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**U.S. Department of Energy**
**Office of Environmental Management**

**The EM Center for Sustainable Groundwater Solutions**
**at the Savannah River National Laboratory**

# Recommendations to Address Technical Uncertainties in the Mitigation and Remediation of Mercury Contamination at the Y-12 Plant, Oak Ridge, Tennessee

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# Recommendations to Address Technical Uncertainties in Mitigation and Remediation of Mercury Contamination at the Y-12 Plant, Oak Ridge, Tennessee

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## Executive Summary

A technical workshop funded by the Department of Energy Office of Environmental Management (EM-22) and organized by the EM Center for Groundwater and Soils was held at the Oak Ridge National Laboratory in January 2008. The workshop was convened at the request of the DOE Oak Ridge Field Office and was focused on the following specific issues:

- Identify technical uncertainties or concerns associated with mercury contamination at Y-12 that may significantly impact schedule or budget
- Identify opportunities for modifying current baseline approaches to either achieve cost reductions and/or technical improvements, or to address technical uncertainties and concerns.

In general, the workshop focused on mercury in the East Fork Popular Creek watershed associated with Y-12; most of the evaluation, however would be generally applicable to other Oak Ridge watersheds. After reviewing the data, interacting with site technical experts and touring the facility, the technical working group evaluated the site using a structured stepwise process. This process involved: 1) developing key assumptions that would guide the effort, 2) developing consensus on important points and developing clear working hypotheses based on both a general and site specific conceptual model, 3) developing science and technology targets, 4) delineating logical subdomains, based on site specific conditions, uncertainties or opportunities, and 5) assessing the scientific needs and environmental opportunities for each subdomain. This structured process encouraged development of creative and diverse ideas and recommendations. Further, the process matched the ideas to the most promising subdomain to encourage efficient and effective implementation of the recommendations. In developing the recommendations for the environmental opportunities for each subdomain, the technical working group specifically highlighted those projects that are relatively inexpensive, that have a relatively low health and safety risk, and that may provide a significant benefit as “Quick Wins.” These Quick Win recommendations, along with the remainder of the recommendations are intended to serve as a resource to support environmental management at the Oak Ridge Reservation.

A significant technical observation of the team was that the level of mercury found in the fish in the East Fork Popular Creek at the Y-12 results from an intricate series of chemical transformations that begins with the initial release of mercury and is followed by a series of changes as the mercury is transported through the shallow soil, to the surface and/or shallow groundwater, and then through the reach of the stream drainage. The concentration of mercury in fish, a potential remedial action endpoint, is better correlated with the concentration of methyl mercury rather than the total mercury concentration in the stream water. The level of methyl mercury in the stream water can be described using a mass balance approach that depends on the concentration of total mercury, methylation processes and rates, and demethylation processes and rates. In recognition of the high level of complexity, the team divided Y-12 into four areas and then made specific technology recommendations for each of these areas. The four areas

include buildings and rubble piles, shallow source zone soil, the Outfall 200 area, and the upper and lower reaches of the East Fork Popular Creek. The team also made specific recommendations for prioritized basic and applied research needs – these fall broadly into the following topic areas:

- Demethylation and methylation processes and rates
- Ecosystem dynamics
- Stream and sediment hydrodynamics

One of the requested deliverables of the mercury workshop was a prioritized list of recommendations for applied science and technology support from EM-22 for mercury issues at Y-12 and Oak Ridge facility. During the workshop, a technology matrix was prepared for each of the four areas described above that identified potentially applicable technologies, and then deemed them as viable-preferred option, viable and not viable. The following list is a compilation of the technologies that preferred viable from each of the matrices. Several of the viable and preferred alternatives were designated as potential "Quick Wins." Quick Win ideas tend to be more mature (can be implemented in less than one year) and may need a relatively small level of funding (<$150K) for bench or field studies to support implementation. Specific projects selected as potential Quick Wins include:

**Domain III (Outfall 200)**

– Use of Stannous Chloride in the NS Pipe to Volatilize Hg
– Addition of Mercury Sequestrants at Outfall 200
– Use Sodium Thiosulfate for Dechlorination at Outfall 200

**Domain IV (Creeks and Streams)**

– Selective physical modifications at areas of methylation
– Addition of trace Se to reduce methylation and/or uptake

A plan that logically integrates some of the recommendations into a coordinated technical approach should be developed with the participation of the relevant Oak Ridge organizations, state and federal regulators and stakeholders. We anticipate that a logical and robust "Quick Win" portfolio will incorporate some type of ecosystem controls, some action(s) near Outfall 200, and possibly some related screening studies. Another very important consideration is that although some of the technologies may be technically viable, they may not be acceptable to site regulators, stakeholders, and site problem holders. Participation of these groups in the decision-making and selection process is crucial.

At this point, it is not appropriate for the technical working group to select the preferred technology portfolio. We recommend that EM-22 funding be used in two stages: The first stage consists of assembling mercury "Tiger Team" to consider the identified Quick Win ideas. This team, through a period of focused and intense effort, would identify and develop a detailed recommendation for consideration by DOE. The resulting plan would lay out a specific set of actions for implementation along with the priority, schedule and resources. The Tiger Team should include key individuals from the diverse groups identified above. For perspective, we believe that the Tiger Team process is a triage that should be performed rapidly and with minimal cost. The goal is to develop consensus and to determine which combination of options provides the most potential benefits within the real-world constraints of the site. Based on the recommendations, DOE EM-22 should consider funding key Quick Win activities as part of a second stage of funding.

## 1.0 Introduction

The Department of Energy Field Office at the Oak Ridge Site requested technical assistance from Department of Energy (DOE)-Environmental Management (EM) to provide technical experts to identify key technical uncertainties and make recommendations for a robust technical strategy to address issues associated with mercury contamination associated with the Y-12 facility. A technical workshop was held at the Oak Ridge site from January 14 – 18, 2008. During the first day of the workshop, both contractor and DOE site personnel briefed the workshop participants, and took them on a tour of the Y-12 facility. On subsequent days, the team reviewed baseline data and reports, asked clarifying questions of site personnel, evaluated work plans, determined critical issues, uncertainties, and recommended alternatives where appropriate. This report documents the team's findings and recommendations.

The specific focus of the technical workshop as requested by DOE-OR was,

> What causes the methylation of Hg? What measures can DOE take to mitigate it in order to decrease the mercury levels in the fish so that the site is in compliance with the Clean Water Act?
>
> The requested deliverable resulting from the workshop is a technical plan that DOE-OR can use to address issues associated with impacts of Hg to the site, specifically, whether the current remediation strategy documented in the current baseline and ROD are appropriate to address cleaning up the ground and surface water and reducing Hg levels in the fish.

## 2.0 History of Environmental Remediation at Y-12

### General Background

Between 1953 and 1983, it is estimated that 240,000 pounds of mercury were released to the East Fork Popular Creek during the operation of the lithium separation processes at the Y-12 Plant. Although the release of high concentrations of mercury from the plant stopped in 1963, mercury continues to be released into EFPC from various point and non-point sources of contamination in the Y-12 complex.

The EFPC can be divided into several discrete sections, the portion that occurs within the Y-12 Plant and the Oak Ridge Reservation Boundary (ORR) is generally referred to as the Upper EFPC (Figure 1.). The EFPC from Bear Creek to its confluence with Poplar Creek near the K-25 Plant is generally referred to as Lower EFPC.

The dry weather loading of mercury to the Upper EFPC has multiple sources, including infiltration of contaminated shallow groundwater into the storm water drain network, dissolution of mercury from the contaminated pipes, advection of contaminated interstitial sediment water into the surface flow, and emergence of contaminated groundwater from the karst system in springs and seeps.

During storm events, the total mercury concentrations in the surface water can increase by over an order of magnitude. This mercury is largely associated with suspended matter that is mobilized from shallow soils, stream bed sediments, and stream banks; the dissolved total mercury levels remain relatively constant over a storm event. Stream discharge, total mercury concentration, and total suspended solids are generally found to be highly correlated during storm events. In 1995, the total mercury release averaged approximately 12-15 gm/day down from 100 gm/day in 1985.

### Past Remedial Efforts

As with most of the large DOE sites, there is a relatively long history of effort directed at mitigation and remediation of soil, stream water, and shallow groundwater contamination at the Oak Ridge facilities. The Reduction of Mercury in Plant Effluents (RMPE) was a multi-stage program that was started in the mid-1980’s that continued through 2001. The focus of this program was to remediate major know sources of mercury and capture mercury-contaminated effluent for treatment. The initial program was designed to reduce the total daily mercury load to the UFEPC to less than five gm/day. The guiding principles of the RMPE program were first to “Isolate and Remove Sources” of waterborne mercury, and second, to “Treat Discharges” if isolation and/or removal were ineffective or infeasible. All sources of Hg-contaminated water were prioritized first by loading (g/day) and second by concentration (ug/L). Initial efforts focused on remediation or treatment of high loading and high concentration sources (e.g., Outfall 49). The most successful RMPE actions were focused on treatment of sump waters, cleaning and relining contaminated drains, minimizing flow through contaminated storm drains. The actions completed under the RMPE program by 1992 resulted in an overall reduction of Hg loading from 150 g/day in 1983 to 15 g/day in 1992.

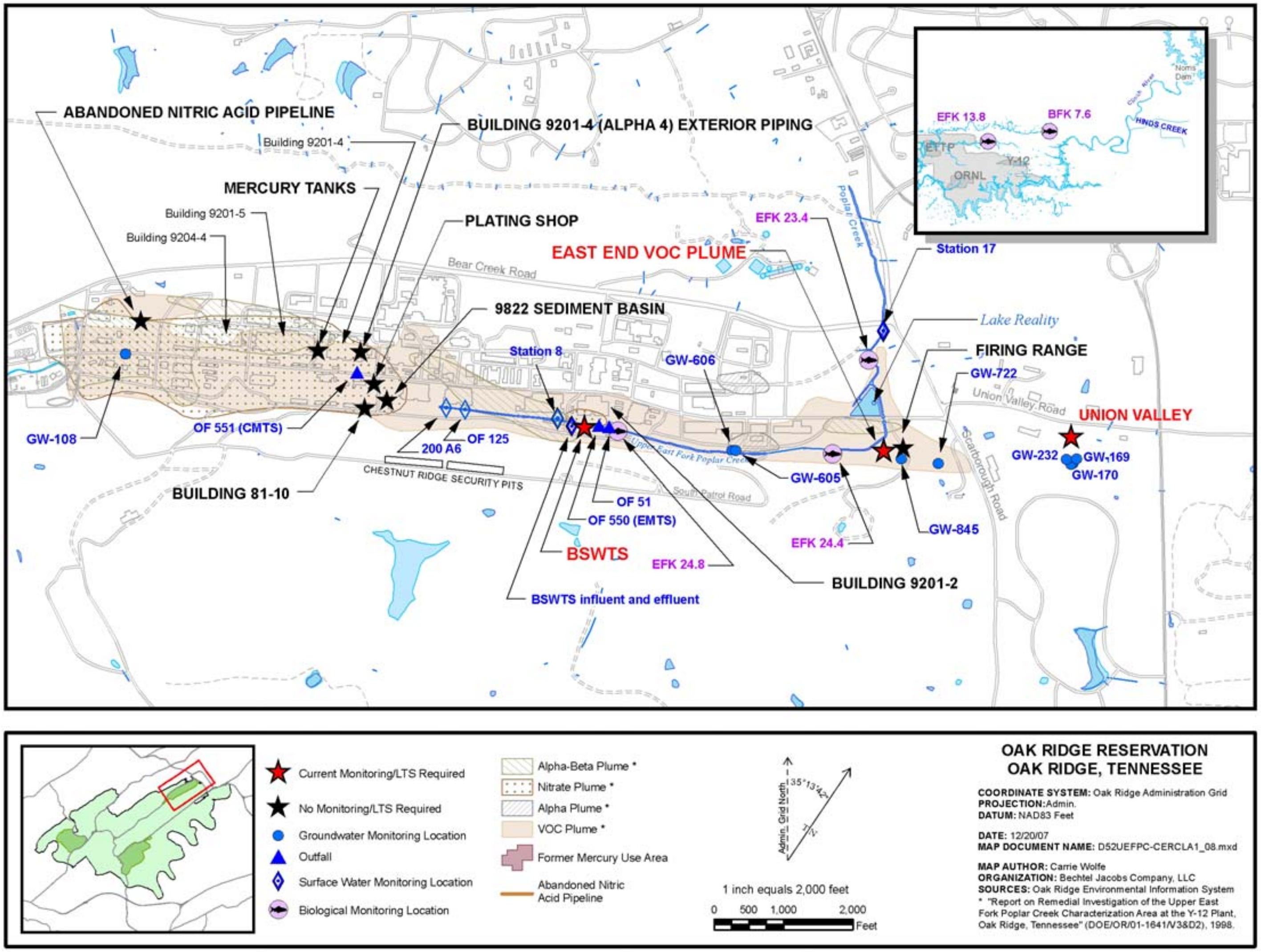


**Figure 1. Map showing the location of the EFPC and infrastructure in the Y-12 complex.**

Several significant remedial and engineering solutions were completed under the RMPE.

