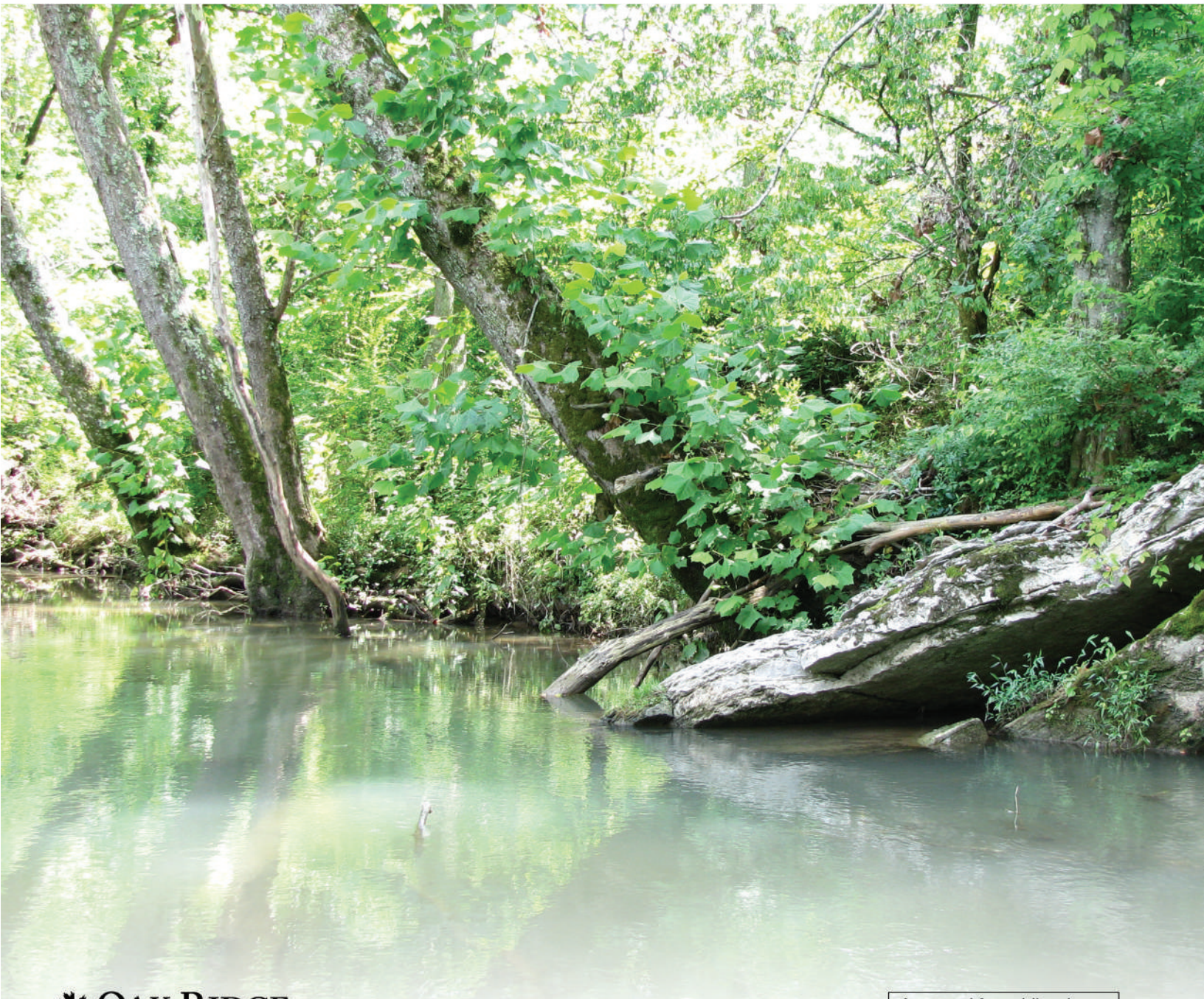
ORNL/SPR-2014/645

Mercury Remediation Technology Development

for Lower East Fork Poplar Creek



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Mark J. Peterson
Scott C. Brooks
Teresa J. Mathews
Melanie Mayes
Alexander Johs
David B. Watson
Monica D. Poteat
Eric Pierce

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Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
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Introduction

Mercury remediation is a high priority for the US Department of Energy (DOE) Oak Ridge Office of Environmental Management (ORO-EM) as a result of large historical losses of mercury within buildings and to soils and surface waters at the Y-12 National Security Complex (Y-12). Along with the Tennessee Department of Environment and Conservation (TDEC) and the US Environmental Protection Agency (EPA), ORO-EM has identified mercury contamination associated with Y-12 as the greatest environmental risk on the Oak Ridge Reservation (ORR). Because of the extent of mercury losses and the complexities of mercury transport and fate in the environment, the success of conventional options for mercury remediation is uncertain. A phased, adaptive management approach to remediation[1], which includes, for surface water, mercury treatment actions in the short-term and research and technology development to evaluate longer-term solutions, has been advocated (US DOE 2014). This document provides a proposed "road map" for conducting research and technology development activities that may lead to effective mercury remediation solutions for East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee.

Significant efforts are under way in Oak Ridge to develop a cleanup strategy and technology development plans that will ultimately decrease mercury concentrations in surface waters and in fish. Two important planning reports were issued in 2014:

1. *Strategic Plan for Mercury Remediation at the Y-12 National Security Complex, Oak Ridge, Tennessee (DOE/OR/01-2605&D2),* providing the overall remediation roadmap for mercury remediation at Y-12
2. *Mercury Technology Development Plan for Remediation of the Y-12 Plant and East Fork Poplar Creek (DOE/ORO-2489),* which highlights the priorities for mercury technology development in Oak Ridge

[1]As used here, "adaptive management" encompasses the concept of decision-making under uncertainty about the outcomes of specific actions, with the goal of identifying effective environmental remedies based on observing effectiveness of interim actions, as well as on results of scientific research comparing multiple causative hypotheses.

-- Strategic Plan for Mercury Remediation at the Y-12 National Security Complex, Oak Ridge, Tennessee (DOE/OR/01-2605&D2)

The research and technology development activities proposed for lower EFPC (LEFPC) are an outgrowth of the conclusions and recommendations described in these two ORO-EM reports. Both documents highlight the need for research and technology development in LEFPC downstream of Y-12.

The broad goal of this document is to offer science-based approaches and ideas to research and technology development activities that may lead to new options for mercury remediation in LEFPC. Proposed is a technology development strategy consistent with the adaptive management paradigm and DOE's Technology Readiness Level (TRL) guidelines. That is, early evaluation should focus on literature review, site characterization, and small scale studies of a broad number of potential technologies (including ideas that may be viewed as higher risk or uncertain but with potentially high payoff). As more information is gathered, an adaptive management approach can be used to focus on technologies that may have the most promise and potential remediation benefit. High merit technologies or strategies will need to undergo more extensive and larger-scale pilot testing before remedial implementation.

The research and technology development approaches for mercury remediation introduced and evaluated in this document are not all encompassing but are based on the following:

- Oak Ridge National Laboratory (ORNL) Environmental Sciences Division (ESD) research staff's understanding of the LEFPC system
- An extensive literature review of the state of mercury remediation science and technology development, as well as on-site data
- An idea-inclusive, broadly-defined review of potential research and technology development approaches that, with increased knowledge and scale of testing, will narrow the options to those most likely to be beneficial
- 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 that would be environmentally disruptive, costly, and potentially ineffective in achieving desired remediation goals

Understanding mercury transport and fate processes in the EFPC system is essential to the development of new technologies and ultimately to the development of remedial options and strategies for the creek. This document includes some background information regarding the current understanding of the EFPC system and the potential approaches and challenges to remediation. The document's principal content is focused on using a broad-based watershed approach to address the mercury issue that includes (1) downstream source control, including soil and groundwater; (2) in-stream sediment and surface water manipulation; and (3) ecological manipulation.

John G. Smith (ORNL) collecting creek bank spiders for mercury analysis.

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THE LEFPC ENVIRONMENT

Site Description

The EFPC drainage basin, which includes EFPC and Bear Creek, is located in east Tennessee within the Ridge and Valley physiographic province of the Southern Appalachians. Parallel northeast-trending ridges constitute the northern (Black Oak Ridge) and southern (Chestnut Ridge) boundaries of the watershed. The primary land cover of the area before European settlement was mature upland and bottomland forest, dissected by small to large streams and rivers as well as small pockets of seep wetlands and hillside prairie communities. In the early part of the 20th century, the area was composed of small farms with a mix of agricultural field and pasturelands, with interspersed woodlands, especially on the ridges. After the US government acquired regional lands for the Manhattan Project during World War II in the 1940s, the city of Oak Ridge was established, and industrial facilities were built to support the war effort, including the Y-12 facility (now the Y-12 National Security Complex) at the headwaters of EFPC and Bear Creek.

Today, the EFPC watershed is located near the northern boundary of DOE's ORR and has an area of 76.5 km^2 from the headwaters to the mouth at Poplar Creek (Fig. 1). Elevations in the basin range from 230 to 290 m. The geology of the watershed is composed primarily of sandstones and dolostones along the ridges, with the valleys underlain by shales, limey shales, and limestones (Hatcher et al. 1992). Recent studies of EFPC bank soils revealed, on average, soils classified as 18% clay, 45% silt, 35% sand,

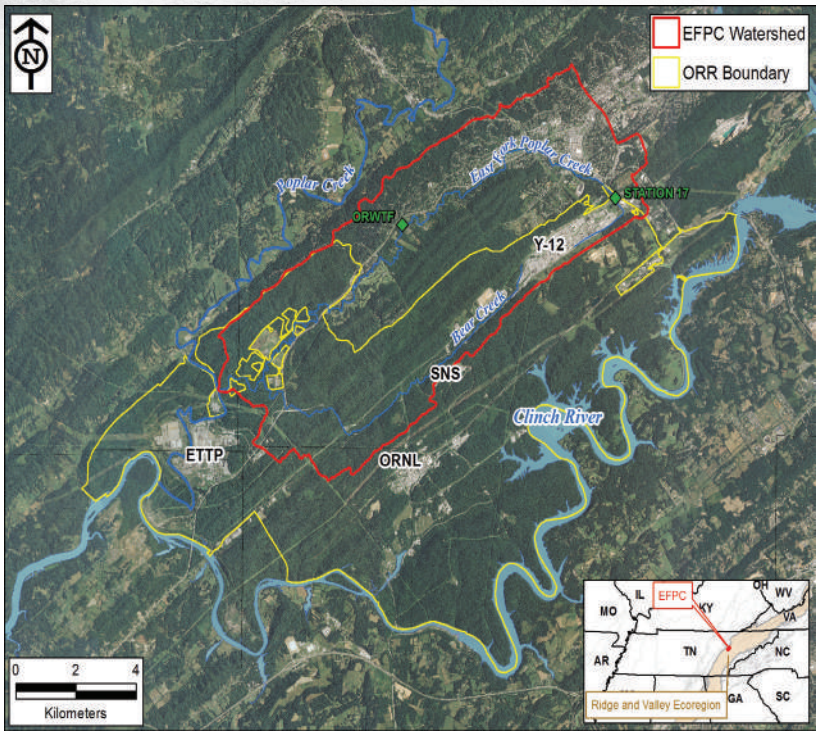


Figure 1. The East Fork Poplar Creek (EFPC) watershed at the northern boundary of the Oak Ridge Reservation (ORR) in Oak Ridge, Tennessee. (Notes: SNS = Spallation Neutron Source; ETTP = East Tennessee Technology Park; and ORWTF = Oak Ridge Wastewater Treatment Facility).

1% gravel, and 22% moisture content. The creek bottom varies throughout its length but has extensive areas of exposed bedrock with sediments most often composed of clays, small gravels, and silt. Although much of the streambed is bedrock, gravel deposits cover about 50% of the stream bottom and contain significant concentrations and mass of mercury in entrained fine particulates (Lockheed Martin Energy Systems Inc. 1996).

EFPC is a third order stream that currently is approximately 25 km (15.5 miles) long. The creek is fed in part by springs on the northwest slope of Chestnut Ridge and the southern slope of Pine Ridge. Spring water enters the Y-12 Complex storm drain network, where it mixes with facility-generated waters (primarily cooling water) and shallow subsurface groundwater before exiting Outfall 200 (OF200) at the western terminus of the creek. The headwaters and a small stream section (~2 km) are located within the Y-12 Complex. A monitoring station, Station 17, located at the stream's edge at the ORR boundary captures daily aqueous mercury concentrations and flow as EFPC enters the city of Oak Ridge. This 2 km segment within the ORR boundary and upstream of Station 17 is defined operationally and administratively as upper East Fork Poplar Creek (UEFPC), while the remaining 23 km downstream of the ORR are defined as lower East Fork Poplar Creek (LEFPC). LEFPC flows outside ORR boundaries for ~15 km through the city of Oak Ridge before re-entering the ORR limits at approximately creek kilometer 8 (Fig. 1). It is in LEFPC that mercury technology development is proposed, as this portion presents unique challenges with respect to mercury cycling, as discussed later in this report.

The stream riparian habitat of EFPC changes dramatically from the headwaters to the mouth (Fig. 2). The first few kilometers of UEFPC are largely straightened channel, with riprap and concrete-lined banks in some sections. Since 1988, the creek has flowed through a concrete diversion channel to bypass a lined basin called Lake Reality, although exchange can occur between the creek and Lake Reality during storms and high flow conditions. The creek flows less than 1 km below Lake Reality before leaving the ORR and entering the city of Oak Ridge, where surrounding land use is largely urban, with a mix of commercial and residential properties bordering the creek. Impervious surfaces within Y-12 and in the city of Oak Ridge, coupled with straightened or altered channel reaches in some sections, contribute to the flashiness of the stream. Large storm events, therefore, are thought to be important in causing high erosion rates and incised banks. Toward the lower portion of the stream section within the city, there is a greater mix of agricultural field and pasture habitat, mixed with secondary growth forest. The lower portion of the watershed within the ORR is largely undeveloped in the stream's riparian zones and consists mostly of mixed hardwood stands, including areas of mature forest. Larger, deeper pools are evident in the lower sections of EFPC, where the stream is often inundated when the downstream reservoir is managed at high pool (by Tennessee Valley Authority [TVA] operations at Watts Bar and Melton Hill dams).

History of Mercury Contamination

The history of Y-12 mercury use and estimated losses—and the extent of downstream contamination in EFPC—is a fascinating story that has been described by many authors over the years (see especially Brooks and Southworth 2011, Loar et al. 2011, Munger 2011) and therefore will be described here only briefly. During the 1950s, the Y-12 Complex conducted industrial-scale lithium isotope separation processes that involved large quantities of mercury. Although mercury control strategies were in place to prevent losses of a costly metal to the environment, approximately 128,000 kg of mercury was thought to have been released into EFPC over the period of 1950–63 (Brooks and Southworth 2011). After that period, industrial use of mercury

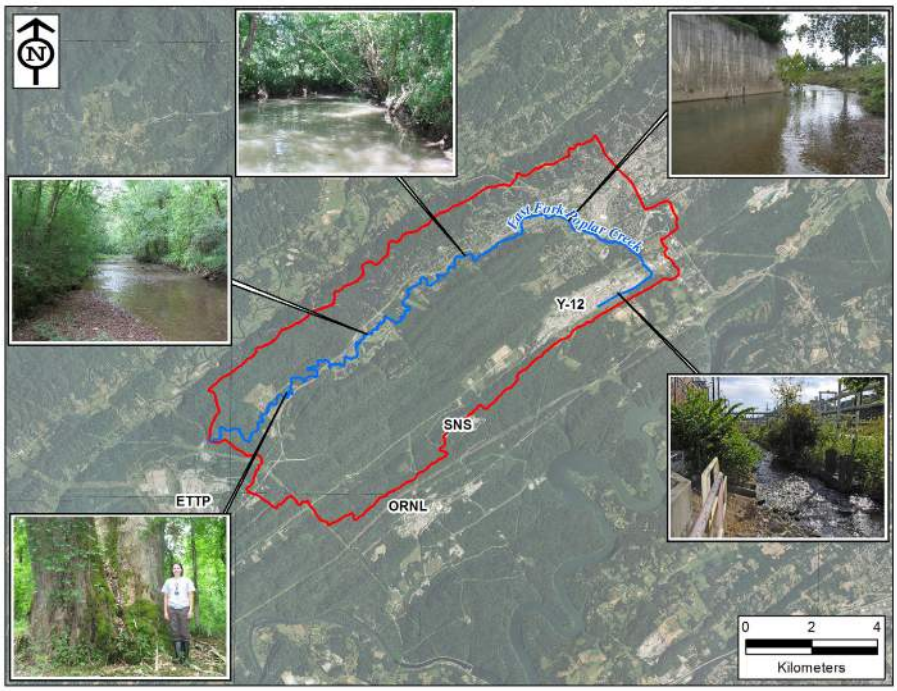


Figure 2. East Fork Poplar Creek and views of stream riparian zones along the creek.

ended, and annual mercury releases from Y-12 decreased substantially. However, lower-level mercury discharges continued from the facility after major operations ended because of past spills near buildings that contaminated surrounding soils and storm drains.

The mercury contamination at Y-12 and EFPC first came to the attention of the public in 1982, when the state of Tennessee posted water and fish advisory signs warning the public of the mercury contamination in EFPC, and more intensive studies of creek contamination began. In 1985, a Clean Water Act National Pollutant Discharge Elimination System (NPDES) permit was issued for the site that required water quality and surface water mercury monitoring, as well as a biological monitoring program that included monitoring of mercury in fish fillets. In 1989, the US Environmental Protection Agency (EPA) placed the ORR, including EFPC and downstream waters, on the National Priorities List, requiring it to be remediated according to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Mercury Regulations and Health Risks

While state and national guidelines for mercury have changed over the years, mercury concentrations in EFPC continue to exceed these guidelines. The State of Tennessee has adopted an Ambient Water Quality Criterion (AWQC) for mercury in surface water of 51 parts per trillion (ppt), which is considered a level that—if not exceeded—will ensure fish do not accumulate mercury concentrations at levels unsafe for recreational anglers. The mercury limits in water are to protect humans from eating contaminated fish; total mercury in EFPC water is not a drinking water or physical contact-related hazard. Total mercury concentrations in EFPC water have decreased substantially over the last few decades, but monitoring data suggests average concentrations in EFPC surface water exceed the 51 ppt limit throughout the creek's length (Fig 3.), prompting TDEC to classify EFPC as an impaired water body (TDEC 2014). In concert with CERCLA interim actions at Y-12, a 200 ppt mercury goal was established at an upstream monitoring station, Station 17 (Fig. 1). Current average annual concentrations exceed that level at Station 17, with a high amount of daily to weekly variation depending on flow.

Over the last few decades, states have increased use of fish-based mercury criteria that provide a better measure of the likely human health risks from fish consumption due to the inconsistent relationship between total mercury in water and in fish. Various environmental factors are known to impact mercury methylation and bioaccumulation. EPA recommends a fish-based ambient water quality criterion of 0.3 parts per million (ppm) methylmercury in fish muscle, and the state of Tennessee has adopted this guideline for issuing fish consumption advisories. On average, fish concentrations range from two- to fourfold higher than the EPA criterion throughout EFPC, prompting the state's "no fishing" advisory. The primary focus of mercury bioaccumulation monitoring in EFPC has been to address human health concerns. Although risks to wildlife are highly dependent on the assumptions used in the risk analysis, mercury concentrations in EFPC fish are in the range of values considered a potential concern to fish-eating wildlife.

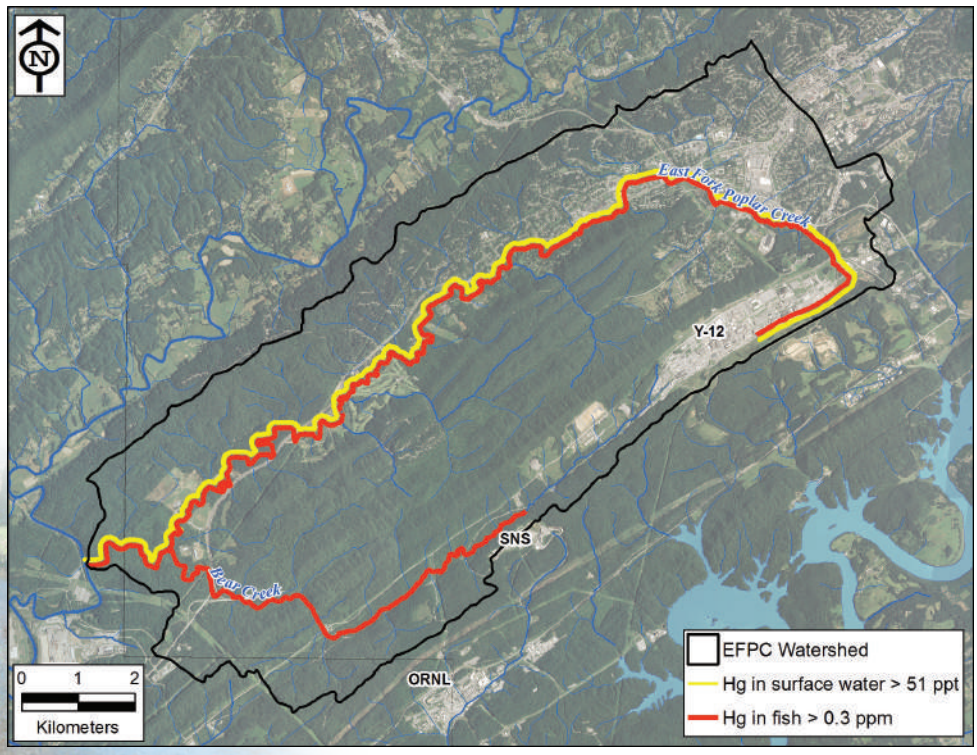


Figure 3. Map showing sections of stream in the EFPC watershed that exceed surface water and fish regulatory guidelines.

Mercury concentrations in EFPC floodplain soils were evaluated as part of a Remedial Investigation/ Feasibility Study (RI/FS) in the early 1990s. A cleanup concentration was developed with regulatory and stakeholder agreement of 400 ppm in soil. Two areas—one just downstream of Station 17, at creek kilometer ~23 (near the National Oceanic and Atmospheric Administration [NOAA] facility) and another in middle EFPC at creek kilometer ~18 (near the old Brunner's Market)—were remediated in the mid-1990s to remove soils with concentrations greater than 400 ppm. In general, mercury concentrations in remaining floodplain soils are higher in the upper third of the creek, with high localized variability (35–250 ppm) (Fig. 4). Recent studies at another mercury-contaminated site, the South River watershed in Virginia, have raised questions regarding ecological risks associated with the terrestrial food chain. As part of the 2011 CERCLA Five Year Review in Oak Ridge, Action Plans were developed to evaluate mercury transport and risk concerns associated with EFPC soils. Those studies are currently underway, and some of the early results provide a basis for technology development in EFPC.

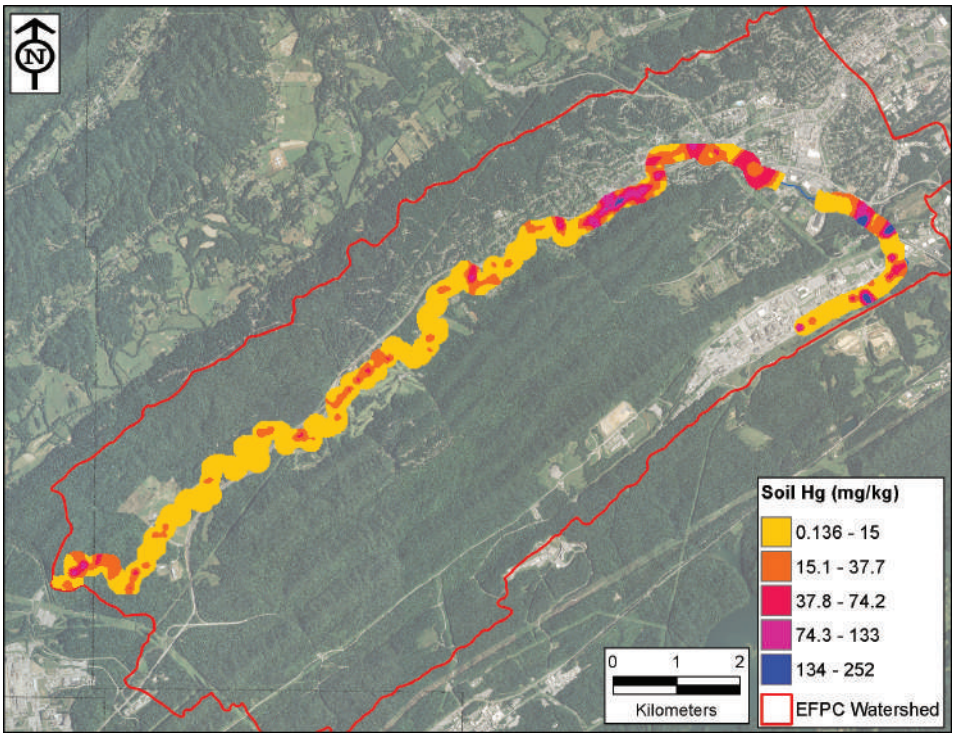


Figure 4. Ranges of floodplain soil mercury concentrations along EFPC. This depiction is not an accurate representation of concentration zones, which are very close to the creek; the soil mercury ranges are expanded for visualization purposes.

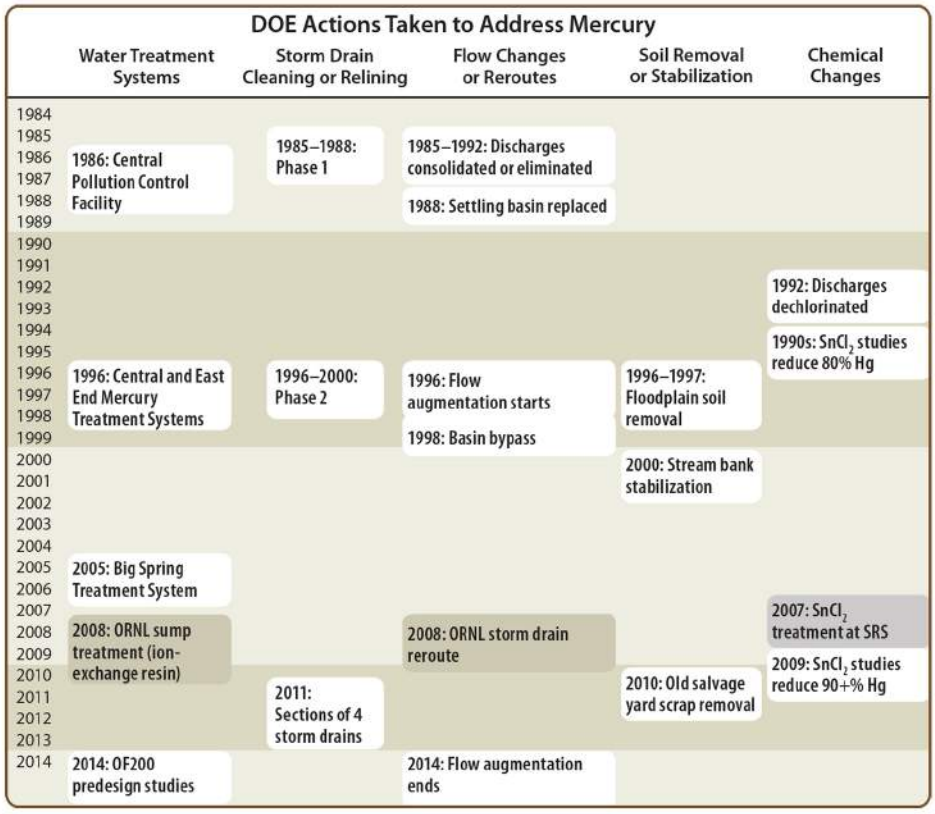


Figure 5. DOE remedial and abatement actions taken to address mercury contamination, 1984–2014. Most actions were taken at Y-12 and downstream; shaded text boxes refer to actions taken at other DOE facilities. The $SnCl_2$ chemical changes were experimentally applied at Y-12 and not implemented as a remedial action.

Mercury Abatement and Remedial Activities to Date

Mercury abatement has been a high priority for DOE and Y-12 over the last 30 years, and considerable technical and financial resources have been applied to the mercury problem. Remedial activities at Y-12 since 1984 have included water treatment, storm drain cleanout and lining, flow changes and reroutes, soil removal and stabilization, and evaluation of chemistry changes (Fig. 5). These actions together have dramatically decreased overall releases of mercury from the Y-12 facility.

Decreases in mercury concentrations in water exiting the Y-12 footprint were most pronounced between 1990 and 2010. However, even after a 30% decline in mercury concentrations in water after the Big Spring Water Treatment System went online in 2005, mercury concentrations in fish did not respond commensurately (Fig. 6). Two recent actions were undertaken at Y-12 to decrease mercury flux: (1) a storm drain cleaning and relining effort was completed in 2011, and (2) flow augmentation (a water piping system that brought Melton Hill Reservoir water into UEFPC) was shut off in spring 2014. The overall benefit of these two actions is currently uncertain but will take some time to evaluate fully.

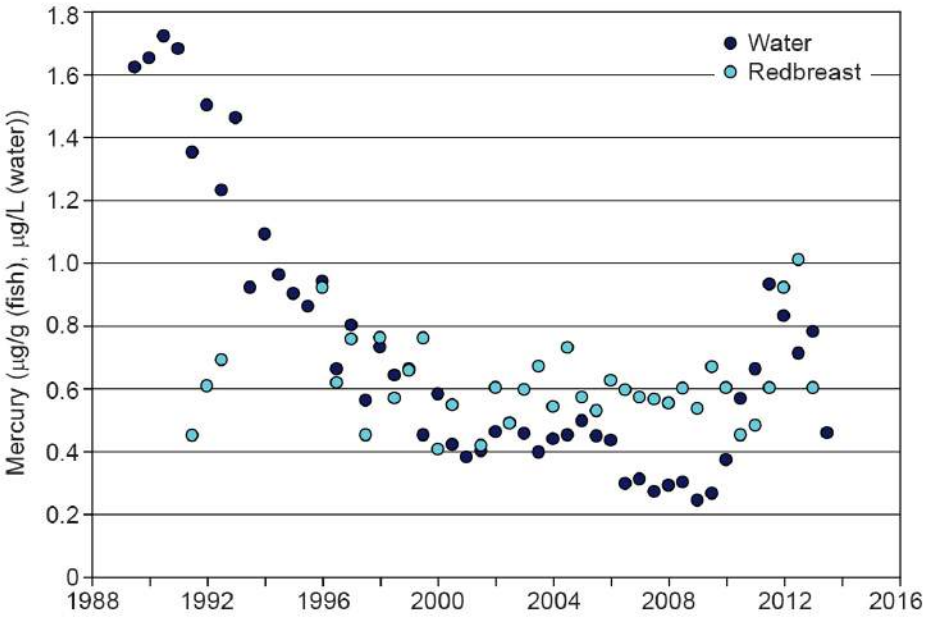


Figure 6. Mean concentration of mercury in redbreast sunfish versus trailing 6 month mean concentration of mercury in surface water, at the most upstream water and fish monitoring locations in EFPC.

