An Integrated, Systems-Based Approach to Mercury Research and Technology Development[1] – 17252

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ABSTRACT

A 3-year strategic planning process was undertaken in Oak Ridge, Tennessee, to develop a research and technology development approach that can help guide mercury remediation in East Fork Poplar Creek (EFPC). Mercury remediation is a high priority for the US Department of Energy's (DOE's) Oak Ridge Office of Environmental Management because of large historical losses of mercury to the environment at the Y-12 National Security Complex (Y-12). Because of the extent of mercury losses and the complexities of mercury transport and fate in the stream environment, the success of conventional options for mercury remediation in the downstream sections of EFPC is uncertain. The overall Oak Ridge mercury remediation strategy focuses on mercury treatment actions at Y-12 in the short-term and research and technology development to evaluate longer-term solutions in the downstream environment. The technology development strategy is consistent with a phased, adaptive management paradigm and DOE's Technology Readiness Level guidelines. That is, early evaluation includes literature review, site characterization, and small-scale studies of a broad number of potential technologies. As more information is gathered, technologies that may have the most promise and potential remediation benefit will be chosen for more extensive and larger-scale pilot testing before being considered for remedial implementation.

Field and laboratory research in EFPC is providing an improved level of understanding of mercury transport and fate processes in EFPC that will inform the development of site-specific remedial technologies. Technology development has centered on developing strategies that can mitigate the primary factors affecting mercury risks in the stream: (1) the amount of inorganic mercury available to the

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[1] This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

stream system, (2) the conversion of inorganic mercury to methylmercury, and (3) the bioaccumulation of methylmercury through the food web. Given the downstream complexities and interdependencies between sources and processes in EFPC, no one task or approach is likely to solve the mercury problem in the creek, thus highlighting the importance of using an integrated, systems-based approach to develop remedial solutions.

INTRODUCTION

Historical operations at the Y-12 National Security Complex (Y-12), located at the headwaters of East Fork Poplar Creek (EFPC), resulted in contaminated buildings, soils, and downstream surface waters, sediments, and biota. Although operational use of mercury ended at the facility in the 1960s, legacy contamination has remained a source to the environment, resulting in water and fish mercury concentrations that exceed human health risk thresholds (Fig. 1). Mercury remediation and abatement has been a high priority for the US Department of Energy (DOE) and Y-12 since the early 1980s, with considerable technical and financial resources applied to the mercury problem. Remedial activities at Y-12 have included water treatment, storm drain cleanout and lining, flow changes and reroutes, and soil removal and stabilization. These actions together have dramatically decreased overall releases of mercury from the Y-12 facility into EFPC.

Mercury concentrations in water leaving the Y-12 facility have decreased tenfold since the 1980s, including a 30% decline in mercury concentrations in water after the Big Spring Water Treatment System went online in 2005. Near Y-12, fish concentrations also declined in the 1980s and 1990s. But since 2000, fish concentrations have not changed—defying expectations that lower mercury concentrations in water would further decrease fish mercury concentrations. Actions at Y-12 appear to have had no significant impact on fish concentrations in downstream EFPC in 30 years of monitoring, with concentrations remaining well above regulatory limits (Fig. 1). The lack of downstream response to Y-12 actions suggests that Y-12 source reduction alone may not achieve the mercury regulatory goals in downstream waters. These findings have instigated an update to the conceptual model for EFPC mercury, with a recognition that an integrated, watershed-scale approach is needed to address the mercury issue. The new strategy includes a continued focus in the short-term on remedial actions at the Y-12 facility—including the construction of a treatment facility at the most contaminated outfall at Y-12—coupled with research and technology development to evaluate longer-term solutions in the downstream environment.

Strategic plans for mercury remediation and technology development at Y-12 and EFPC were updated in the 2014–16 timeframe, with significant input from regulators, facility operators, environmental managers, scientists, engineers, and the public. Stakeholders increasingly understand that mercury concentration, methylation, and bioaccumulation processes in the creek are complex and driven not only by mass of mercury in the system but also by physical, chemical, and ecological factors in the receiving stream. Understanding mercury transport and fate processes in the entire EFPC system was deemed essential to the development