Lake Reality Bypass – Lake Reality is an engineered retention pond that is located on the east end of UEFPC in Y-12. It was designed to collect and retain spills from Y-12 and to buffer peak stream flow. In 1996, a temporary bypass of the pond was constructed to minimize export of methyl mercury produced in the pond to the downstream reach of the EFPC. This bypass was later made permanent after it was demonstrated that the pond was acting as a source of methyl mercury to the downstream system.

Treatment of Outfall 51 Discharge – Outfall 51 drains a large spring adjacent to Building 9201-2 that discharges into the Upper East Fork Poplar Creek. Water flows from the spring through Outfall 51, a culvert that empties into UEFPC. Since 2005, the water from the spring and the sumps in Building 9201-2 has been collected and treated.

Treatment at N/S pipes – The headwaters of the UEFPC arise at the N-S drainage pipe in Y-12 where water from the pipe discharges into an open channel. The flow in the N/S pipe is composed of water pumped from building sumps, storm drains, natural springs, and treated water from one or more of the west end treatment works. Approximately 6 m downstream from this discharge source, water from the Clinch River is added to maintain a NPDES required base flow.

**Ongoing Remediation and Research Efforts**

In addition to the implementation of new EM-22-funded engineering and technology initiatives at Y-12, an effective path forward for addressing mercury remediation and abatement in East Fork Poplar Creek (EFPC) will continue to be dependent on contributions from ongoing monitoring programs and research activities. The Y-12 Complex's Biological Monitoring and Abatement Program (BMAP), which is conducted by staff from Oak Ridge National Laboratory, has provided a critical long-term measure of change in fish mercury concentrations in EFPC (1985-2008). The evaluation of changes in fish mercury concentrations over time provided by BMAP have been particularly important in assessing the success of ongoing remediation and abatement efforts. Monitoring of mercury concentrations in water is also critical to understanding mercury processes in EFPC. Mercury concentrations in EFPC are routinely measured by both B&W Y-12's Environmental Safety and Health Organization and Bechtel Jacobs Water Resources Restoration Program (BJC's WRRP). B&W Y-12's routine monitoring is guided by the Tennessee Department of Environment and Conservation's Clean Water Act NPDES permit requirements, while BJC's requirements are dictated by CERCLA Record of Decision-based performance measures.

As needed to address specific issues and to implement effective decision-making, both the Y-12 facility and the CERCLA contractors have conducted special investigations deemed important to understanding the mercury problem in EFPC. Most recently, a jointly-performed synoptic survey of mercury in various EFPC media was conducted in an effort to evaluate recent mercury flux. These findings are particularly important to DOE and their contractors, as the State of Tennessee is planning to issue a mercury Total Maximum Daily Load (TMDL) for EFPC, which could impact Y-12's regulatory requirements as well as BJC clean-up decisions. It's important for DOE and regulators alike that there is good understanding of the current mercury situation in EFPC and that future actions are effectively targeted.

The ORNL Science Focus Area under the Office of Science's Environmental Remediation Sciences Division (ERSD) has a strong focus with regard to biogeochemical transformation of mercury at the shallow groundwater and surface water interfaces. The program targets the fundamental mechanisms by which inorganic Hg is transformed into methylmercury (MeHg) in stream ecosystems and, particularly, the processes that control the formation of MeHg production to bridge the gap between field observation and process-based understanding. This research program focuses on the following primary objectives:

- Elucidate the rates, mechanisms and controls of abiotic and microbial processes affecting Hg speciation and transformation, and resolve how and what critical Hg precursors are produced, transported and subsequently methylated in the ecosystem, and

- Develop and validate models to understand in detail the biochemical and biophysical mechanisms of transformation between major Hg species and MeHg.

Currently, a few strains of sulfur reducing bacteria that may produce MeHg are being investigated. In the next five years, the program will focus on fundamental mechanistic investigations with regard to rate and transformations, specifically, to assess roles of geochemical conditions and speciations on net methyl mercury production. Hg speciation and transformation in relation to redox reactions of aqueous species (e.g., Fe, dissolved oxygen (DO), DOM, S) and solution pH, Eh, ionic strength and composition will be evaluated. Rates of microbial methylation influenced by available Hg species will be studied. The role of specific moieties of NOM (e.g., semiquinones) in abiotic Hg methylation and demethylation will be elucidated, and the role of reduced thiols and carboxyls in the NOM in the formation of complexes and stabilization of solid-phase Hg species (e.g., HgS) will be investigated to understand the availability of Hg for biological methylation. Sulfur reducing bacteria are the dominant microbes responsible for Hg methylation, but other groups of microbes that contribute directly or indirectly to net MeHg production [e.g., by generating Fe(II)] will be studied. Fundamental insights will be gained by studying the structural changes induced by $Hg^{2+}$ and methyl mercury and the functional relationships of the *mer* operons in demethylation and *mer* operon signaling to DNA via RNA. Chemical and photochemical redox transformation of Hg is also underway to resolve surface catalyzed reactions by particulates and surface adsorbed species [e.g., reduced Fe(II) and DOM] of both abiotic and biological origin. Both conceptual and numerical models will be used at appropriate scales to interpret reaction mechanisms. Measurement of actual rates of MeHg production and demethylation in microcosms will confirm these observations with data from contaminated and reference sites. The results of the research will be communicated to DOE ORO site managers and problem holders.

A comprehensive mercury strategy for EFPC will require multiple programs and components. Although each of the above programs have slightly different goals and objectives, aligned together they are most likely to be effective in achieving mercury reductions in fish. Continued source reduction and characterization activities are needed as part of the CERCLA baseline activities (BJC). Monitoring is needed to evaluate the success/failure of actions relative to CWA and TMDL requirements (Y-12/BMAP). The Office of Science research will be used to better understand mechanisms of mercury methylation and bioaccumulation (for more effective decision making). Finally, new strategies, tools, and technologies need to be vetted in addition to the planned CERCLA actions to be successful (EM-22).

## 3.0 Technical Assessment

### Description of the Problem

The technical assistance panel used structured stepwise process to evaluate the issue of mercury at Y-12. First, a consensus was developed on key assumptions and the relevant background scientific and technical information. Then, a site-specific conceptual model of the Oak Ridge site was formulated – this model defined a series of key settings in the Oak Ridge ecosystem, and then identified both uncertainties and opportunities for those settings. This evaluation and matching process proved to be a powerful tool to focus the team and led to specific recommendations.

### Technical Evaluation Process

The technical working group evaluated the site using the following structured stepwise process in their evaluation: 1) developing key assumptions that would guide the effort, 2) developing consensus on important points and developing clear working hypotheses based on both a general and site specific conceptual model, 3) developing science and technology targets, 4) delineating logical subdomains, based on site specific conditions, uncertainties or opportunities, and 5) assessing the scientific needs and environmental opportunities for each subdomain. This structured process encouraged development of creative and diverse ideas and recommendations. Further, the process matched the technology solutions to the most promising subdomain to encourage efficient and effective implementation of the recommendations. In developing the recommendations for the environmental opportunities for each subdomain, the technical working group specifically highlighted those projects that are relatively inexpensive, that have a relatively low health and safety risk, and that may provide a significant benefit as "quick wins" for consideration by Oak Ridge management, technical staff, regulators, and stakeholders.

### Key Assumptions

As described above, Oak Ridge has performed numerous and diverse activities to reduce the efflux of mercury into its surrounding environment. These efforts include process modifications, removal (excavation) and physical isolation (e.g., "bank stabilization") of contaminated soil and sediment, water treatment, lining or replacement of mercury contaminated underground lines ("clean water through clean pipes"), flow management, pond replacement and bypass, facility decommissioning, and other activities. The impacts of these remedial actions on the concentration of mercury in local streams has been carefully measured and monitored.

In the Upper East Fork Poplar Creek in Y-12 near the effluent discharge location, early actions taken to reduce mercury releases resulted in a clear concomitant reduction of mercury in both the water and fish tissue (Figure 2, a). Between the 1980s and 2005, for example, total mercury concentrations in water in the uppermost reaches of this stream decreased from ≅1 ug/L (≅1000 ng/L) to ≅0.5 ug/L (≅500 ng/L) and concentrations in the fish tissue decreased from ≅2 ug/g to ≅0.6 ug/g. This trend was significant because it demonstrated clear progress toward reducing mercury concentrations in fish tissue that would be protective of humans consuming the fish (i.e., guidelines for fish tissue concentrations have ranged from about 1 ug/g to 0.3 ug/g during this time period). At sampling locations further from facility discharges (Figure 2, b), a more complex pattern has been documented – total mercury concentrations in the water decreased as a result of remedial actions (from ≅1 ug/L (≅1000 ng/L) to ≅0.4 ug/L (≅400 ng/L)), but concentrations in the fish remained relatively stable (≅0.8 ug/g). Follow up research has documented the importance of mercury speciation to the observed concentrations in fish tissue. Fish tissue concentration is related to methyl mercury (rather than total mercury) and differences in the trends in time and space are ultimately explained in terms of complex, inter-related and interacting transport and transformation processes.

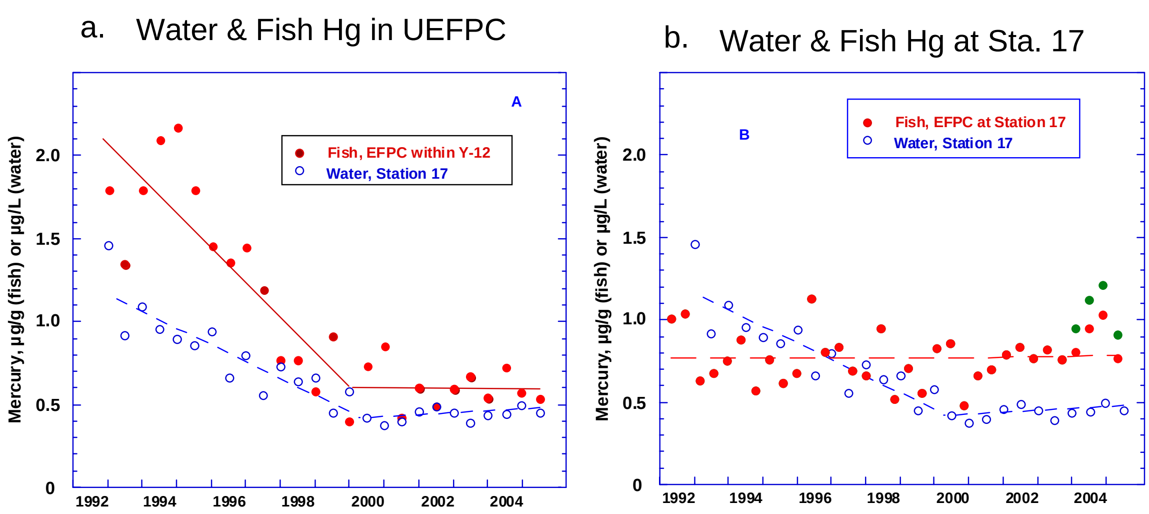


**Figure 2. Trends in water and fish concentrations in (a) the upper portion of East Fork Poplar Creek and (b) at a more distant sampling location.**