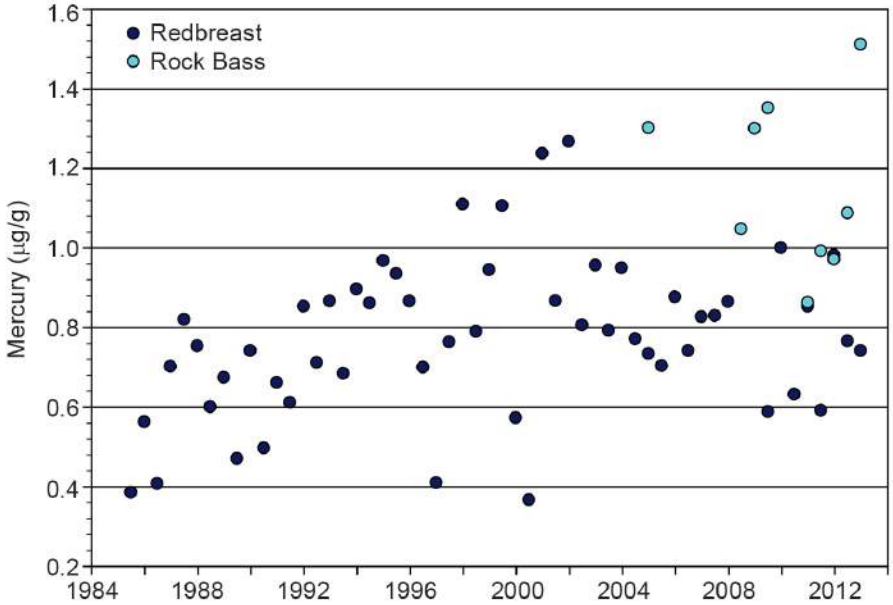


Figure 7. Mean mercury concentration in muscle tissue of redbreast sunfish and rock bass at the most downstream monitored site in EFPC.

Approximately 10 miles downstream, mercury concentrations in fish have not changed significantly in the 30 years of monitoring EFPC (Fig. 7), although the trends are obfuscated by changes in the dominant fish species present. 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. It is increasingly apparent that mercury concentration, methylation, and bioaccumulation processes in the creek are complex and are driven not only by mass of mercury in the system but also by physical, chemical, and ecological factors in the receiving stream.

Despite 34,220 m^3 of soil >400 ppm mercury being removed from the LEFPC floodplain in the 1996–97 floodplain remediation, extensive lower-level zones of contaminated soils and sediments remain in the downstream environment. Investigation continues into 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. EFPC surface water and sediments will be addressed in a future CERCLA Record of Decision. A major goal of environmental management (EM) research and technology development in LEFPC is to develop strategies for reducing human and ecological risk while avoiding environmentally destructive and costly large-scale soil and sediment removal.

Mercury Complexities in LEFPC

Mercury is a unique contaminant with multiple forms that each act differently in the environment and have different levels of health risks (Fig. 8). Although the initial form of mercury at Y-12 was elemental mercury (Hg[0]), and significant levels of Hg(0) remain in buildings used for mercury processing at Y-12 and in nearby soils, most of the mercury leaving Y-12 in water is mercuric mercury (Hg[II]) bound to particles as inorganic Hg(II) ionic compounds or complexes. Mercury in downstream soils and sediments is also primarily inorganic complexes. The total mass flux of inorganic mercury in EFPC is dominated by the transport of particles that are associated with mercury. Mercury-enriched particles are entrained in the streambed as they gradually move through the system, with most of the mercury being on silt- and clay-sized particles. Fine particles are retained in coatings of biofilms that cover hard surfaces of the streambed and within the gravel reaches of the stream. Stream sediments contain a substantial inventory of stored mercury that may be transported during high-flow events and accumulated at lower flows.

Dissolved inorganic mercury is assumed to be the form of mercury that acts as a direct precursor for the formation of methylmercury by microorganisms. Methylation is carried out by sulfur- and iron-reducing microorganisms, as well as methanogens, and syntrophic, acetogenic, and fermentative Firmicutes (Gilmour et al. 2013b, Parks et al. 2013), and is well known to be associated with redox transition zones where aerobic (oxygen-rich) conditions grade into anaerobic (oxygen-poor) zones.

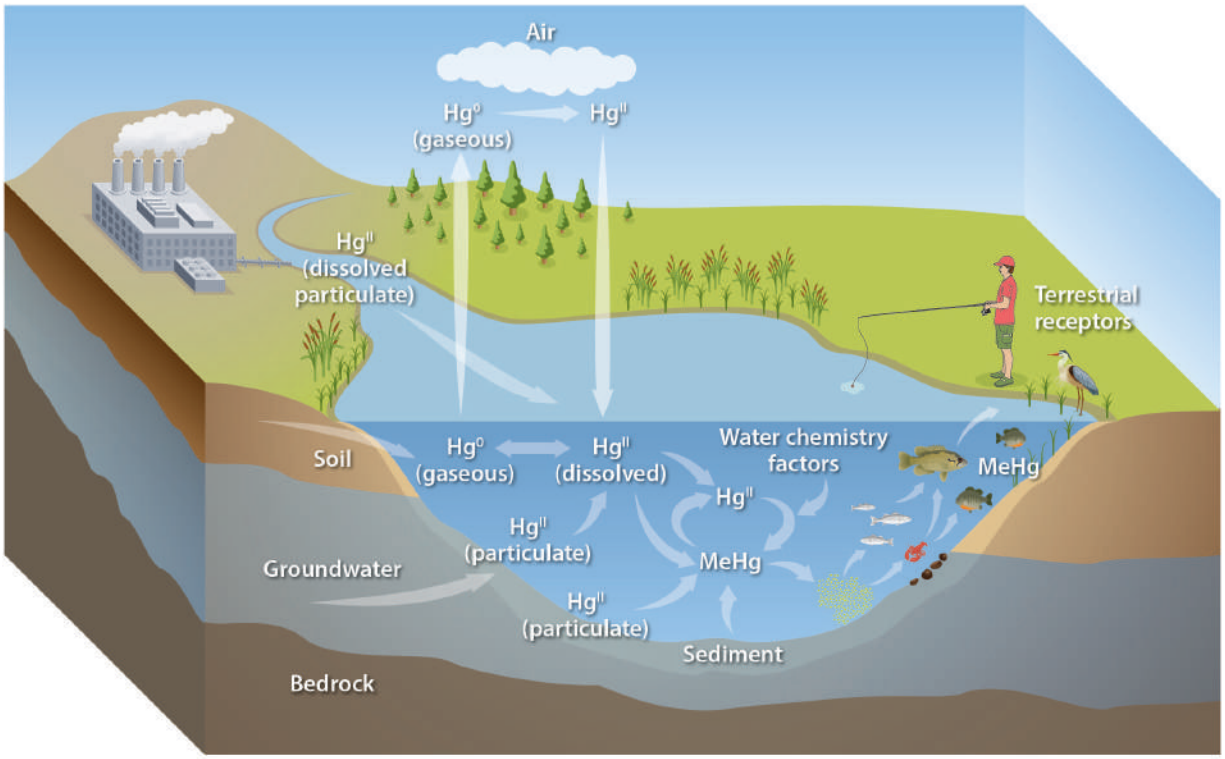


Figure 8. A simplified diagram showing mercury forms and transformations in the environment.

Forms of Mercury in the EFPC Environment

- **Elemental (Hg[0])**
  - As metallic vapor, "liquid," or bound in mercury containing minerals
  - High quantities in buildings and soils at Y-12; rarely detected at high concentrations downstream
- **As ions (Hg[I] and Hg[II])**
  - In solution or bound in ionic compounds or complexes (e.g., inorganic salts: mercuric sulfide [HgS], mercuric oxide [HgO], and mercuric chloride [HgCl2])
  - Most common form in the downstream environment (soils, sediments, surface water)
- **Organic mercury (e.g., CH_3Hg)**
  - Bound to inorganic or organic particles/matter by ionic, electrophilic, or lipophilic adsorption
  - Methylmercury readily accumulates in food chain and is a known neurotoxin

Methylmercury is a known neurotoxin, is accumulated by organisms low on food chains such as periphyton (algae), and can biomagnify at each step from invertebrates to prey fish to predator fish. Primary routes of methylmercury exposure to higher-level aquatic organisms, as well as terrestrial receptors such as humans or wildlife, are through the food chain (i.e., ingestion) rather than direct surface water uptake. In EFPC, a fish consumption advisory and associated posting of the creek ensures fish are not eaten by recreational anglers.

The methylation and bioaccumulation processes pose unique challenges for remediation. Methylmercury cannot be targeted for removal as part of a typical contaminated soil removal action. Mercury concentrations in fish are a function of the magnitude of the inorganic mercury source, and also the methylation rate and the nature of the food chain. Many environmental factors, both chemical and biological, affect mercury methylation and bioaccumulation including pH, suspended solids, dissolved organic matter, flow rate, sediment attributes, and the microbial and biological communities present (Fig. 9).

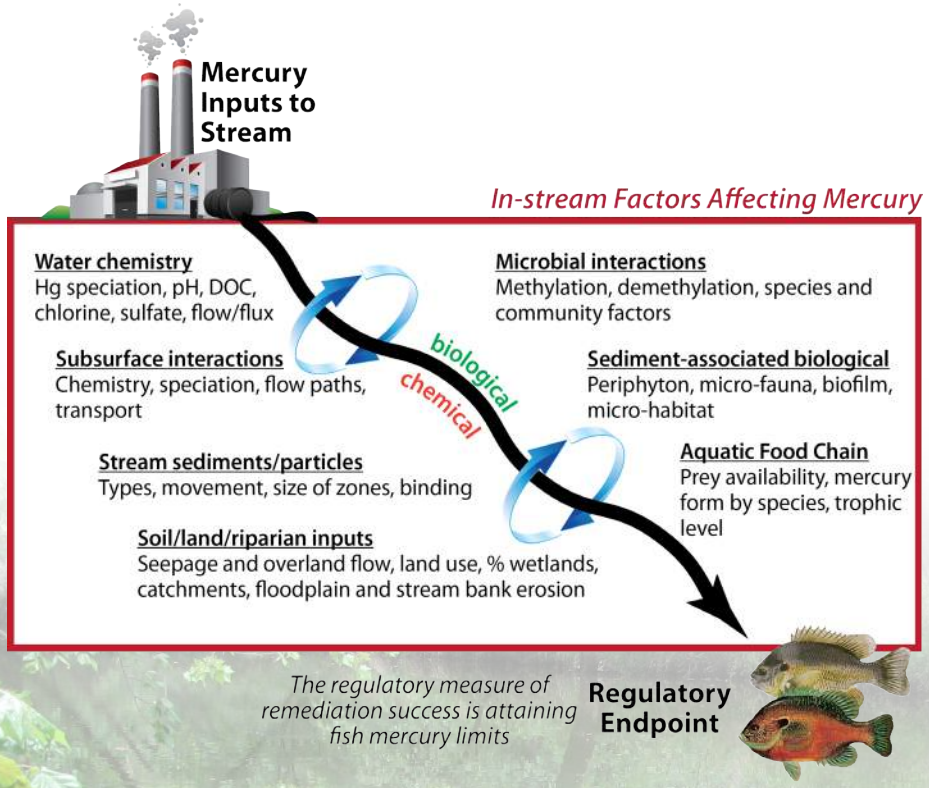
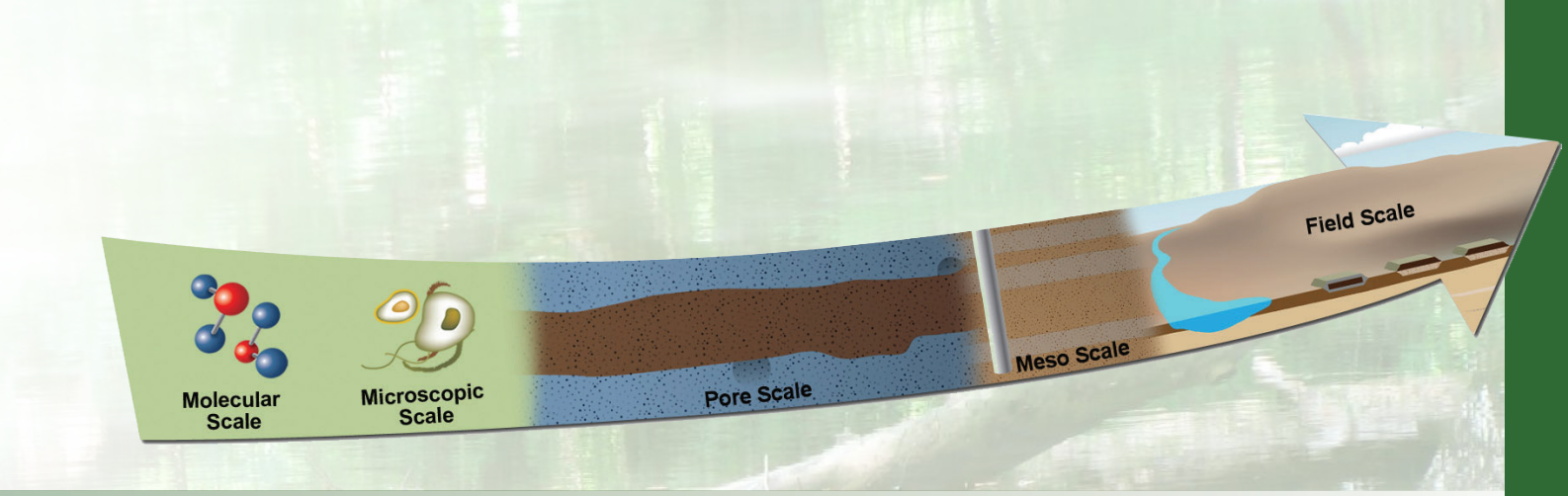


Figure 9. In-stream chemical and biological factors affecting mercury methylation and bioaccumulation.



APPROACH TO LEFPC MERCURY TECHNOLOGY DEVELOPMENT

DOE-EM Technology Development

The DOE Office of Environmental Management (EM) is responsible for cleanup and risk reduction of the environmental legacy from the nation's nuclear weapons production and nuclear energy research. Cleanup of remaining EM sites represents one of the largest, most complex, and formidable environmental restoration challenges in the world (Pierce et al. 2009). Furthermore, the soil and groundwater problems that remain, such as mercury at the Oak Ridge Reservation, present a significant challenge for the technical community (Pierce et al. 2009, NRC 2009). The large projected cost for the remaining soil and groundwater cleanup is because of the complexity of the problems, volume of contaminated media, limitations of existing baseline technology, and use of conservative standard-based closure requirements.

Over the past decade, DOE EM has used roadmaps and other formal plans to describe science and technology gaps and to develop work needed to fill those gaps, with the goal of successfully addressing many of these "first of a kind" subsurface challenges. These roadmaps included the Groundwater Vadose Zone Integration Project Roadmap (US DOE 1998, US DOE 2000), A National Roadmap for Vadose Zone Science and Technology (US DOE 2001), and more recently DOE EM's Cleanup Technology Roadmap (US DOE 2008). There is also extensive information and recommendations provided by the National Research Council (NRC) in its reviews of various DOE roadmaps (NRC 1999, NRC 2000, NRC 2001, NRC 2004, NRC 2009). In 2009, NRC's review of DOE's Cleanup Technology Roadmap stated that "the unique chemical, physical, and radiological properties of waste and contamination at the EM cleanup sites and the unique subsurface characteristics of the sites themselves require special capabilities of the sites and their associated national laboratories…." The review also stated that "the scientific and technical state of the art will evolve during the next 30 years of EM site cleanup program, as well as public expectations for the cleanup goals. EM…will be required to keep up with these evolutions to provide up-to-date basis for cleanup decision" (NRC 2009). In the 2009 publication, the NRC identified the following two prioritization needs for the Groundwater and Soil Remediation Roadmap:

- Gap 1: The behavior of contaminants in the subsurface is poorly understood.
- Gap 2: Site and contaminant source characteristics may limit the usefulness of EM's baseline subsurface remediation technologies.

DOE's success in addressing these "first of a kind" challenges requires bridging the gap between basic science and "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 Complex. 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 that affect DOE's ability to address this problem successfully. All of the aforementioned NRC recommendations are reflected in the Mercury Remediation Strategy (US DOE 2014), a recent mercury technology development (TD) document (DOE/ORO-2489), and this document.

The mercury TD plans outlined in this document seek to implement a systems-based approach (e.g., watershed-scale) to identify effective remedial options and create a framework for defining and achieving sustainable remedial endpoints within acceptable timeframes. Systems-based approaches for remediation require the integration of site information with a detailed understanding of the physical, chemical, and biological processes that control contaminant movement. The

approach provides a complete picture of the system and allows for 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 fully accounts for watershed-scale risks to human health and the environment.

A key component in evaluating the success of a remediation strategy is the development and implementation of an integrated monitoring strategy used to build, test, and verify the conceptual site model, which is then refined and used to inform, develop, and refine monitoring plans (Bunn et al. 2012). This monitoring strategy is a critical aspect for achieving a scientifically and technically defensible regulatory approved end-point. An end-point is a risk-informed remediation goal or scenario permitted by environmental regulations that protects human health and the environment (Gerdes et al. 2013). It can be an interim remediation target or the final remedial action that enables a path for the transition from active cleanup to closure. It may consist of interim remedial milestones and transition points and/or regulatory alternatives to standards-based remediation. The mercury cleanup strategies and approaches outlined in this document have a foundation in use of a systems-based (e.g., watershed-scale) approach to remediation with a targeted end-point in mind (i.e., targeted methylmercury fish tissue concentration below 0.3 µg/g).

Use of the Technology Readiness Approach

The Technology Readiness Approach will be adopted to develop suitable technologies and strategies for LEFPC mercury remediation. DOE EM adopted the National Aeronautics and Space Administration/DOE methodology for evaluating technology maturity (US DOE 2009). This approach integrates Technology Readiness Assessments (TRAs) and Technology Maturation Plans (TMPs) into the critical decision process for project execution. The TRAs are designed to determine the development stage and to assess whether the technology or approach to remediation has matured enough to be inserted into the project design and execution schedule. The TMPs provide a roadmap or set of steps required to increase the maturity of a remediation approach such that the technology can be inserted into the project execution schedule. A key component in the maturation process is the Technology Readiness Level (TRL) scale (Fig. 10), which is used in TRAs to evaluate maturity based on prescribed criteria (Table 1). The TRL scale can be group into the following three categories:

- Applied Research—research targeted to a specific technology need (TRLs 1–3)
- Technology Development—feasibility demonstration of a science-derived technology or concept (TRLs 4–6)
- Technology Maturation—technology demonstration leading to implementation (TRLs 7–9)

The TRL scale moves a remediation technology or approach from concept through bench- and mesoscale testing to field-scale demonstration. Concept evaluation involves understanding existing and potential science and technologies, primarily through evaluation of existing approaches (literature searches, etc.), bench- and mesoscale testing, and field characterization (to understand the system for technology application and future remediation). Bench- and mesoscale testing are designed to evaluate the feasibility of the concept and to test a variety of expected conditions with the goal of identifying limitations and refining the overall concept. The field-scale demonstration is designed to test the concept under field relevant conditions with the initial goal of identifying the limitations and refining the concept and with the final goal of testing the refined concept at the engineered-scale before full deployment. This process represents an effective management tool for reducing technical risk and minimizing the potential for technology-driven cost increases and schedule delays. Technology development activities in LEFPC are expected to span the range of TRLs 1–6 (Applied Research and Technology Development). Engineered and full-scale technology deployment would most likely only occur within the CERCLA decision-making process, typically as a chosen outcome of a Feasibility Study.

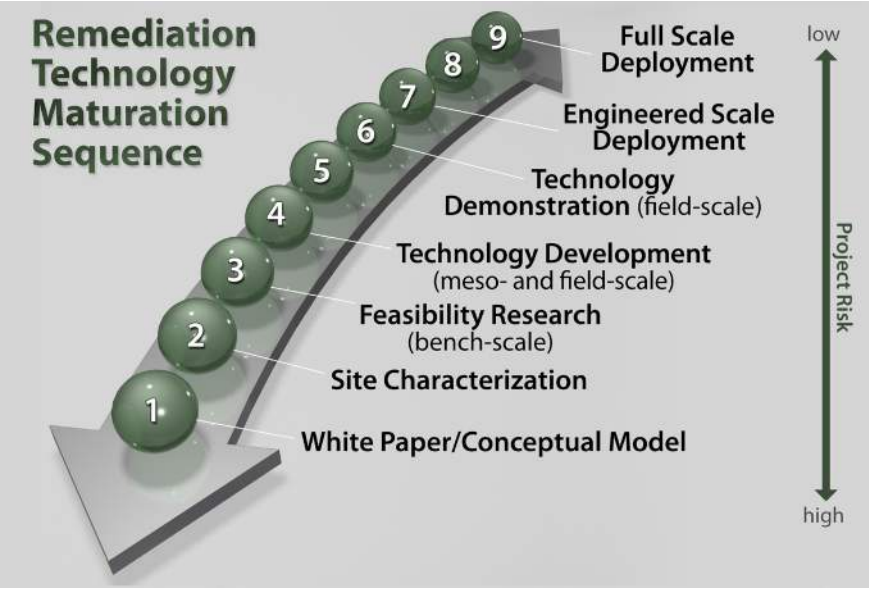


Figure 10. Mercury technology maturation sequence.

Table 1. Description of Technology Readiness Levels and the potential application of mercury technology development

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description	Mercury TD	Mercury TD Description
System Operations	TRL 9	Actual system operated over the full range of expected conditions		Full scale operations	Operate system and monitor remedial effectiveness
System Commissioning	TRL 8	Actual system completed and qualified through test and demonstration	Technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development	Full scale commissioning and testing	Make minor adjustments to the system design and implement
	TRL 7	Full-scale, similar (prototypical) system demonstrated in relevant environment	Prototype full-scale system. Represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment		Implement system at field scale and test the various components to make certain system is functioning properly
Technology Demonstration	TRL 6	Engineering/ pilot-scale, similar (prototypical) system validation in relevant environment	Representative engineering scale model or prototype system, which is well beyond the lab scale tested for TRL 5. Represents a major step up in a technology's demonstrated readiness	Engineering scale deployment at field scale	Test system concept at an engineered scale for the 24-km creek and identify challenges in the deployment strategy
Technology Development	TRL 5	Laboratory scale, similar system validation in relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects.	Field scale testing	Test system concept at the field-scale to evaluate the influence of field conditions on planned deployment strategy. Iteratively refine concept at mesocosm scale to improve system response
	TRL 4	Component and/or system validation in laboratory environment	Basic technological components are integrated to establish that the pieces will work together. This is relatively "low fidelity" compared with the eventual system	Laboratory to mesocosm scale testing	Test concepts at a mesocosm scale to evaluate impact of different system components under a variety of conditions in a controlled setting. Test a variety of field relevant conditions to iteratively refine concept and deployment strategy
Research to Prove Feasibility	TRL 3	Analytical and experimental critical function and/or characteristic proof of concept	Active research and development is initiated. This includes analytical studies and laboratory scale studies to physically validate the analytical predictions of separate elements of the technology		Reduce the number of concepts/ ideas and focus on most promising approaches based on test results collected, site conceptual model, and scientific understanding of the system
	TRL 2	Technology concept and/or application formulated	Invention begins. Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumption	Laboratory scale testing	Evaluate a variety of concepts and ideas at a bench/laboratory scale to quickly test a wide range of expected conditions. This selection process will need to be informed by the site conceptual model and scientific understanding of the contaminant and environment
Basic Technology Research	TRL 1	Basic principles observed and reported	Lowest level of technology readiness. Scientific research begins to be translated into applied research and development (R&D)	White paper/ research concept	Describe concepts and ideas

Research and Technology Development in Oak Ridge

There is a long and rich history of EM research and TD activity in Oak Ridge, centered initially on groundwater and waste related issues. In the 1980s to early 1990s as part of the EM50 program, major research and technology investments included efforts to understand radionuclide movement in groundwater near ORNL and to develop technologies to stabilize radioactive waste. Follow-on research and technology development was initiated in upper Bear Creek at the Integrated Field Research Challenge near the S-3 ponds, where DOE's Office of Science funded research that started in the 1990s. The focus of the Integrated Field Research Challenge has been on understanding the transport and fate of uranium, nitrates, and other contaminants in groundwater, as well as development of reactive barrier technologies.

Relative to mercury, a 25 year record of research achievement has led to various actions that have improved the mercury situation in Oak Ridge (Fig. 11). Research to identify sources of mercury within Y-12 first began in the 1980s, especially within Y-12 storm drains. Later in the 1990s to early 2000s, more significant annual research and technology development investments were made through the Reduction of Mercury in Plant Effluents program, resulting in a number of small-scale but successful abatement actions (Fig. 11). These small-scale investigatory studies continued in the 2000s, primarily conducted by ORNL staff to better understand long-term monitoring results. In 2008 there was a renewed focus on mercury technology development, when a Technical Assistance Team supported by DOE EM Headquarters visited Oak Ridge and provided recommendations for potential mercury remediation "quick wins." Follow-on studies focused on OF200 and the potential for use of stannous chloride (SnCl) treatment, as well as the role of flow management in mobilizing mercury in sediments. In 2011 a Conceptual Model of mercury flux at Y-12 was published, helping to focus the cleanup community on the importance of OF200 as a source of mercury

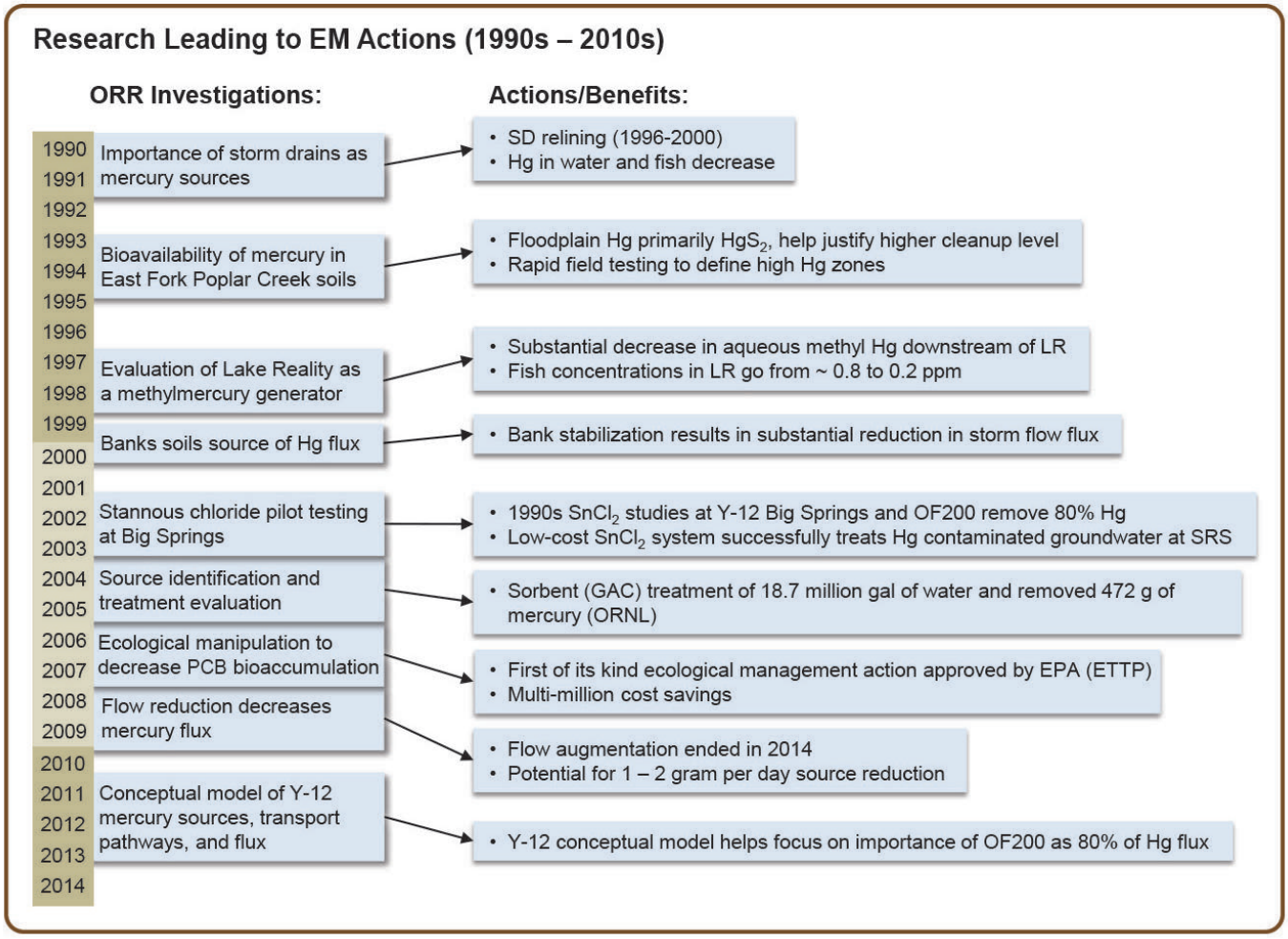


Figure 11. Timeline highlighting various research activities in Oak Ridge that have led to Environmental Management (EM) actions and benefits, 1990s–2010s. (Notes: SD = storm drain; LR = Lake Reality, SRI = Savannah River Site).

to downstream waters. Most recently, consistent with increased national level emphasis on bringing science into EM decision-making, a congressional line item provided funding for mercury technology development in Oak Ridge, including a focus on the LEFPC issue.