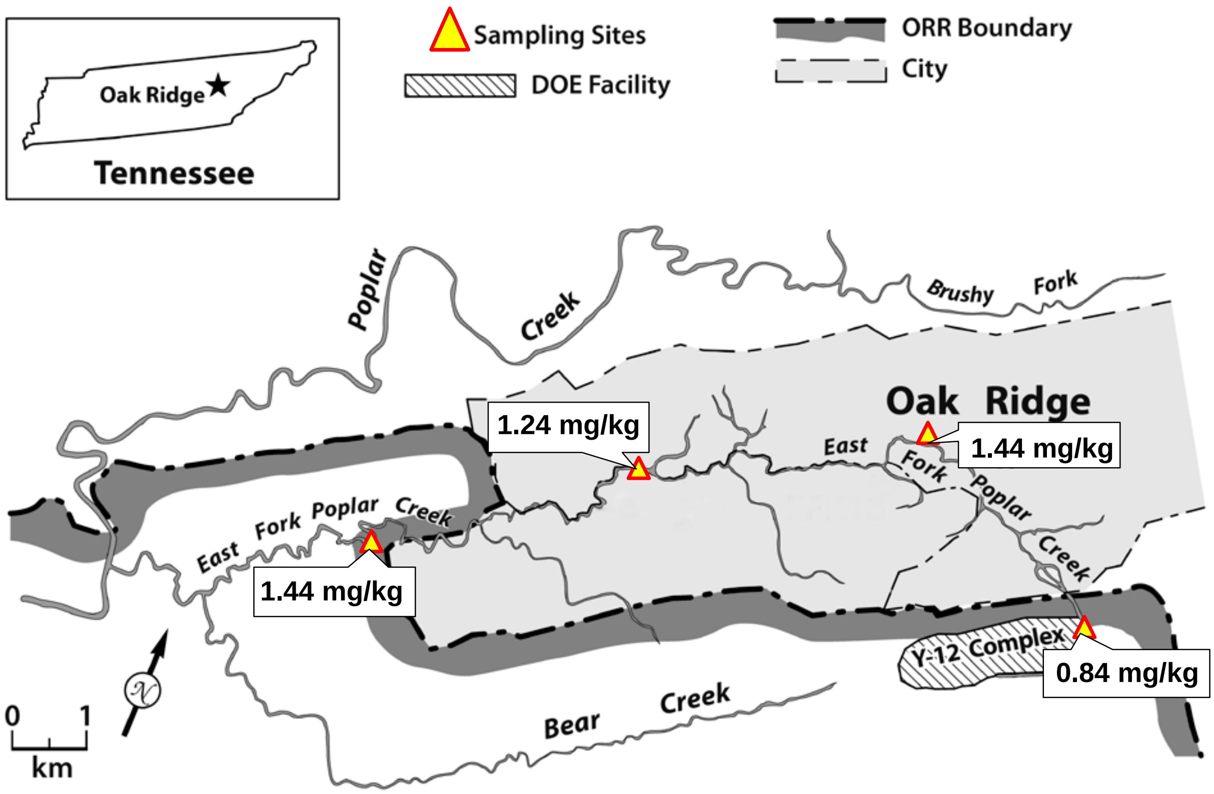

Fig. 1. Mean mercury concentrations in rock bass (*Ambloplites rupestris*) at four locations in East Fork Poplar Creek, Oak Ridge, Tennessee. Six fish were collected from each site in the fall of 2014. The EPA-recommended fish-based methylmercury criterion is 0.3 mg/kg.

of new technologies and ultimately to the development of remedial options for the creek. The role of historically deposited mercury found in floodplain soils, groundwater, bank soils, and sediments—relative to present-day mercury releases from Y-12 at the stream's headwaters, has been a focus of recent research.

Presented herein is the strategic framework that has defined EFPC research and technology development activities over the last 2 years. A major goal of research and technology development in EFPC is to offer innovative, science-based solutions that may reduce human and ecological risk while avoiding environmentally destructive and costly large-scale soil and sediment removal.

TECHNOLOGY DEVELOPMENT APPROACH

To address EFPC mercury contamination, DOE has adopted a phased, adaptive management approach to remediation, which includes mercury treatment actions at Y-12 in the short-term and research and technology development (TD) to evaluate longer-term solutions in the downstream environment [1]. In 2014–15, a technology development strategy for EFPC was developed, consistent with the adaptive management paradigm and DOE's Technology Readiness Level (TRL) guidelines (Fig. 2, [3]). That is, early evaluation should focus on planning, literature review to understand current mercury remediation options, site characterization, and small-scale studies of a broad number of potential technologies. As more information is gathered, more of the focus will be on technologies that may have the most promise and potential remediation benefit. Depending on early study results, high merit technologies or strategies may undergo more extensive and larger-scale pilot testing before a remedial action is chosen.