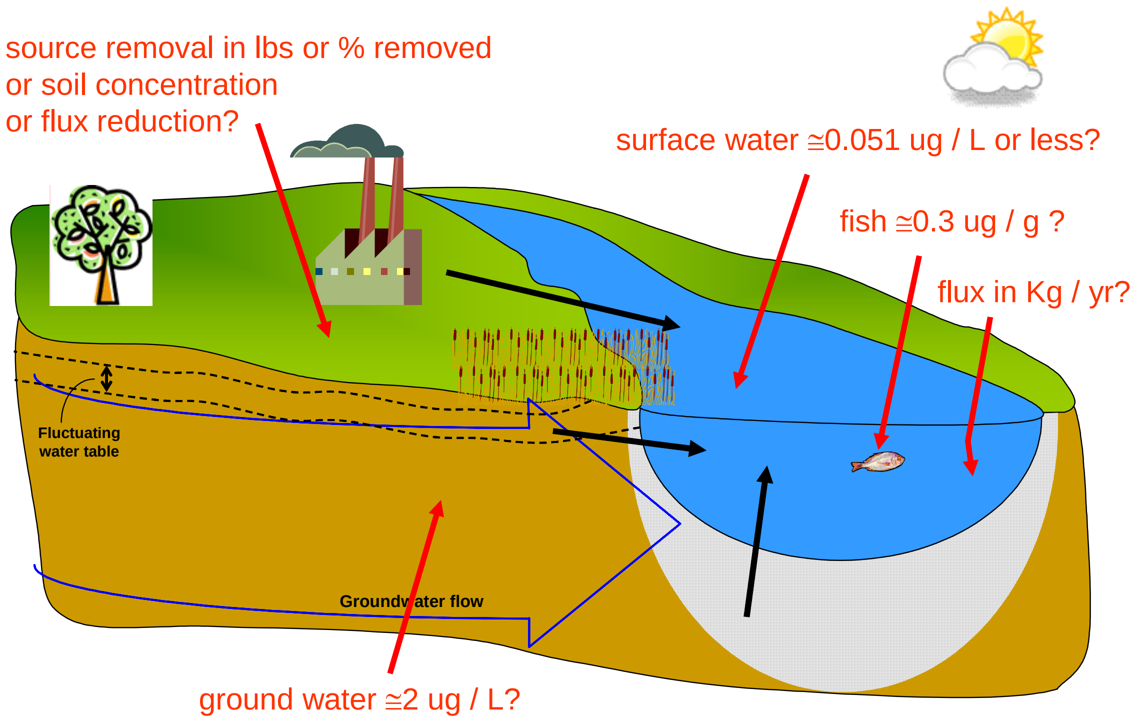


**Figure 3. Examples of divergent metrics applied to environmental remediation activities for soil, sediment, groundwater and surface water**

An important factor that challenges institutional consistency in the remediation and management of mercury at Oak Ridge is the fact that different regulatory protection and cleanup programs utilize widely divergent metrics of success. For CERCLA (Comprehensive Environmental Resources Compensation and Liability Act) and similar decontamination and decommissioning actions, the target metric is often mass or volume removed, residual soil concentration, or flux leaving the source. For surface water, several target metrics are viable including total mercury concentration (e.g., ug/L), total mercury load (e.g., Kg/yr), fish tissue concentration (e.g., ug/g), or some other parameter (e.g., methyl mercury concentration). NPDES (National Pollutant Discharge System) rules for surface water tend to be set in terms of total contaminant concentration or toxicity while related TMDL (Total Daily Maximum Load) limits are expressed in terms of either total concentration or total load (often based on meeting a critical objective such as fish tissue). These divergent approaches are depicted in Figure 3. Developing an improved understanding of the processes that link the various compartments to each other (soil → shallow groundwater → surface water → fish) is a key step in developing a more consistent and comprehensive environmental strategy for mercury.

National data suggest a clear trend toward the use of fish tissue concentration as the ultimate basis for setting standards. Further, many watersheds throughout the country are considered impaired due to mercury and the data suggest that achieving fish tissue target levels of 0.3 ug/g is challenging in many environments. In the case of the Oak Ridge

Reservation, where large amounts of mercury have been handled through the years, these ecosystem targets will be even more challenging. Nonetheless, a consensus assessment and assumption of the technical assistance team was that developing a consistent site-wide basis for assessing the effectiveness of remedial actions is an important step in making progress. This basis should be developed in collaboration with state and federal regulators with clear agreement on the ultimate objectives of the remediation activities and the primary metric(s). If, as we assumed, controlling fish tissue concentrations is the ultimate metric of success, the linkage of the proposed actions to the expected magnitude and time-frame of beneficial reduction in fish tissue concentration would be a factor in selecting among remedial options. The team further noted that this type of an approach would encourage creative and diverse ideas that can be combined to yield cost effective progress. Even if these actions do not achieve 0.3 ug/g in a short period of time, they could demonstrably reduce fish tissue to levels that are "as low as reasonably achievable."

> Key point:
>
> Activities that reduce the fraction of mercury converted to methyl mercury within stream water and stream sediment, or actions that alter stream food chain dynamics are potentially important to addressing mercury at Oak Ridge. These activities may have as much, or more, impact on reducing mercury in fish tissue as reductions in the releases of total mercury or reduction of streambed/floodplain inventories of mercury

In summary, the technical assistance team used several key assumptions during the technical deliberations: 1) fish tissue concentration is the limiting, most conservative, ecosystem protection endpoint because of the high degree of food-chain bioconcentration and biomagnification of methyl mercury species, 2) trends in regulatory standards indicate an increasingly emphasis on fish tissue concentrations as the nominal endpoint, and 3) a variety of activities are potentially viable to mitigate Oak Ridge mercury contamination on the surrounding environment. As a result of these assumptions, the technical assistance team deliberations were predicated on a two-pronged philosophy in which mercury remediation actions are needed to both reduce mercury releases and to disrupt the linkage between mercury releases and fish uptake.

**Conceptual Model of Mercury -- General**

Several watersheds have received mercury discharges from Oak Ridge operations over the years. One of the most important, East Fork Poplar Creek, has been studied and has been the target of a range of remedial activities. Data from this watershed were the primary basis for the technical assistance team discussions, evaluations and recommendations. Since East Fork Poplar Creek is generally similar to the other areas of Oak Ridge, many of the recommendations would be applicable to those areas as well.

A relatively complete descriptive conceptual model for mercury is presented in Appendix C. This conceptual model is based on a substantial body of scientific literature and based on data from geographically diverse sites (including data from the DOE Oak Ridge Reservation, other watersheds in region, the Everglades in Florida, the European Union, Canada, and many others). The technical assistance team believes that the existing research forms an intellectual foundation for future efforts at Oak Ridge and that the recommended applied science and environmental management activities build on that foundation. Key features of the conceptual model are depicted in Figure 4. The right side of this model is the traditional graphic presented in the mercury literature and it shows the complex transformations of mercury in surface water and bottom sediments,. To adequately depict the relevant Oak Ridge scenario, the left side of the figure was added depicting the source, the soil (vadose zone), and the shallow groundwater.

Figure 4 has important ramifications – it suggest challenges exist for understanding mercury dynamics in all of the identified compartments and in developing technically based linkages between actions in one compartment (e.g., soil excavation) and impacts in another compartment (e.g., methyl mercury and fish tissue concentration in surface water).

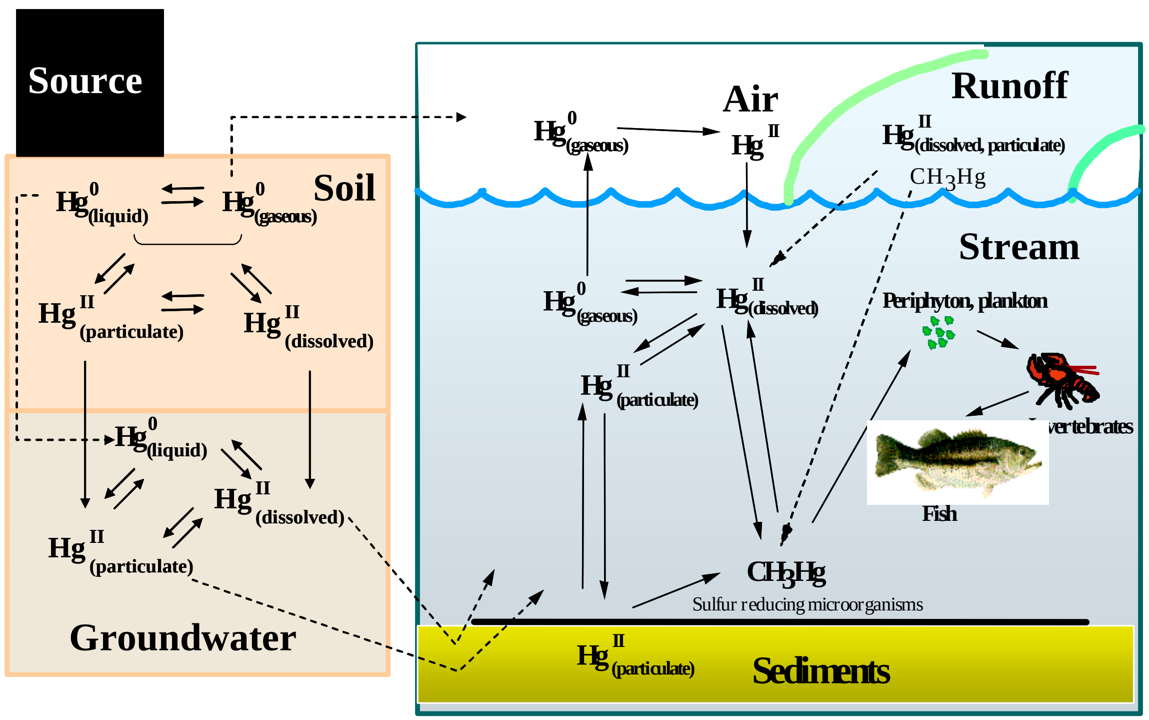


**Figure 4. Block diagram showing some of the key mercury transformations in different compartments of the environment**

As noted above, a relatively detailed conceptual model for mercury is provided in Appendix C; relevant highlights of that text include:

- Speciation of mercury in the environment is governed by geochemistry and microbial activity.
- Mercury occurs in three oxidation states, elemental (Hg0), mercurous (HgI) and mercuric (HgII). In groundwater, the most mobile form of mercury are dissolved neutral complexes of HgII (such as HgCl20). In surface water, uptake in fish is associated with organic forms of mercury such as methylmercury.
- Mercury in sediment is generally found in association with organic matter, sulphide or both (or sometimes as elemental "beads" or amalgams).

- In many aquatic systems biotic methylation appears to produce almost all the methylmercury and sulphate-reducing bacteria (SRBs) are often mediators of the methylation process.
- Degradation (demethylation) of methylmercury is also controlled by microbial processes but photodegradation is also important within the photic zones of aquatic systems
- The production (and degradation) of methylmercury depends on such factors as the availability of Hg (II), oxygen concentration, pH, redox potential, presence of sulphate and sulphide, salinity, sunlight, and the nature and presence of organic carbon and other organic and inorganic agents.
- The predominant form of mercury in fish is methylmercury (MeHg) and is most often derived from microbial processes in the environment that convert inorganic mercury forms to methylated forms that are accumulated and "magnified" within food chains leading to fish and other organisms that consume fish.
- The discharge of inorganic mercury to water bodies as a cause of fish contamination with methylmercury was first recognized in the late 1960s and efforts to reduce loading, at least from point sources, began in the early 1970s. Thus, there are now numerous sites around the world where long-term monitoring data is documenting the recovery of Hg-contaminated fisheries. A common temporal trend observed at sites where point source loading was initially high (e.g., kg/day) and then sharply reduced or eliminated is a rapid decline in mercury in fish in the receiving water bodies
- Mercury in fish at many river and lake sites that experienced early high Hg loadings have not fully recovered even after more than 30 years (e.g., South River in Virginia, Onondaga Lake in New York). The reasons for failure of fish to fully recover vary somewhat from site to site but typically include: 1) continued residual loading from the point source(s) and 2) accumulation of mercury within the receiving water body and/or riparian terrestrial system that is continuing to feed mercury back to the water column and biota for long periods after the original source of contamination is curtailed.
- One novel hypothesis concerning recovery of Hg-contaminated implicates mercury-resistant bacteria in suppressing production and persistence of methylmercury where water concentrations of inorganic mercury are sufficiently high to stimulate and maintain resistance mechanisms in indigenous bacteria. These mechanisms include MerA-mediated reduction of mercuric ion and MerB-mediated demethylation and can significantly affect the amount of methylmercury that is available for entry into the aquatic foodweb. According to this hypothesis successful efforts to reduce loading of inorganic mercury may ultimately deactivate these mechanisms and cause unexpected spatial and temporal trends in mercury in fish. For example, fish mercury concentrations may increase downstream from a point source even as total mercury is decreasing over the same distance.

**Conceptual Model of Mercury in the East Fork Poplar Creek**

The technical assistance team considered the general conceptual model with a focus on the issues of the East Fork Poplar Creek in Oak Ridge. This section outlines the scientific hypotheses that are, or will need to be, tested to explain the spatial and temporal patterns in mercury in EFPC water and fish. The hypotheses are mainly limited to those related to mercury and methylmercury in creek water but it is understood that identifying the correct explanations for these will lead to an explanation for methylmercury in prey species, fish and aquatic wildlife. The hypotheses are not mutually exclusive, i.e., more than one mechanism or process may explain the distribution and behavior of mercury in the EFPC. The list is not final as new data from the EFPC or findings elsewhere may suggest additional hypotheses and indicate key areas where the multiple hypotheses should evolve.

