methylmercury bioavailability and bioaccumulation in simplified aquatic food chains using the radiotracers $^{203}Hg$ and $Me^{203}Hg$ in water collected from different ORR streams.

- **Evaluate potential stream responses to proposed mercury remedial actions.** The primary effort in FY 2013 was to evaluate mercury and tin responses to a stannous chloride treatment system at the Savannah River Site. Work has been completed and a manuscript that summarizes the findings has been submitted [17]. Results will be useful in evaluating the potential for application of a similar treatment system in Oak Ridge. This work was conducted in collaboration with Savannah River National Laboratory and Savannah River Ecology Laboratory.

### Adapting Existing and Designing New Novel In Situ Treatment Approaches for Mercury Remediation

Because of the heterogeneous distribution of mercury contamination in the soil and sediment underneath the Y-12 NSC, the traditional "dig and haul" approach to remediation will be extremely expensive and has the potential for releasing significant mass of mercury to the environment during and after excavation activities. Additionally, access to contamination zones may be limited due to site infrastructure, and the cost of treatment and disposal of mercury wastes poses significant risk. To address this risk, ROMIC-AFRI conducted a broad literature survey of promising mercury treatment technologies. In addition to the literature review, research activities have focused on laboratory-scale experiments to evaluate the effectiveness of two plausible treatment options identified during the literature review, thermal and chemical treatment amendments. Thermal treatment, which is being conducted in conjunction with Khlopin Radium Institute under the DOE-EM international program, has focused on the use of a novel microwave heating approach that requires less energy in comparison with the baseline technology—vacuum assisted vapor desorption. Chemical treatment has been focused on a previously attempted remediation strategy, engineered polysulfide. The polysulfide approach relies on the hydrolysis process of polysulfide to control sulfur release and react with mercury in the subsurface to convert elemental mercury to a more stable less mobile and toxic form of mercury (e.g., cinnabar or meta-cinnabar). Laboratory scale experiments were initiated on pure elemental mercury and aged mercury beads, and these tests will be scaled up in the coming years.

## SUMMARY

The DOE-EM Office of Soil and Groundwater-sponsored and ORNL-led ROMIC-AFRI has been conducting applied research and technology development activities to address the legacy mercury issue on the ORR. These efforts have result in the development of new and innovative approaches including (1) new mercury detection methods; (2) a more detailed understanding of elemental mercury distribution, speciation, and transformation in subsurface sediments; (3) evaluation of sorbent materials for the removal of waterborne mercury; and (4) an evaluation of thermal (microwave based) and chemical treatment approaches for mercury contaminated media. Finally, a conceptual model of mercury mobility within the EFPC system was developed, and this information has become the foundational document in the development of the recently released DOE-EM Oak Ridge Operations Office Mercury Remediation Strategy. The Mercury Remediation Strategy represents a long-range plan for mercury cleanup within the Y-12 NSC.

DOE's successful implementation of sustainable cleanup solutions requires bridging the gap between basic science and "needs driven" applied research. 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. Using ROMIC-AFRI to address knowledge gaps in the understanding of mercury biogeochemistry, predict mercury fate and transport at a watershed scale, reduce the volume of contaminated media, and provide the scientific and technical basis for on-site disposal will enable the effective remediation of legacy mercury at the Y-12 NSC.

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