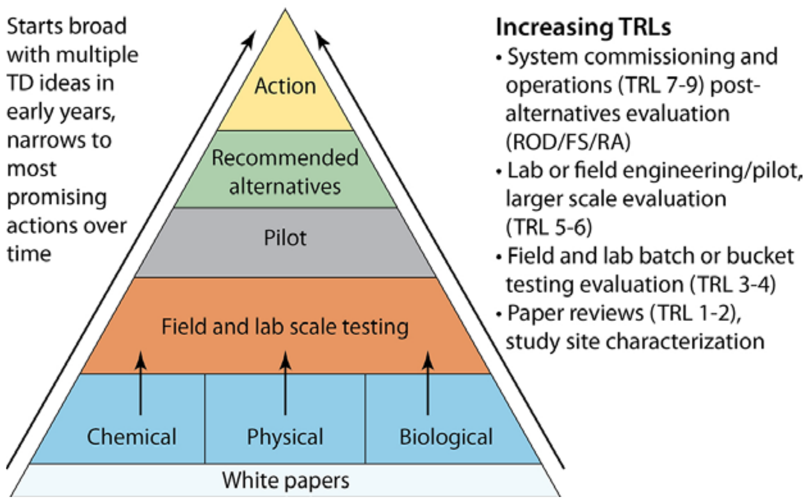

Fig. 2. A technology development pyramid utilizing DOE's Technology Readiness Level (TRL) guidelines [2,3].

As a first step in the TRL process, the TD team conducted a strategic planning process [3]. The strategy was informed by the following:

- An understanding of past and current research and monitoring results within EFPC
- A recognition of the chemical uniqueness, complexity, and dynamic environmental behavior of legacy mercury in stream environments
- An extensive literature review of the state of mercury remediation science and technology development
- An understanding of the overall strategy, priorities, and timeline of mercury remediation activities in Oak Ridge
- A desire to avoid large-scale removal of downstream soils and sediments which would be environmentally disruptive, costly, and potentially ineffective in achieving desired remediation goals
- An evaluation and ranking of potential mercury technology applications tailored to the EFPC system

An outcome of strategic planning was the development of a systems-based approach (e.g., watershed-scale) to identify effective remedial alternatives and technologies and create a framework for defining and achieving sustainable remedial endpoints (i.e., a targeted methylmercury fish-tissue concentration below 0.3 µg/g) within acceptable timeframes. Systems-based approaches for remediation require the integration of site data with a detailed understanding of the physical, chemical, and biological processes that control contaminant movement before selection of a remedial option. The technique provides a complete picture of the system and enables a remedial team to determine the nature and extent of the problem, develop and refine the site conceptual model in an iterative fashion, and select a remediation strategy that accounts for the risks to human health and the environment.

In EFPC, the primary human and ecological risks are associated with eating mercury-contaminated fish. Three key factors determine the level of mercury contamination in fish: (1) the amount of inorganic mercury available to an ecosystem, (2) the conversion of inorganic mercury to methylmercury, and (3) the bioaccumulation of methylmercury through the food web ([4], Fig. 3). One or more of these factors may be the primary driver for elevated mercury concentrations in fish. For example, there are waterbodies that receive substantial atmospheric inputs of mercury, but because of advantageous water chemistry and food chain factors, fish concentrations in those waterbodies are relatively low. Conversely, total mercury inputs can be low, but some waters with large and older fish can have mercury concentrations that are a health concern. Each of the three major factors affecting mercury concentrations in fish can be influenced by a complex array of potential controlling variables, as listed in Fig. 3.

The three major factors controlling mercury bioaccumulation are closely aligned with three regulatory goals in EFPC: the reductions of mercury flux, water concentration, and fish concentration. Three study tasks were defined to evaluate ideas for controlling these variables (Fig. 4). Task 1, Soil and Groundwater Source Control, focuses on addressing downstream mercury sources to the creek, especially floodplain and bank soils, and groundwater. Task 2, Sediment and Water Chemistry Manipulation, centers on manipulation of in-stream processes, including the many water and sediment chemistry factors that affect mercury methylation. Task 3, Ecological Manipulation, seeks ways to manipulate the food chain at both lower and higher levels of organization to decrease mercury concentrations in fish. Because the physical, chemical, and biological factors that affect mercury processes in the creek are interdependent and interrelated as well as complex, an early focus has been on obtaining a watershed-scale understanding of the system. Consistent with the TRL approach, controlled field and laboratory testing will be conducted increasingly over time to investigate potential technological solutions that may be effective in EFPC.