The hypotheses listed are presently restricted to possible explanations for the observed dissolved phases of total and methyl Hg in the creek. This is not to imply that particulate phases are unimportant or will not be included in further hypothesis formulation and testing. Dissolved phases are undoubtedly in equilibrium, or quasi-equilibrium, with particulate phases so that hypotheses posed for one phase can provide insight into the other phase. Dissolved phases are inherently the more reactive and bioavailable than particulate phases and thus deserve primary attention.

| WORKING HYPOTHESIS TO EXPLAIN DISSOLVED Hg IN EFPC |
|---|
| 1) Plant site is a significant point source<br>a. Surface water effluents<br>b. Shallow groundwater inputs |
| 2) Sediments within plant site are point source(s). Hg-contaminated sediment, including possibly free elemental Hg, is present in sufficient quantities and in “soluble” enough form(s) to account for the observed increase in dissolved mercury downstream of the plant site. |

| |
|---|
| 3) Shallow groundwater and/or tributary inputs downstream of plant site are significant source(s)<br>a. Point sources (springs, tributaries, STPs)<br>b. Area sources (seepage through stream bed) |

| |
|---|
| 4) In-stream bed sediments downstream of plant site are significant source(s)<br>c. Historic deposits<br>d. Ephemeral deposits |

| |
|---|
| 5) Floodplain soils are significant source(s)<br>a. In situ leaching (e.g., alluvial GW, see 3b)<br>b. Bank erosion (see 4b) |

| |
|---|
| 6) Atmospheric inputs are a significant source<br>a. Historic (watershed soils, see 3b and 5a)<br>b. Current direct deposition |

| WORKING HYPOTHESIS TO EXPLAIN <u>METHYL Hg</u> IN EFPC |
|---|
| 1) Ex situ generation and input<br>a. Floodplain including riparian wetlands<br>b. Effluents (STPs, urban runoff, alluvial GW inputs) |
| 2) In situ generation<br>a. Within bed sediments w/o periphyton/biofilm<br>b. Within periphyton/biofilm mats<br>c. Within water column |
| 3) Spatial (longitudinal) trends in methyl Hg concentrations in water and fish are being regulated by the activities of Hg-resistant bacteria that reduce net methylation rates.<br>i. Lower than expected in UEFPC based on total Hg<br>ii. Higher in LEFPC because resistance mechanism is attenuated by lower total Hg |

These working hypotheses were converted into a graphical representation (Figure 5) to help organize the follow-on deliberations. This graphic is a more site specific representation of the earlier block diagram in which key local features (history, scale, heterogeneities, engineered features, etc.) are captured and highlighted. This figure captures technical issues (such as controlling biogeochemical processes) and also lists potential targets/opportunities for technology to improve environmental management of mercury at this site.

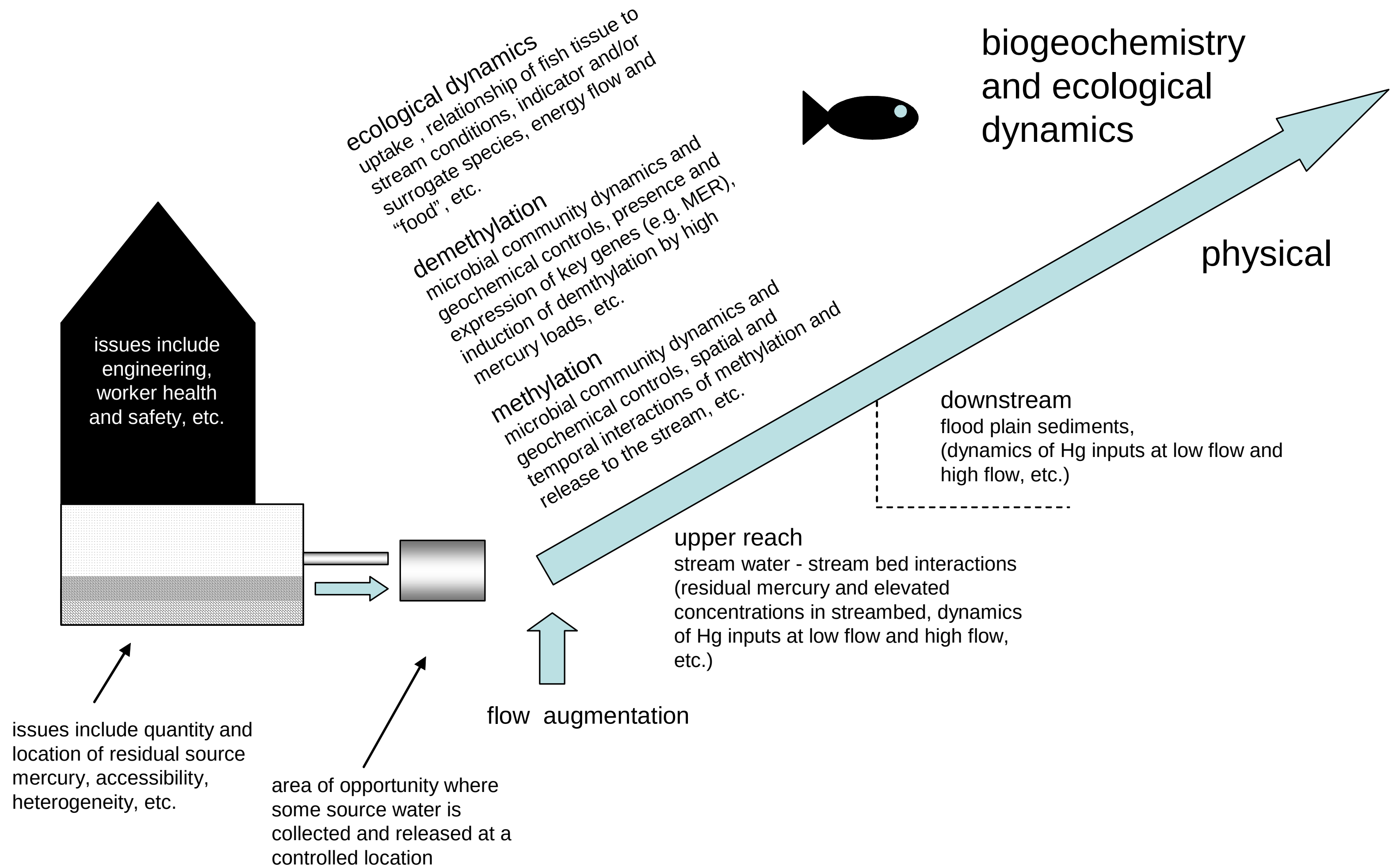


**Figure 5. Summary depiction of site specific mercury conditions In the East Fork Poplar Creek watershed, Oak Ridge**

**Technical Evaluation Results – Basic Science and Technology**

The table of multiple working hypotheses above leads directly to the target areas that require additional basic and applied research efforts. The technical working group supports investment in this portfolio by the DOE Office of Science (through the Science Focus Areas and related funding mechanisms). The hypotheses were organized into the following summary topic areas:

- Demethylation and methylation processes and rates
- Ecosystem dynamics
- Stream and sediment hydrodynamics
- Relating mercury source areas actions to stream impacts (this is the long term goal and includes modeling of release processes, subsurface speciation and transport, hydrodynamics, stream transformations, and food chain uptake)

**Technical Evaluation Results – Applied Science and Engineering**

Examination of Figure 6 suggests that the overall issues of mercury in the East Fork Poplar Creek watershed can be logically organized into four zones, or subdomains. The subdomains identified during the review were:

I. Buildings / Rubble
II. Source Zone Soil
III. Outfall 200 Area
IV. Upper and Lower Reaches of Creek

The subdomains were defined based on having one or more key characteristics that relate directly to scientific challenges or environmental management opportunities. In general, similar mercury transformation and transport processes occur within each subdomain. In some cases a subdomain is also based on a unique physical location and access (e.g., III). These subdomains were used in the last phase of the evaluation to develop highly targeted and specific recommendations specific to Oak Ridge. Each subdomain was assigned to one or more technical working group participants who evaluated uncertainties and opportunities. The evaluation was documented in an excel spreadsheet that describes the proposed technology/strategy, the objective, advantages, disadvantages and other information, including a summary statement. The workshop participants were also requested to highlight potential “Quick Wins.” Quick Wins are selected as viable projects that are relatively inexpensive, that have a relatively low health and safety risk, that can be implemented in a relatively short timeframe (< 1 year), and that may provide a significant benefit. All of the contributions were discussed in detail and vetted by the entire team. Thus, the results of this triage process represent consensus of the group.

Following the figure, the results for each of the subdomains are provided in turn.

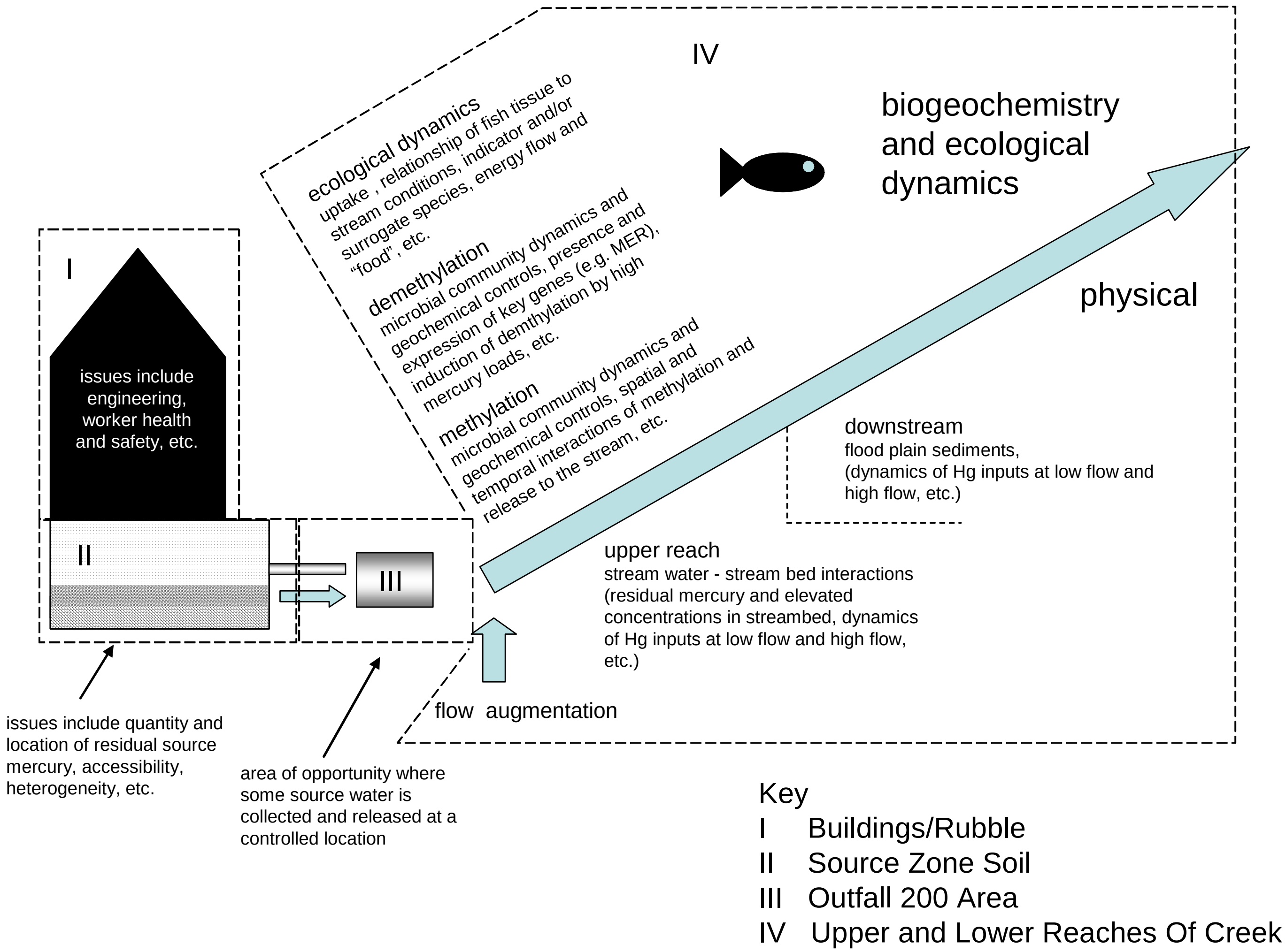


**Figure 6. Subdomains identified to assist in evaluation of mercury in the East Fork Poplar Creek watershed, Oak Ridge**

**SUBDOMAIN I – BUILDINGS / RUBBLE**

Efforts in this zone generally fall within the category of facility decontamination and decommissioning. An overarching conclusion of the panel is that, with adequate funding, this type of effort is relatively straightforward and that technologies, infrastructure, and a skilled workforce exists to support the work. The two broad classes of action that are applicable in this zone are: 1) to decommission the materials in a safe manner for disposal or processing (e.g., thermal) at an approved location either on-site or offsite, or 2) immobilize or encapsulate the contaminated material. Table 1 is a summary of the team deliberations. Work in Zone I will benefit from ongoing applied research and technology development related to on-site chemical analysis and screening of debris, and the potential to segregate wastes and reduce the volume of waste requiring disposal or processing. The technical working group noted that these technical improvements have the potential for significant cost savings and the potential to reduce short term risks (e.g., to workers). However, the linkage of Zone I technology improvements to the environmental endpoint of bioavailable mercury and fish tissue concentration in zone IV is weak – it is unlikely that such technology targets would substantively contribute to advancing Oak Ridge toward the broader goal of mitigating impacts to the receiving stream ecosystem in the vicinity of the plant in the near term or medium term time-frame. The workshop participants support technology developments in Zone I, but the priority of these developments was viewed as lower that the priorities in some of the later zones. DOE programs such as the Small Business Innovative Research (SBIR) program may be a promising avenue to support the necessary technology development in this subdomain. There were no potential Quick Wins identified in Subdomain I.