Moving forward, research and technology development to address mercury in LEFPC must be sequenced to fit within the overall mercury remediation strategy and timeline (Table 2). Ultimately, the magnitude of potential remedial actions in the downstream environment will depend in part on the performance of recent and future remedial actions at Y-12, including storm drain cleanout/rerouting activities, flow augmentation shut-off, and the success of the OF200 Mercury Treatment Facility. However, current expectations are that Y-12 actions will not be able to result in meeting regulatory limits in the downstream environment, and downstream actions at some point are anticipated.

The research and technology development activities proposed for LEFPC in the next few years will support a CERCLA Alternatives Evaluation for LEFPC that is estimated to be performed in the fiscal year 2021 timeframe (Table 2). In the years leading to 2021, studies should be conducted in a phased, adaptive management approach to reduce uncertainties, to better define and target potential actions or use of new technologies, and to increase efficiencies in characterization, targeted removal and treatment, and waste disposition. As an adaptive plan consistent with the Technology Readiness Level approach, this strategy is expected to evolve dependent on (1) the results of early studies, (2) available funding, and (3) future sitewide remediation priorities and timelines.

Table 2. As of 2014, planned mercury-related remedial activities in Oak Ridge, Tennessee. Based on draft plans in the Y-12 Mercury Remediation Strategy (US DOE 2014).

Planned Mercury Remediation Activities	Fiscal Years 2014–2046						
	14–17	18–22	23–27	28–32	33–37	38–42	43–46
Outfall 200 Mercury Treatment Facility Planning and Construction							
Mercury Treatment Facility Operation							
LEFPC Research and Technology Development							
LEFPC Alternatives Evaluation							
Possible Follow-On Actions							
Mercury Use Facilities Decontamination and Decommissioning and Remedial Actions							
Other Mercury Related Remedial Actions and Records of Decision							

TARGETED RESEARCH AND TECHNOLOGY DEVELOPMENT

Targeted field and laboratory studies are proposed to investigate the use of physical, chemical, and biological manipulations to decrease the primary regulatory concerns in LEFPC: mercury flux, concentration, and bioaccumulation. **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 potential manipulation of in-stream processes, including the many water and sediment chemistry factors that affect mercury methylation. **Task 3, Ecological Manipulation,** investigates methods to manipulate the food chain at both lower and higher levels of organization to decrease mercury concentrations in fish. Together, the three study tasks focus on manipulating the key factors that affect mercury concentrations in fish in the downstream environment[1] (Fig. 12). Because the physical, chemical, and biological factors that affect mercury processes in the creek are interdependent and interrelated as well as complex, the research approach advocated here focuses first on obtaining a watershed-scale understanding of the system. Technology development activities should focus on control strategies that provide potential benefits in decreasing mercury flux, surface water concentration, and bioaccumulation.

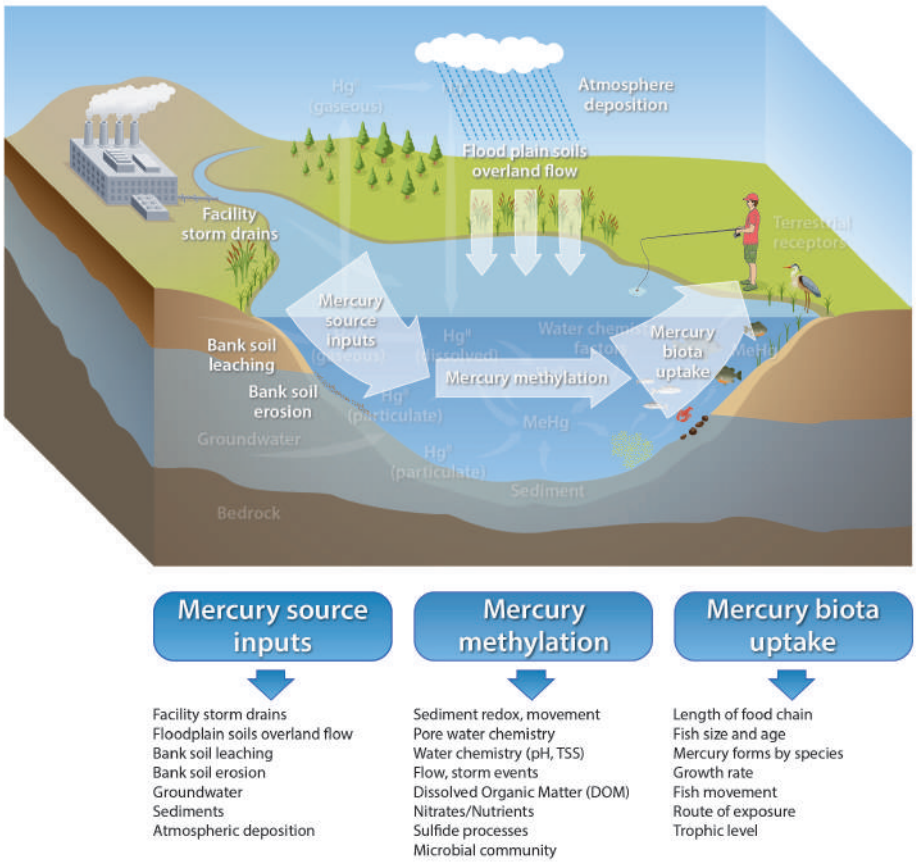


Figure 12. Research and technology development tasks are proposed to address the three major factors affecting mercury concentrations in fish.

[1]Three key factors determine the level of mercury contamination in fish—the amount of inorganic mercury available to an ecosystem, the conversion of inorganic mercury to methylmercury, and the bioaccumulation of methylmercury through the food web.

-- USGS Circular 1395 (Wentz 2014)

Soil and Groundwater Source Control

SOIL

Role of Bank and Floodplain Soil Inputs

As previously stated, a remedial action removed more than 34,000 m^3 of floodplain soils with mercury concentrations exceeding 400 mg/kg in the early 1990s. Recently, downstream bioaccumulation and magnification of mercury in fish continues in spite of decreasing releases from Y-12, strongly suggesting that processes in the stream and its environs are contributing to bioaccumulation. In fact, soils and sediments downstream of Y-12 account for > 80% of the annual export of mercury to the watershed (Southworth et al. 2013). Mercury is in several redox and chemical states in soils—elemental, mercury sulfide precipitates, and associated with soil and organic particles through sorption reactions. As mercury is eroded from bank and floodplain soils, it contributes to the concentration of total mercury in the water column and sediments. Bioavailability refers to the ability to be transformed into dissolved mercury complexes that may be assimilated by microbes or periphyton. The extent of bioavailability of the form of mercury in soils influences the extent to which eroded sediments containing mercury contribute to methylmercury (MeHg) production.

The LEFPC creek bank soils have never been systematically characterized for bioavailability, for mercury and MeHg concentrations, or for susceptibility to erosion. Characteristics influencing soil fluxes into EFPC include soil texture, stability measures such as plastic or liquid limits, the slope angle of the banks, stream water velocities, and vegetation characteristics. Trees, bushes, and other vegetation may enhance the stability of creek banks through the depth, density, and frequency of roots and fungal mycorrhizal growths. However, falling vegetation may contribute to overall destabilization of the banks. Seasonal processes such as strong storms and freeze–thaw also can erode bank and floodplain soils. Basic information is not available on erosion patterns of floodplain and bank soils along LEFPC's entire reach.

Mercury is found in the elemental form, precipitated as mercury sulfides, and sorbed onto minerals and soil organic matter (Barnett et al. 1997, Barnett and Turner 2001). Soil chemical characteristics—such as organic carbon and sulfur content, surface area, oxidation and reduction potential, pH, and cation exchange capacity—govern the strength of bonds between sorbed mercury and soil particles. Precursors for MeHg involve dissolved mercury bonded with dissolved organic carbon, particularly thiol-containing organic functional groups. Sulfate and iron-reducing microorganisms are generally responsible for methylation (King et al. 1999). Mercury that bonds weakly to soil components may be more susceptible to transformation to dissolved mercury. Mercury bonded strongly to soils may not be bioavailable, even if it becomes eroded into the creek, and there are indications that bioavailability decreases with age. To understand how particle-associated mercury from creek bank and floodplain soils contributes to MeHg production, the extent of bioavailability of mercury in the soils should be known.

Addressing these key knowledge gaps will enable the targeting of remedial activities to locations having the highest risk, where risk is defined by both erosion potential and mercury concentrations. With greater

Key concepts

- Soils and sediments account for >80% of annual export of mercury to the EFPC watershed
- Eroding floodplain soil banks deliver fluxes of mercury into EFPC
- Reducing mercury fluxes into EFPC should decrease mercury available for methylation
- The bioavailability of eroded mercury to the microbial community is an important control on MeHg production

scientific knowledge, remedial options can target locations to have the greatest effect (Fig. 13). One concept for targeting solutions refers to the reach of the creek—where making key improvements in select locations only is expected to disproportionately reduce mercury fluxes to the creek system.

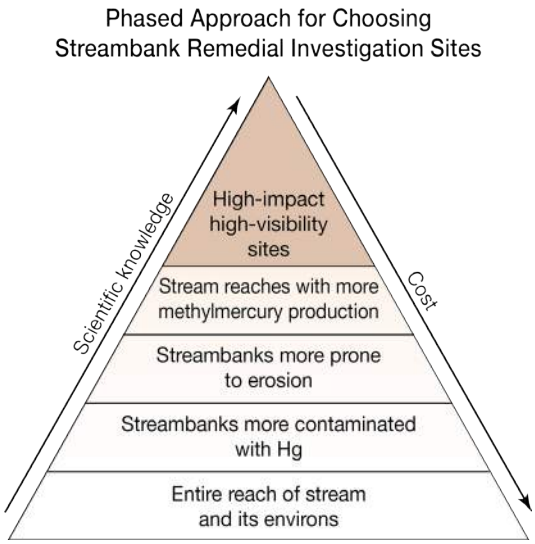


Figure 13. Phased approach for choosing stream bank remedial investigation sites and to determine target areas for remediation.

The first step in this approach is to identify locations that are susceptible to erosion and that contain high mercury (or MeHg) concentrations. As part of earlier research, ORNL staff implemented two interrelated approaches to obtain quantitative estimates of stream bank erosion. The first uses Global Positioning System (GPS)-referenced video mapping of the entire length of LEFPC to its confluence with Poplar Creek. The second approach involves the installation of erosion pins at a few sites identified from the video survey to ground-truth the estimates originating from the video survey.

A GPS-based, kayak-mounted above-water and underwater video mapping and electronic sensor system—a technology developed by Dr. Paul Ayers at the University of Tennessee and applied for a unique purpose in LEFPC—was used to survey stream bank and erosion conditions on EFPC in March, July, and August 2013 (Fig. 14). Each kayak was equipped with three mounted GPS-based video cameras pointing right, left, and forward. The cameras recorded georeferenced digital video of the stream banks, and side-pointing lasers measured stream width. During the "leaf-on" survey, light meters also were mounted on both of the kayaks to get estimates of the length of stream that was covered by canopy. Stream and bank attributes were acquired from interpretation of the recorded video and kayak sensor measurements, such as the angle of the bank slope, slope height, coverage by plants, riparian diversity, light intensity, and river width. Basic information on the direction of the creek and stream water velocities also was measured. A modified Bank Erosion Hazard Index (BEHI) score was determined from bank height, bank angle, surface cover, and riparian diversity information. BEHI scores were converted to erosion susceptibility ratings. The radius of curvature determined from the location of GPS points was used to calculate Near Bank Stress (NBS) scores. The BEHI and NBS scores were used to estimate total stream bank erosion and identify locations of high erosion and stream bank rescission (Fig. 14) using the North Carolina Piedmont Region Bank Erosion Prediction Curves (Doll et al. 2002).

Key questions

- What is the distribution of physical properties of creek bank and floodplain soils, and how do physical soil properties control erosion potential?
- How do seasonal changes (e.g., freeze-thaw and storm events) affect erosion of bank and floodplain soils?
- How are mercury and MeHg concentrations in floodplain and bank soils distributed, and how are concentrations related to soil physical and chemical characteristics?
- How can we limit releases of mercury to the creek associated with bank and floodplain soil erosion?
- How do different soil-based technologies interact with each other and control the overall response of mercury concentrations in fish?

The second technique involved the use of erosion pins, which measured erosion and deposition in specific locations identified from the BEHI and NBS scores (Fig. 15). The method consists of driving a narrow diameter metal

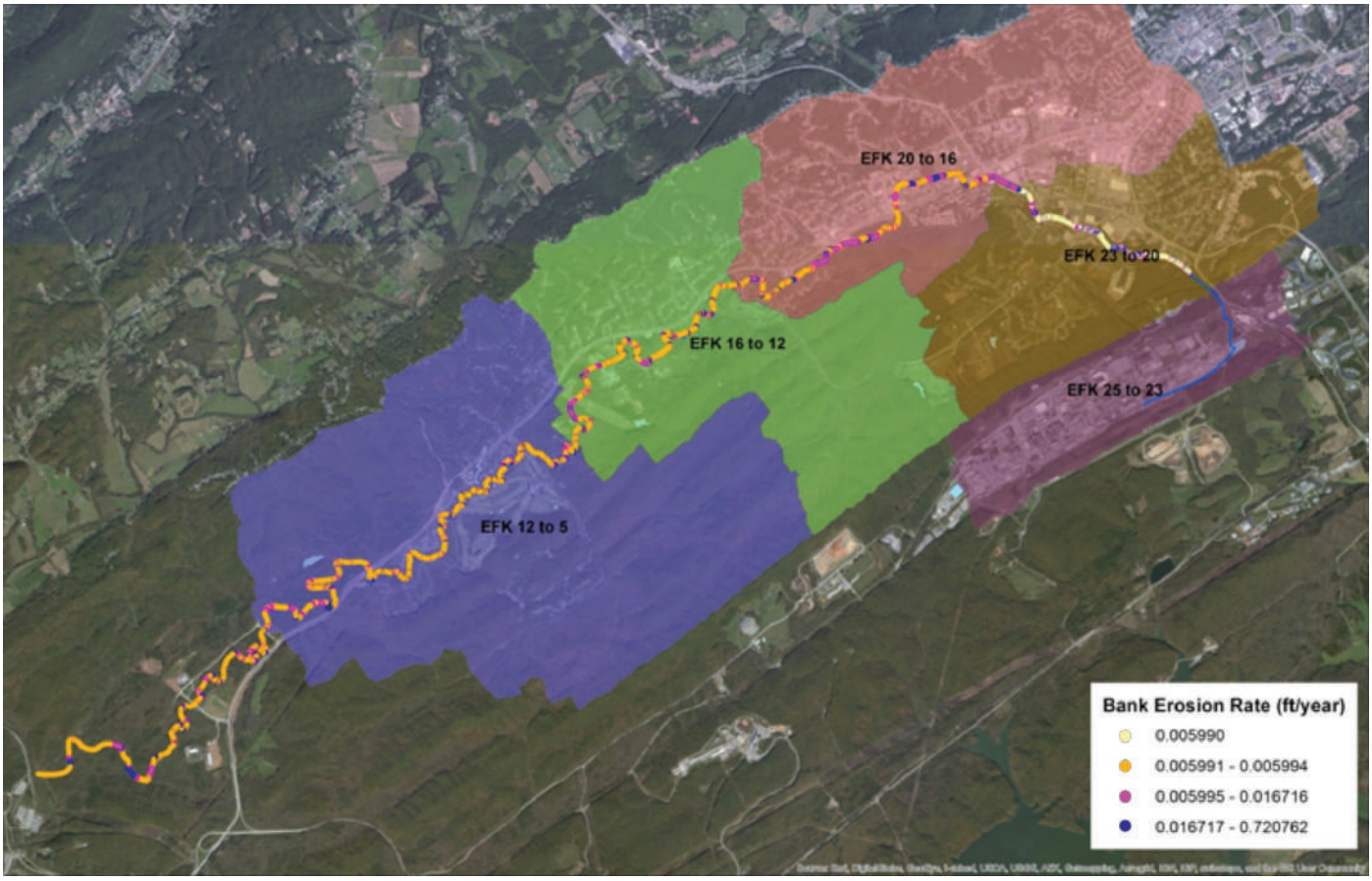


Figure 14. Bank erosion rates across East Fork Poplar Creek calculated from GPS-mounted kayak surveys. (Note: EFK = East Fork Kilometer).

rod into the stream bank until it is flush with the surface. To quantify erosion, the length of exposed pin is measured as a function of time, usually quarterly or bi-annually, or is associated with seasonal timing. Deposition or erosion is measured similarly after carefully exposing the tip of the pin after burial. Mean bank erosion rates are calculated and are combined with measurements of reach length and bank height to estimate volume and mass of erosion.

The bank erosion studies have provided a significant addition to the scientific understanding of the importance of bank soils to LEFPC. However, information is still lacking on the distribution of physical and chemical characteristics of the bank soils. In addition, data is needed to relate measured and predicted erosion rates to mercury and MeHg concentrations throughout the creek. Preliminary results demonstrate little relation between mercury concentrations at repeated sampling locations, suggesting that repeated, or more spatially explicit, sampling will need to be conducted to understand spatial and temporal variability. Subsequent erosion measures can be targeted to locations with high erosion rates and high mercury or MeHg concentrations. In addition, this level of information will be necessary to choose sites to test different treatment alternatives. Before soil remedial approaches are tested in a significant way in the field, an understanding of the soil's physical properties, chemistry, erosive properties, and bioavailability is needed.

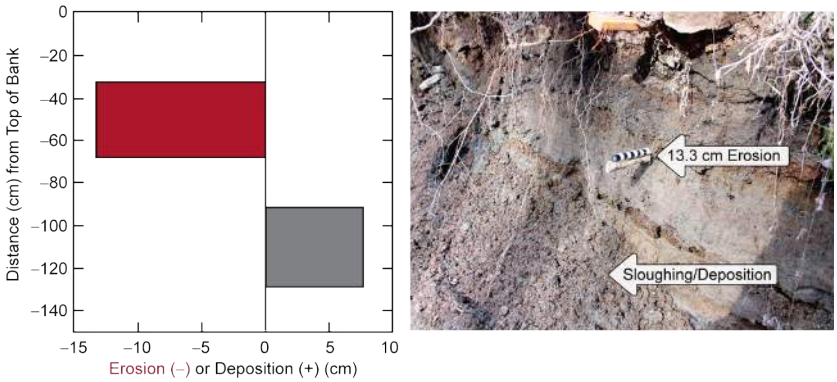


Figure 15. An erosion pin survey at EFK 22, showing pins highlighted with arrows (right) and the erosion and deposition in the graph (left). The images reveal erosion in the upper pins and sloughing and deposition at the lower pins.

Potential Soil Technologies

After determining where to target remedial efforts, the question becomes which remedial activities can effectively and economically prevent releases of creek bank and floodplain soils. Remedial options range from "no action" to "removal and reburial," but there is general scientific consensus that neither of these options meets the needs for site cleanup (Looney et al. 2008). Current data suggests that remedial actions focused only on Y-12 are unlikely to fully address mercury contamination in the downstream environment, especially at the lower end of the creek where methylation rates are high. Removal and reburial is likely to be disruptive to the local communities and environment and may be prohibitively expensive if deployed over significant reaches of the creek; furthermore, there are significant questions regarding the likelihood that soil removal will have its intended benefits in decreasing fish concentrations. The goal of soil technology development is to find alternative approaches that reduce mercury fluxes while avoiding large-scale soil removal. Some potential soil stabilization approaches and technologies that are being investigated for LEFPC are presented in Table 3.

Optimal technology development in LEFPC may involve some combination of bank stabilization strategies in key locations, while seeking to both preserve and enhance the existing environment. For example, bank stabilization may be accomplished using armoring, decreasing the slope of creek banks, and removing unstable trees. Proactive measures such as stabilizing the slope with native plants or other materials could further reduce erosion and would be necessary to recover from bank or vegetation removal activities. Geosorbents designed for uptake of mercury or MeHg could be applied with other stabilization measures or could be designed to function as a stabilization technology. The creek could be reconfigured and diverted away from high erosion sites. Plant root characteristics can promote stabilization of soils and potentially also promote geochemical conditions to inhibit methylmercury production. The South River and the South Fork of the Shenandoah River in western Virginia provide an example of bank stabilization and sorbent deployment to reduce mercury contamination in a stream environment similar to LEFPC (Rhodes et al. 2009, DuPont 2012 2013, Stahl et al. 2014).

There is great potential to combine one or more of these approaches and, in fact, a need to test and potentially deploy multiple approaches because some locations may not be suitable for all technologies. Further, some technologies may be in conflict with each other. Therefore, a solid testing plan will be needed to investigate promising approaches singly and in combination with other technologies. As discussed above, baseline conditions are necessary for identifying testing locations and for proving treatment responses. Remedial technology applications at Lavaca Bay, Texas, involved large-scale dredging and groundwater treatment but failed to decrease mercury concentrations in fish to the desired extent because of ongoing mercury releases from shorelines and marshes (Bloom et al. 1999, US EPA 2011, Matthews et al. 2013). Halting the source of mercury fluxes to Onondaga Lake, New York, also failed to reduce mercury concentrations in fish, most likely because lakebed sediments continued to produce MeHg. Later, however, increases in lake nitrate concentrations were correlated with reduced MeHg production (Henry et al. 2013). A comprehensive and coordinated effort to reduce floodplain and creek bank erosion in EFPC should result in an improved creek environment. As discussed above, a solid scientific basis is needed to choose locations for testing and later implementation of remedial activities as well as to monitor response from baseline conditions to prove that remediation also reduces mercury fluxes and mercury concentrations in fish.

Potential Sorbent Technologies

Although stabilization structures may prevent erosion of mercury-contaminated creek sediments and bank soils, dissolved mercury or methylmercury may migrate across physical barriers and contribute mercury flux to the downstream environment. In situ stabilization of

Stream restoration in Bear Creek, Oak Ridge, Tennessee.

Table 3. Potential soil remedial technologies and approaches for LEFPC

Technology	Description	Objective	Positives	Negatives	Technical Maturity	Research Needs	Overall Evaluation
Bank or floodplain soil removal	Removal of soils with significant bioavailable mercury	Minimize releases of bioavailable mercury to creek	Permanent source removal	Environmentally disruptive. High public visibility. Volume of low contamination is large. High potential cost	Common remedial approach with history of use in EFPC watershed	Lack of understanding of what constitutes bioavailable mercury in bank soils	Viable but not preferred unless hot spots of bioavailable mercury are identified
Bank stabilization through physical armoring	Armoring of bank soils susceptible to erosion with riprap, geotextiles, etc.	Minimize erosive release of particle-associated mercury into EFPC	Straightforward to implement	Environmentally disruptive. Continued maintenance and monitoring is required. Delivery of sunlight may enhance methylation in the water column	Common remedial approach with history of use at EFPC	Identification of "high-risk" locations with high mercury and erosion potential. Demonstrate that reducing erosion reduces mercury concentrations in fish	Viable if bank soils contribute to mercury accumulation in fish
Reduction of slope angles of bank soils	Reducing bank slope angles to minimize erosion	Minimize erosive release of particle-associated mercury into EFPC	Straightforward to implement	Environmentally disruptive. Continued maintenance and monitoring is required.	Common remedial approach to prevent bank erosion	Identification of "high-risk" locations with high mercury and erosion potential. Mercury by depth into bank not well known	Viable if bank soils contribute to mercury accumulation in fish. Less certain to provide significant decrease in erosion
Removal of unstable vegetation	Remove trees and vegetation that are at risk of falling and destabilizing bank channels	Prevent treefalls that destabilize bank soils	Straightforward to implement. Can be coupled with armoring, bank slope angle reduction, and/or new plantings	Environmentally disruptive. Continued maintenance and monitoring is required. Effect of changes in sunlight on bioaccumulation not well understood	Common remedial approach for erosive creek banks	Identification of "high-risk" locations with high mercury and erosion potential. Demonstrate that reducing erosion reduces mercury concentrations in fish	Viable if benefits to mercury loading to stream and fish can be demonstrated
Stabilize creek bank and floodplain soils with native plants	Plant rhizomous native plants along creek banks and in floodplain soils	Reduce or minimize erosion of floodplain and bank soils	High potential to enhance existing environment. High potential to reduce erosion. Can be coupled with vegetative removal, reduction of bank slope angles, and armoring	Uncertain target locations for deployment. Continued maintenance and monitoring is required	Stream riparian restoration commonly deployed on Oak Ridge Reservation	Identification of high-risk mercury sources that are also susceptible to erosion. Requires demonstration that reducing erosion also reduces mercury concentrations in fish	Viable if benefits to mercury loading to stream and fish can be demonstrated
Sorbents to capture mercury and MeHg	Sorbents are applied to bank soils to accumulate mercury and prevent release to EFPC	Prevent mercury and MeHg from being released from bank soils	High potential for sequestration of mercury and MeHg. Can be coupled with vegetative removal, reduction of bank slope angles, and armoring	Method for stabilizing added sorbents is required. Potential high cost of sorbents. Uncertain target locations for deployment. Continued maintenance and monitoring is required	Field demonstrations are few. Deployment will require skill and experience	Requires testing to identify appropriate sorbents. Sorbents must have long-term chemical and physical stability and retention capacity	Viable, but more research is needed
Relocate creek channel	Identify locations for diversion of existing creek and reroute creek to flow through areas with lower mercury loading	Reduce or eliminate reaches where mercury is being released through erosion or where methylation is significant	Permanent solution to problem areas. Contaminated soils are left in abandoned channel	Much of surrounding land is privately owned. Extremely costly	Strategy has been deployed on smaller scale on the Oak Ridge Reservation	Identification of role of bank soils. Demonstrate that reducing erosion reduces mercury concentrations in fish	Viable but not preferred in most locations because of land ownership

mercury-contaminated soils is considered a viable option for application at Y-12 and EFPC. The amendment of creek sediments or stream banks with sorbents aims to capture mercury species within a high affinity sorbent matrix and thus limits migration. Sorbent amendments are a low-impact, low-cost approach for stabilization of contaminated soils and sediments (Ghosh et al. 2011). Many sorbents used for ex situ stabilization of heavy metals have also been considered for in situ stabilization. The primary mode of action is strong binding of contaminant species

to the sorbent material, resulting in a reduction in the pore water concentration. However, sorbent amendments raise many questions regarding long-term effectiveness and stability, ecological impact, and sorbent delivery and mixing. The following technology development strategy comprises evaluation of sorbent materials suitable for application in situ, followed by thorough testing under field-relevant conditions from laboratory to microcosm to pilot scales. The goal is to identify sorbent materials and related engineering solutions with minimal impact on the ecosystem and long-term stability, resulting in a sustained reduction in the concentration of methylmercury available for bioaccumulation in EFPC.

The use of sorbents for the removal of mercury and other heavy metals from aqueous solutions has been investigated extensively. Major classes of sorbents with potential for application in aquatic ecosystems include carbon adsorbents (active carbons, biochars) (Di Natale et al. 2006, Gomez-Eyles et al. 2013), mineral adsorbents (silica gels, activated alumina, oxides of metals, hydroxides of metals, zeolites, clay minerals, pillared clays, porous clay heterostructures), natural and synthetic polymers (functionalized resins), metalorganic microporous materials, and composite and mixed adsorbents (Blanchard et al. 1984, Chen et al. 1999, Chiarle et al. 2000, Walcarius and Delacote 2005, Chang et al. 2007, Shafaei et al. 2007, De Canck et al. 2010) (Table 4, Fig. 16). In a typical treatment process, mercury-contaminated water is passed through a sorbent bed where mercury is adsorbed and removed from the water. The sorbent capacity of the bed is dependent on its surface area, pore size distribution, and surface chemistry. The effectiveness of adsorption is sensitive to a variety of water characteristics, such as co-contaminants, competing metals, and ligands. Co-contaminants may outcompete mercury for surface sites on the sorbent, and an abundance of sufficiently strong aqueous ligands can keep mercury in solution and bioavailable. In addition, suspended solids, organic compounds, and biological growth can cause fouling and plugging of the sorbent. The vast majority of published studies to evaluate sorbent materials for removal of mercury or other heavy metals are centered on industrial waste streams and ex situ treatment technologies.

A literature review of sorbent-based approaches for the remediation of metal-contaminated soils and sediments indicates that the most promising technologies to date are based on activated carbons and biochars (Beesley et al. 2010, Ghosh et al. 2011, Asasian and Kaghazchi 2012, Gomez-Eyles et al. 2013). Activated carbons and biochars can be produced from renewable, low-cost biomass feedstocks; show low inherent toxicity (Jonker et al. 2009, Janssen and Beckingham 2013); and effectively reduce the diffusive flux of contaminants into the water column and subsequent uptake by organisms. Although some findings presented in these studies are certainly relevant to the development of in situ soil and sediment treatment strategies for various contaminants, the unique biogeochemistry of mercury in aquatic ecosystems requires additional considerations. Furthermore, the ecological risks and long-term effects associated with in situ amendments need to be evaluated.

Potential Sorbent Materials

Laboratory experiments can be used to evaluate sorbents with the goal to select a limited set of sorbents to prevent the migration of dissolved mercury and MeHg species from mercury-contaminated soils and sediments into the surface water. Sorbent performance can be evaluated in a series of small-scale laboratory studies, which should be guided by the following criteria: theoretical sorption capacity, partition coefficient K_D, leaching of contaminants, impact on soil/sediment chemistry, and biology and cost. Sorbent materials under consideration for further laboratory evaluation comprise several classes of materials and are listed in Table 4.

In addition to commercially available sorbents, biochars, brass granules, and a novel lignin carbon fiber-based material developed at ORNL also can be

Table 4. Commercial and non-commercial sorbent materials under consideration

Sorbent	Type	Est. K_D (L/kg)	Capacity (mg Hg/g)	Maturity	Cost	Research Needs
Thiol-SAMMS	Functionalized silica (thiol functionalized)	?	600	Medium	High	K_D, test for leaching
Organoclay™ MRM	Functionalized clay (sulfur impregnated)	?	20–100	Medium	High	K_D, test for leaching
Organoclay™ PM-199	Functionalized clay	~500	?	Medium	High	K_D, sorption capacity, test for leaching
SediMite™	Activated charcoal (pelletized)	>10,000	?	Medium–high	Medium	K_D, sorption capacity, test for leaching
Nanomyte® Mergon-AG	Activated charcoal	>10,000	40	Medium	High	K_D, test for leaching
Calgon TOG-LF 80 × 325	Activated charcoal (bituminous coal-based)	>10,000	?	Low	Medium	K_D, sorption capacity, test for leaching
Biochar	Natural charcoal (softwood)	>1,000	?	Low	Low	K_D, sorption capacity, test for leaching
Lignin carbon fiber (LCF)	Carbonized lignin (hardwood lignin)	?	?	Low	Low	K_D, sorption capacity, test for leaching
Brass granules	Cu/Zn alloy, immobilized Hg(II) by amalgamation	?	50	Low	Medium	K_D, test for leaching of Cu^{2+} and Zn^{2+}

evaluated. Lignin carbon fibers (LCFs) are a low-cost, renewable alternative to carbon fibers derived from petroleum-based precursors. Lignin is an inexpensive, high-carbon by-product of pulp and paper production as well as biorefineries (Eberle et al. 2013). The globally available lignin resource is enormous. Up to 40 million tons/year can potentially be isolated from the world's kraft pulp mills without adversely affecting mill operations, offering significant cost advantages. Although the limited strength of LCF reduces its usefulness in structural applications, a porous graphitic structure, high surface area, low cost, and ability to process LCF into large mats make it a potentially interesting material for sorbent applications (Fig. 16).