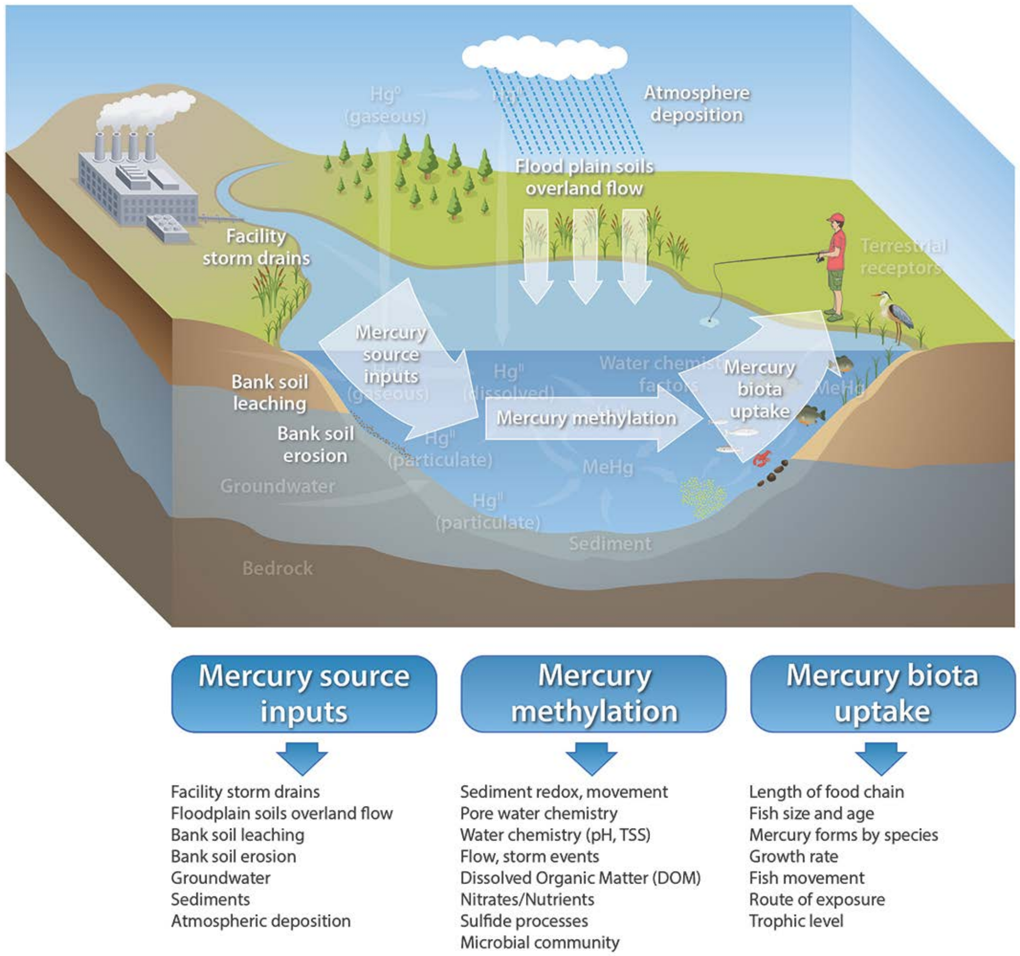

Fig. 3. Conceptual model showing the three major factors affecting mercury concentrations in fish as well as a list of potential East Fork Poplar Creek variables that may influence those factors [3].

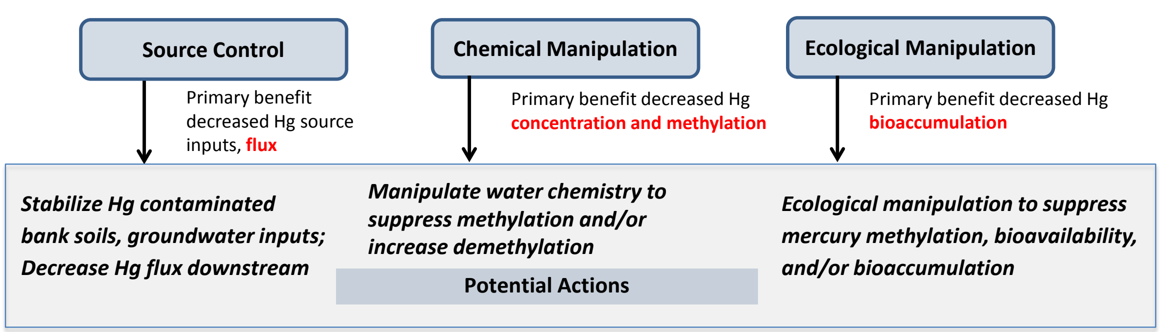

Fig. 4. A framework for development of research and technology tasks designed to interrupt the mercury transport, methylation, and bioaccumulation processes in East Fork Poplar Creek [3].