**SUBDOMAIN II – SOURCE ZONE SOIL**

As above, efforts in this zone are also associated with facility decontamination and decommissioning. The array of technologies for the source soil is more varied than the technologies for building and rubble. These technologies involve bulk removal (large scale excavation and hot spot excavation), thermal treatment (removal), sequestration (thermal-chemical immobilization), physical mobilization or extraction, in situ vitrification, grouting, capping / water diversion, sequestration (chemical reagents), and chemical mobilization / extraction. As noted in the summary information provided in Table 2, several of these technologies were identified as viable and several as not viable. The viable technologies were generally recommended only if certain conditions are present at the site. As in Zone I, technology improvements in support technologies such as field screening and onsite analysis tools, including instruments such as the membrane interface probe, were identified as viable and desirable.

The technical working group noted that these technical improvements have the potential for significant cost savings and the potential to reduce short term risks (e.g., to workers). However, the linkage of Zone II technology improvements to the environmental endpoint of bioavailable mercury and fish tissue concentration in zone IV is weak – it is unlikely that such technology targets would substantively contribute to advancing Oak Ridge toward the broader goal of mitigating impacts to the receiving stream ecosystem in the vicinity of the plant in the near term or medium term time-frame. The workshop participants support technology developments in Zone II, but the priority for these activities was viewed as lower that the priorities in some of the later zones. As above

SBIR is a potential source of technology development.  There were no potential Quick Wins identified in Subdomain II.

**Table 1.**

**Subdomain I -- Buildings and Rubble**

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Removal and Offsite Disposal** | Physically remove buildings and rubble The resulting solids are handled and sent for offsite disposal or treatment at an appropriate facility. Waste segregation and reduction (e.g., by field screening) may be possible. | Reduction of mercury and reduction of the associated mercury release and timeframe. | Baseline technology. | High cost -- large scale operation has significant worker health and safety issues/requirements. There is a potential for mobilizing mercury or for fugitive emissions as building materials are broken up and handled. If buildings and slabs are removed (or if water is used for dust control, mercury may be mobilized and released from underlying soils). Removal of the mercury inventory from buildings/scrap may not result in a reduction of mercury in the creek or in fish tissue. | Mature | If applied on a large scale, a minimal program of research would help mitigate identified negatives. Significant engineering, planning and implementation costs. | Viable |
| **Onsite Treatment Or Encapsulation** | Remove mercury from building materials or rubble (vacuum processes or thermal treatment), stabilize mercury (sulfur compounds or other stabilizing compounds), or encapsulate rubble or building materials (polymers, grouts etc.). | Removal or isolation of mercury based on specific characteristics of the wastes. | If applied strategically and tactically, these technologies may provide a useful adjunct to removal and disposal. | Will require research on effectiveness for each application scenario. In many cases, the research might not result in a deployable technology. Removal of the mercury inventory from buildings/scrap may not result in a reduction of mercury in the creek or in fish tissue. | Generally immature | Significant | Needs to be examined on a case by case basis. |
| **Field analysis and screening tools for rubble and wastes** | Instrumentation to screen wastes and rubble -- primarily for waste segregation. | Support waste segregations so that the amount of wastes requiring disposal is reduced. | If applied strategically and tactically, these technologies may provide a significant cost savings. | Will require research on performance and regulatory acceptability. Reducing the amount of mercury contaminated buildings/scrap for processing and disposal will not result in a reduction of mercury in the creek or in fish tissue. | Variable maturity | Moderate | Potentially viable and recommended if implementation can be performed cost effectively and regulatory acceptance is obtained. |

**Table 2.**

**Subdomain II -- Source Zone Soil and Shallow Subsurface Contamination**

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Excavation (large scale)** | Physically remove all forms of mercury throughout a large area along with the bulk soil matrix using excavating equipment. The resulting solids are handled and sent for offsite disposal or treatment at an appropriate facility. Waste segregation and reduction (e.g., by handling clean overburden) may be possible but segregation using size separation (successfully applied for some metals) is unlikely for mercury. | Reduction of mercury inventory in the upper sediment zone and reduction of the associated mercury release and timeframe. | Baseline technology. | High cost -- large scale operation has significant worker health and safety issues/requirements. Requires complete access to the overlying ground surface. Destroys subsurface infrastructure and generates a large quantity of secondary waste. Requires large quantities of clean backfill. There is a potential for mobilizing mercury or for fugitive emissions as soil is disturbed and handled. Removal of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Mature | If applied on a large scale, minimal research needs, but significant engineering, planning and implementation costs. | Viable but not recommended -- Due to the identified negatives, the panel does not recommend large scale excavation. |
| **Excavation (hot spot)** | Physically remove all forms of mercury in targeted "hot spots" (along with the bulk soil matrix) using excavating equipment. The resulting solids are handled and sent for offsite disposal or treatment at an appropriate facility. Waste segregation and reduction (e.g., by handling clean overburden) may be possible but segregation using size separation (successfully applied for some metals) is unlikely for mercury. | Reduction of mercury inventory in the upper sediment zone and reduction of the associated mercury release and timeframe. | Baseline technology. | Medium to high cost (depending on scale and quality of supporting data) and potential for significant worker health and safety issues/requirements. Requires complete access to ground surface overlying the target zone. Destroys subsurface infrastructure in the target zone and generates secondary waste. Requires clean backfill. There is a potential for mobilizing mercury or for fugitive emissions as soil is disturbed and handled. Leaves mercury in the unexcavated soils around the hot spots. Removal of mercury inventory in the hot spots may not result in a reduction of mercury in the creek or in fish tissue. | Mature | Additional characterization of the source area to identify and refine the location of residual elemental mercury. Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Viable but not recommended unless additional research identifies a clear target and confirms a linkage of the potential mercury reduction to broader remedial action objectives. |

**Table 2. (continued)**

**Subdomain II -- Source Zone Soil and Shallow Subsurface Contamination**

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Thermal Treatment (vapor extraction)** | Closely spaced heaters raise the temperature of the target zone (>> 250C). Concurrent vapor extraction in heated wells removes the subsurface vapors for mercury collection/treatment. Commercially available as "In Situ Thermal Desorption" or ISTD. | Reduction of mercury inventory using high temperature to volatilize/remove residual source elemental mercury in the upper sediment zone and reduction of the associated mercury release and timeframe. | Removes elemental mercury without excavation. | High cost / uses significant amount of energy. Requires complete access to the overlying ground surface (heater spacing typically less than 3 m). Due to access requirements and temperatures, this technology may damage or destroy many types of subsurface infrastructure (similar to excavation). There is a potential for mobilizing mercury as water is removed and heat is applied or for fugitive emissions from shallow heated soils -- careful control and capture is required. Removal of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Medium -- ISTD has been used at a number of sites for organic contaminants. Mercury application has been studied at the laboratory scale and the results including information for design published in the peer reviewed literature. | Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Viable but not recommended unless 1) additional research identifies a clear target, 2) value engineering shows that technology is competitive with "hot spot" excavation, and 3) research confirms a linkage of the potential mercury reduction to broader remedial action objectives. |
| **Sequestration (heat and sulfur)** | Heat the subsurface and add elemental sulfur to immobilize mercury in geologically stable immobilized forms. This could be applied as a combination technology (e.g., ITSD with sulfur added late in the process). Some conceptual development to apply at lower temperatures have been speculated. | Immobilization of mercury and reduction of the associated mercury release and timeframe. | Stabilizes elemental mercury in target zone without excavation. | Requires significant development with no assurance of deployable technology. Significant cost and schedule risk. All of the logistical negatives of thermal treatment (vapor extraction) are probable. Removal of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Immature / conceptual | Substantial process related research and development would be needed (lab and field and multiple scales). Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Not Viable at this time -- Due to the identified negatives, the panel does not recommend this approach unless there are significant advancements that would reduce the cost and schedule risks and provide for a more certain and robust design. |

## Table 2. (continued)

### Subdomain II -- Source Zone Soil and Shallow Subsurface Contamination

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Physical Mobilization / Extraction** | Use vibration, sonic energy, pressure, and/or other physical energy to mobilize elemental mercury liquid for collection. | Reduction of mercury inventory in the upper sediment zone and reduction of the associated mercury release and timeframe. | Removes elemental mercury without excavation. | Requires significant development with no assurance of deployable technology. Similar technologies (applied to hydrocarbons) increase extraction by several percent but leave large residuals in place. It will be difficult to reliably collect mobilized mercury. Reduction of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Immature / conceptual | Substantial process related research and development would be needed (lab and field and multiple scales). Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Not Viable at this time -- Due to the identified negatives, the panel does not recommend this approach unless there are significant advancements that would reduce the cost and schedule risks and provide for a more certain and robust design. |
| **In Situ Vitrification** | Use plasma torch or joule heating to volatilize and remove mercury and convert the remaining matrix into a stable glass waste form. Offgas is collected for treatment. | Removal of mercury and physical stabilization of matrix to "eliminate" mercury release and timeframe. | Removes elemental mercury and stabilizes residual soils without excavation. | Requires significant development with no assurance of deployable technology. High cost and high energy use. Requires significant access to the target zone and has health and safety issues associated with high temperatures, subsidence, etc. There is a potential for mobilizing mercury as water is removed and heat is applied or for fugitive emissions from shallow heated soils -- careful control and capture is required. Removal of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Immature / conceptual (for this application) | Substantial process related research and development would be needed (lab and field and multiple scales). Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Not Viable at this time -- Due to the identified negatives, the panel does not recommend this approach unless there are significant advancements that would reduce the cost and schedule risks and provide for a more certain and robust design. |

## Table 2. (continued)

### Subdomain II -- Source Zone Soil and Shallow Subsurface Contamination

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Grouting** | Inject grout or gel to encapsulate and/or isolate residual source mercury | Stabilize mercury in target zone and minimize the movement of water through contaminated zone. | Stabilizes mercury residual soils without excavation. | Requires significant subsurface access and past grouting research has had variable success. Deployment in low permeability portions of the site would be difficult. There is a significant potential to displace mercury and release it from the source. Stabilization of mercury inventory in the source zone and reduction of water infiltration may not result in a reduction of mercury in the creek or in fish tissue. | Immature / conceptual | Substantial development would be needed. Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Viable but not recommended unless 1) additional research identifies a clear target, 2) the potential mobilization risks are mitigated, 3) value engineering shows that technology is competitive with "hot spot" excavation, and 4) research confirms a linkage of the potential mercury reduction to broader remedial action objectives. |
| **Capping / Water Diversion** | Install surface caps, surface water drainages, and/or capillary barriers to reduce water migration through contaminated source areas. | Stabilize mercury in target zone by reducing the movement of water through contaminated zone. | Stabilizes soils with residual mercury without excavation. Baseline technology. Implementable with well researched performance monitoring available. | Requires complete access to surface. Not be effective for mercury source below the water table or in areas with fluctuating water table (may have limited applicability to Y-12). Stabilization of mercury inventory in the source zone and reduction of water infiltration may not result in a reduction of mercury in the creek or in fish tissue. | Mature | Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to identify areas where there is sufficient vadose zone with mercury source above the water table). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Viable but not recommended unless additional research identifies a clear vadose mercury source target and confirms a linkage of the potential mercury reduction to broader remedial action objectives. |