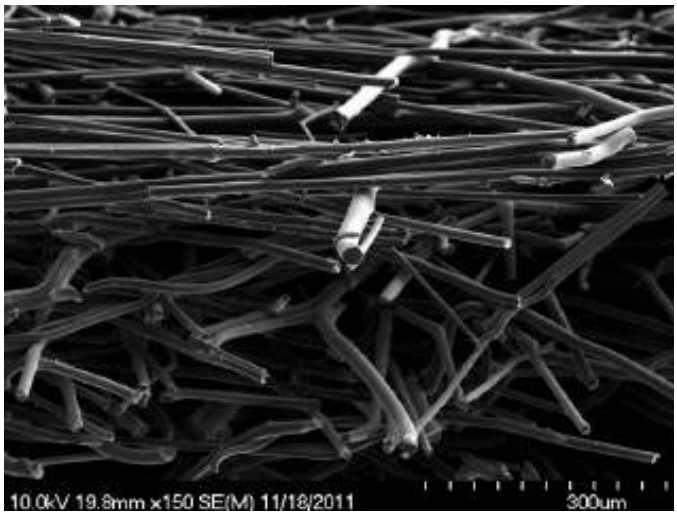


Figure 16. Top: Melt-blowing process for the production of lignin carbon fiber mats. Below: Scanning electron microscopy image of a lignin carbon fiber mat reveals a network of interconnected fibers.

Soil Research and Technology Development Needs

Science-based solutions are needed to develop strategies and technologies to address LEFPC soil contamination. Initial technology development activities should include assessments of the site to refine the conceptual model, testing of potentially applicable sorbents, and planning of technology development field tests. A broad-based review and approach to technology testing should be considered in the initial years, followed by progression to deployment of the most promising technologies at a pilot scale in the field.

Watershed-scale sampling of bank soils is needed, including determination of particle size distribution and mercury concentrations. Initial surveys of banks soils in EFPC have revealed substantial spatial and temporal variability in mercury and MeHg. Understanding that variability, coupled with characterization of bank erosion potential, is essential to identifying fluxes of soils, mercury, and MeHg into EFPC. A key early research goal is to use field characterization data to identify high-priority locations for remedial solutions. In addition, these efforts can help establish baseline conditions necessary for identifying the efficacy of technology testing and future remedial solutions.

Lab-scale tests with a variety of sorbent materials are needed to identify effective and economic materials capable of retaining mercury and MeHg for significant periods. Limitations to using sorbents for soil remediation often center on appropriate application at the test site and understanding effectiveness over longer time scales. Therefore, it will be important over time that tests scale up in terms of realistic representation of EFPC, including spatial and temporal considerations. Sorbent efficacy will need to be field-tested, preferably in a realistic on-site setting under semi-controlled conditions. It is likely that sorbents will eventually need to be applied in concert with other bank rehabilitation methods, such as vegetation removal, reducing bank angles, bank stabilization through physical armoring, and vegetative re-plantings to stabilize creek banks.

Consistent with the adaptive management approach, promising ideas from field and laboratory testing should move forward and up the technology readiness ladder. Monitoring baseline conditions and manipulation responses is essential to determining the outcomes of tests and identifying the most promising technologies for full scale implementation.

GROUNDWATER

Role of Groundwater Inputs

Shallow groundwater adjacent to EFPC may play a significant role in mercury cycling and dynamics in the creek, but this has gone largely uncharacterized to date. When considering stream flow, the dominant image that comes to mind is that of unidirectional downstream water flow and solute transport. Nevertheless, as pointed out long ago, "the stream is not a pipe" (Bencala 1993). Rather, streams are integrated into a complex network of flow paths in which water and solutes move into and back out of hyporheic zones and subsurface areas. Local-scale interactions are controlled by the relative magnitudes of groundwater flow, surface water flow, and water elevations. Evidence collected to date suggests that in some EFPC riparian zones, MeHg concentrations in groundwater can be much greater than in the surface water. Total dissolved mercury in groundwater, however, tends to be lower than in creek water. The extent to which groundwater may be a source of MeHg to the surface water is unknown.

Although the extent to which groundwater inputs to the stream has not been characterized, the recent evidence of higher concentrations of MeHg in groundwater near where the Mill Branch tributary meets EFPC suggests that even a small discharge of this groundwater could affect the surface water MeHg balance (Fig. 17). Although microbial community analyses have not been completed in groundwater along EFPC, evidence of anaerobic microbial processes, including nitrate and sulfate reduction and low dissolved oxygen, are observed. Anaerobic processes

Figure 17. Location of floodplain wells installed in the floodplain behind the TVA substation near EFK 15.7. The approximate locations of East Fork Poplar Creek and Mill Branch have been drawn on the figure (screen capture from Google Earth; aerial imagery date April 2013). Distance from the edge of the creek bank to wells MBFP-01, -02, and -03 is 1.2–1.5 m; well MBFP-04 is ~12.5 m from creek.

(i.e., in the absence of oxygen) are key for the production of MeHg, because a variety of terminal electron acceptors such as oxygen and nitrate must be exhausted before MeHg production commences. In most aquatic systems, microbial iron and sulfate reducers, as well as fermentors and methanogens, are largely responsible for MeHg production.

Interestingly, the relationships between total mercury and MeHg in the creek and groundwater are quite different (Fig. 18). The extent of the contribution of groundwater to surface water is likely to change as a function of season. For example, in fall and winter, trees do not remove as much moisture from the vadose zone, causing groundwater to rise and feed into EFPC. In the growing season, trees remove more moisture from the vadose

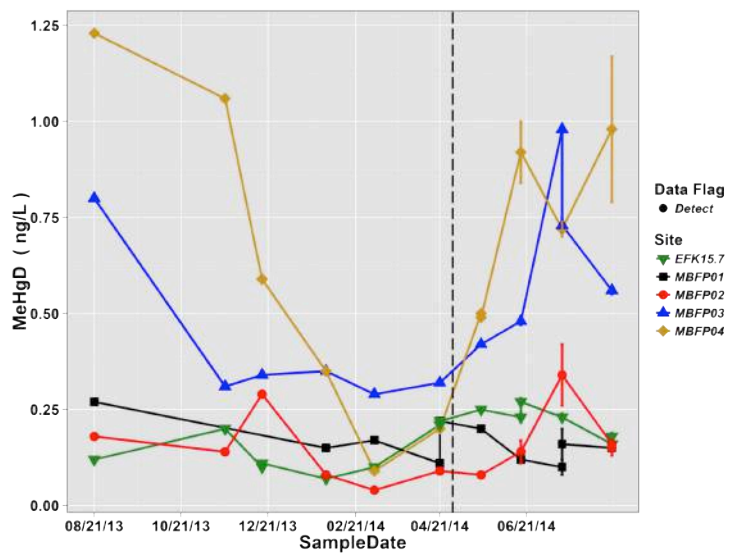


Figure 18. Concentrations of dissolved (< 0.2 µm) methylmercury (MeHg) in surface water (EFK 15.7) and groundwater (MBFP01 to MBFP04). The vertical dashed line indicates the cessation of flow augmentation near Outfall 200 inside the Y-12 Complex. Error bars indicate ± 1 standard error of the analytical measurement. Error bars not visible are smaller than the symbol size.

zone, and EFPC may be a "losing" stream (i.e., the stream infiltrates to recharge groundwater). Stream infiltration may also include dissolved organic matter and nutrient inputs, which are critical for fueling microbial community processes. Therefore, understanding seasonal constraints on groundwater–surface water interactions is key for understanding the overall role of groundwater as well as to design, if needed, remedial technologies to address groundwater mercury flux.

Potential Groundwater Technologies

Although early studies have shown at some groundwater locations a seasonal pattern of mercury and MeHg concentrations, a direct measure of the role

of groundwater in MeHg fluxes to the creek has not been conducted. Nor is it understood if there are spatial or temporal considerations that are important to that flux. The significance of these processes must be determined before any remedial approaches are considered. Therefore, early assessment of groundwater technologies should focus on understanding the role of groundwater on methylmercury processes in the creek.

If the groundwater source of methylmercury is found to be significant and widespread, then specific remediation approaches (Table 5) can be evaluated. These may include reactive capping along groundwater discharge areas, biological or geochemical additions to promote demethylation and/or minimize methylation in groundwater, decreasing or eliminating groundwater–surface water exchange, and vegetation plantings to alter nutrient availability or enhance phytoremediation. For the first two technologies in particular, understanding if the groundwater acts as a "point source" contributing MeHg to the stream at isolated locations may determine the feasibility of the approaches. If groundwater discharge is diffuse, technologies likely cannot be employed at enough locations to significantly affect fluxes or alter the chemistry. However, if groundwater discharge occurs at select locations, technologies may be used to aid in reducing fluxes or altering groundwater composition.

A wide array of technologies can be developed to minimize the production and release of MeHg into LEFPC if groundwater is demonstrated to be an important source. Reactive capping technologies can utilize materials

Table 5. Potential groundwater remedial technologies and approaches for LEFPC

Technology	Description	Objective	Positives	Negatives	Technical Maturity	Research Needs	Overall Evaluation
Reactive capping	Minimizes groundwater and MeHg fluxes into EFPC	Reduce MeHg fluxes to EFPC	If MeHg fluxes are isolated, targeted alteration of hydrology and reaction to attract MeHg and Hg could be effective	Uncertain spatial extent of groundwater discharge zones	Long history in groundwater discharge zones for other contaminants	Understanding of MeHg production in groundwater and release to surface water. Understanding of subsurface flowpaths as a function of seasons	Promising. Depends on spatial extent of groundwater MeHg production. Depends on whether groundwater is a point source to EFPC or if interactions are diffuse
Lining bed and banks of EFPC	Minimizes water and MeHg fluxes into EFPC. Minimizes nutrient fluxes into groundwater	Reducing or eliminating groundwater and surface water interactions	Effective means of eliminating groundwater and surface water interactions	Could conflict with overall stream ecosystem restoration. Intrusive and costly	Very mature. History of deployment in UEFPC and other locations	Understanding of methylmercury production in groundwater and release to surface water. Understanding of subsurface flowpaths as a function of seasons	Very conventional technology but inconsistent with overall habitat restoration goals
Altering groundwater chemistry	Alter groundwater chemistry to promote demethylation	Minimize the net release of MeHg	Potential to alter MeHg production before groundwater enters EFPC	Does not remove source. Will require long-term and continuous treatments. Many available technologies; e.g., altering oxygen content, nutrient load, engineered remedial additions	Common technique for other contaminants	Requires understanding of MeHg production in groundwater and release to surface water	Could be effective if groundwater is an important and widespread source of MeHg to EFPC. Best if there are isolated discharge zones of groundwater
Altering microbial community composition	Alter groundwater chemistry to promote demethylation	Minimize the net release of MeHg	Potential to alter MeHg production before groundwater enters EFPC	Does not remove source. Will require long-term and continuous treatments. Microbial community composition is complicated	Less commonly employed than geochemical manipulations	Understanding of MeHg production in groundwater and release to surface water	Could be effective if groundwater is an important and widespread source of MeHg to EFPC. Best if there are isolated discharge zones of groundwater
Vegetative plantings	Alter groundwater chemistry and microbiology to minimize methylation and/or to minimize water flux	Minimize the net production and release of MeHg	Amenable to ecosystem restoration efforts. Plantings are appropriate for shallow groundwater MeHg source.	Does not remove source. Complex processes involving vegetation, microbes, and groundwater chemistry	Less commonly employed to alter shallow groundwater chemistry	Understanding of MeHg production in groundwater and release to surface water	Only incremental benefit likely.
Phyto-remediation	Plantings to promote uptake of Hg by plants	Hg removal	Potential for source removal without earth removal. Can be coupled with creek restoration efforts	Requires continual removal, replanting, and disposal. Potential for release of Hg from leaves	Commonly employed in shallow groundwater systems	Understanding of plant uptake of Hg and MeHg	Not preferred because of risk of continual maintenance

Key questions

- To what extent does methylmercury production in groundwater contribute to surface water fluxes?
- To what extent do nutrient contributions to groundwater contribute to methylmercury production?
- How does the seasonal variation in groundwater–surface water exchange affect methylmercury release in EFPC?
- How can the production of methylmercury in groundwater be minimized?
- How can the release of methylmercury from groundwater to surface water be minimized?
- Can targeted vegetation plantings minimize the production and release of methylmercury?

with new sorbents or compounds to minimize the release of MeHg and total mercury along the boundary of groundwater discharge. Reactive capping can also promote demethylation. Flow barriers such as creek bed liners, perhaps developed for the specific EFPC conditions, can minimize groundwater–surface water interactions. However, widespread bed lining activities would be at odds with other targets focusing on ecological stream restoration and enhancing benthic communities, and such activities could be prohibitively expensive. Once the chemistry and microbial conditions in groundwater are known, targeted additives or alterations of groundwater microbiology or chemistry could alter gross or net methylation. For example, technologies that encourage oxygenation and aerobic conditions can minimize MeHg production and/or promote demethylation, and these kinds of technologies have been applied in groundwater scenarios for many other contaminants. Technologies that alter the microbial community and minimize growth conditions for methylators can also reduce production of MeHg. Vegetative plantings can be used to alter the hydrological balance between groundwater and surface water and minimize groundwater discharges. Plantings can also alter the nutrient balance of groundwater through uptake or release, thus altering the growth conditions of the methylating microbial community. Finally, phytoremediation techniques may be used to promote the uptake of MeHg and mercury.

As discussed above, most of these technologies require one key aspect to succeed. The release points of groundwater MeHg to surface water must be spatially isolated. In other words, selective application of the technologies is required to minimize cost and maximize effectiveness. Vegetative plantings, however, may be readily deployed along the entire floodplain and near-bank environment.

Groundwater Research and Technology Development Needs

Science-based solutions are needed to develop strategies and technologies to address LEFPC groundwater contamination, if characterization studies determine that groundwater is a significant source of MeHg to the creek. Initially, scientific investigations should be conducted to form the basis of a detailed conceptual model describing the system, functional compartments, and rates and mechanisms of interactions between groundwater and surface water. Subsequently, a variety of remedial technologies should be tested at the lab, pilot, and reach scale as well as monitoring baseline and manipulation conditions.

Technology development initially should involve basic characterization of surface water–groundwater interactions at one or more locations. The goal of such studies would be to identify the extent of fluxes in terms of volume of water and concentration of mercury and MeHg. If fluxes are significant, tracer injections could be used to identify the release points of groundwater to EFPC, as a function of season and water table, and to determine whether groundwater fluxes are point sources or diffuse sources. The type of remedial technology appropriate for testing will be highly dependent on the nature of the surface water–groundwater interactions. Diffuse exchange will point toward more engineered solutions, such as reactive capping, vegetative plantings, and lining the creek. Point sources will support more targeted solutions, such as altering groundwater chemistry, phytoremediation, or affecting the microbial community composition. As always, multiple technologies ultimately may need to be deployed. Altering groundwater chemistry or microbial community composition would need to be first tested in the laboratory, while other technologies can be tested only in the field.

Surface Water and Sediment Manipulation

SURFACE WATER

Role of Surface Water Chemistry

The water chemistry domain comprises water within the creek and water that fills the spaces between rocks, sand, and finer particles on the creek bed. The transition zone between this surface water and the groundwater is frequently referred to as the hyporheic zone and is an area known to be active for mercury methylation. The factors controlling mercury cycling and MeHg production in surface waters of streams and rivers are complex, and some interact in ways that are known, while others likely interact in ways that have yet to be elucidated. Although a great deal of mercury research has been conducted in aquatic environments, most has taken place in coastal and estuarine environments (Heyes et al. 2006, Hollweg et al. 2009, Liu et al. 2009), lakes (Hintelmann et al. 2000, Guevara et al. 2009), reservoirs, and wetlands (Mitchell and Gilmour 2008, Mitchell et al. 2009), leaving rivers and streams less well studied in comparison.

A number of water chemistry parameters are correlated with methylmercury production and accumulation by biota (Table 6). The mechanism underlying these observations may reflect a combination of effects related to mercury or MeHg speciation (e.g., aqueous-solid partitioning, association with dissolved organic matter), the activity of methylating or demethylating bacteria causing changes in net MeHg concentration, or direct effects on organisms' accumulation efficiency. The site-specific form of the relationship between these parameters and mercury cycling, MeHg production, and bioaccumulation in the EFPC ecosystem is not known.

A number of watershed-scale factors can affect MeHg levels in surface water and fish in EFPC. For streams across the United States, there is a positive correlation between wetland area and MeHg concentration in water (Wentz et al. 2014; Fig. 19). EFPC has very low wetland

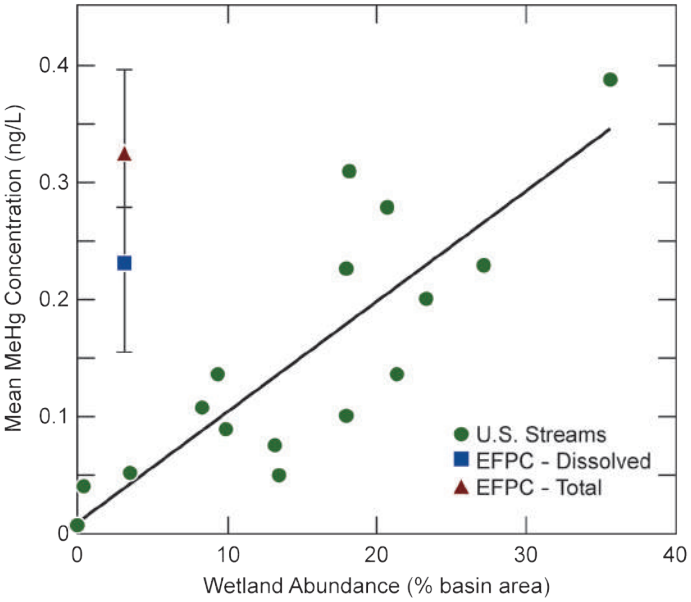


Figure 19. Mean MeHg concentration in water versus wetland abundance for streams in the United States and East Fork Poplar Creek. Data for EFPC are from creek kilometer 5.4 (adapted from Wentz et al. 2014).

Table 6. Summary of state of understanding of factors and variables affecting Hg fate and transformation in the environment

Factor	Variable	Trend	Mechanism
Form of Hg and MeHg in system	Solid phase	Hg sorbed onto solids or in a precipitate may not be available for methylation	
		MeHg sorbed onto particles not accumulated via uptake routes dependent on dissolved concentration. This MeHg may also be unavailable for demethylation	Decreases dissolved MeHg available for uptake or demethylation
	Dissolved phase	Positive relationship between Hg concentration and MeHg production up to a limit	
	Hg ageing	"Fresh" or newly added Hg to a system more available for methylation	Freshly added Hg not yet complexed/sorbed with highest energy sites, more labile for exchange/uptake by methylating bacteria
Water chemistry	pH	Inverse relationship between pH and MeHg bioaccumulation for benthic inverts, fish, and loons	May affect both methylation and demethylation
			Hg sorption increases with pH, decreases Hg available for methylation
			Hg(II) solubility decreases with increasing pH making Hg less available for methylation
			Aqueous speciation of Hg(II) is pH-dependent, may result in species less available for methylation
			Hg(II) photoreduction increases with pH. The Hg(0) formed may not be available for methylation and also can escape aquatic system via evasion
			Dependence of bacterial methylation and demethylation activity on pH not known
			Unknown effect on uptake by biota
	Alkalinity	Alkalinity negatively correlated with Hg concentration in biota	Unknown
	DOC quantity and quality	Opposing trends are observed depending on DOC quality factors, precise nature of those factors not well defined, effects likely highly site-specific	Complex relationship between DOC quality, concentration, Hg and MeHg aqueous complexation and partitioning to solid phase, and microbial activity
		Positive relationship between labile OC and methylation	Increased supply labile C increases microbial activity until other nutrient limitations come into play
			Short-term intense activity in response to labile OC could result in anaerobic conditions favoring mercury methylation
		MeHg associated with high molecular weight DOM leads to less bioaccumulation	
		Positive relationship between DOC concentration and Hg transport and dissolved Hg	Hg-DOM complexes can increases Hg solubility/ aqueous phase partitioning
		DOM can enhance Hg(II) photoreduction and MeHg photodemethylation	Unclear; strong thiolate binding in DOM enhances energy transfer from excited triplet state of aromatic moieties in DOM
	Dissolved oxygen	No methylation in presence of oxygen.	Bacterial mercury methylation occurs only in anaerobic environments. All known methylating bacteria do so only under anaerobic conditions (Fe[III] reduction, SO_4 reduction, fermentation, methanogenesis)
	Nutrient status	Nitrate—addition could either increase or decrease Hg methylation	If nitrate is not a limiting nutrient, its addition could inhibit conditions/ microbial metabolisms associated with Hg methylation - Fe(III) and SO_4^{2-} reduction, fermentation, methanogenesis
			If nitrate is a limiting nutrient, its addition could stimulate microbial activity, including Hg methylation
		Iron—increased supply of Fe(III) can increase methylation	Fe(III) addition may stimulate methylating Fe[III]-reducing bacteria
		Sulfate—an upside-down "U" response of Hg methylation to SO_4 addition is seen	When SO_4^{2-} concentration limits sulfate reduction, addition of sulfate increases Hg methylation. Eventually, addition of excess sulfate limits methylation due to excess sulfide production. In presence of excess sulfide, greater fraction of dissolved Hg forms charged Hg-S species (less bioavailable) and promotes precipitation of poorly soluble Hg/Fe(II)/S(II) phases

Factor	Variable	Trend	Mechanism
	Other	Selenium—inverse relationship between selenium concentration in water and MeHg in biota	Unknown. May affect Hg(II) availability for methylation via aqueous complexation or precipitation of Hg with selenite. May affect methylation activity of bacteria. May affect MeHg uptake or depuration processes by biota.
		Molybdate—in laboratory studies, molybdate is used as a specific inhibitor of sulfate reducing bacteria. MeHg production in these studies is substantially decreased or eliminated when molybdate is added	Multiple modes of action; primary mode may be interference with sulfate uptake
Physical/ Environmental	Water temperature	Positive correlation between temperature and methylation activity	Microbial activity increases with temperature as permitted by other limiting nutrients in the system
			Higher activity may induce zone of anoxia favoring mercury methylation
	Light	Enhanced photoreduction of Hg(II) with increased sunlight. Resultant Hg(0) lost from system via volatilization	
		Enhanced photo-demethylation with increased sunlight	
		Increased primary and secondary production yields greater growth efficiency in fish—lower Hg concentration in tissues	
	Large woody debris	Large woody debris traps leaves, fine-grained sediment creating areas that may have high methylation potential	Accumulation of fine-grained sediments and entrained organic materials (detritus, aquatic vegetation, leaves, etc.) create anaerobic zones favoring the production of methyl mercury by anaerobic bacteria

coverage (3% by area), and many of these areas are not well connected hydrologically to the main creek channel. EFPC has six to eight times more MeHg than other streams with similar wetland coverage (Fig. 19). These results suggest that wetlands are not primary source contributors to MeHg in EFPC. Atmospheric mercury deposition is another primary source of mercury to watersheds but is thought to be a trivial component of the mercury mass balance in EFPC—contributing an estimated 0.0002% mean annual daily load of mercury to the creek. Additionally, atmospheric deposition alone in nearby creeks does not result in fish that exceed human health guidelines.

Total mercury concentrations in LEFPC surface water exceed the State of Tennessee's AWQC, with the largest percentage of surface water mercury concentrations composed of inorganic mercury bound to particles. The LEFPC mercury mass balance is, therefore, driven by source mercury inputs including the point source discharge of mercury from Y-12 as well as redistribution and transport of legacy mercury within the watershed (e.g., bank soils, sediments). The role of current releases of mercury from Y-12 vs. downstream historical sources on mercury methylation is not well understood and is an area of investigation, as is the role of downstream water chemistry factors on methylation. The importance of various environmental factors on mercury methylation is evident in the fact that total mercury surface water concentrations decrease with distance downstream, while MeHg increases. MeHg is generally assumed to be the form of mercury that is assimilated and bioaccumulated. While this is true in many non-polluted sites, it is worth considering that in an industrially contaminated setting with very high mercury concentrations, such as EFPC, inorganic mercury may also contribute to mercury body burden (Hines et al. 2000, Horvat et al. 2003). If this is the case, then decreasing waterborne mercury concentration should lead to rapid decreases in fish mercury because inorganic mercury is eliminated from tissues more rapidly than MeHg (Trudel and Rasmussen 1997). Therefore, actions targeted at lowering inorganic mercury concentration may directly lower mercury accumulation in EFPC biota in addition to lowering the supply of mercury for methylation by bacteria.

Key questions

- What changes in mercury and MeHg flux occur along the length of EFPC? Can these indicate "hot spots" of MeHg production?
- Are mercury and MeHg dynamics during high flow events indicative of any significant out-of-stream sources of these constituents to the creek?
- What are the water quality characteristics of zones where MeHg is produced? What actions might be taken to mitigate MeHg in those zones?
- How does mercury methylation potential for EFPC samples respond to changes in water chemistry?

> Freshwater streams are relatively underrepresented in the mercury and MeHg research literature, leaving important gaps in understanding and limiting the knowledge base on which informed decision support rests.

Potential In-Stream Water Chemistry Manipulations

The goal of water chemistry manipulation technologies is to disrupt mercury transport and loading, aqueous partitioning, methylation, and exposure/bioaccumulation mechanisms. By decreasing total and methylmercury concentrations in surface water, the expectation is decreased flux of these constituents and their concentration in fish tissue. New water chemistry manipulation strategies and technologies are sought to effectively decrease mercury bioavailability and bioaccumulation, while limiting impacts to the environment or costly soil removals.

A number of environmental or physical factors may play a direct role in mercury transformations and accumulation in EFPC and potentially may be manipulated to benefit the mercury issue (Table 7). To be comprehensive, a number of factors known to affect mercury transformations are discussed here as possibilities for manipulation. Although it is well known that certain in-stream factors affect mercury methylation, manipulating those factors to decrease methylation is an approach that needs targeted applied research and technology development, including, for EFPC, a thorough understanding of water chemistry–mercury interactions in the system.

For example, two major factors known to affect mercury transformation and methylation processes are water temperature and light. There is a positive correlation between water temperature and methylation activity. Creek temperature could be manipulated by supplementing flow with cooler water at several locations along the creek, although making significant temperature changes in a watershed the size of EFPC is likely to be problematic. Altering the light regime by controlling canopy cover could make beneficial use of mercury's photochemical reactions. For example, photoreduction of Hg(II) to Hg(0) and volatilization of the latter from the water could lower mercury concentrations. Similarly, photodegradation of MeHg could decrease the amount of MeHg available for biouptake. However, the sunlight–mercury relationship needs to be studied in EFPC, especially relative to periphyton growth and food chain dynamics that affect mercury bioaccumulation.

Mercury accumulation in biota is negatively correlated with both pH and alkalinity. The underlying mechanism responsible for these correlations is not known. However, EFPC water is mildly alkaline (pH 7.5–8), well-buffered hard water (158 mg/L as $CaCO_3$) because of the underlying carbonate rock terrain through which it flows. Remediation actions designed to further increase either the pH or alkalinity would not seem to be worthwhile.

Bacterial mercury methylation occurs in anaerobic environments. EFPC surface water and most of the water flowing through the coarse-grained bed are well oxygenated. Nevertheless, in some locations, there are fine-grained channel margin deposits and other areas with decreased exchange of sediment pore water with the surface water. Additionally, many of these locations contain excess labile organic carbon (e.g., from entrained organic detritus). Either of these conditions, or their co-occurrence, can result in the depletion of dissolved oxygen in the sediment pore water. In these anaerobic environments, both Fe(III) and sulfate-reducing microbial populations are more active, creating conditions favoring the production of MeHg. The identification and targeted aeration of such zones may disrupt MeHg production.

Properties of naturally occurring dissolved organic matter (DOM) have been correlated with mercury and MeHg concentrations as well as with methylmercury production and bioaccumulation. DOM properties are highly site-specific, resulting in complex and sometimes contradictory trends reported in the literature. In EFPC, changes in DOM as one travels downstream should discourage mercury methylation and accumulation. However, these changes are gradual and may be overwhelmed by counteracting changes in other controlling variables. It may be possible to add greater amounts of DOM to inhibit MeHg production and accumulation. Extensive characterization and experimentation are required to generate the needed knowledge base to support such action.

The concentration of nutrients other than dissolved oxygen can affect MeHg production. Our understanding of the mode of action of nutrients on MeHg concentration is best for the microbial community response, although other environmental compartments (e.g., aquatic macrophytes) may contribute in ways that are not currently known. Nitrate, if present in non-limiting concentrations, can inhibit MeHg production by favoring nitrate-reducing communities. There are no known nitrate reducers capable of MeHg production. In Onondaga Lake, MeHg concentration in the water column and biota decreased with increases in nitrate concentration. Suppression of methylating sulfate-reducing bacteria in the presence of higher nitrate concentration is believed to be responsible.

The behavior of a lake versus a flowing creek in response to nitrate addition may be very different. In contrast, if nitrate is a limiting nutrient, then adding nitrate to a system could generally stimulate MeHg production via general stimulation of microbial activity. Because of diffuse inputs within Y-12 to UEFPC and discharge from the Oak Ridge Wastewater Treatment Facility (ORWTF), EFPC is eutrophic along its length with respect to nitrate and meso- to eutrophic with respect to phosphate concentrations.