SUMMARY OF STUDY FINDINGS TO DATE

The systems-based research and technology development approach summarized herein (and detailed in Peterson et al. 2015 [3]) was used to conduct and prioritize research activities over a 2-year period from 2014 to 2016. The approach was vetted to multiple organizations and has strong stakeholder support. Because mercury sources and processes are interconnected it was recognized that a systems approach (i.e., watershed-scale) is needed to mitigate mercury issues in the downstream environment.

Early research has focused on understanding the system so that targeted technologies and strategies can be developed. For Task 1, Soil and Groundwater Source Control, field studies to date have pointed to the importance of bank soils as a source of mercury flux in EFPC, especially in the upper sections of the creek, and have found seasonally high methylmercury in shallow groundwater. Initial technology feasibility studies have focused on laboratory evaluation of sorbent-based technologies with the potential to limit mobilization of dissolved mercury species from stream banks, and thereby minimize the potential for production and bioaccumulation of methylmercury. Current studies also identify leaching of other species from sorbents (e.g., sulfate, organics), which could interfere with sorbent efficacy by, for example, promoting methylation. Future studies will evaluate partitioning of mercury species between contaminated EFPC soils and sorbents.

For Task 2, Water Chemistry and Sediment Manipulation, a new stream gauging and water quality station has been established. A combination of grab sampling and autonomous water quality monitoring is used. In combination with data from other locations along the creek, stream reaches that are sources of mercury and MeHg are being identified, enabling assessments of whether future targeted remedial actions could be effective. Recent study has shown that flow changes from the facility have resulted in changes in mercury speciation in downstream surface waters. Closer to Y-12, phased laboratory- and field-scale experiments are being conducted to assess the role of upper EFPC chemistry on mercury mobilization and the forms of mercury present. Early laboratory studies have shown that exposure to chlorination and dechlorination chemicals can enhance the release and mobilization of soluble mercury(II) from beads of elemental mercury and stream sediments. Alternative treatment methods that might reduce mercury fluxes to EFPC have been identified for further assessment.

The primary long-term goal of Task 3, Ecological Manipulation, is to reduce mercury bioaccumulation in fish through sustainable ecological manipulations. This task has been focused on understanding bioaccumulation and food chain effects from algae to invertebrates to fish. Analyses of methylmercury in prey and trophic status using stable isotopes have been early focuses of field studies. Those data are now being used to quantify the trophic transfer efficiency of mercury through the EFPC food chain and to identify the critical linkages for mercury transfer to fish. Long-term fish and invertebrate community data are being used to model and predict the effect of food changes on fish mercury concentrations. Currently, the introduction of native mussel species is being evaluated to determine their potential to reduce mercury flux and fish bioaccumulation in EFPC.

CONCLUSIONS

A science-based, stepwise approach to remediation technology development, well vetted to the stakeholder community, is advocated. The strategic plan for mercury remediation technology development in EFPC was developed using DOE adaptive management and TRL guidelines, coupled with an updated conceptual model of the system based on recent detailed study. The technology development approach was further vetted and supported by multiple stakeholders over a 3-year strategic planning process in 2014–16.

The preliminary findings from 2 years of research and technology development studies are providing new insights into the processes and variables affecting mercury flux, methylation, and bioaccumulation. Systems-level studies have pointed to the importance of upstream creek bank soils as a source of mercury to the creek, the importance of flow and other water chemistry characteristics on the form of mercury, and the role of methylmercury found in prey species on fish receptors.

With a better understanding of the watershed system, remedial technologies and strategies are being assessed for potential future application or targeted action. An underpinning driver for this research is the desire to avoid large-scale removal of downstream soils and sediments that would be environmentally disruptive, costly, and potentially ineffective in achieving desired remediation goals. The watershed approach is advocated because it considers all the contributing factors that affect mercury transformations in the complex EFPC environment. Understanding all the potential outcomes of environmental change may lead to opportunities for managing and restoring the stream for natural resource benefits and/or water quality enhancements.

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ACKNOWLEDGEMENTS

We would like to thank URS | CH2M Oak Ridge LLC (UCOR), especially Jimmy Massey and Dan Macias, and the US Department of Energy Office of Environmental Management, especially Brian Henry and Jason Darby, for project oversight and funding. We also thank the Y-12 Compliance Department for support of the Biological Monitoring and Abatement Program that evaluates fish mercury trending in EFPC. Oak Ridge National Laboratory is managed by UT-Battelle for DOE under contract number DE-AC05-00OR22725.