**Table 2. (continued)**

**Subdomain II -- Source Zone Soil and Shallow Subsurface Contamination**

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Sequestration (liquid reagents)** | Add chemical reagent solutions to reduce the rate of release from source zone mercury. Examples of potential reagents might include electron donors, inorganic or organic sulfates/sulfites, elemental or mineral solids, phosphates, etc. | Stabilize mercury in target zone by limiting oxidation at the metal interface and formation of sequestering solids/minerals. | Stabilizes soils with residual mercury without excavation. | Requires significant development with no assurance of deployable technology. Requires significant access to the target zone. There is a potential for mobilizing mercury as reagent is flushed through the site. Stabilization of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Immature / conceptual | Substantial process related research and development would be needed (lab and field at multiple scales). Careful study would be needed to assure that the added chemicals would not cause harmful collateral impacts. Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Not Viable at this time -- Due to the identified negatives, the panel does not recommend this approach unless there are significant advancements that would reduce the cost and schedule risks and provide for a more certain and robust design. |
| **Chemical Mobilization / Extraction** | Add chemical reagent solutions (lixiviants) to mobilize and release from source zone mercury. Examples reagent might include electron acceptors, halides, organic solvents, etc. | Extraction of mercury from a target zone and reduction of the associated mercury release and timeframe. | Reduces mercury residual soils without excavation. | Requires significant development with no assurance of deployable technology. Requires significant access to the target zone. Technology works by mobilizing mercury as reagent is flushed through the site and careful control to avoid unintended releases are crucial. Reduction of mercury inventory in the source zone may not result in a reduction of mercury in the creek or in fish tissue. | Immature / conceptual | Substantial process related research and development would be needed (lab and field and multiple scales). Careful study would be needed to assure that the added chemicals would not cause harmful collateral impacts. Additional characterization of the source area to identify and refine the location of residual elemental mercury and information on hydrology and geology (to allow efficient design). Additional studies of the impacts (value) of removal of source inventory in terms of reducing mercury in the creek or in fish tissue. | Not Viable at this time -- Due to the identified negatives, the panel does not recommend this approach unless there are significant advancements that would reduce the cost and schedule risks and provide for a more certain and robust design. |

**Table 2. (continued)**

**Subdomain II -- Source Zone Soil and Shallow Subsurface Contamination**

| Technology / Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | Overall |
|---|---|---|---|---|---|---|---|
| **Field analysis and screening tools for rubble and wastes** | Instrumentation to screen soil -- primarily for targeting removal or treatment (hot-spot) actions and for waste segregation. Example technology is the membrane interface probe (MIP) used with a cone penetrometer or Geoprobe. | Support field efforts so that the amount of removal or treatment is reduced. | If applied strategically and tactically, these technologies may provide a significant cost savings and significantly improve the spatial coverage and quality of characterization information. | Will require research on performance and regulatory acceptability. Will not result in a reduction of mercury in the creek or in fish tissue. | Variable maturity | Moderate | Potentially viable and recommended if implementation can be performed cost effectively and regulatory acceptance is obtained. |

**SUBDOMAIN III – OUTFALL 200 AREA**

Zone 3 (Outfall 200 and point sources of mercury within the karst system and streambed in the reach immediately downstream from that outfall) is the source of most of the base flow mercury loading to EFPC. As a consequence, the uppermost 800 meters of stream after it emerges from the storm drain network can be regarded as a "point" source affecting the remaining watershed downstream. Mercury inputs to surface water in this subdomain are somewhat unique in they are accessible and are comprised primarily of dissolved, highly reactive, bioavailable forms of mercury. This combination of access and chemistry provides several opportunities for alternative strategies to reduce the accumulation of methylmercury in fish throughout the entire stream system. Those strategies are outlined in Table 3 and described in the following sections. Several Quick Win strategies for Subdomain III were identified by the technical working group.

<u>In-situ air stripping</u> {Potential Quick Win}

Most of the flow in the storm drain system above Outfall 200 contains residual chlorine (TRC) 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 Outfall 200 contains reactive dissolved Hg(II). Studies carried out by the Y-12 Reduction of Mercury in Plant Effluent Program (RMPE) demonstrated that after removal of residual chlorine (necessary to eliminate toxicity of the discharge) mercury in this effluent could be converted to volatile Hg(0) by the addition of nearly stoichiometric amounts of stannous chloride. It was hoped that the Hg(0) would be rapidly lost via volatilization in the shallow, well mixed reach of stream below Outfall 200, but photo-oxidants in the water prevented the reduction of mercury in stream water exposed to sunlight. 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.

The main storm drain above Outfall 200 (N/S pipe) provides a second potential opportunity to employ in-situ reduction of Hg(II). In the dark, enclosed system, photo-oxidation would not be a concern. If the dechlorination location was relocated to a point within the N/S pipe well upstream from Outfall 200, a acceptable reductant, such as stannous chloride or ferrous sulfate, could be added at ppb concentrations to convert Hg(II) to Hg(0) at the site of dechlorination. Volatilization of Hg(0) would need to be enhanced by the addition of air from a bubbler line on the bottom of the pipe and forced ventilation of the section of pipe between the dechlorination/reduction site and outfall 200 to remove gaseous mercury. If successful, such an approach might be capable of removing 80 - 90% (~ 5 g/d) of the base flow mercury now exiting Outfall 200. Although the actual mass of Hg vented to the atmosphere as a result of implementing this technology will be relatively small (5 g/d), the mercury could be removed from the air stream using cartridge of sorption media (such as sulfur impregnated activated carbon). In this configuration, the stripping gas could be operated in a loop – gas would be collected from the outfall pipe headspace and treated with sorbent installed in the low pressure inlet to air compressor. The compressor would provide the pressurized air for the sparge line installed in bottom of the outfall pipe.

Positive attributes of this strategy include its technical simplicity and low cost. The system would require reagent storage and dosing equipment combined with a bubbler tube, pressurized air supply, and forced ventilation system. It would generate little or no secondary waste, and the required reagents would be added at trace concentrations and are of low aquatic toxicity. Experimental stannous chloride addition to EFPC previously received regulatory approval. Negative attributes include the addition of chemicals to stream water and the unknown effect on methyl mercury production. The process would be sensitive to residual disinfectants, inhibitors, and oxidants that may degrade the efficiency of the chemical reduction of mercury. If successful, this strategy would only affect Hg in Outfall 200.

The concept using $SnCl_2$ reduction/air stripping to remove Hg from contaminated ground water was developed at ORNL, with pilot plant tests run at the DOE Y12 and Savannah River (SR) facilities. A full scale treatment system is now operating at SR. Before this strategy could be implemented, research would be needed to reconfirm the treatability of the discharge under current wastewater conditions and to engineer reagent delivery, ventilation, and sparging systems. This technology was designated as viable, and conditionally recommended.

<u>Addition of Hg sequestrants at Outfall 200</u> {Potential Quick Win}
As noted above, mercury at Outfall 200 is maintained in a highly reactive, dissolved Hg(II) form that will readily react with potential sequestrants. Numerous possible additives exist, most of which react Hg with a sulfur moeity. Possible additives include organic thiols, inorganic sulfides, selenium or sulfur-containing amino acids. The objective would be to convert inorganic Hg 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 Hg from downstream sources by taking advantage of the natural photo-oxidation/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 Outfall 200. If successful, that could very inexpensively reduce Hg bioaccumulation in the creek. The chemistry of Hg sequestration is well known, and the concept has been utilized in soils. It hasn't been intentionally applied to aerobic surface waters. Sequestrants might also have the potential to reduce dissolved concentrations of other trace metals in EFPC, reducing the possibility that these have sub acute ecological effects. Like air stripping, the effectiveness of sequestration is likely to be limited to Hg coming from Outfall 200, unless a slow-release form is developed. 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 amount that could be added.)

A significant, but not daunting, amount of study would be required prior to implementation, testing the reactivity, kinetics, and environmental persistence/bioavailability of reaction products of various sequestrants. Aqueous sulfide is probably most 'off the shelf' technology. MSE is currently investigating use of cysteine in microcosm studies under DOE funding.

Change to sodium thiosulfate as dechlorinating agent at Outfall 200 {Potential Quick Win}

The Outfall 200 discharge is presently dechlorinated by the addition of a slight excess of ammonium bisulfite to eliminate toxicity associated with residual disinfectant chlorine. Empirical 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 thiosulfate. This action stimulated visible changes in the streambed biofilm, undoubtedly associated with a change in microbial ecology and growth of organisms that utilized thiosulfate. Based on these observations, the panel evaluated a strategy that proposes switching the dechlorinating agent at Outfall 200 to thiosulfate, and adjusting the dosage to promote the microbial degradation of excess thiosulfate in the stream. Microbial degradation of thiosulfate may alter the microbial ecology to disfavor methylating microorganisms, or may generate sulfur-containing chemicals that sequester inorganic Hg and render it less bioavailable. Thiosulfate is commonly used in industrial discharges as a dechlorinating agent, although other chemicals are typically used for treating high volume flows.

Positive aspects of this strategy include its simplicity - merely changing from one dechlorination chemical to another and adjusting the dose rate. Cost would be low compared with many other remedial measures. Thiosulfate is low in toxicity, and implementation would represent a low risk experimental approach. This approach has several negative attributes. Thiosulfate would be more expensive and more cumbersome than the present dechlorinating agent. It has never been intentionally studied as an ecological tool for control of Hg methylation and bioaccumulation; thus, its efficacy is speculative. Altering the composition of the streambed microflora has the potential for adverse ecological and aesthetic effects. If effective, the downstream persistence of the effect is unknown.

This strategy could be safely implemented with little additional research, although the implementation itself would constitute a significant research effort. The ecological monitoring program already in place in EFPC would evaluate whether or not it was effective and ecologically benign. If effective, it would be valuable to have in place a research effort to determine what mechanisms account for the observed reduction in mercury bioaccumulation.

Eliminate or Move Flow Management

As a result of negotiations between DOE and the Tennessee Dept of Environment and Conservation (TDEC), 18,000 $m^3$/d of raw water is added to the flow of UEFPC (flow management) at a site near Outfall 200 to maintain a stable minimum flow. The additional flow dilutes waterborne inorganic mercury but increases overall Hg inputs by enhancing advection of contaminated interstitial water from downstream sediment beds into the surface flow. The streambed Hg source is localized in a short reach of stream 100 meters below Outfall 200 where metallic Hg is deposited on a clay hardpan underlying soft sediments armored by a layer of gravel. Eliminating raw water inputs or moving the discharge point downstream below streambed source area could lower Hg inputs by 2 g/d. The water added by flow management typically contains substantially higher concentrations of suspended solids (TSS) that the Outfall 200 discharge it dilutes, facilitating the conversion of dissolved Outfall 200 Hg to particle-associated forms.

Discontinuing flow management would provide an immediate decrease in Hg loading to EFPC, and would possibly be helpful in complying with load restrictions arising from a TMDL determination. The decreased loading would result in decreased aqueous Hg below the point where flow management was added if it were moved rather than eliminated. Reduced TSS and higher aqueous Hg concentrations would favor uptake of inorganic mercury by photosynthetic organisms in the streambed biofilm, possibly reducing methylmercury production.  Negative aspects of this strategy include a two to three-fold increase in mercury concentration in the upper reaches of EFPC, and loss of the beneficial ecological effects associated with dilution of other solutes and stabilization of in-stream temperatures. This action would only affect a portion of the Hg load to the creek (the Outfall 200 source would not change), and, if flow augmentation was eliminated, would not be expected to reduce methylmercury bioaccumulation. Reduced TSS in the streamflow would alter the transport dynamics of inorganic mercury in the ecosystem. The effects on Hg methylation and bioaccumulation are unknown.

Discontinuation of the flow management system would be easily accomplished, but moving the discharge point downstream would require engineering and construction of a new discharge. Lower TSS would facilitate direct uptake of Hg by diatoms/algae in biofilm, perhaps competing with methylating microorganisms. Research is needed into relative bioavailability of  Hg for methylation  when sorbed by inorganic particulates versus primary producers versus bacteria before the effects of this action on bioaccumulation could be predicted.

Control of Hg mobilization within the shallow karst system

Metallic mercury within the solution cavity network underlying EFPC acts as a continuous source of both Hg(II) and Hg(0) to shallow groundwater flowing through the that network. Most of that flow emerges in a large spring 800 downstream from Outfall 200, but it is possible that streambed seeps also act as discharge points. Introducing material to the subsurface flow system that coats Hg deposits and impedes dissolution could possibly reduce the rate of dissolution of Hg from these deposits.

Positives associated with this action are that it would interdict a difficult source without extensive excavation and expense. Effective implementation of this technology would include development of an improved conceptual model of the karst system which would be difficult and expensive.   In addition, most of the Hg input to EFPC from the karst system is currently captured and treated in the Big Spring Treatment system (BSTS), and therefore this action would have relatively little impact on aqueous mercury concentration or loading. Any unintended consequences of actions affecting solute transport in the karst system would be hard or impossible to rectify. There is no currently available technology for effectively coating metallic mercury in water, therefore this option could not be employed without substantial R&D.