Because sulfate-reducing bacteria (SRB) were for a long time the only known group of bacteria capable of methylating mercury, a great deal of research has studied the relationship between sulfate concentration and methylmercury production. In general, an upside-down "U" response is observed. At low sulfate concentration, sulfate limits the activity of SRB, while MeHg production increases with increasing sulfate concentration. Eventually, at higher sulfate concentration, the production of excess sulfide limits MeHg production because a greater fraction of the inorganic mercury becomes bound in less bioavailable forms (either charged HgS aqueous complexes or poorly soluble HgS solid phases). Sulfate concentrations in

Table 7. Summary of potential remediation alternatives based on understanding of factors and variables affecting Hg fate and transformation in the environment summarized in Table 6.

Factor	Variable	Remediation Alternative/ Approach	Mode of action	Note/ Comment
Form of Hg / MeHg in system	Dissolved phase	Monitored natural recovery	Hg concentrations will naturally decline over time	Length of time to achieve objective not known
				Little to no improvement expected without substantial source reduction from Y-12
				Public perception hurdle
		Pump and treat	Creek flow diverted to engineered water treatment facility to remove Hg	
		Deploy removable sorbents	Dissolved Hg concentration lowered via sorption onto solid phase that can be removed and replaced as needed	
		Phytoremediation	Hyperaccumulating vegetation will remove Hg from solution and can be harvested for disposal	
		Restart flow augmentation, locate injection point at/ near Station 17	Dilution of source from Y-12 will decrease concentration of inorganic Hg available for methylation leading to lower MeHg concentration	
	Solid phase	Addition of sulfide	Increases Hg precipitation into poorly soluble and nonbioavailable phases	Sulfide toxicity; oxidation of sulfide generates acid; increasing neutrally charged Hg(II)-S species may increase Hg methylation; oxidation of sulfide to sulfate may stimulate methylation; overloading sulfide promote anoxia favoring methylation; what controls bioavailability of Hg for methylation poorly known
		Sorbent addition to water	Removes dissolved Hg from aqueous phase decreasing available Hg for methylation	
	Hg aging	Significantly decrease or cease inputs of "fresh" Hg from Y-12	Older Hg in the system less available for methylation	Relative bioavailability of fresh Hg from Y-12 assumed to be higher than Hg currently in the system
Water chemistry	pH and Alkalinity	Determine pH and alkalinity least favorable for MeHg uptake in EFPC and adjust creek to that value	Unknown, responds to empirical negative correlation among pH, alkalinity, and MeHg accumulation	May require long-term titration of flowing water body. EFPC currently well-buffered system in the mildly alkaline pH range
	Dissolved oxygen	Targeted aeration of fine-grained deposits, hyporheic zones where methylation suspected of occurring	Introduction of dissolved oxygen disrupts anaerobic microbial metabolisms associated with methyl mercury production	May not effectively penetrate fine grained deposits, hyporheic zones without large-scale direct intervention
	DOC quantity and quality	Amend EFPC with high molecular weight recalcitrant natural organic matter	Hg and MeHg associated with high molecular weight DOM less available for methylation and biotic uptake, respectively	Empirical observations from literature. Specific DOM structure-activity relationships are not known and likely are highly site/ DOM specific

Factor	Variable	Remediation Alternative/ Approach	Mode of action	Note/ Comment
Nutrient status	Nitrate	Nitrate additions	Greater availability of nitrate will inhibit microbial Fe(III) and SO_4 reduction, and methanogenesis —the bacterial metabolisms associated with methyl mercury production	Increased nitrate concentrations in Onondaga Lake deemed responsible for lower MeHg concentrations and accumulation in biota
				EFPC currently eutrophic throughout with respect to nitrate due diffuse release from Y-12 and point discharge from ORSTP. EFPC meso- to eutrophic with respect to phosphate
	Sulfate	Sulfate additions	Addition of excess sulfate will generate excess sulfide, resulting in forms of Hg less available for methylation	May inadvertently increase methylation, system may be C limited so SO_4 addition may not be useful
				EFPC naturally has relatively high levels of SO_4^{2-} already (~30 mg/L); further additions may not be useful.
	ORSTP	Stricter controls on nutrient (nitrate, ammonium, phosphorus) discharge	Nutrient discharges from the ORSTP outfall into EFPC may be stimulating activity within the creek, promoting an undesirable increase in Hg methylation and/or biotic uptake	
	Selenium	Addition of selenium to lower MeHg concentration in water and biota	Unknown	Concerns over selenium toxicity make this approach unlikely
	Molybdate	MeHg generation is significantly decreased to completely halted in laboratory incubations amended with millimolar amounts of sodium molybdate	Molybdate inhibits the activity of sulfate reducing bacteria, some of the most important mercury methylating bacteria	Relatively large amounts of molybdate (> 100 mg/L) are needed for effective inhibition
				Unknown if molybdate would inhibit other known classes of Hg methylating microorganisms (Fe(III) reducers, fermenters, methanogens) but it is not a specific inhibitor of these microorganisms
				Unknown if sulfate reducers are the primary methylators in EFPC
				Secondary effects of molybdate on other parts of the ecosystem (e.g., toxicity, effects on Hg uptake by higher organisms)
				Sulfate reducers adapt to molybdate under constant exposure – inhibitory effect is lost
Physical/ Environ-mental	Water temperature	Lower water temperature by manipulating flows	Decreased microbial activity will decrease MeHg production	Unknown response of rest of trophic structure and consequent MeHg concentration in biota
				Potentially large capital investment and ongoing operations and maintenance costs
	Light	Remove creek canopy cover	- Greater light penetration will enhance photoreduction of Hg(II) to Hg(0); volatilization of this out of creek water - Greater light penetration will lower MeHg concentration in water via photodemethylation	Removal of trees/ canopy cover may be counterproductive with respect to bank stabilization efforts or would need to be conducted in conjunction with active bank management
				Increased light penetration may accelerate growth of submerged aquatic vegetation which may enhance MeHg formation via (i) trapping fine sediments, creating anoxic zones, (ii) providing labile organic detritus stimulating anoxia and microbial activity
				Canopy removal likely increase water temperature which may increase MeHg production
	Large woody debris management	Removal of large woody debris, debris blockages	Decreases buildup of fine-grained deposits and accumulation of vegetation/ detritus which enhance mercury methylation	

local creeks naturally have a fair amount of sulfate (~15 mg/L), and EFPC carries higher concentrations (~30 mg/L) because of inputs from the Y-12 Complex.

Other elements have also been shown to affect MeHg production or bioaccumulation in fish. Molybdate (MoO_4^-) is used in laboratory experiments as a specific SRB inhibitor. When MoO_4^- is added to pure cultures of SRB or sediment slurries at appropriate concentrations, sulfate reduction stops, as does MeHg production. Molybdate may interfere with sulfate reduction through several proposed mechanisms, but it remains unclear if its effect on MeHg production is caused by general inhibition of SRB activity or acts specifically in the mercury methylation biochemical pathway. MeHg concentration in biota is negatively correlated with selenium concentration in water. The exact mechanism is unknown, and several possibilities exist. Similar to sulfide, complexation or precipitation of inorganic mercury with selenite may decrease the bioavailability of mercury for methylation. As with molybdate, selenite inhibits the activity of SRB, although the effect on MeHg production by these bacteria has not been studied. Finally, selenium may affect MeHg uptake by biota. Regardless of mechanism, amending EFPC with either molybdate or selenium faces a number of scientific uncertainties and seems unlikely to obtain regulatory approval.

A comprehensive discussion of treatment alternatives to be evaluated should include monitored natural recovery (MNR). Far from a "do-nothing" approach, MNR involves detailed, ongoing, and adaptive monitoring of critical parameters in the impacted area and its environs. This approach and its attendant issues have been discussed in depth in many other documents (e.g., National Research Council 2000), and these will not be reviewed in detail in this document. The MNR approach may be appropriate and may have regulatory approval for select contaminants in certain settings. Nevertheless, its implementation can be faced with opposition from a variety of local community concerns (e.g., the no-action perception, things may get worse, uncertain and long timeline to achieve objectives). Additionally, the scientific evidence suggests that MNR may not be appropriate in the case of mercury contamination.

A comprehensive land management strategy for the EFPC watershed developed with the goal of improving creek water quality and helping address the mercury challenges could be developed. Changing patterns of land cover and land use within the EFPC watershed can counteract other actions designed to decrease MeHg in fish. Increases in impervious land cover can increase stormflow runoff that can deliver particulate mercury to the creek. Additionally, this extra water can exacerbate flooding and the associated creek bank erosion. Forest cover can increase deposition of reactive mercury to the creek during leaf fall in the autumn, and shading of the creek by the canopy could create conditions that increase MeHg in fish. The effect of canopy cover changes on microbial and periphyton communities also is uncertain. Active management of large woody debris throughout the creek would decrease accumulation of fine-grained deposits in their vicinity. Such actions would lower the number of places in the creek that harbor active MeHg production. Any tree management strategy would have to consider impacts on bank stability and private landowners (maintaining an aesthetic for their land). Finally, other improvements to water quality may be counteracted by other diffuse inputs along the creek. For example, targeted actions in Y-12 to decrease nitrate discharge

may be counteracted by fertilizer application at multiple locations along the creek (e.g., homeowners, golf course). Development of a watershed approach to managing and restoring the system for natural resource benefit, water quality enhancement, and mercury-associated risk reduction is deemed worth further investigation.

The Role of Y-12 Fluxes and Chemistry on LEFPC

The influence of the Y-12 Complex at EFPC's headwaters on downstream water chemistry and mercury fluxes and concentrations is well known. OF200 discharge from the western portion of Y-12 is the major source of base flow mercury loading to LEFPC (Peterson et al. 2011). Multiple outfalls downstream of OF200 within the eastern portion of Y-12 and the UEFPC stream channel itself also contribute important but smaller fluxes of mercury to LEFPC. Mercury in surface water in this upper reach is accessible, under DOE control, and primarily dissolved Hg(II), a highly mobile, reactive, and bioavailable form of mercury. This combination of access and chemistry provides an opportunity to manipulate the water chemistry to reduce the flux of mercury and accumulation of methylmercury in fish throughout the entire LEFPC stream system.

An important goal is to assess alternatives to current chemical treatment and discharge practices and/or implement chemical manipulations in surface water that would reduce mercury migration to LEFPC and mercury bioavailability. DOE EM has plans to construct a water treatment facility at OF200 to remove mercury and, therefore, chemical manipulation alternatives would need to be compatible and complementary to those plans. This could include targeting outfalls other than OF200, reducing mercury fluxes in the interim period before construction of the treatment plant, and implementing best management practices that could reduce the flux of mercury to the treatment plant, thereby reducing treatment and waste disposal costs.

Extensive spills of liquid Hg(0) in buildings, soils, and storm drains are the sources of the dissolved mercury in UEFPC surface water (Fig. 20). The Hg(0), which has a relatively low solubility, is oxidized by manganese and other metal oxides found in soils (Fig. 21) and by chemical oxidants (e.g., chlorine) found in process waters discharged into the storm drains and creek. The Hg(0) found in Y-12 storm drains is exposed to some anthropogenic chemicals on a continuous basis, while other chemicals are only discharged episodically (Table 8). Chlorine, dechlorination chemicals (ammonium bisulfite), and steam plant corrosion inhibitors (primarily amines) are released on a continuous basis. Treatment chemicals from cooling tower blowdown water are used and discharged only on an intermittent basis, primarily in hot weather. Many of these continuous and intermittent use chemical discharges are known to or have the potential to affect the form and total flux of mercury to LEFPC.

Y-12 process water contains residual chlorine that, when discharged to the storm drain system, can react and oxidize the dissolved and liquid Hg(0) beads present and transform them to the more soluble and mobile Hg(II) form. ORNL has recently measured free chlorine concentrations as high as 3.4 ppm in the Y-12 storm drain system. Preliminary laboratory testing conducted by ORNL has shown that exposing Hg(0) beads to tap water with residual chlorine of <3 ppm results in the formation of ~70 times more dissolved Hg(II) than beads placed in distilled water. This suggests that exposure of Hg(0) in the storm drain system to residual chlorine results in the formation of soluble Hg(II) species. The formation of Hg(II) species could result in substantially increased total mercury fluxes to LEFPC. Ammonium bisulfite is currently used as the primary dechlorinating agent at Outfalls 200 and 21 before discharge to the creek.

> Hg(0) beads exposed to residual chlorine in storm drains may result in the formation of ~70 times more dissolved Hg(II)

Amines and other chemicals are used in the treatment of boiler system equipment. Amines have the potential to form complexes with Hg(II) (Mousavi 2011). Amines can also react with chlorine to form chloramine. Chloramine, an oxidizing agent similar to chlorine, is also probably capable of oxidizing Hg(0) to Hg(II) but has a much longer half-life than other forms of chlorine and may release ammonia when degraded.

Chlorination byproducts like trihalomethanes and haloacetic acids form through the reaction of chlorine

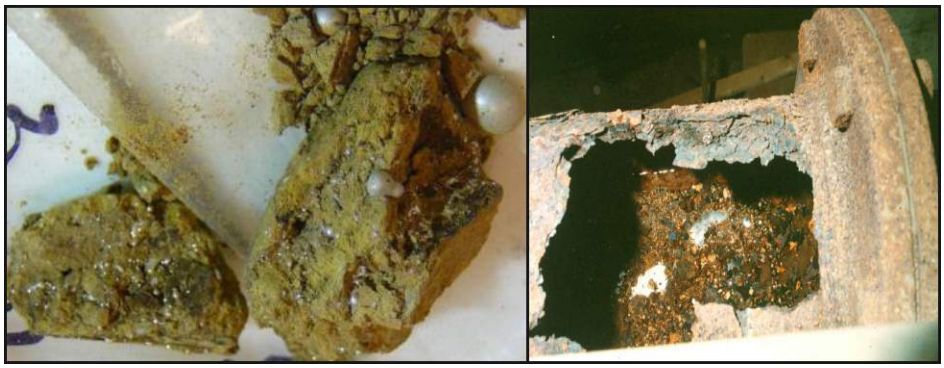


Figure 20. Beads of Hg(0) found in soil cores collected near an old Y-12 mercury use facility (left) and a Y-12 storm drain (right).

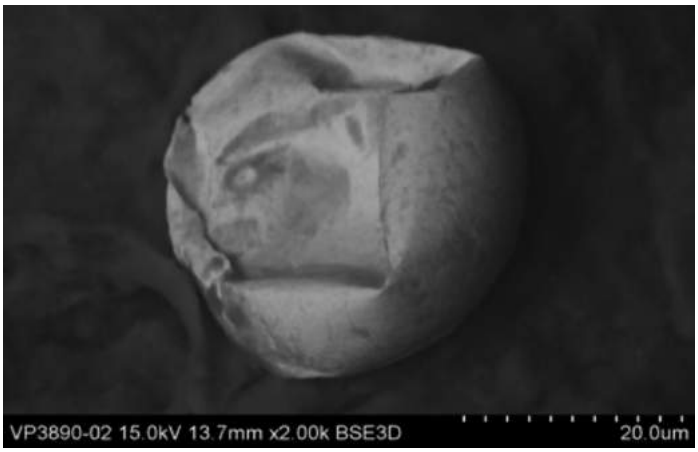


Figure 21. Scanning electron microscope image of soluble HgO coating formed after Hg(0) bead was exposed to manganese oxides.

with other chemicals or trace amounts of organic carbon. Historical sampling data from the Oak Ridge Environmental Information System (OREIS) shows that chlorination byproducts are frequently detected in the west end storm drain system (e.g., OF150). The chlorination byproducts that are similar to other carboxylic acids also have the potential to form complexes with Hg(II) (Mousavi 2011). Binding of Hg(II) to organics can affect bioavailability of Hg(II) in aquatic ecosystems (Haitzer et al. 2002) and limits Hg(II) availability to methylating bacteria (Ravichandran 2004).

Intermittent industrial wastewater discharges to the storm drain occur on a regular basis; specifically the operation of Y-12 cooling towers requires the use of a variety of chemicals for corrosion control, acid cleaning, microbiological control, and antifoaming agents and surfactants (Table 8). Blow down cooling water is released to the storm drains episodically during warm months. The chemicals released probably have a variety of impacts on the mercury contacted within the storm

Table 8. Summary of some Y-12 water treatment chemicals used in UEFPC

Treatment/Use	Amounts	Chemical Ingredients and Potential Impacts
Process water supplied by city is chlorinated (CL_2, NaHOCl, etc.) throughout storm drain system	3.4 ppm detected in Y-12 storm sewers	May oxidize Hg(0) found in storm drains to more soluble Hg(II). Chlorine can be transformed to chloramine and chlorination byproducts like trihalomethanes and haloacetic acids through reaction with other chemicals or organic carbon. Potential impacts of these byproducts on Hg mobilization should be considered
Ammonium bisulfite is used at OF200, OF21, and OF109 for dechlorination	Used in slight excess to remove chlorine	Removes chlorine, but dechlorination byproducts may remain or be altered further (see previous row). Some oxygen may also be removed
Boiler system steam plant condensate related; Corrosion inhibitor	Suggested: 5–40 ppm	Cyclohexylamine, alkyl diaminopropane, ethanolamine–mines can react with chlorine to form chloramine, which has a much longer half-life than other forms of chlorine and which may release ammonia when degraded.
Corrosion inhibitor	6–12 ppm	Phosphoric acid, tetrapotassium pyrophosphate (potential to bind mercury), potassium hydroxide, chlorotolyltriazole sodium salt
Corrosion inhibitor	1–2 ppm	Sodium hydroxide, chlorotolyltriazole sodium salt
Corrosion inhibitor	1–2 ppm	Sodium hydroxide, ethylenediamine tetraacetic acid, tetrasodium salt (known chelating agents), and sodium molybdate (inhibit sulfate reducing bacteria and Hg[II] methylation by ~95%)
Acid cleaner	Suggested: 5–20%	Hydrochloride (can precipitate Hg_2Cl_2)
Microbiological control	Suggested: 16–120 ppm	Sodium dichloro-s-triazinetrione dihydrate (hydrolizes to form hypochlorous acid, HOCl)
Microbiological control	Suggested: 12–36 ppm	1-bromo-3-chloro-5,5-dimethylhydantoin
Anti-foaming agent	Suggested: <1 ppm	Oil based, silicon emulsion in aqueous solution
Surfactant	Suggested: 50–100 ppm	L-aspartic acid (amino acid)
Microbiological control	Suggested: 2.5 ppm	Ammonium bisulfite (see above)

drains, depending on the specific chemicals released; however, the overall impact of the chemical releases is most likely an increase in the Hg(II) flux leaving Y-12. ORNL observed and conducted opportunistic sampling from OF160 during an episodic release of process water on May 18, 2012 (the source of which was not determined). Flow and mercury concentrations were elevated during this sampling event, with total mercury detected at 6.1 ppb and 92% of the total being dissolved and in the Hg(II) form. Four days later when OF160 was resampled after the release had stopped, the flow from the outfall was much lower, and total mercury was only 0.4 ppb, with 88% in the dissolved Hg(II) form. The net impact of the release of cooling tower blow down water is an increase in the flux of mercury to LEFPC because of the temporary increase in flow and chemical interactions with mercury occurring within the contaminated storm drains.

Potential Reduction of Mercury Fluxes from Y-12 to LEFPC

A variety of alternatives (Table 9) to current chemical treatment and discharge methods used in Y-12 industrial processes, in addition to controlled chemical additions and manipulations, can be considered to reduce mercury fluxes and forms that enhance migration of mercury to LEFPC. Because the effects of some of the numerous chemicals present in UEFPC water (Table 8) on mercury forms and transport are not well understood, a systematic phased approach of alternatives identification and evaluation, combined with laboratory- and field-scale experiments, is needed to test and select viable alternatives for implementation. This is particularly true for the large assortment of chemicals (Table 8) currently used for the treatment of cooling tower blow down water (see Table 9, alternative 3) and other intermittent industrial discharges to the storm drains. This process will require continuing discussions with Y-12 utilities and other Y-12 divisions to better understand chemical usage types, quantities and timing of discharges, and institutional capability to make alterations to current systems.

Eliminating or reducing chlorine concentrations in the storm drain system could significantly reduce the amount of soluble Hg(II) produced as chlorinated water comes in contact with liquid and dissolved Hg(0) and could reduce the total mercury discharged to LEFPC under baseflow conditions (see alternative 1 on Table 9). Decreased chlorine concentrations in the storm drain system could be accomplished by conducting dechlorination of the process water before or just downstream of discharge points to the storm drain, especially in areas where Hg(0) contamination is known to exist. Although technologically feasible, this would require some operational modifications at Y-12 to achieve the objectives. However, making these changes could have a substantial beneficial impact on the flux and form of mercury leaving Y-12 and is considered a high priority from a cost–benefit perspective.

Although ammonium bisulfite is currently used as the primary dechlorinating agent at Y-12 outfalls, several other chemical substitutes, such as sodium thiosulfate, ascorbic acid, and hydrogen peroxide, are known to be effective low toxicity substitutes (Looney et al. 2008). Observations of mercury concentrations in bass in a stream at the DOE Paducah Gaseous Diffusion Plant found that mercury bioaccumulation decreased after the facility began dechlorinating sanitary wastewater treatment plant discharge by dosing with high quantities of sodium thiosulfate. This action stimulated visible changes in the streambed biofilm, undoubtedly associated with a change in microbial ecology and growth of organisms that used thiosulfate. These observations suggest that switching the dechlorinating agent at OF200 to thiosulfate and increasing the dosage to promote the microbial degradation of excess thiosulfate in the stream could lead to a microbial ecology that disfavors methylating microorganisms and/or generates sulfur-containing chemicals that sequester inorganic mercury and render it less bioavailable (see alternative 2 in Table 9). However, during field testing activities for a $SnCl_2$ treatment alternative, it was observed that the addition of thiosulfate temporarily increased mercury flux in a portion of the North/South pipe because of mercury complexation and desorption of mercury from the tunnel walls (Southworth et al. 2009). This temporary increase in mercury flux related to the use of thiosulfate is a concern that would have to be resolved before full implementation. Testing would need to be conducted to confirm that at higher dosage and higher thiosulfate concentration levels, the reactions would be driven toward the formation of mercury sulfide complexes, and desorption of mercury would not be an issue.

Substituting thiosulfate would be more expensive and cumbersome than using ammonium bisulfite, but it could be consistent with the approach of treating multiple lower flows upstream of OF200 or other storm drains at or near the discharge points of chlorinated water to the storm drain system (see alternative 1 in Table 9). It has never been intentionally studied as an ecological tool for control of mercury methylation and bioaccumulation; thus, its efficacy is speculative. Altering the composition of the microflora has the potential for adverse ecological and aesthetic effects, but this is likely to be limited to within the Y-12 boundaries and in the storm drain system and should, therefore, have little impact on LEFPC active methylation. If effective, monitoring of the downstream persistence and efforts to determine what mechanisms account for the observed reduction in mercury bioaccumulation would be warranted.

Adding sulfide or other compounds (e.g., sodium sulfide) above OF200 or in other storm drains could change the highly reactive Hg(II) to insoluble HgS or other forms of mercury that may be less prone to MeHg formation (Looney et al. 2008). As noted above, mercury at OF200 under baseflow conditions is in a highly reactive,

Table 9. Alternative chemical treatment and manipulation options

Technology	Description	Objective	Implementability	Recommendation
Alternative Treatment Methods				
(1) Reduction of chlorine in storm drains	Remove chlorine farther upstream closer to or before discharge point to storm drains to limit Hg(0) oxidation to Hg(II)	Minimize oxidation of Hg(0) in storm drain system to more soluble Hg(II) form to reduce mercury flux to LEFPC during baseflow conditions	Would require some changes to Y-12 infrastructure, but changes would not be that difficult to implement	Conduct lab and field testing to confirm that implementation will result in desired reduction in mercury flux. Chlorination byproducts that remain might still impact mercury mobility
(2) Alternative dechlorination chemicals	Replace the present dechlorinating agent (ammonium bisulfite) with sodium thiosulfate, and adjust dosage to promote microbial degradation of excess thiosulfate in stream	Microbial degradation of thiosulfate may alter microbial ecology to disfavor methylating microorganisms (e.g., thiobacillus), and/or may generate sulfur-containing chemicals that sequester inorganic mercury and render it less bioavailable	Thiosulfate is commonly used for dechlorination at DOE facilities. Research into whether it is effective and what mechanisms account for any observed reduction in MeHg bioaccumulation is needed	Additional studies are needed to assess reactivity, kinetics, and environmental persistence, bioavailability, and methylation of reaction products
(3) Alternative treatments or elimination of chemical treatments	Many of the chemicals listed in Table 8 transform the Hg(0) to the more mobile Hg(II) or may complex with Hg(II) and enhance migration to LEFPC. Alternative chemicals or treatment options should be considered. For example, UV treatment methods might reduce the need for certain treatment chemicals	Limit mercury oxidation and mercury complexes that enhance migration of mercury to LEFPC	Would require changes to Y-12 infrastructure	Conduct an assessment of current chemical treatment practices to determine if there are better chemicals or alternative treatments that can reduce chemical discharges
Chemical Manipulations or Additions				
(4) Addition of mercury sequestering agents	Mercury at OF200 is maintained as a dissolved, highly reactive Hg(II) species that will readily react with potential sequestrants. Possible additives include organic thiols, inorganic sulfides, sulfur containing amino acids	Convert mercury to nonbioavailable forms that will not be methylated in downstream reaches of LEFPC	Chemistry is well known, but limited past application to aerobic surface waters	Viable alternative, although would require additional studies to assess reactivity, kinetics, and environmental persistence/ bioavailability of reaction products
(5) Chemical reduction (e.g., stannous chloride) followed by vapor stripping	Move dechlorination point to a site within a pipe. Add reductant to discharge to convert Hg(II) to volatile Hg(0) and provide a mechanism for volatilization, while ventilating the system to remove volatilized mercury in the air	Reduction of inorganic mercury load from the Y-12 mercury sources to LEFPC	Concept developed at ORNL and pilot tests have been completed at ORNL and Savannah River Site. Full scale system operating for groundwater at Savannah River Site (Looney et al. 2003)	Viable alternative, although would require additional studies. Because full-scale treatment plant is being built at OF200, consider as an alternative for other outfalls
(6) Chemical additions to reduce mercury in fish and/or methylation	Chemicals that can reduce the methylation of mercury and uptake in fish like selenium (Southworth et al. 1994) and molybdate (Chen et al. 1997) could be metered into the creek	Reduce methylation of mercury in LEFPC. Molybdate is known to inhibit growth of sulfate reducing bacteria known to methylate mercury, and selenium has been shown to reduce MeHg in fish	Could be regulatory and technical issues to overcome because additions would have to be conducted in LEFPC where methylation is occurring	Additional assessment would need to be conducted to determine if regulatory and technical issues are too great. Would require testing before implementation

dissolved Hg(II) form that will readily react with potential sequestrants. Numerous possible additives exist, most of which react to mercury with a sulfur moeity. Possible additives include organic thiols, inorganic sulfides, selenium, or sulfur-containing amino acids. The objective would be to convert inorganic mercury to stable non-bioavailable forms that would not be methylated in the downstream reaches of EFPC. A slow release form of sequestrant (such as encapsulated nanoparticles) might be capable of sequestering mercury from downstream sources by taking advantage of the natural photooxidation/reduction cycle.

One advantage of this approach is that it might be possible to merely add sequestrant to dechlorination chemicals that are already added continuously at OF200 and other outfalls. If successful, that could very inexpensively reduce mercury flux to LEFPC. Sequestrants might also have the potential to reduce dissolved concentrations of other trace metals in EFPC, reducing the possibility that these have subacute ecological effects. The effectiveness of sequestration is likely to be limited to mercury coming from OF200 and other UEFPC outfalls, unless a slow-release form is developed that has a chance to migrate downstream to LEFPC or that can be added in LEFPC. It would also require regulatory approval, and the toxicity of potential reagents would be a limiting factor (i.e., low AWQC for sulfide would limit the amount that could be added). Additional study would be required before implementation, reactivity testing, kinetics, and environmental persistence/bioavailability of reaction products of various sequestrants. Aqueous sulfide is probably the most "off-the-shelf" technology.

Chemical reduction in darkened pipes followed by air stripping (Table 9, Option 5) has been successfully field tested at Y-12 upstream of OF200, where over 90% of the Hg(II) was reduced to the volatile Hg(0) form (Southworth et al. 2009, Southworth et al. 2010a, Looney et al. 2008). Most of the flow in the storm drain system contains residual chlorine because of the discharge of chlorinated process water (drinking water from the City of Oak Ridge water supply system) from various uses (primarily cooling water). The residual chlorine is aggressive in its oxidation and solubilization of mercury, and as a result, the mercury in water exiting OF200 and other outfalls contains reactive dissolved Hg(II).

Studies carried out at Y-12 demonstrated that after removal of residual chlorine, mercury in this effluent could be converted to volatile Hg(0) by the addition of nearly stoichiometric amounts of stannous chloride. Looney et al. (2003) performed pilot scale research showing that the technology is applicable to contaminated groundwater under controlled conditions, and the technology has now been implemented full scale on a pump-and-treat system at the DOE Savannah River Site. Although this strategy was not considered for OF200 treatment, it could be a viable approach at a smaller scale in other mercury contaminated storm drains. Before this strategy could be implemented, research would be needed to reconfirm the treatability of the discharge under current and changing flow conditions and to engineer reagent delivery, ventilation, and sparging systems.

Chemical additions (e.g., selenium and molybdate) could also be conducted at Y-12 to reduce mercury methylation and uptake of MeHg in fish downstream

Water chemistry sampling in East Fork Poplar Creek.

(Table 8 and Table 9, Option 6). The use of selenium compounds to reduce mercury in fish and other biota has been investigated in both controlled mesocosms (e.g., Rudd and Turner 1983) and whole lake experiments (Parkman and Hultberg 2002). In addition, there are examples where unintentional selenium inputs (Chen et al. 2001) or removals (Southworth et al. 1994) have provided an opportunity to observe the response of MeHg in fish. Certain oxyanions like molybdate are known to inhibit methylation by suppressing the activities of SRBs (Chen et al. 1997, Compeau and Bartha 1985). Although it may be possible to implement these types of chemical additions in a way that will not be impactful or toxic to other biota, there are significant regulatory and technical issues to overcome. These types of chemical additions may be less effective near Y-12 and may need to be targeted to areas in LEFPC where methylation of mercury is known to be occurring. In addition, confirmation would be needed that the environmental impacts of chemical additions like these are consistent and not detrimental to other watershed actions being taken.