Continue projected CERCLA actions

The current strategy for reducing mercury bioaccumulation in EFPC focuses on reducing inorganic mercury concentrations in water. Future actions include removal of contaminated sediments and soils, cleaning/relining contaminated storm drains, and limiting the infiltration of shallow groundwater through Hg-contaminated soils.

This strategy employs actions that have often effectively reduced Hg inputs in the past. It has also appeared to be successful at reducing Hg bioaccumulation at a single site within the Y-12 facility. It has been approved in the CERCLA regulatory process, and funding for continued efforts is likely.

The largest negative associated with this strategy is that its success is dependent upon inorganic Hg concentration in water being reduced to the point where it limits methylmercury production in EFPC. Reductions in Hg inputs achieved to date have not been successful at achieving this goal throughout most of EFPC. The degree of further reduction in aqueous inorganic mercury needed to achieve acceptable methylmercury concentrations in fish is thus not known, and could be lower than is technically achievable. A potential unintended consequence of reducing shallow groundwater inputs to contaminated storm drains could be an increase in mercury transport if it induces the intrusion of chlorinated process water from storm drains into Hg-contaminated footers/backfill, solubilizing Hg that eventually re-enters the surface flow. There is a very real probability that after all CERCLA actions are completed, that goal will not have been reached.

**Table 3.**

**Subdomain III -- Outfall 200 Area**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| In situ Air Stripping (Volatilization Using Stannous Chloride) | Move dechlorination point to a site within N/S pipe well upstream from Outfall 200. Add stannous chloride to discharge to convert mercury to volatile Hg(0) and provide a mechanism for volatilization, while ventilating the system to remove volatilized Hg in the air. | Reduction of inorganic mercury load from the Y-12 west end mercury sources to the upper reach of East Fork Poplar Creek | Technically simple to implement and low cost. Consists of reagent storage and dosing system combined with a sparger or physical agitation. No secondary aqueous waste. Possible elimination of up to 5 g Hg/d from baseflow. Experimental addition of $SnCl_2$ to EFPC has previously received regulatory approval. | Reduces total mercury load to stream but may not reduce methyl mercury or mercury in fish tissue. Adds trace levels of tin to water. Process is sensitive to disinfectants, inhibitors, and other potential process chemicals that may reduce effectiveness or cause the process to fail. Previous data indicated that sunlight inhibits process so need to be done within the pipe. May not achieve complete treatment. | Concept developed at OR. Lab and pilot tests completed at OR and SR. Full scale system operating for GW at SR. | Reconfirm treatability under current wastewater conditions (for the range of flow and chemical conditions). | Viable and recommended if treatability study is successful, and if reduction in total inorganic mercury load is desired. |
| Addition of Hg sequestrants at Outfall 200 | Hg at Outfall 200 is maintained as a dissolved, highly reactive Hg(II) species that will readily react with potential sequestrant. Possible additives include organic thiols, inorganic sulfides, S-containing amino acids. | Convert Hg to non-bioavailable forms which will not be methylated in downstream reaches of EFPC. | Possibly achieved by just adding sequestrant along with dechlorination chemicals. If successful, could very inexpensively reduce Hg bioaccumulation | Effectiveness likely to be limited to Hg coming from Outfall 200, unless a slow-release form is developed (a.g., encapsulated nanoparticles?) Would require regulatory approval, low AWQC for sulfide would limit amount that could be added. | Chemistry is well known, concept utilized in soils. Hasn't been intentionally applied to aerobic surface waters | Testing reactivity, kinetics, and environmental persistence/bioavailability of reaction products of various sequestrants is needed. Aqueous sulfide is closest 'off the shelf' technology. MSE currently investigating use of cysteine in microcosm studies under DOE funding | Viable, recommended. Has potential for large savings, early attainment of AWQC compliance at Y-12, more problematic downstream |

**Table 3. (continued)**

**Subdomain III -- Outfall 200 Area**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| Change to sodium thiosulfate as a dechlorinating agent. | 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, or may generate sulfur-containing chemicals that sequester inorganic Hg and render it less bioavailable | Simple change in an ongoing process. Low toxicity, empirical evidence suggests that it can reduce mercury bioaccumulation. Relatively low risk experimental approach | More expensive, more cumbersome than the current dechlorinating agent. Has not been intentionally studied as an ecological tool for control of Hg methylation. Possible adverse ecological and aesthetic effects. Downstream persistence of effect unknown. | Thiosulfate is commonly used to dechlorinate small discharges at DOE facilities. | Research into whether it is effective and what mechanisms account for any observed reduction in MeHg bioaccumulation is needed. | Viable, recommended but not preferred option at this time -- additional research is needed. |
| Eliminate/move flow management | Move the discharge point for flow management to a site closer to Station 17 or eliminate it entirely | Reduce the dissolved mercury input from contaminated sediments to surface flow in UEFPC | The addition of 18,000 m3/d of raw water to the flow of UEFPC (flow management) dilutes waterborne inorganic mercury but may increase overall Hg inputs by enhancing advection of interstitial water from downstream sediment beds into the surface flow. Eliminating raw water inputs or moving the discharge points downstream below streambed source areas could lower Hg inputs by 2 g/d. Elimination of TSS inputs associated withy raw water may alter Hg transport dynamics in EFPC, with unknown effects on bioaccumulation. | Flow management has positive ecological effect on stream biota, and dilutes Hg and other solutes. Elimination from UEFPC would raise waterborne Hg concentration. Would only affect a portion of Hg load to the stream. Not likely to dramatically affect Hg bioaccumulation | Readily applicable, movement would require engineering and constructing a new discharge point. | Total elimination would raise waterborne inorganic Hg concentration in UEFPC. Lower TSS would facilitate direct uptake of Hg by diatoms/algae in biofilm, perhaps competing with methylating microorganisms. Research is needed into relative bioavailability of Hg for methylation when sorbed by inorganic particulates vs. primary producers vs. bacteria. | Viable, not recommended unless incremental change in Hg loading is deemed necessary (TMDL). |

**Table 3. (continued)**

**Subdomain III -- Outfall 200 Area**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| Control of Hg mobilization within the shallow karst system (Outfall 51 source control) | Uncaptured fraction of Outfall 51 spring flow contributes reactive, dissolved Hg to EFPC surface flow. Source of the Hg in the spring is upstream, likely metallic Hg in solution cavity network. | Hg in spring is assumed to arise from the dissolution of Hg()) and Hg(II) from deposits of metallic mercury in the solution cavity network. Rate of dissolution and subsequent transport could be reduced by adding material to the subsurface flow system that coats mercury deposits and impedes dissolution. | Would interdict a difficult source without extensive excavation and expense. | Most of this source is presently treated by BSTS, wouldn't remove a big fraction of current loading. Unintended consequences of actions affecting solute transport in karst system could be hard to rectify. Not currently available technology for effectively coating metallic Hg in water. | Very immature | Would require extensive research before application | Not presently viable, needs research, would only affect a fraction of Hg load |
| Continue projected CERCLA actions | Removal of contaminated sediments, cleaning/relining contaminated storm drains, limiting infiltration of rainwater | Further reductions in Hg loading to UEFPC | Already approved in CERCLA process, employs actions that have effectively reduced Hg inputs in the past. Hs had success in reducing Hg bioaccumulation at one site in UEFPC | Success is totally dependent upon inorganic Hg concentration in water being reduced to the point where it limits methylmercury production in EFPC. Reductions in Hg inputs achieved to date have not been successful at achieving this throughout most of EFPC. Reducing groundwater inputs to contaminated storm drains could have unintended effects on mercury transport if it induces the intrusion of chlorinated process water from storm drains into Hg-contaminated footers/backfill. | Mature technologies previously employed at the site, except for actions that limit infiltration, lower shallow water table. | There is a need to define an appropriate 'target' concentration for inorganic Hg concentration in EFPC. Reasonable but optimistic estimates used for setting preliminary cleanup goals were clearly too high. | Viable. These efforts are proceeding towards a goal that may (or may not) be adequate to meet emerging environmental endpoints. Need continued efforts to determine appropriate target concentration. Should proceed along with development/testing of alternative strategies |

SUBDOMAIN IV – UPPER AND LOWER REACHES OF STREAM

Subdomain IV is the most complex and diverse environmental zone in the EFPC system. This subdomain is also the key area where critical mercury transformations occur and in which uptake into the food chain occurs. These characteristics provide both challenges and opportunities. As a result, the technical working group developed the most diverse and voluminous set of possible strategies and identified many significant uncertainties and research needs. In the simplest sense, the goals of all of the strategies developed by the team there fit in to a few broad classes:

1) remove mercury (sediment or soil removal)
2) physically block, stabilize or isolate mercury (bank stabilization, relocate creek channel, stabilize floodplain using plants, reestablish a lake or pond in flow system)
3) non biological actions to reduce mercury uptake (modify physical conditions in stream, selenium amendment, photochemical inhibitors)
4) microbial ecology modifications to reduce mercury transformation, accumulation and uptake (decrease methylation processes or increase demethyhlation processes)
5) innovative fisheries management (remove contaminated fish, stock fish with a lower accumulation potential, add clean food for fish).

These strategies are presented in this order, with summary evaluations, in Table 4. The technical working group coalesced around the position that actions in subdomain IV have a high potential to reduce the mercury in the food chain and that many of the possible actions are potentially cost effective – several were identified as potential Quick Wins. Some of the most promising ideas, however, were those that rely on understanding and manipulating microbial ecology. The technical working group believes that more research is needed to realize the full potential of these concepts and urge funding by the Office of Science and other basic science funding agencies.

<u>Sediment/Soil Removal</u>

This would be a selective "removal" action targeting sediment and/or soil deposits demonstrated empirically to contain mercury in form(s) that are bioavailable. The objective would be to reduce or eliminate releases of bioavailable mercury to the East Fork Poplar Creek. It would require sampling to identify and delineate "reaches" of the creek where mercury is entering, or could enter, the water column in, for example, "dissolved" form where dissolved might be defined as "0.45 micron pore filtering passing", by molecular weight cutoff (e.g., <5000 MWCO) or by some other easily measured form of mercury, including simply methylmercury. One might search for such reaches by close-interval surface or hyporheic water sampling, or by performing a simple aqueous extraction of soils and sediments. Once identified the deposits of soil or sediment would be removed by dredging or mechanical excavation and disposed of by upland land filling. This type of action is neither innovative nor high risk beyond the identification of material for removal. In effect the original ROD for LEFPC required selective removal of floodplain soil where the objective was limited to protection of human health and not reduction of mercury in fish.

<u>Bank Stabilization</u>

If historical deposits of Hg-contaminated soil or sediment were determined to be eroding or subject to erosion within any part of EFPC, and further, to be releasing mercury in bioavailable form(s) to surface water, then it could be effective to prevent further erosion by stabilizing the subject deposits. The objective of this action would be to reduce or eliminate further inputs of bioavailable mercury. For such action to be effective it would first be necessary to determine whether "particle-associated " mercury in these deposits is, or could become, bioavailable when resuspended/redistributed within the creek. Secondly it would be necessary to identify and delineate those banks that are the major contributors to this loading. The stabilization of riverbanks is well-developed technology with much experience/expertise available from other federal agencies such as the U.S. Army Corps of Engineers. This option would require a long-term commitment to monitoring and maintenance of stabilized banks, as well as early demonstration that it was effective in reducing mercury in fish.

Relocate Creek Channel

Creek channel relocation would be a selective action targeting bypass of a specific creek reach containing bioavailable mercury with the objective of reducing the input of inorganic bioavailable mercury or methylmercury to the system. As with a removal action this approach would require sampling to identify and delineate "reaches" of the creek where mercury is entering, or could enter, the water column. Some portions of the channel of East Fork Poplar Creek have already been relocated although not for the purpose described here. Urban development with Oak Ridge has resulted in some channelization and relocation of the creek, for example, near the intersection of Illinois Ave and Oak Ridge Turnpike. Similarly, much of the original UEFPC channel has been altered and/or relocated. Candidate channel sections for selective relocation exist in both upper and lower EFPC if identified to be contributing to the mercury in fish and there is DOE precedent and engineering experience with reconstruction of stream channel on the ORR (e.g., tributaries to Bear Creek and White Oak in Melton Valley).

Stabilize floodplain and stream bank soils using native plants

This option is similar to bank stabilization techniques designed to limit floodplain and stream bank mercury inputs to the stream, but is less obtrusive than conventional earth moving options. The goal of this option is to plant highly rhizomous, native plants along drainage ways and eroded bank areas that are high in mercury. Before this option is attempted, a more in-depth evaluation of the role of riparian and floodplain sources on mercury bioaccumulation is needed. Further, assuming that floodplain mercury is a significant source to downstream waters, a survey of floodplain hotspots would be needed to better target plant restoration efforts. This option offers an additional advantage in that the efforts over the long-term could enhance natural resources. Unlike major earth moving activities which can be problematic to implement on private lands, floodplain stabilization efforts using plants could be encouraged by providing technical advice or plant specimens to watershed organizations or landowners. Increasingly, there are more refined methods for bank stabilization using plants, although plantings are less permanent than structural changes, especially without continued plant management. This option is more viable if conducted in conjunction with other remediation techniques, including bank armoring efforts. Planting alone is unlikely to result in fish reaching mercury concentration targets.