Water Chemistry Research and Technology Development Needs

Approaches are needed to decrease total mercury and MeHg concentrations in EFPC surface water. Research designed to decrease total mercury concentration and flux should be closely coupled with evaluations of Y-12 discharges, bank soil erosion, groundwater–surface water interfaces, and sediment transport. Research and technology development is needed to evaluate managing EFPC water chemistry for the purpose of decreasing net methylmercury concentration. This may be achieved by (1) decreasing microbial mercury methylation either through direct intervention in microbial metabolism or rendering inorganic mercury to a form that cannot be methylated, (2) increasing microbial or abiotic demethylation, (3) sequestering methylmercury out of the water column and associated with a solid phase that is not available for biological uptake, (4) effecting changes to water conditioning chemicals or the storm sewer dechlorination process within Y-12 to decrease mercury flux exiting OF200, or (5) some combination of the preceding items. Natural synergies among this and other domains (e.g., soil, ecology) would be maximized through close collaboration and information exchange, consistent with the watershed approach.

Evaluations of potential water chemistry manipulations in the creek depend in part on a thorough understanding of current stream chemistry conditions, especially in light of flow augmentation ending in May 2014 that most certainly affected in-stream chemistry. Additional flow and water chemistry stations in the creek are needed to provide useful information toward that understanding of stream conditions. Nearer Y-12, it is well known that existing operations affect the water quality and water chemistry in the creek. The role of chemicals present in EFPC water because of ongoing plant operations on the forms of mercury present and mercury methylation processes should be evaluated in a phased approach using a combination of laboratory- and field-scale experiments.

The water chemistry evaluations both at Y-12 and in-stream provide the basis for follow-on studies that will conduct direct manipulation of water chemistry factors to decrease mercury methylation. Consistent with the TRL approach, manipulation studies need to start at the bench-scale and, if promising, move to field- and pilot-scale studies. Because it is impossible to replicate stream water chemistry conditions in the laboratory, testing of potential technologies designed to decrease mercury methylation would benefit from use of LEFPC water in a semi-controlled environment, such as in stream-side tanks and channels.

SEDIMENT

Role of Sediments on Mercury Cycling

Factors controlling mercury partitioning between dissolved and particle-associated phases and those controlling sediment transport and storage are key to understanding mercury sources, reactivity, bioavailability, transport, and inventory in EFPC. Review of the salient literature provides general trends and important controlling variables. Nevertheless, the magnitude and rates of these processes and their potential interactions are highly site-specific and require detailed characterization across a range of seasonal, temporal, and hydrologic conditions to provide comprehensive conceptual understanding and, eventually, for that understanding to be used effectively in decision support and remediation action.

In the absence of dissolved sulfide, the majority of mercury and MeHg in EFPC is either associated with particles (sorbed or [co]precipitated solids) or present in the aqueous phase predominantly complexed with dissolved organic matter (Riscassi et al., in prep, Dong et al. 2009, Southworth et al. 2013, Southworth et al. 2010). This is consistent with numerous other studies conducted in diverse environments across the globe. Previous work has estimated that >80% of annual mercury export from EFPC is from sediment transport (Southworth et al. 2013, Southworth et al. 2010). Similarly, a detailed study of EFPC mercury and MeHg dynamics for water year 2013 (October 1, 2012, through September 30, 2013) showed that 99% of mercury and 87% of MeHg flux were caused by particle transport (Riscassi et al., in prep). Streambank soils, bed sediments, and surface biofilms throughout EFPC exceed the sediment quality guideline (SQG) consensus-based threshold effect concentration (TEC; below which adverse toxicity effects are not expected) of 0.18 mg/kgdw proposed by MacDonald et al. (2000). Most also exceed the consensus-based probable effect concentration (PEC;

above which adverse toxicity effects are expected) of 1.06 mg/kgdw (Southworth et al. 2013; Southworth et al. 2010; Donovan et al. 2014; Brooks et al., in prep).

Much of the EFPC streambed is bedrock with ~50% overlain by boulders, cobbles, gravels, and entrained finer particulates. The thickness of this overlying layer varies but is generally quite thin, less than 18 inches in most places. Fine-grained sediment occurs primarily as fine-grained channel margin (FGCM) deposits and interstitial sediment between coarser material on the streambed. The areal extent and properties of fine particle deposits have not been accurately determined, constituting a large area of uncertainty in understanding the EFPC system. However, their extent is less than the exposed bedrock and coarse-grained portions of the bed and, in general, is restricted to lower stream velocity areas near the creek banks and downstream of obstructions or large woody debris piles. Studies of other metal and radionuclide contaminants demonstrate that the concentration of the element increases with decreasing sediment particle size. This can be an important indicator of the retention mechanism by the solid phase (e.g., sorption versus [co]precipitation). Additionally, this has implications for mercury resuspension and transport under various hydrologic regimes. For example, fine particles are more easily resuspended and transported under high recurrence–interval flow events.

Little data exists on the concentration of mercury as a function of particle size for EFPC creek sediment. Work conducted under the In-Stream Contaminant Study by TVA (1985) suggested relatively low enrichment factors for creek sediments, generally less than 5, in finer particles (< 63 μm) relative to coarser particles (63 < x < 500 μm). The enrichment factor showed weak and non-significant increase with distance from the Y-12 Complex. More recent work by Donovan et al. (2014) and ORNL researchers also indicated a relatively weak enrichment factor that decreased with downstream distance. The differences reported likely reflect the many changes to EFPC over the 30 years separating these studies, including improved water quality and decreased mercury discharges from the Y-12 Complex, implementation of flow augmentation, stream bank stabilization actions along UEFPC in Y-12, and targeted removal of highly contaminated floodplain soils at two locations along LEFPC. Our present understanding of the creek sediment is incomplete with regard to a number of characteristics likely to play central roles in mercury transport, storage and inventory, and availability for methylation.

Another major source of uncertainty is the lack of information regarding stability of the EFPC streambed with respect to, for example, sediment residence time and gravel/cobble movement. Given that much of the creek channel is bedrock or covered with a relatively thin veneer of unconsolidated material, it seems reasonable that much of the erosive force of the stream under baseflow and stormflow conditions will be directed toward reworking and transporting the bed sediments or lateral erosion of the creek banks as opposed to vertical streambed incision. In addition to their importance in mercury and MeHg flux described above, fine-grained deposits foster development of the anaerobic conditions favoring mercury methylation. Retarded movement of aerobic surface water through these deposits allows development of anaerobic conditions supporting microbial metabolisms (Fe[III] and sulfate reduction, fermentation, methanogenesis) associated with mercury methylation. Large, stable, or accreting FGCM deposits may provide local hotspots of MeHg production.

Previous work has identified the mineral metacinnabar (ß-HgS) as the dominant form of mercury in EFPC floodplain soil. Less detail is available for bed sediments. The form of mercury in creek bed sediments has been studied using a selective sequential extraction procedure (Bloom 2003). In this procedure, sediments are treated with a sequence of increasingly aggressive chemical extractants, and the mercury released in each operationally defined pool is quantified. Greater than 97% of the mercury was found to be associated in highly sequestered forms—extractable only with strong base, concentrated strong acid, or aqua

East Fork Poplar Creek sediment samples.

regia (hydrochloric + nitric acids)—putatively corresponding to organo-complexed, strongly inorganically complexed, and HgS solid phases, respectively (Southworth et al. 2010, Brooks et al., in prep). Results of sequential extraction tests are suggestive of geochemical modes of an element's sequestration, and the results described above may be viewed as encouraging but incomplete. For example, they do not provide information in the rate of incorporation into or release from solids, nor do they address re-equilibration among different pools on the solid phase. More detailed understanding of the rate and extent of mercury release from creek sediments would support targeted efforts to enhance sequestration of mercury onto sediments, thereby decreasing MeHg production.

Potential Sediment Control Technologies

Many of the potential control technologies that address the sediment compartment fall into two broad categories. First, technologies that increase partitioning of mercury and MeHg onto solids may render them unavailable for methylation or biotic uptake, respectively. This can be achieved using sorptive media, including reactive caps, or additions that favor solid phase (co)precipitation. Second, to the extent that creek bed sediment stabilization will decrease sediment export, these technologies will also decrease mercury and MeHg flux from the system. Table 10 presents a summary of potential sediment manipulation technologies and strategies, with an assessment of their potential for application in LEFPC.

Sorbent amendments of soils and sediments are deemed to be some of the most promising soil and sediment control technologies under consideration for LEFPC. The effectiveness of sorbent amendments is determined by the partitioning of mercury species between sediments and pore water (Fig. 22). Sorbent amendments that reduce the total concentrations of mercury and MeHg species in the pore water should be effective in reducing bioavailability to organisms. Sediments with low native sediment:water partition coefficients (K_D) for mercury and MeHg should be most effectively treated. Thus, any sorbent amendments compete for mercury and MeHg with the existing binding capacity of organic matter and other constituents present in the sediments. Therefore, the effectiveness of the sorbent not only depends on its sorption capacity and chemistry, but also on the K_D and the concentration of natural organic matter in the system. Additional technology development opportunities relative to the use of sorbents were provided in this report's soil section. Bank soils and sediments are intrinsically linked, with strong evidence that bank soils contribute substantially to the sediment load in EFPC; sorbents and stabilization technologies may need to be similar in approach and application.

The relationship between mercury and organic matter in the creek is important to mercury cycling and methylation processes. It was previously shown that the association of mercury with DOM in EFPC water is kinetically controlled, with the fraction of stannous chloride reducible mercury decreasing from 90% to 27% from the mercury source to a site 2.5 km downstream (Miller et al. 2009). Laboratory experiments have demonstrated that mercury forms stronger complexes with DOM in a time-dependent manner (Miller et al. 2012). Thus, mercury complexed by DOM may become less accessible for exchange reactions with functional groups on sorbent surfaces, which may affect the effectiveness of sorbents significantly. Inorganic mercury and methylmercury sorb strongly to natural organic matter (NOM) in sediments and soils. The concentration of NOM in sediments is a strong predictor of total mercury and MeHg partitioning between the bulk phase and pore water (Marvin-DiPasquale et al. 2009, Gilmour et al. 2013a). Interaction studies under

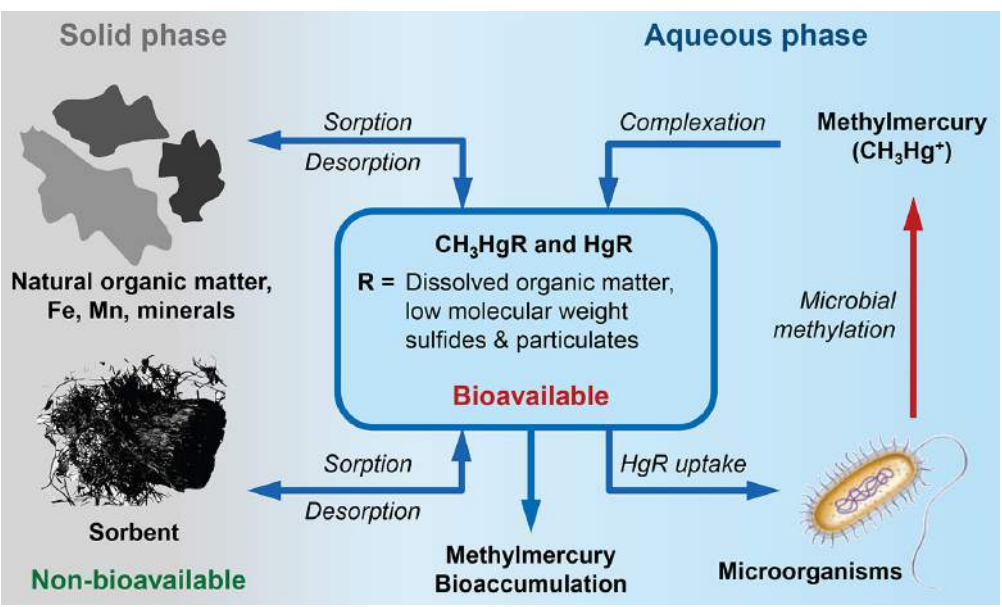


Figure 22. Key processes controlling the partitioning of mercury species between aqueous and solid phase (natural organic matter, minerals, and sorbent amendments). A pool of mercury species associated with dissolved organic matter and colloidal particles is bioavailable for uptake and methylation by microorganisms. Irreversible sorption of dissolved mercury and methylmercury species to the solid phase lowers the concentration of bioavailable species and thus limits both uptake by methylating microorganisms and bioaccumulation. The effectiveness of the sorbent for a particular contaminant is determined by its partitioning coefficient, K_D, which is defined by the concentration in the sorbent divided by the concentration in the aqueous phase.

Table 10. A summary-level description of potential sediment control technologies and strategies, and their potential for use in LEFPC

Technology	Description	Objective	Pros	Cons	Technological Readiness	Needs
Monitored natural recovery	Active monitoring and assessment of creek, biota, and environs	Allow contaminated sediments to flush out of the system during normal baseflow and storm events	(i) Nondisruptive of ecosystem, private property (ii) possibly lower cost	(i) Length of time to achieve objective not known, (ii) little to no improvement expected without substantial source reduction from Y-12	High. Straightforward to apply, but uncertain effectiveness in LEFPC	Quantitative hydrological model(s) of sediment transport in EFPC
Sediment excavation	Remove contaminated sediments from creek	To remove Hg from the ecosystem	Hg permanently removed from system	(i) Extremely disruptive of system, (ii) little to no improvement expected without substantial source reduction from Y-12	Moderate. Technologies are well known but application in LEFPC is uncertain	Physical extent of contaminated sediments
Aerate anoxic sediments	Introduce dissolved oxygen into anaerobic creek sediments	Stop Hg methylation by inhibiting activity of bacteria that create MeHg	Disrupt a source of MeHg in the creek	Needs to be highly mobile/relocatable as distribution of anoxic sediments may be highly variable in space and time	Low. Research needed	Effective aeration technology, mobility design
Sorbent addition	Add natural or engineered sorbents to sediments	To make Hg/MeHg less soluble and bioavailable	Lowers Hg concentration in water and biota	Duration of effectiveness unknown	Low. Research needed	Sorbent evaluation; long-term data to evaluate performance, avoid unintended negative consequences
Sequestrant addition	Add reagents that alter form of Hg in system	To make Hg/MeHg less soluble and bioavailable	Lowers Hg concentration in water and biota	Duration of effectiveness unknown	Low. Research needed	Sequestrant evaluation; long-term data to evaluate performance, avoid unintended negative consequences
Sediment freezing	Freeze highest risk sediments for removal	Remove sediment source from system	Removal method may prevent mobilization common with conventional excavation	Possibly high cost for removal, drying, and waste disposal. Limited spatial range of application	Low. Limited application in creek environments	Design data, feasibility evaluation for access options to small stream
Reactive sediment caps	Mat with embedded reactive material placed over top of sediment (e.g., BentoMat®, AquaBlok®, Reactive Core Mat™, GeoWeb® with sorbent, etc.)	Stabilizes fine-grained sediment deposits; decreases flux of Hg and MeHg across the sediment cap	Potentially easy installation and low maintenance	Possible bypass flow; disruptive of benthic ecosystem	Moderate. Research needed to evaluate long-term effectiveness	Rate and extent of Hg/MeHg uptake and release; physical durability of mats under real conditions (dynamic flow, damage from wildlife and debris)
Sediment grouting	Inject grout into sediments with or without functionalized additives	Holds sediments in place and removes Hg/MeHg from interstitial pore water	Depending on polymer morphology, could still allow water exchange between benthic habitat and surface water	Has been successful in groundwater applications, untried in flowing surface waters	Low. Research needed.	Durability of grouts when mixed with sediments and under natural conditions of flow, Hg/MeHg uptake and release

Key questions of early research

- What is the stability of creek sediment bedforms (fine-grained channel margin deposits, gravel sour, etc.)?
- What is the distribution of mercury among different particle size classes of creek sediment?
- Is the form of mercury similar across different particle size classes of creek sediment?
- What is the areal extent of fine-grained deposits in EFPC? Do they harbor conditions favoring production of MeHg?

controlled conditions have shown that mercury binding to DOM at low mercury/DOM ratios ([mercury]/[DOM] < 0.001) is mainly because of thiol functional groups (Drexel et al. 2002). Different types of DOM (e.g., humic acids, fulvic acids) all show similar binding constants. At higher mercury-to-DOM ratios, the available thiol sites become saturated, and mercury exhibits lower binding constants, mainly to carboxyl and amine groups. Thus, the interaction of mercury species with organic matter depends largely on functional groups, which are primarily influenced by the pH in the system (protons compete with mercury for binding sites).

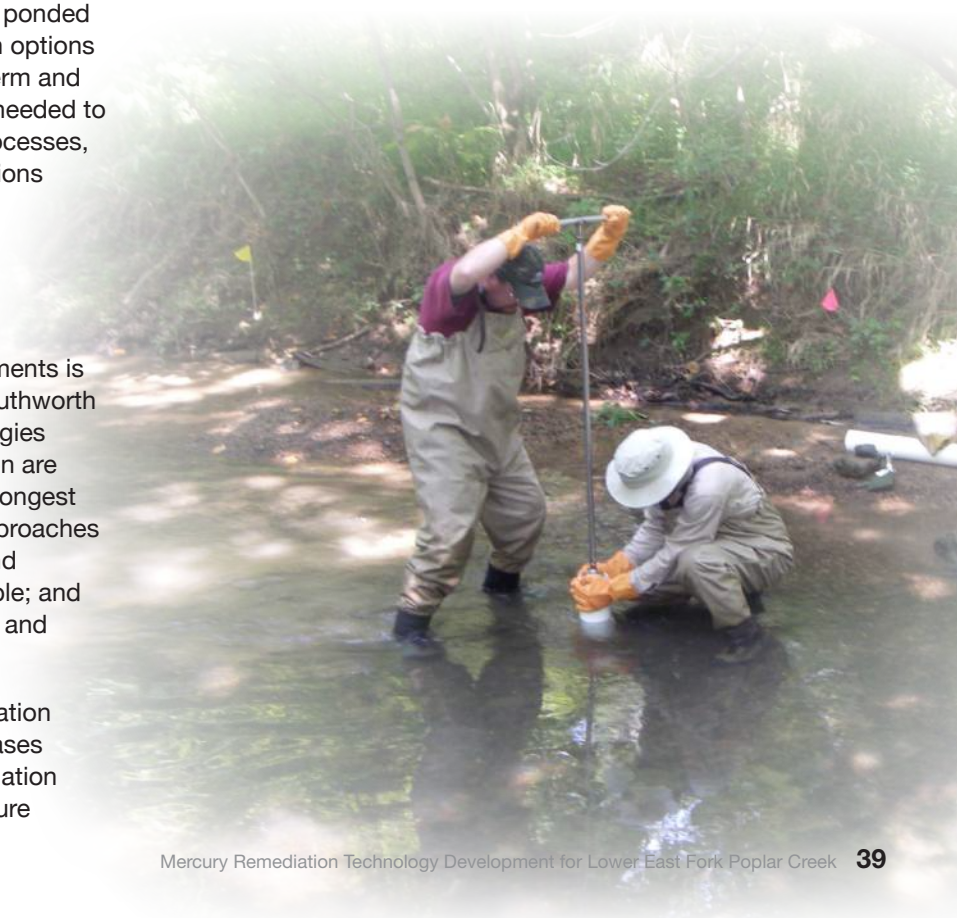
Sediment stabilization technologies coupled with reactive caps or sorptive media may decrease resupply of dissolved mercury from the sediment reservoir. Potential stabilization approaches were described in the soil section of the report. Sediment stabilization strategies are well known but have been applied more commonly in ponded environments. Sediment barriers and stabilization options can be difficult to deploy and retain in the long-term and can be environmentally destructive. Research is needed to evaluate the role of sediments on methylation processes, with the hope of implementing more targeted actions where methylmercury production is greatest.

Sediment Research and Technology Development Needs

Mobilization of mercury from streambed sediments is a major source of mercury export from EFPC (Southworth et al. 2010). Remediation strategies and technologies targeting creek sediment and mercury stabilization are critically needed and must be informed by the strongest site-specific knowledge base possible. These approaches should target both (i) sequestration of mercury and MeHg, rendering them less mobile and bioavailable; and (ii) stabilization of sediment against resuspension and downstream transport.

Because of the paucity of site-specific information regarding key sediment characteristics, initial phases of technology development must provide a foundation of characterization information that can guide future design evaluations, consistent with the phased TRL approach. A better understanding of spatial variability of mercury in creek sediments longitudinally, including areal extent of fine-grained channel margin deposits in EFPC, is needed. Specific sediment characterization needs for LEFPC in the short-term include (1) quantification of total mercury as a function of sediment particle size along the length of EFPC; (2) form of mercury on the sediment particles (e.g., sorbed, precipitated); (3) rate and extent of mercury/MeHg release from sediments into the aqueous phase; (4) rate, extent, and stability of mercury/MeHg repartitioning behavior from sediments onto added natural and engineered sorbent materials; and (5) strength of sediment stabilizing formulations when mixed with sediment.

Initial characterization of materials from the field can inform laboratory-scale evaluation and screening of a variety of options. With new knowledge about the system, laboratory studies are needed to evaluate the effectiveness and long-term stability of various sorbents under the conditions identified for EFPC. As promising sorbent materials are identified, scale-up and testing of the technologies from lab mesocosms to pilot scale is required. Stream-side tank or channel testing would enable evaluation at relevant scales under well-controlled field-relevant conditions. Future research activities and technology development should center on using LEFPC-specific sorbent, barrier, or stabilization technologies and strategies to target specific high contamination zones.



Ecological Manipulation

Photo courtesy of the Knoxville News Sentinel

ECOLOGY

Role of Ecology in EFPC

Mercury is a risk to humans and wildlife primarily through the food ingestion route of exposure. In contrast to virtually all other metals, mercury (especially in its organic form, methylmercury) biomagnifies or becomes increasingly concentrated as it is transferred through aquatic food chains to higher trophic levels, namely to fish. Consequently, the consumption of mercury-contaminated fish is the primary exposure route to humans (Fig. 23). For this reason, the National Recommended Water Quality Criterion (NRWQC) for mercury is based on a fish tissue concentration rather than an aqueous mercury concentration because the tissue concentration (0.3 mg/kg) is considered to be a more consistent indicator of exposure and risk to humans.

Although most mercury in the environment is inorganic mercury, a small proportion of total mercury (HgT) is microbially transformed to MeHg in the aquatic ecosystem (Fig. 24). Anoxic, reducing environments such as wetlands are considered mercury-methylating "hotspots," where inorganic mercury is methylated primarily by sulfate- and iron-reducing bacteria. However, recent research has highlighted freshwater streams as sites of mercury methylation, with favorable conditions for methylation including increased temperatures, the presence of certain filamentous algae, and the presence or absence of certain organic nutrients (Tsui et al. 2010). The methylation of mercury from periphyton- and macrophyte-associated bacteria also has highlighted additional

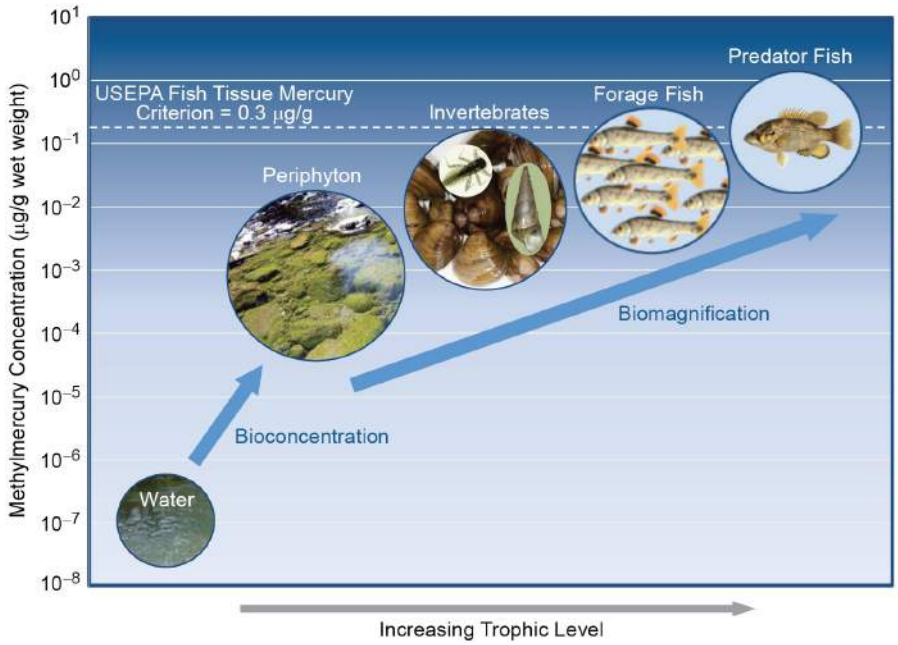


Figure 23. Methylmercury (MeHg) concentrations in aquatic organisms rise with each additional step up the food chain. The highest concentrations of MeHg are generally found in fish at the top of the food chain. Modified from Wentz et al. 2014.

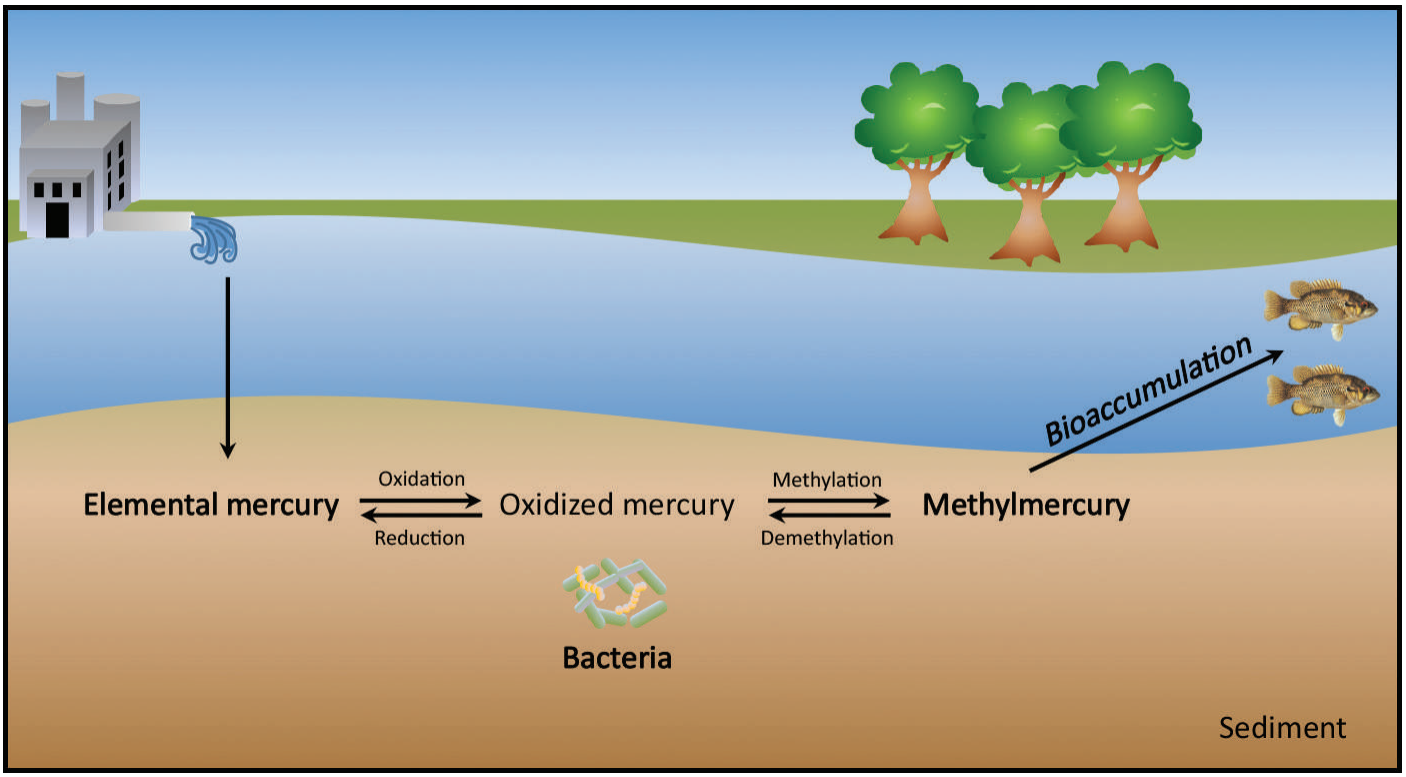


Figure 24. In anoxic conditions (e.g., in sediments of freshwater streams), mercury is methylated by sulfate- and iron-reducing bacteria. Methylmercury (MeHg) is then more bioavailable to the aquatic food web.

opportunities for mercury methylation within freshwater streams (Acha et al. 2012).

Methylmercury readily crosses cell membranes and binds with proteins, forming complexes that mimic essential amino acids. For this reason, MeHg is highly bioaccumulative, becoming incorporated into protein-rich tissues (e.g., muscle; typically MeHg is >95% of the HgT in fish fillets) with long residence times. In aquatic animals, MeHg uptake rates from water and assimilation efficiencies from food are high, while elimination rates are low, leading to a progressively increasing concentration within an organism over time. This also leads to a progressive concentration of mercury within a given food chain as MeHg is transferred from one trophic level to the next.

One of the challenges to effective remediation at mercury-contaminated sites is that while mercury body burdens in fish are often more closely linked to aqueous MeHg than inorganic mercury concentrations (Tom et al. 2010), MeHg production is not easily predicted or controlled. For example, in systems contaminated by atmospheric deposition with low aqueous HgT concentrations (< 10 ng/L), there is a correlation between Hg(II) and MeHg concentrations (Kelly et al. 1995). However, in point-source contaminated systems, waterborne inorganic mercury concentrations may range over several orders of magnitude, while MeHg concentrations in water and biota seldom differ by more than tenfold (Southworth et al. 2004). Decreasing aqueous inorganic mercury concentrations and loading may often be a more achievable remediation goal than decreasing MeHg concentrations, but this approach has led to mixed results in terms of responses in fish bioaccumulation. A number of source control measures have resulted in rapid responses in lake or reservoir fisheries (Joslin 1994, Turner and Southworth 1999), but examples of similar responses in mercury-contaminated stream ecosystems are less common. Recent work suggests that fish in stream systems actually may be more susceptible to mercury bioaccumulation than those

Key Concepts

- **Mercury, especially methylmercury, biomagnifies, with concentrations increasing through the aquatic food chain.**
- **The consumption of mercury-contaminated fish represents the largest source of this neurotoxin to humans. The US Environmental Protection Agency recommends a fish tissue guideline of 0.3 mg/kg in methylmercury in fish fillet.**
- **Because fish accumulate mercury through their diet, understanding food web interactions is the key to controlling mercury concentrations in fish.**

in lakes, highlighting the need to better understand the ecological drivers of mercury bioaccumulation in stream-dwelling fish (Chasar et al. 2009, Ward et al. 2010a). While inorganic mercury concentrations play a part in determining overall mercury concentrations in fish, methylation efficiencies and food web pathways are also important in determining fish tissue concentrations.

Effective mercury remediation in EFPC requires not only an understanding of the nature and magnitude of mercury inputs, but also knowledge of the extent to which these inputs must be controlled to achieve the desired reduction of mercury contamination in biota necessary to meet the NRWQC. However, because mercury is accumulated predominantly through the food chain rather than through aqueous exposure, understanding food web structures and transfer pathways for mercury to fish is a key component to successfully implementing strategies to mitigate mercury bioaccumulation. Uptake at the base of the aquatic food chain (algae/periphyton, invertebrates) is the most important concentration step for mercury (with mercury concentrating over 10,000-fold between water and algae; Fig. 23). However, while the relationship between mercury concentrations in water and fish has been characterized, the transfer pathways from the base of the food chain remain largely unknown.

Potential Ecological Manipulation Strategies

An important research and technology development need is to quantify the trophic transfer efficiency of mercury through the EFPC food chain and identify the critical linkages for mercury transfer to fish. By understanding these critical linkages, design strategies can be developed to sustainably alter, or manipulate, the aquatic food chain to mitigate mercury transfer to fish.

The trophic cascade hypothesis—one of the principal paradigms in ecology—describes food web interactions as a balance of resources and energy such that nutrient inputs set the maximum potential productivity of a system. Deviations from this maximal production are due to food web interactions (e.g., grazing, predation) (Fig. 25). These principles from basic ecology have been applied for decades as a water resources management tool to restore water quality in lakes (Berg et al. 1994, Carpenter et al. 1985, Danger et al. 2008, DeBoom and Wahl 2014), wildlife and fisheries management (Stow et al. 1995), and crop protection (Engler and Rogoff 1976). By manipulating a given trophic level, it is possible to alter other trophic levels across the food web. Thus, it is also feasible to mediate undesirable attributes at one trophic level by altering another trophic level (e.g., the bioaccumulation of contaminants in a given species) (Fig. 26).

More recently, these principles have been applied for the remediation of contaminated sites because the removal or introduction of key species can alter the bioaccumulation of contaminants through altering habitat,

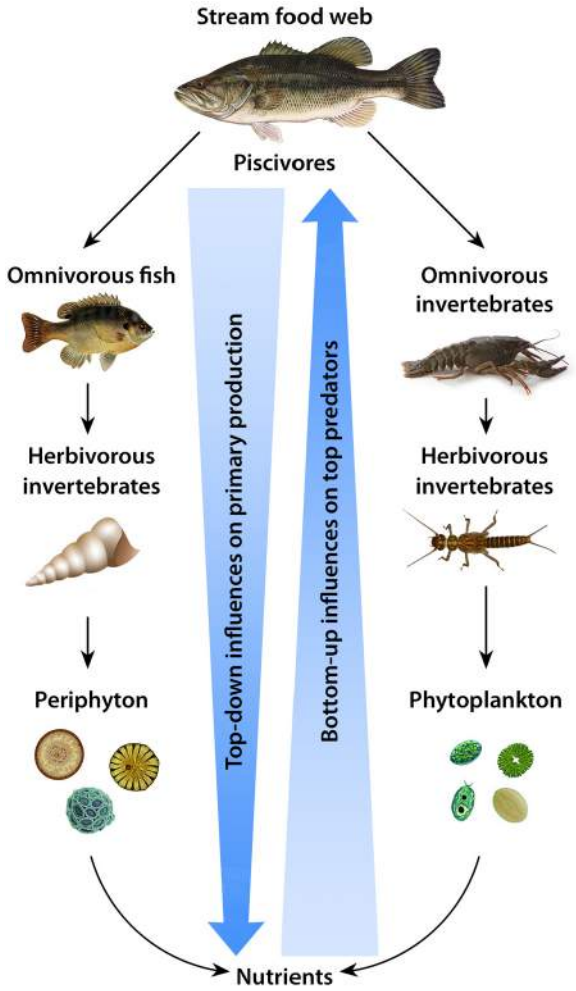


Figure 25. The trophic cascade hypothesis states that primary production in aquatic systems is affected by the feeding of fish. Conversely, the fish populations in aquatic systems are affected by primary production. Adapted from Carpenter and Kitchell, 1988.

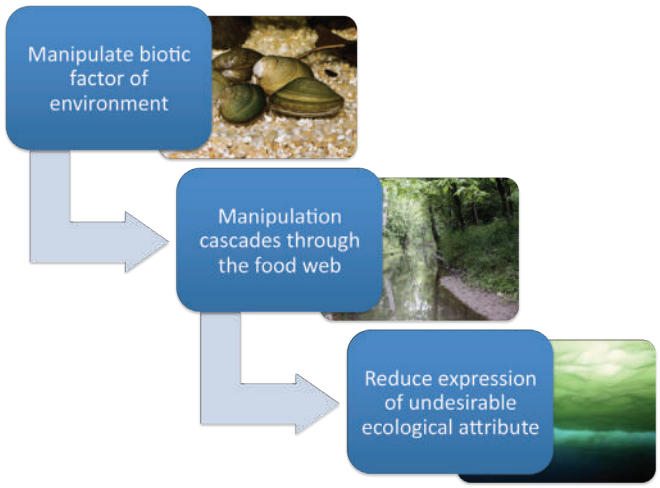


Figure 26. Flow diagram depicting the basis of ecological manipulation throughout the food web. Alteration of one trophic level can cascade throughout the food web, mitigating the expression of undesirable ecological attributes.

removing contaminants, or altering contaminant transfer processes. These ecological manipulations have been applied at different stages in the aquatic food chain, depending on the ecosystem and contaminant concerned. For example, phytoremediation—the use of green plants and their associated microorganisms to stabilize or reduce contamination in soils or water—has been used since the 1990s in both terrestrial and aquatic systems. The addition of filter feeding invertebrates, especially bivalves, has been shown to be effective in removing metals, organochlorines, and hydrocarbons from aquatic environments (Gifford et al. 2005, Gifford et al. 2004). Adding or removing fish species can have effects on contaminant bioaccumulation (including mercury) on shorter time scales (Lepak et al. 2012, Lepak et al. 2009, Masson and Tremblay 2003, Sharma et al. 2008, Sharma et al. 2011), but management strategies on how to maintain lower contaminant concentrations over the longer term are required.

Using ecological manipulation techniques to mitigate contaminant bioaccumulation is a newer, unconventional approach in remediation practices worldwide, but there are cases of multi-trophic level manipulations that have been successful. For example, to reduce polychlorinated biphenyl (PCB) bioaccumulation in fish at the K-1007-P1 Pond on the Oak Ridge Reservation, rooted plants were introduced to stabilize PCB-contaminated sediment; long-lived and top predator fish species were removed; and smaller, shorter-lived native fish species were overstocked. Within 5 years of remedial activities, PCB concentrations in bluegill, the target bioindicator species, had fallen below remedial goals (US DOE 2014) (Fig. 27).

In mercury-contaminated sites, ecological manipulations as remediation strategies are vastly understudied and not well understood when compared with chemical and physical remediation strategies. Across comprehensive reviews on mercury remediation (Davis et al. 2012; Hinton and Veiga 2001; Mailman et al. 2006; Randall and Chattopadhyay 2013; Wang et al. 2012; Wang et al. 2004), ecological manipulations are rarely mentioned in remediation strategies. In fact, only five strategies of ecological manipulation are cited: phytoremediation (Wang et al. 2012), the addition of fish to lower mercury concentrations in fish by increasing fish growth rates (Mailman et al. 2006), the removal of trees from the riparian zone to reduce mercury methylation by removing sources of organic carbon (Mailman et al. 2006), the burning of the riparian zone before flooding to reduce the organic carbon available for mercury methylation (Mailman et al. 2006), and the exclusion of prey fish from areas with high MeHg production during specific times of the year (Davis et al. 2012). Overall, ecological manipulations

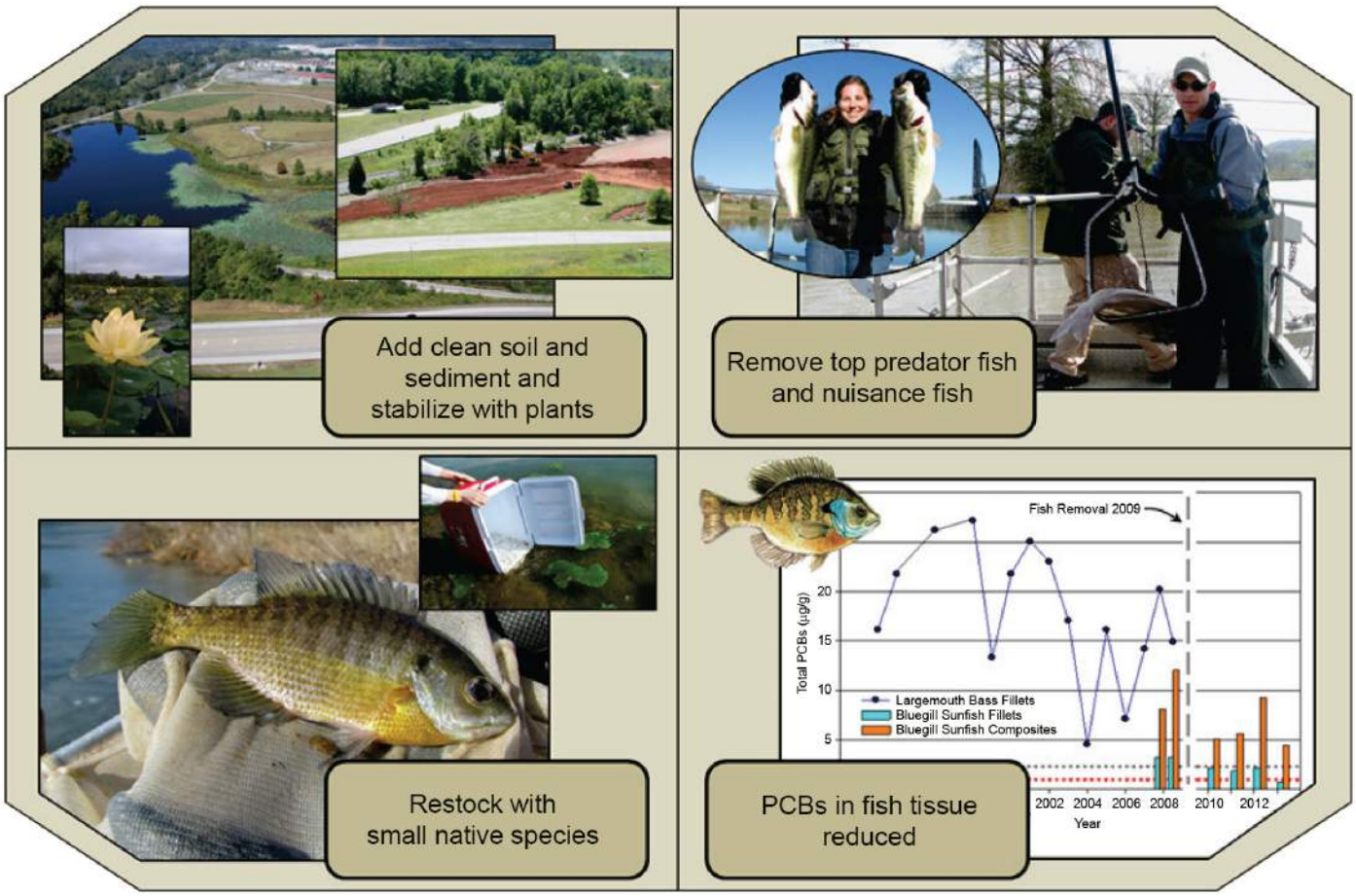


Figure 27. A number of ecological remediations were successful in lowering PCB concentrations in fish tissue at the K-1007-P1 Pond on the Oak Ridge Reservation. Data courtesy of ORNL's Biological Monitoring and Abatement Program.

represent a novel mercury remediation approach with the potential to reduce mercury bioaccumulation sustainably within EFPC.

Ecological manipulation with the end goal of reduced mercury bioaccumulation in fish can occur at different trophic levels of the food chain. The following subsections describe potential ecological manipulations at successive steps up the food chain, starting at the base of the food web with primary producers (algae/periphyton), and continuing on through primary (invertebrates), secondary (fish), and tertiary (fish) consumers.

Potential Manipulations of Primary Producers

Uptake at the base of the aquatic food chain is the most important concentration step, with mercury concentrating over 10,000-fold between water and algae. Primary producers within stream ecosystems are extremely important in food web dynamics. Through bottom-up processes, primary producers in an ecosystem can control growth and community structure. Primary producers not only provide food and structure for higher trophic levels but also heavily influence biogeochemical cycling of nutrients as well as contaminants within freshwater systems (Hill et al. 2010). While the relationship between mercury concentrations in water and fish has been characterized in EFPC, the transfer pathways from the base of the food chain remain largely unknown.

Periphyton—a consortium of algae, bacteria, protozoa, fungi, other invertebrates, and detritus (Eminson and Moss 2007)—is important in the loading of mercury within stream ecosystems into the food web in two ways:

1. Periphyton bioconcentrates mercury into the base of the food web.
2. Bacteria associated with periphyton can transform inorganic mercury to MeHg.

Because of the dual nature of periphyton's effect on mercury movement in the food web, it is crucial to consider manipulations involving periphyton when considering mercury remediation.

The approaches to ecologically manipulate primary producers that will be discussed in the following subsections include phytoremediation, increasing riparian shading, and manipulating of the bacterial community.

Phytoremediation

Phytoremediation is a type of bioremediation that uses plants to mitigate environmental contamination. Although most studies have focused on terrestrial systems, phytoremediation is the most-studied ecological manipulation approach used as a remediation strategy at contaminated sites (Susarla et al. 2002, Wang et al. 2012). A related technique, phycoremediation, uses macro- or micro-algae to remediate contamination and can be used in aquatic systems. Phytoremediation encompasses at least four separate processes that can remediate soils and sediments—contaminants can be accumulated in the plant biomass (phytoextraction); inactivated or immobilized at the root zone (phytostabilization); absorbed and released into the air (phytovolatilization); or modified to result in their inactivation, degradation, or immobilization (phytotransformation) (Rhodes 2013). Overall, the use of phytoremediation in mercury-contaminated sites has shown promise (Mishra et al. 2008, Rai 2008).

In aquatic systems, many species of macrophytes have shown potential in hyperaccumulating mercury, especially within their root systems, leading to a decrease in mercury concentrations in the surrounding environment. However, phytoremediation in mercury-contaminated aquatic sites is generally regarded as risky, predominantly because of the elevated mercury methylation that occurs at the root-associated periphyton of macrophytes (Mauro et al. 2002). More recently, the use of microalgae, either in continuous culture or immobilized in a permeable matrix, has been suggested as a way to sorb dissolved contaminants, including mercury (Barkley 1991, Bayramoglu et al. 2006, de-Bashan and Bashan 2010, Pena-Castro et al. 2004, Travieso et al. 2002). This technology is relatively immature and, because of implementation constraints, may be more suitable for use in UEFPC than LEFPC.

Major advantages to phytoremediation include a low implementation cost and ability to monitor mercury concentrations within the plant (Wang et al. 2012). This allows for feasible implementation and monitoring the impact of the manipulation. Phytoremediation is also considered less harmful to the environment than many other remediation technologies because it can utilize naturally occurring organisms (Rhodes 2013). These plants could potentially serve as an improved habitat for resident species. Overall, phytoremediation can be less disruptive to a pre-existing ecosystem.

However, there are many pertinent drawbacks in the use of phytoremediation in EFPC, especially because of mercury's unique biogeochemical cycle within freshwater systems. Phytoremediation is very site specific, so while it is well studied and has been implemented at other contaminated sites, a unique plan would have to be made for its implementation in EFPC. A main concern would be the propensity for macrophytes to be important sites of mercury methylation (Cosio et al. 2014). Phytoremediation also takes time to make marked reductions in mercury concentrations within an environment (Fuller 2003). Additionally, the survival of the plants could be affected by mercury toxicity (Rhodes 2013). The management of mercury-containing biomass harvested from EFPC could be costly. Further, this technology is relatively immature in development for mercury remediation in aquatic systems.

Increase Riparian Shading

The uptake of mercury into periphyton is the most important concentration step in the food web, with mercury concentrating more than 10,000-fold in algae from dissolved exposures. Further, periphyton also includes bacteria that can methylate mercury, causing higher dissolved concentrations of MeHg. This MeHg can then be introduced into the aquatic food web if taken up by closely associated algae. By controlling periphyton growth by increasing canopy cover to affect irradiance, it could be possible to affect mercury methylation and bioaccumulation. Increasing canopy cover through planting trees also stabilizes the banks of EFPC, further reducing mercury inputs into the system.

An increase in riparian shading could affect photosynthetic productivity in primary producers. If shading effectively decreased aquatic primary production, it is possible that both MeHg production and bioaccumulation at the base of the food chain could be decreased (Feminella et al. 1990). However, there are potential drawbacks to this ecological manipulation. Methylmercury can undergo photodemethylation in the presence of sunlight, leading to reductions in MeHg concentrations in water, which could affect food web concentrations (Mauro et al. 2002, Tsui et al. 2013). Blocking sunlight through shading could itself cause an increase in MeHg by disallowing photodegradation. Further, increased benthic periphyton biomass has been shown to cause decreases in mercury concentrations within the food web through density dilution (Chen and Folt 2005, Ward et al. 2010). Increasing periphyton concentration via phosphorus additions has even been suggested as a remediation technology through the density dilution effect. With decreased periphyton concentrations, any effect from “density dilution” would be removed. Lastly, the added organic carbon from the new allochthonous sources would have unknown effects on mercury bioavailability and mercury methylation rates within EFPC.

There is much conflicting information on how the manipulation of periphyton concentrations at a contaminated site affects bioaccumulation throughout the food web, and because periphyton abundance and effects on mercury/MeHg production and cycling have not been characterized, it is not possible to predict how manipulating periphyton communities would affect mercury cycling in EFPC. The geochemical cycling of mercury makes it especially hard to predict an ecosystem-wide response. Laboratory and mesocosm studies on the effectiveness of periphyton manipulation could further inform the use of this technology in EFPC.

Manipulate Bacterial Community

In situ bioremediation via the manipulation of the bacterial community has the potential to reduce mercury bioaccumulation throughout the food web by reducing the MeHg available for bioaccumulation. Reductive demethylation of MeHg is mediated by the *mer*-operon system, which degrades MeHg into elemental mercury and methane. Oxidative demethylation degrades MeHg to inorganic mercury, carbon dioxide, and small amounts of methane (Hsu-Kim et al. 2013). Seeding EFPC with a species of demethylating bacteria could reduce mercury bioaccumulation by reducing the amount of MeHg available for bioaccumulation.

Disadvantages associated with bacterial community manipulation mainly concern the introduction of a foreign organism into an established community. First, a demethylating bacterial species would have to be selected. There is no guarantee that this bacterium would be able to compete for survival in EFPC because of various physical, chemical, or biological parameters. The bacterial strain could demethylate MeHg in laboratory conditions or even in other streams, but if conditions are not conducive to its survival, the bacteria will die out after seeding. Lastly, the effectiveness of this technology is unknown.

Potential Manipulations of Invertebrates

Invertebrates serve as an important link in the freshwater food chain—they are the primary consumers that link the primary producers of the stream ecosystem with fish species. Bivalves in particular have many crucial roles in freshwater ecosystems. Freshwater mussels are filter feeders that can feed on bacteria, bacteria-sized particles, algae, zooplankton, detritus, and dissolved organic matter in the water column (Vaughn and Hakenkamp 2001, Vaughn et al. 2008). Juvenile mussels and some invasive mussels are also known to pedal feed—that is, feed on bacteria and algae from the sediment (Vaughn and Hakenkamp 2001, Yeager et al. 1994). Further, mussels are known to burrow into sediment, effectively aerating it through bioturbation, which could possibly stimulate bacterial metabolism and increase bacterial food resources (Vaughn et al. 2008).

Bivalves have been used in contaminant remediation practices worldwide because of their propensity to hyperaccumulate and store contaminants, particularly metals but also organochlorines and hydrocarbons, within their body tissues without succumbing to toxic effects (Gifford et al. 2007, Gifford et al. 2005, Gifford et al. 2004). However, a recent literature search found no study that has of yet explored the use of bivalves in mercury remediation other than as a tool to monitor the success of other remediation efforts (Beckvar et al. 2000).

Mussels could play an important role in the availability of MeHg to enter the EFPC food web. Because mussels filter particulates from the water column (and possibly sediment), they can affect mercury bioaccumulation throughout the food web by exerting effects on periphyton, dissolved organic matter, methylating bacteria, and dissolved mercury concentrations (Dieguez et al. 2013,

Pickhardt and Fisher 2007). However, no studies have described the abilities of native EFPC mussels to filter particulates and/or mercury from the water column or sediment bed. Therefore, their effects on mercury bioavailability remain largely unknown.

Research is needed to evaluate whether there are potential benefits to using native bivalves for mercury remediation within EFPC. By reintroducing native bivalves into EFPC, the concentration of periphyton (including the associated bacteria that can methylate mercury) would likely decrease in the water column and, possibly, in the sediment. This could decrease mercury methylation. The bioturbation of mussels would oxygenate the anoxic sediments, potentially further decreasing the methylation of mercury. Interestingly, spent mussel shells have been shown as a possible way to remove metals from contaminated environments, with shells extracting more than twice their weight of lead from water (Tudor et al. 2006). It is possible that this would also lower mercury bioaccumulation. Lastly, the consumption of dissolved organic matter could also remove associated mercury from the system and into the tissue of the mussels. These could all reduce MeHg concentrations within EFPC, leading to decreased MeHg bioaccumulation throughout the EFPC food web.

There are many uncertainties to bivalve addition that need further investigation. Shells of alive and spent mussels are prime habitat for periphyton, which could cause an increase in periphyton along the benthic zone, potentially causing an increase in mercury methylation. Another potential avenue for increased mercury methylation by way of bacteria is the consumption of bacterial predators. Without these predators, bacterial growth could increase. By consuming dissolved organic matter, inorganic mercury could become more bioavailable for uptake (Chiasson-Gould et al. 2014), increasing the amount of mercury within the food web. Lastly, healthy mussel communities generally occur as complex multispecies assemblages (Vaughn et al. 2008), and it is unknown how a single-species seeded population of mussels would fare in EFPC.

Because this approach is novel in mercury remediation, there are many unknowns that must be explored. For example, a mussel species must be selected that can survive (and thrive) in EFPC. One important factor in this survival is choosing a species that uses a native host fish (e.g., bluegill) in its early parasitic life stage. The filtration rate of selected mussel species would give an idea of how effective this ecological manipulation might be in removing particulates from the water column. In addition, further experiments could shed light on the inclination of selected mussel species to obtain food via water filtration or pedal feeding.

Globally, freshwater mussels are among the most threatened group of aquatic organisms, rapidly losing biodiversity (Atkinson et al. 2011, Vaughn and Hakenkamp 2001). In EFPC, native mussels may have been impacted negatively by past industrial stressors to the creek. The reintroduction of native species (see Table 11 for 13 potential species, three of which have been recorded in EFPC as of 1997) would be a chance to not only lower MeHg bioaccumulation within the food web (Fig. 28) but also to repopulate a native, extirpated species into its natural habitat.

Potential Manipulations of Fish

Fish are of particular importance in mercury-contaminated sites because of their link to human health; the most common exposure route of mercury to people in the United States is through the consumption of fish containing MeHg. Because of this, monitoring programs at impacted sites commonly examine mercury concentrations in the water column as well as in fillets of upper trophic level fish.

The Y-12 Biological Monitoring and Abatement Program (BMAP) has been monitoring mercury concentrations in target fish species at several sites along EFPC since the 1980s (Southworth et al. 2011). Over the years, several fish species have been collected for mercury monitoring throughout EFPC, with concentrations varying with the size, life span, and trophic level of the fish. For more than 20 years, the primary target species for mercury monitoring in EFPC for human health concerns has been the redbreast sunfish (*Lepomis auritus*), although in recent years rock bass (*Ambloplites rupestris*) have replaced redbreast as the most abundant sunfish species at many monitoring sites. Fig. 29 shows spatial trends for mercury concentrations in fish collected in and downstream of EFPC in spring/summer 2013.

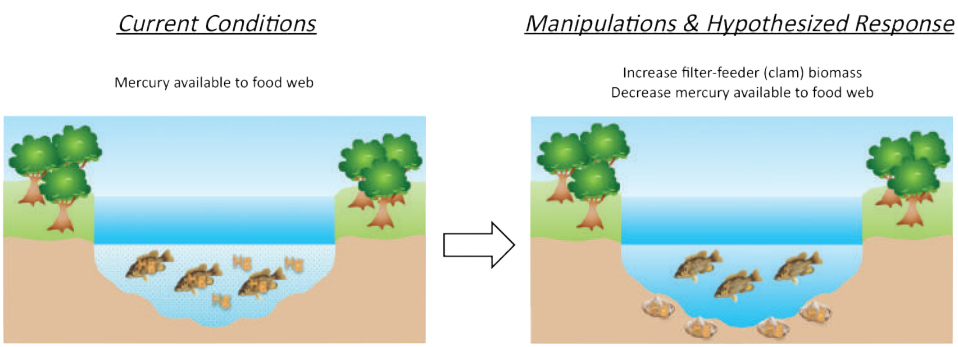


Figure 28. The introduction of filter feeders could decrease the availability of mercury to the food web, decreasing the mercury concentration in fish tissue.

Table 11. Potential freshwater mussel species for ecological remediation of EFPC

Name	Family	Maximum size (mm)	Habitat	Known host fish suitable for EFPC	Status (1993)
Actinonaias ligamentina[a] "Mucket"	Unionidae	140	Main channels in runs and riffles; depth of 3 ft or less; prefer gravel, cobble, mud	Bluegill, rock bass	Stable
Amblema plicata "Threeridge"	Unionidae	170	Small streams to big rivers; prefer clay, mud, sand, and gravel; most common in 1–3 ft of water	Bluegill, rock bass	Stable
Eliptio dilatata "Spike"	Unionidae	120	Reservoirs; less than 2 ft of water in upper Clinch River; prefer firm substrate of course sand and gravel; moderately strong current	Banded sculpin, rock bass	Stable
Lampsilis cardium "Plain pocketbook"	Unionidae	140	Moderate to strong current; tolerant to pollution; prefer coarse gravel and sand; between 2 and 20 ft of water	Bluegill	Special concern
Lasmigona costata "Flutedshell"	Unionidae	190	Moderately strong current; prefer coarse sand and gravel; 3 ft of water or less	Bluegill, rock bass	Stable
Ligumia recta "Black sandshell"	Unionidae	160	Strong current; prefer coarse sand with gravel and cobbles; several inches to 6 ft of water	Bluegill	Special concern
Pleurobema cordatum "Ohio pigtoe"	Unionidae	80	Large rivers; 18–24 ft of water; prefer firm substrate	Bluegill	Special concern
Quadrula metanerva "Monkeyface"	Unionidae	110	Swift current; clean water; prefer gravel	Bluegill	Stable
Strophitus undulatus "Creeper"	Unionidae	90	Adaptable; high gradient to meandering or channelized rivers	Bluegill	Stable
Toxolasma parvus "Lilliput"	Unionidae	30	Small to large rivers, lakes and ponds; prefer mud, sand, and fine gravel	Bluegill	Stable
Utterbackia imbecillis "Paper pondshell"	Unionidae	100	Shallow banks; prefer fine mud and sand	Bluegill, rock bass	Stable
Villosa iris[a] "Rainbow"	Unionidae	75	Clean, well-oxygenated water; less than 3 ft of water; prefer gravel and sand; moderate to strong current	rock bass	Stable
Villosa vanuxemensis[a] "Mountain creekshell"	Unionidae	70	Small headwater creeks; very clean water; prefer gravel and sand	Banded sculpin	Special concern

Note: All information from Parmalee and Bogan 1998.
[a] Signifies specimen (alive or shell) was observed in 1997 by J. G. Smith (US DOE 1997).

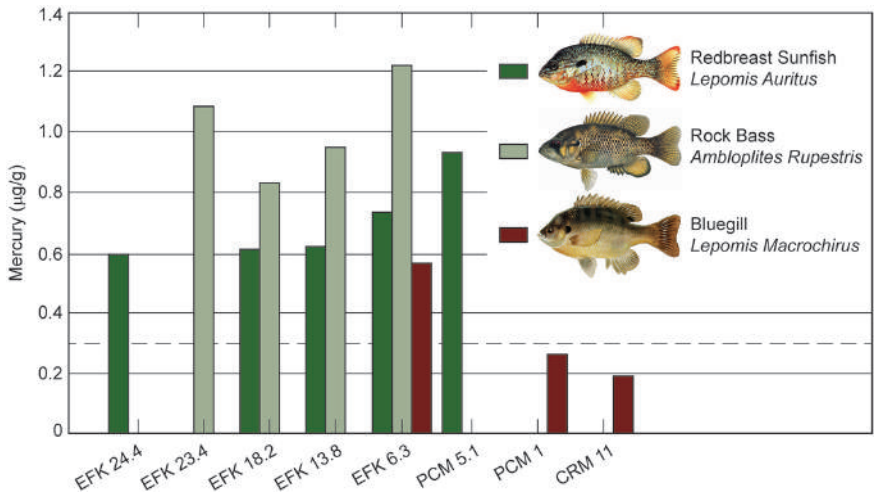


Figure 29. Mercury concentrations (µg/g) in fish fillets at sites within and downstream of EFPC. All fish were collected in spring or summer of 2013. Dotted line signifies the NRWQC fish tissue concentration of 0.3 mg/kg. Data courtesy of ORNL's BMAP. (Notes: CRM = Clinch River Mile; PCM = Poplar Creek Mile.)

Several key points are illustrated in Fig. 29:

- Within EFPC, mercury concentrations in a given fish species have historically risen with increasing distance downstream. This is likely because aqueous MeHg concentrations rise with increasing distance downstream (although this is not true of aqueous total mercury concentrations).
- At a given collection site/season, mercury concentrations follow a similar trend of rock bass > redbreast > bluegill (*Lepomis macrochirus*). This is likely because of dietary preferences in these fish species, with rock bass feeding on prey items (e.g., crayfish, juvenile fish) that are higher on the food chain than the preferred prey items of redbreast and bluegill (e.g., aquatic insects).
- Downstream of EFPC, mercury concentrations in sunfish decrease with increasing distance downstream, consistent with dilution from the point source.

Approaches to ecologically manipulating the fish community, including stocking a lower trophic level fish and removing highly contaminated, predatory fish, are discussed in the following subsections.

Stocking a Lower Trophic Level Fish

Mercury bioaccumulation is strongly correlated with feeding guild and size (Peterson and Van Sickle 2007). Because mercury (particularly MeHg) bioaccumulates with each successive step up the food chain, fish that feed on benthic invertebrates will inherently accumulate less mercury than piscivorous fish. The insectivorous food chain is shorter than the piscivorous food chain, restricting the opportunity for mercury to biomagnify up the food chain.

Few studies have looked at the effects of stocking fish with lower bioaccumulation potential to decrease fish tissue concentrations contaminants, and only one focused on the effects on mercury bioaccumulation. Lepak et al. (2012) found that by stocking a high quality, low mercury bioaccumulating fish species, mercury concentrations in the resident predatory fish were reduced via growth dilution (Fig. 30). However, this effect was short lived because mercury concentrations rebounded the following year. Table 12 shows potentially promising candidates for stocking in EFPC; these species are native and/or locally abundant and prefer habitats similar to those in EFPC.

There are advantages to stocking lower trophic level fish. They inherently bioaccumulate less mercury than fish higher on the food chain. Because these fish are not

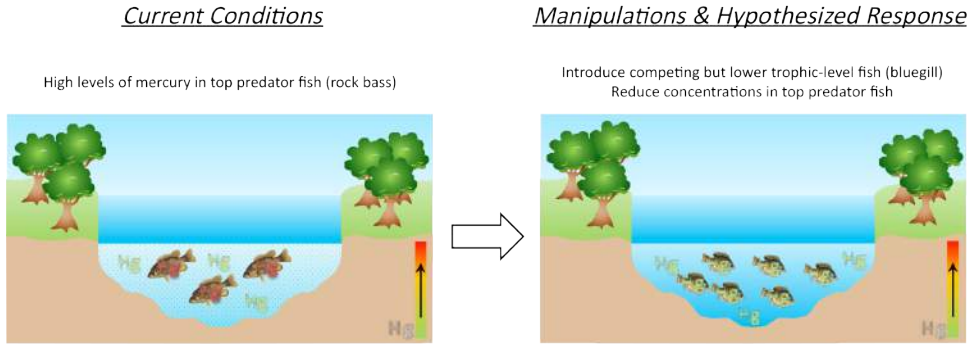
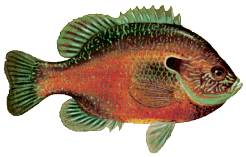


Figure 30. Hypothetical effects of manipulating fish communities in EFPC to introduce lower trophic level fish and/or removing higher trophic level fish on mercury bioaccumulation. These manipulations may reduce the mercury concentrations in top predator fish in the system. Adapted from Carpenter and Kitchell 1988.

Table 12. Descriptions of habitat, prey, and water quality of candidate fish for restocking in EFPC

Fish species	Habitat	Prey	Water quality
Bluegill (*Lepomis macrochirus*)	Juveniles— just above the vegetation, prefer calm water with fine substrates Adults— More generalist, usually high in the water column, above vegetation	Small-bodied invertebrates, particularly insects (both aquatic and terrestrial)	pH range: 7.0–7.5 dH range: 10–15 Temp: 1–22°C
Longear sunfish *(Lepomis megalotis)* 	Clear, shallow to moderately deep, still waters with vegetation	Primarily aquatic and terrestrial insects, occasionally small fish	Unknown
Redear sunfish *(Lepomis microlophus)*	Prefer large, clear, low -gradient streams, slow currents, pools with vegetation	Primarily feed on aquatic insects; feed secondarily on copepods, clams, crayfish	pH range: 6.7–8.6 dH range: 5–12.3 Temp: 6.5–27°C

Notes: dH = dissolved hardness; pH = potential of hydrogen.

piscivorous, a step allowing for further biomagnification of mercury is removed from the system. As a stand-alone remedial option, this ecological manipulation is generally thought of as a temporary solution (Stow et al. 1995), however, because these fish usually have to be restocked after the initial stocking to maintain low mercury concentrations. Stocking of lower trophic fish may be done best in conjunction with other management strategies.

Removing Highly Contaminated, Predatory Fish

Predatory fish removal is a food chain manipulation that can decrease the overall fish tissue concentration of mercury in EFPC. “Intensive fishing” has been proposed as a control of mercury concentrations in fish tissue for over 30 years (Gothberg 1983, Verta 1990). Reductions in mercury concentrations in the remaining fish were attributed to either increased fish growth—a dilution effect in the remaining population—or alterations in the food web. The growth dilution of MeHg in fish also has been corroborated by more recent experimental data (Ward et al. 2010). The overall success of overfishing led to the hypothesis that food web manipulation could be a viable means of lowering MeHg levels within fish tissue at mercury-contaminated sites.

Fish removal has been used in a few instances throughout the past 11 years with mixed results (Hakanson et al. 2003, Masson and Tremblay 2003, Sharma et al. 2008, Sharma et al. 2011). Generally, studies find that removing larger fish will cause a decrease in mercury concentrations in remaining fish, possibly due to growth dilution from increased biomass (Sharma et al. 2008). Others have seen increases in fish mercury tissue concentrations after fish removal (Hakanson et al. 2003). However, these studies use intensive fishing as a means to remove targeted fish species. Therefore, they do not completely remove the target population and must keep intensive fishing measures in place to continue to see results.

An advantage to this method is that effects are instantaneous. A decrease in fish mercury concentrations may be evident immediately. By shortening the food chain in EFPC, the opportunity for another step of bioaccumulation is removed. By totally removing the target predatory fish species and the establishment of a less bioaccumulative species, it may be possible to see these effects extend long-term. However, preventing reestablishment of the predatory fish species may require active fish management or use of fish barriers to keep out the higher trophic level fish species. These barriers must withstand flooding events to be effective, although there is now extensive research into electronic barriers associated with carp migrations in the Great Lakes and elsewhere. These new technologies offer opportunities to better manage stream fish populations, similar to ponds and lakes. Barriers, however, may disrupt

migratory patterns of other fish as well as cause a loss of genetic diversity in the remaining fish populations (Novinger and Rahel 2003). Long-term fish management and monitoring may be needed.

Summary of Potential Ecological Manipulation Techniques

Table 13 presents a summary of potential ecological manipulation techniques. Some of the more conventional ecological remediation technologies (e.g., phytoremediation) may not be ideal for mercury-contaminated sites because of the complex geochemical cycle of mercury in freshwater environments. However, other less-utilized ecological manipulations may be suitable for EFPC remediation (Table 13). Based on the information compiled, the most promising ecological manipulations to pursue include fish community manipulation (removal of predatory fish and stocking of lower trophic level fish), the introduction of native bivalves, and increasing riparian shading. Table 13 lists research needs to address before implementation of these ecological manipulations.

At the base of the food web, manipulations such as decreasing periphyton abundance via riparian shading and the introduction of native bivalves offer new ways to manipulate mercury bioaccumulation in the food web. Understanding how changes in periphyton biomass affect mercury bioaccumulation throughout the food web in the laboratory would give us insight on how riparian shading would affect mercury bioaccumulation in the environment. Likewise, by better characterizing the effects of mussel filtration on particulate abundance in the water column using laboratory experiments, researchers can begin to understand the effects that mussels could have on mercury cycling and bioaccumulation in EFPC.

For the proposed fish manipulations to be viable options in EFPC, there must first be an understanding of food web dynamics throughout the community. Few studies have examined the effects of fish community manipulation on mercury bioaccumulation within aquatic ecosystems. Further, none have looked at the combined effects of removing predatory high trophic level fish and the stocking of lower trophic level fish. ORNL's success with this combination of manipulations in reducing PCB concentrations in K-1007-P1 Pond gives optimism to the success of these manipulations in reducing mercury bioaccumulation in EFPC. Caging and mark/recapture studies would further determine the likelihood of success of these technologies within EFPC.

Ecological Manipulation Research and Technology Development Needs

As with any other remediation technology, effective food web manipulations require a comprehensive understanding of the system being manipulated (Lepak et al. 2009). In addition to monitoring mercury concentrations in target fish species, BMAP has been monitoring fish and benthic macroinvertebrate community structures over time since the 1980s (Peterson 2011). Whereas the current understanding of mercury bioaccumulation in EFPC is limited to a few target fish species, the fish and macroinvertebrate community data sets provide valuable information on the food web structures and, therefore, on the potential opportunities for ecological manipulations.

Figure 31, created with BMAP data, shows that the species richness of both fish and benthic macroinvertebrates is greater at downstream locations than at upstream locations, suggesting a more complex food web in LEFPC than in UEFPC (Fig. 32). More steps within a food web allow for greater mercury biomagnification from primary producers to the top predatory species. This, along with the spatial trends in aqueous MeHg concentrations in EFPC, could explain the trends in fish mercury concentrations throughout the creek. While controlling MeHg production may not be a realistic goal with the current understanding of mercury methylation dynamics, manipulating the food web structure to encourage the colonization of lower trophic level fish may be more achievable on time scales relevant to remediation decisions. This would provide an opportunity for decreased mercury bioaccumulation and potentially decreased ecological and human health exposure and risk.

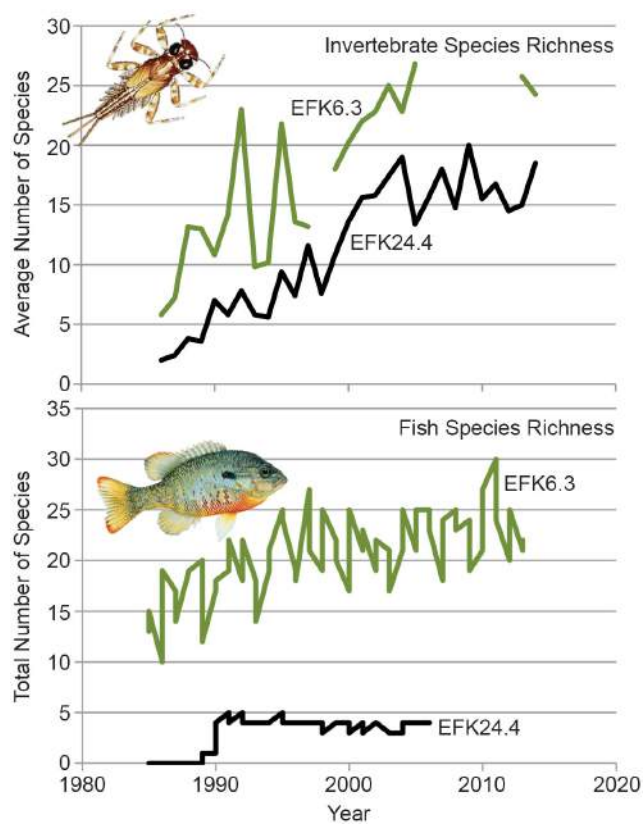


Figure 31. Invertebrate and fish species richness over time at upstream (East Fork Kilometer [EFK] 24.4) and downstream (EFK 6.3) sites of EFPC. Data courtesy of ORNL's BMAP.

Table 13. Potential ecological manipulation techniques in EFPC

Technology	Description	Objective	Pros	Cons	Research Needs
Phyto-remediation	Add vegetation in the streambed to remove Hg from the sediment and water column	Remove Hg and MeHg from water column and sediment and into plant biomass	Relatively low cost; plants can be easily monitored	MeHg can be passed up the food chain after accumulation in plants; Hg II can be transformed into MeHg by bacteria associated with plants; takes time	Effects of macrophytes on Hg methylation in sediments; species of plant suitable for EFPC
Phyco-remediation	Add algae in continuous culture or immobilized in soluble matrix to remove Hg from water column	Remove Hg (and MeHg) from water column and onto algal cells	Microalgae are efficient at metal sorption	Requires water to be forced through tanks or over columns for sorption; may be more suitable for use in UEFPC than LEFPC	Suitable species for EFPC; infrastructure needs
Increase riparian shading	Add vegetation to the riparian zone to decrease the sunlight available to stream, reducing the concentration of primary producers	Reduce the production of MeHg; reduce the uptake of Hg II and MeHg into the food web	Decreased periphyton density will decrease the production of MeHg; bank stabilization	Decrease in photodegradation of MeHg; no density dilution effect; more organic carbon in stream to promote methylation; potential effectiveness unknown	The effects of allochthonous input into stream food webs and Hg bioaccumulation; the effects of decreased periphyton concentrations on the food web
Manipulation of bacterial community	Add bacteria with a lower threshold for mer gene induction	Reduce the production of MeHg in water and sediment	Decreased MeHg concentrations in water and fish; potential low cost	Need the right bacteria for demethylation; this bacteria strain may not compete/survive in EFPC; potential effectiveness unknown	Species of bacteria suitable for EFPC
Zooremediation (introduction of native bivalves)	Seed the stream with native bivalves that will filter Hg and MeHg from the water column, as well as filter Hg-methylating bacteria from the water column	Reduce the amount of Hg and MeHg in the food web	Decrease the concentration of periphyton in the water column and potentially sediment, thereby decreasing potential methylating bacterial populations; decrease amount of Hg available in the water column for bioaccumulation; increase the aeration in anoxic sediments; increase habitat for macroinvertebrates; reintroduce and restore native mussel populations	Shells offer habitat for periphyton, causing an uptick in periphyton concentration and potential uptick in Hg methylation; small founder population can lead to low heterozygosity; mussels can stimulate bacterial production by eating bacterial predators; mussels generally occur in complex multispecies assemblages; potential effectiveness unknown	The filtration rates of chosen mussel species; the effects of mussel introduction on the food web dynamics; the optimal population density of a reintroduced native mussel
Overstocking of lower trophic level fish	Add fish that are known to accumulate low levels of MeHg	Reduce the fish concentrations of MeHg; shorten the food chain	Lower trophic level fish accumulate less Hg via diet; doesn't require instream fish management	Temporary solution; need for restocking	Community-wide effects; need a better understanding of food chain dynamics to understand consequences of stocking fish
Removal of highly contaminated fish	Selectively remove highly contaminated species using electrofishing techniques	Reduce the fish concentrations of MeHg; shorten the food chain	Immediate effect of lower fish concentrations of Hg; can have long lasting effects if done properly	Will require fish barriers; will require long-term fish management	Community-wide effects; need a better understanding of food chain dynamics to understand consequences of removing fish

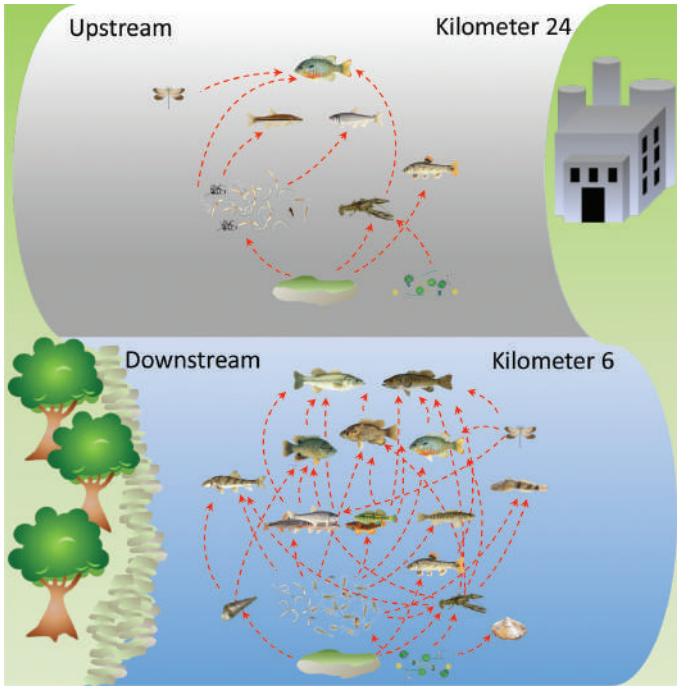


Figure 32. Depiction of food web structures (created from fish and benthic macroinvertebrate community data obtained from BMAP) at upstream and downstream monitoring sites within EFPC. The food web downstream (kilometer 6) is much more complex than the food web upstream (kilometer 24). More steps in the food chain enhance mercury bioaccumulation, leading to higher mercury concentrations in fish tissue.

The BMAP community data provides useful information on food web interactions, but to design ecomanipulation strategies that could be effective in reducing mercury bioaccumulation in fish, it is necessary to characterize the mercury transfer efficiency within the food web. Field surveys are proposed to collect biota from different trophic levels throughout EFPC for mercury, MeHg, and stable isotope analysis to deduce trophic structure (Fig. 33) (Cabana and Rasmussen 1994). By quantifying the mercury transfer within EFPC food webs, researchers can identify the key linkages for mercury transfer and identify manipulation strategies to decrease that transfer. Further, as with any remediation action, a thorough baseline characterization is needed before manipulation to discern the effectiveness of the action. Once the field characterization is completed, a detailed food web complete with mercury transfer can essentially provide a road map outlining key focus areas of efficient mercury transfer, which may be amenable to manipulation. From this road map, detailed "pilot" studies at the mesoscale (e.g., in stream-side tanks) are needed to assess the effects of manipulations in the laboratory before field implementation.

The data gathered from field surveys can be used in conjunction with historical BMAP data to create a conceptual model of mercury transfer through the food chain at various locations throughout the stream. This model can identify key trophic linkages where ecological manipulations have the potential to be effective, but before full scale implementation, it is necessary to do pilot scale tests to examine the survival and effectiveness of the species listed in Tables 11 and 12 and to gain information on optimal implementation specifications (e.g., initial population densities, deployment locations). By conducting studies using the TRL approach, technologies and approaches that have the most merit can move beyond laboratory and field testing to larger-scale pilot testing. Key early research and technology development activities should focus on the following:

- Experiments to examine the effects that riparian shading may have on MeHg production and bioaccumulation
- Determination of effects that the addition of native mussel species may have on dissolved and particle-associated mercury and MeHg within the creek
- Determination of the effects of mussel filtration on nutrient uptake and secondary effects of MeHg production by periphyton
- Experiments to examine the effect of fish population density on mercury and MeHg bioaccumulation
- Experiments to examine the effects of stocking mussels and lower trophic level fish on mercury bioaccumulation throughout the food chain

Figure 33. ORNL scientists and University of Michigan collaborators collect biota samples from the field.

CONCLUSIONS AND FUTURE DIRECTIONS

The research and technology development activities reviewed and proposed in this document offer science-based approaches and ideas that may lead to new options for mercury remediation in LEFPC. Proposed is a technology development strategy consistent with the adaptive management paradigm and DOE's TRL guidelines. The approach follows a "pyramid TD approach" (Fig. 34). That is, early evaluation needs to focus on literature review and white paper evaluations, site characterization, and small-scale studies of a broad number of potential technologies (including ideas that may be viewed as higher risk or uncertainty but with potentially high payoff). As more information is gathered, an adaptive management approach can be used to conduct testing and to focus on technologies that may have the most promise and potential remediation benefit. High merit technologies or strategies will need to undergo more extensive and larger-scale pilot testing before remedial implementation.

Future directions for mercury research and technology development in LEFPC will be defined to a large degree by the overall remediation strategy and priorities in Oak Ridge, the financial and technical resources that are available, and an iterative, adaptive management approach that relies on the findings from earlier research. Using DOE's current mercury remediation timeline, a remedial alternatives evaluation for LEFPC would be conducted in 2021. As proposed here by ORNL scientists, the research and technology development activities conducted between now and then would provide the necessary time and resources to find the most effective remedial strategies for addressing the complex mercury issue in LEFPC.

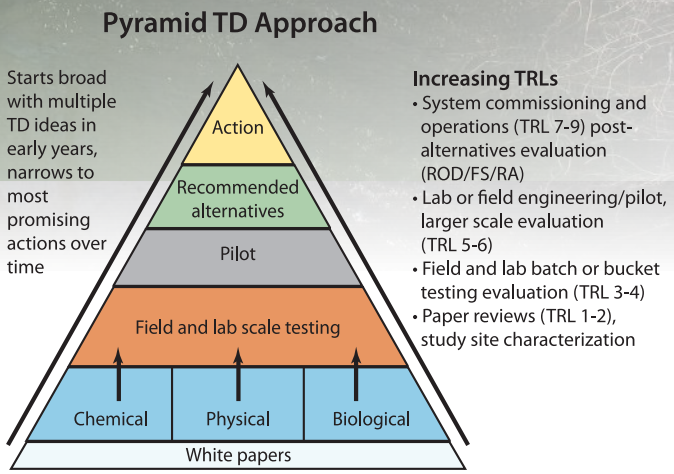


Figure 34. Pyramid technology development approach.

As a first step in research and technology development in LEFPC, a conceptual model that provides a better understanding of mercury sources, transformations, transport, and fate processes in the EFPC system is essential (Fig. 35). Very little is known about mercury and especially MeHg levels in various source compartments (e.g., bank soils, sediments, groundwater, lower trophic level biota), and the spatial and temporal variability found within the watershed. Near-term field surveys should obtain a more comprehensive and scientifically valid characterization of mercury content in within-stream media. Further, the environmental factors that affect mercury flux, methylation, and bioaccumulation in LEFPC are poorly understood, and early studies should obtain data that may be useful in defining future system management or manipulations that may decrease mercury methylation and bioaccumulation. Lab-scale and meso-scale testing of potential strategies and technologies should be conducted concurrent with field studies. See summary of research and technology development needs on following page.

SUMMARY OF RESEARCH AND TECHNOLOGY DEVELOPMENT NEEDS[a]

A watershed-scale evaluation of mercury distribution and temporal variation in EFPC and an understanding of the environmental factors affecting mercury processes in the creek:

- Conduct stream bank soil surveys in summer and winter, including evaluation of particle size distribution and mercury concentrations
- Identify susceptible stream bank sites in terms of both erosion potential and mercury or MeHg concentrations
- Identify the extent of potential fluxes of mercury in groundwater to the creek in terms of volume of water and concentration of mercury and MeHg
- Establish creek gauging and water chemistry stations to understand flow and water quality dynamics on mercury flux and methylation. This is especially important information to obtain after Y-12 flow augmentation has ended.
- Conduct limited field sampling to help quantify the impacts of facility chemical usage on the forms and magnitude of mercury transported from UEFPC to LEFPC
- Evaluate the forms and distribution of mercury in sediments throughout EFPC
- Collect biota samples for mercury and MeHg analysis from sites throughout EFPC to better understand mercury distribution throughout the food chain, including algae, invertebrates, and prey fish that rarely have been analyzed historically

Concurrent and follow-on laboratory-scale studies designed to develop technologies and strategies that might be applied to LEFPC:

- Conduct lab-scale tests with a variety of sorbent materials, for soil and sediment application, designed to identify effective and economic materials capable of retaining mercury and MeHg for significant periods.
- Conduct testing of alternative chemical treatment methods that may benefit mercury release or transformation at the Y-12 facility
- Test altering groundwater chemistry or microbial community composition if groundwater is found to be an important source of MeHg to the creek.
- Examine the effects in the laboratory that riparian shading/light may have on MeHg production and bioaccumulation in algae
- Determine in the laboratory the potential effects of mussel filtering on algae biomass, nutrient uptake, and dissolved and particle-associated mercury and MeHg in the creek

Meso- and pilot-scale studies of potential technologies and system manipulations:

- Scale-up of potential technologies and strategies is needed to evaluate technology readiness. A near-stream flow-through Field Research Station (FRS) is advocated for controlled streamside testing.
- Streamside testing would involve pumping of mercury-contaminated EFPC water into a streamside facility where various sediment, water chemistry, and ecological amendments can be tested as to their efficacy in decreasing mercury concentrations.
- Test technologies under longer-term, site-specific creek exposures, addressing a major hurdle in application and scale up of laboratory findings.
- Test potential for using multiple strategies and technologies. For example, sediment sorbent application combined with mussel addition and fish population management can be a separate treatment option.
- Use FRS meso-scale testing to inform potential pilot-scale application of a technology or strategy within the creek.

[a]Research and technology development needs described in this document are those proposed by ORNL scientists. Implementation is subject to funding availability.

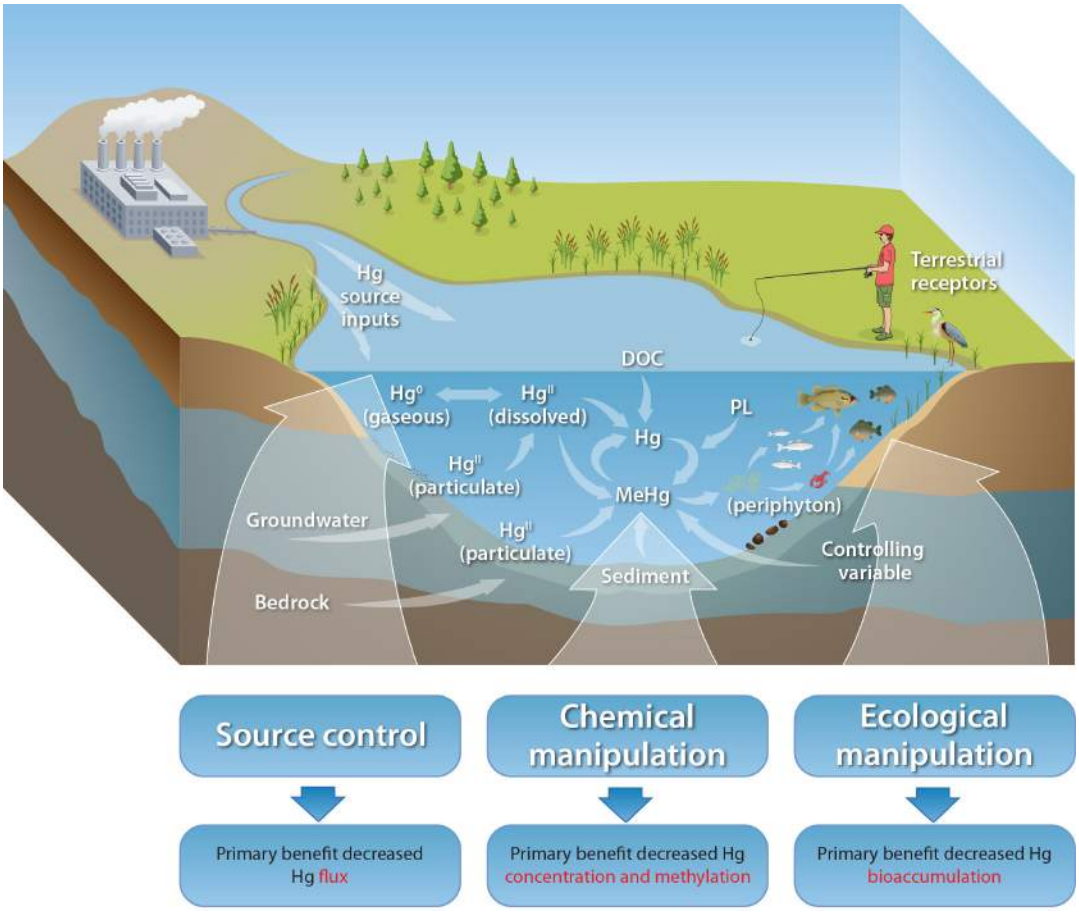


Figure 35. Three categories of potential remedial actions designed to interrupt the mercury transport, methylation, and bioaccumulation processes in LEFPC.

Proposed here is a broad-based watershed approach to address the mercury issue that includes (1) landscape-scale source control, including soil and groundwater; (2) in-stream sediment and surface water manipulation; and (3) ecological manipulation (Fig. 35). These three domains (source and transport, methylation, food chain) are the primary major factors that control mercury levels in fish. A focus of mercury technology development should be on those tools and strategies that can interrupt the mercury transport, methylation, and bioaccumulation processes in LEFPC. An underpinning aspect of 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 LEFPC environment, and it may provide opportunities for managing and restoring the system for natural resource benefit and water quality enhancement.

Acronyms and Abbreviations

AWQC	ambient water quality criteria
BEHI	Bank Erosion Hazard Index
BMAP	Biological Monitoring and Abatement Program
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DOC	dissolved organic carbon
DOE	Department of Energy
DOM	dissolved organic matter
EFK	East Fork kilometer
EFPC	East Fork Poplar Creek
EM	environmental management
EPA	US Environmental Protection Agency
ESD	Environmental Sciences Division
FGCM	fine-grained channel margin
FRS	Field Research Station
FS	Feasibility Study
GPS	Global Positioning System
HgS	mercuric sulfide
HgT	total mercury
IFRC	Integrated Field Research Challenge
K_D	low native sediment:water partition coefficients
LCF	lignin carbon fiber
LEFPC	lower East Fork Poplar Creek
MBFP	Mill Branch floodplain
MeHg	methylmercury
MNR	monitored natural recovery
MTF	Mercury Treatment Facility
NBS	Near Bank Stress
NOAA	National Oceanic and Atmospheric Administration
NOM	natural organic matter
NPDES	National Pollutant Discharge Elimination System
NRC	National Research Council
NRWQC	National Recommended Water Quality Criterion
OC	organic carbon
OF200	Outfall 200
OREIS	Oak Ridge Environmental Information System
ORNL	Oak Ridge National Laboratory
ORO-EM	Oak Ridge Office of Environmental Management
ORR	Oak Ridge Reservation
ORSTP	Oak Ridge Sewage Treatment Plant
ORWTF	Oak Ridge Wastewater Treatment Facility
PCB	polychlorinated biphenyl
PEC	probable effect concentration
ppm	parts per million
ppt	parts per trillion
RA	Remedial Action
RI	Remedial Investigation
RSI	Restoration Services, Inc.
SQG	sediment quality guideline
SRB	sulfate-reducing bacteria
TD	technology development
TDEC	Tennessee Department of Environment and Conservation
TEC	threshold effect concentration
TMP	Technology Maturation Plan
TRA	Technology Readiness Assessment
TRC	total residual chlorine
TRL	Technology Readiness Level
TSS	total suspended solids
TVA	Tennessee Valley Authority
TWRA	Tennessee Wildlife Resources Agency
UCOR	URS | CH2M Oak Ridge LLC (UCOR)
UEFPC	upper East Fork Poplar Creek
USGS	US Geological Survey
WBS	Work Breakdown Structure
Y-12 or Y-12 Complex	Y-12 National Security Complex

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