Return Lake Reality and Upper EFPC to 1985 conditions

In the 1980's, mercury concentrations in fish in EFPC displayed a strong correlation with inorganic mercury concentrations. Inorganic mercury concentrations in water and fish decreased with distance downstream of Y-12, with fish in lower EFPC near the current target concentrations in fish of 0.3 mg/kg. If 1980s-like conditions were still present in EFPC, the 90% decrease in inorganic mercury loading since that time may have resulted in a commensurate decrease in fish. To restore environmental factors thought to be most important in driving the 1980s correlation, this option involves restoring of 1980's conditions in Lake Reality, similar to the old New Hope Pond environment, and shutting off flow management and dechlorination activities (which were implemented in the 1990s).

Establishment of a highly vegetated Lake Reality retention basin would increase the effectiveness of the basin as a sediment trap. Based on the historical patterns of mercury bioaccumulation associated with changes in chlorine inputs in EFPC, increasing potable (chlorinated) water inputs could have a positive impact on mercury concentrations, although the relationship is not well understood and more research is needed. Changes to dechlorination would likely render the upper 1 -2 km of EFPC toxic due to residual chlorine inputs. Although shutting off flow management and dechlorination activities would be easy to implement, wholesale changes to flow and chlorine input in EFPC is unlikely to receive regulatory and public approval because of the toxicity issue. Restoring Lake Reality to a system dominated by rooted, submerged aquatic vegetation is a more doable action, but it would take some time to establish these conditions, and the success of this action alone in reducing mercury levels in fish is uncertain. This is another option that could use further research. A small pilot field study would be relatively straightforward to set up in Lake Reality or the bypass channel, where underlying assumptions could be tested.

Modify in stream physical conditions to affect ecology and bioaccumulation
The use of mercury sequestrants and other options associated with changes in water chemistry are highlighted in Zone 3. This option is meant to address potential changes in stream aqueous conditions far downstream of outfall sources of mercury. Primarily through changes in flow management and instream/riparian habitat, key factors affecting mercury methylation and bioaccumulation can be manipulated, including temperature, amount of total suspended solids, sedimentation, amount of sunlight, and algal/vegetation characteristics. These changes can affect the mercury uptake process, and/or can affect the stream's ecology in a beneficial way. For example, warmer stream temperatures and greater suspended particles and nutrient enrichment would favor low mercury species such as bluegill and stonerollers, but limit high mercury species such as rockbass. An advantage of EFPC is that unlike most streams, the aqueous conditions are more controllable by modifying facility inputs and flow management at the stream's headwaters. Bringing in more clean sediment via flow management could also be beneficial, in overlying more contaminated sediments or increasing particle-associated, and less bioavailable, mercury. Proposed actions such as changing flow, stream temperature or TSS may be straightforward; however, the effect of these changes on mercury bioaccumulation is unknown. This option is amenable to controlled scientific

study. This option is unlikely alone to reduce mercury in fish to target levels, but might be a viable option in concert with other source reduction options.

### Selenium Amendment {Potential Quick Win}

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, 2000) that have provided an opportunity to observe the response in tissue concentrations in fish. Early whole lake treatments in Sweden produced troubling results when fish disappeared from some treated lakes due to the toxic effects of this chemical if the dose is not carefully controlled (Parkman and Hultberg 2002). Later whole lake treatments in Sweden at lower doses have apparently been very successful at significantly reducing mercury in fish and biota in the treated lakes (Hultberg 2003; Hultberg 2006). Unfortunately there have been no studies of the application of selenium in stream or river systems although some lake systems with high water renewal rates (<< 1 year) have been treated and studied (Hultberg 2003). Water and biological tissue concentrations that are likely to cause toxicity are fairly well known (Hamilton 2003, 2004) and thus it should be relatively easy to establish a dosing system to stay below toxic concentrations. An application at the DOE Y-12 Plant would be especially amenable for an application because the facility sits astride the headwaters and is already dosing to dechlorinate chlorinated effluents. Application downstream might require development of a sparingly soluble matrix containing selenium that could be scattered in the streambed. The early Swedish work actually employed selenium imbedded in a rubber matrix for the purpose of achieving a prolonged slow release.

### Addition of photochemical inhibitors to upper EFPC

Photochemical processes (both reduction and oxidation) drive the cycling of waterborne Hg (including particle-associated Hg) between Hg (0) and Hg (II), possibly generating reactive Hg species that are key precursors for MeHg production. Preliminary studies at ORNL suggest that the entire water column inventory of inorganic Hg in contaminated streams such as EFPC can undergo an oxidation/reduction cycle in less than a day. If the rate of microbial production of methylmercury is limited by the concentration of ephemeral forms of inorganic Hg (including Hg (0)), interfering with the photochemical redox cycle has the potential to reduce aqueous methylmercury concentrations, and consequently, mercury bioaccumulation in fish.

Photochemical processes can be enhanced or impeded by various chemicals that scavenge reaction intermediates or block critical wavelengths of light. The addition of low concentrations of photochemical inhibitors, (probably dyes) to the shallow-illuminated upper reaches of EFPC may be effective at preventing the formation of important methylation precursors. Alternatively, impeding photochemical oxidation while allowing photochemical reduction to proceed would allow aqueous Hg (0) to build up and be lost to volatilization, reducing total waterborne mercury concentrations.

This approach could potentially be relatively inexpensive and simple, and may have little effect on the ecology or appearance of the stream. However, it is speculative and theoretical, without a solid foundation of research to support it. There may also be regulatory constraints against adding photochemical inhibitors to public waters. However, dyes such as Aquashade are commonly added to privately controlled ponds to inhibit the growth of aquatic vegetation (both algae and rooted plants).

This is a relatively unexplored area of research that might shed knowledge on the global cycling of mercury. Simple experiments such as light/dark microcosms, sampling fish for mercury analysis from ponds treated with photochemical inhibitors such as Aquashade could provide an indication of whether this approach has promise.

Strategies that Manipulate Microbial Ecology

The technical working group developed several ideas that are all based on manipulation of microbial ecology. These include:

- Increase demethylation by bioaugmentation
- Increase demethylation by GMO bacteria
- Increase demethylation by geochemical manipulation
- Decrease methylation by bioaugmentation
- Decrease methylation by geochemical manipulation

These ideas, while related in a general way, exhibited key differences so each is described separately in Table 4. The strategies are broadly differentiated into those that increase demethylation and those that decrease methylation. Within each category, the manipulation methods include bioaugmentation (adding appropriate naturally occurring organisms), manipulation of geochemistry, and for demethylation, adding genetically modified organisms (GMO). In practice, these strategies could be used alone, in combination with each other, or in combination with other stream based actions. The net result of the ecological changes is lower methyl mercury concentration in the water and lower fish uptake – conceptually these strategies partially decouple the total mercury in the stream water from the form(s) of mercury available for uptake into the food chain.

Two overarching conclusions that from the evaluation process were: 1) microbial ecology based strategies are some of the most promising ideas for long term application in the Oak Ridge environment, and 2) significant advancement in basic science and understanding is needed for reliable application of any of these strategies (or a combination of strategies. Thus, this is a prime target for investment by the DOE Office of Science and other basic science funding agencies.

This research should focus on elucidating rates, mechanisms and controls of microbial (and abiotic) processes affecting Hg speciation and transformation, and resolve how critical Hg precursors are produced, transported and subsequently methylated in the ecosystem. Funding should be used to develop and validate models to understand in detail the biochemical and biophysical mechanisms of transformation between major Hg species and MeHg. To be useful, the research will need to mechanistically relate Hg speciation and transformation to coupled with redox reactions of aqueous species (e.g., Fe, dissolved oxygen (DO), DOM, and S) and determine the influences of parameters such as pH, Eh, and ionic strength. The research should clarify the microbial ecology of key transformations (e.g., sulfate reducing bacteria are the dominant microbes responsible for Hg methylation, but other groups of microbes also contribute directly or indirectly to net MeHg production)

Remove highly contaminated fish

The basic premise of this option is that removing the most highly contaminated fish can interrupt the contaminant exposure pathways that lead to ecological or human receptors. The focus of the contaminant pathway interdiction is at the higher food chain level, in contrast to conventional options where interdiction is at the soil or sediment source level. Interdiction at the food chain pathway could be advantageous in that the action results in immediate risk reduction that is independent of the success of source control actions. Fish can be removed using a combination of electrofishing and netting techniques, and the carcasses disposed of in a nearby soil pit or landfill. Fish removal actions have been applied at the K901A pond at ETTP, and fish management actions for reducing PCB risk have been vetted and approved by regulators in association with a Non-Time Critical Removal Action at the K-1007-P1 Pond at ETTP (Peterson et al. 2005). Removing high risk fish in EFPC is particularly doable upstream of the Lake Reality bypass weir, where upstream movement and repopulation by larger fish is unlikely.

This option is less manageable with distance downstream and the open creek system where fish can migrate into areas where fish were removed. Continued removal of large fish would be needed long-term in those stream sections, unless a weir or dam is created downstream that would prevent fish migration. Based on past experience in Oak Ridge, there is some public sensitivity to killing fish, although other fish removal options have received public support in Oak Ridge. An effective argument would need to be made regarding the benefits of the action, which might include removal of nonnative fish species (e.g., carp and redbreast sunfish) while enhancing native fish populations. Fish management techniques such as electrofishing and netting are relatively routine tools, but the application of these tools for bioaccumulation reduction is limited. Research needs include a better understanding of unintended consequences of food chain manipulation on mercury processes.

<u>Add fish with low bioaccumulation potential</u>

This fish management option involves stocking (i.e., adding) of fish species that accumulate low levels of methylmercury. Fish species such as bluegill, trout, and topwater cyprinids obtain a significant portion of their diet from terrestrial sources; primarily adult terrestrial insects that fall into the water or deposited surface water larvae like mosquitoes or midges. For these fish species, a significant portion of their diet is, therefore, relatively uncontaminated with mercury. These insectivorous food chain pathways are also shorter pathways than piscivorous fish, limiting biomagnification. This option is less time intensive than in stream management of fish populations. Fish hatchery trucks can distribute fish into the stream at bridges found throughout the length of East Fork Poplar Creek.

If high numbers of uncontaminated fish are released, this option assumes that stocked fish would out compete resident contaminated fish populations. Successful competition would be dependent, however, on effective stocking rates, timing of stocking (to maximize fish egg predation for example), temperature requirements for stocked species (this could be managed by changes in flow management), and a detailed understanding of species to species relationships in the wild. Frozen Head State Park, a short distance from Oak Ridge, has a creek similarly sized as East Fork that has a put-and-take rainbow trout fishery. Understanding the impact of that annual stocking on resident sunfish could be useful in evaluating the efficacy of this option in East Fork Poplar Creek. Unlike fish removal, risk reduction could take years with stocking until fish populations are completely replaced. Fish hatchery and stocking operations are standard fish management practices, but application of these tools for bioaccumulation reduction is limited. Prior to whole scale stocking of fish, this option could be readily investigated by blocking a small section of stream to undergo stocking and see how resident fish populations are affected.

The potential impact of this option may be limited due to the fact that bluegill collected from the EFPC contains approximately 70-85 percent of the MeHg concentration at the same site. While this option has the potential to reduce overall mercury levels in fish, the actual impact to the environment and environmental risk may be relatively low.

<u>Add uncontaminated food for fish</u>

Large fish receive most of their mercury body burden through the food chain. This option would attempt to convert the food base for these large fish from in stream sources to manual feeding of uncontaminated food. To cover enough of the stream to be effective, fish feeders, which are commercially available, would be placed near the stream and regular release of uncontaminated food pellets would be provided to the stream. For fish that eat the uncontaminated food, some reduction of mercury in fish tissue would be expected with this option. However, fish would also be expected to continue to take advantage of in stream sources, and dramatic decreases in fish mercury content are unlikely. Fish feeders are unlikely to reach most of the fish population in EFPC without significant effort, and the ability to train significant numbers of fish to eat polluted food is uncertain. It's possible that providing significant additional food sources to the stream could increase nutrients significantly, and there may be unintended consequences of creating a larger fish population that is larger, and more contaminated, than current. This option has never been done before to reduce contamination in fish. A field scale effort could be conducted to evaluate the success of introducing uncontaminated food on fish body burdens, but research effort would probably be better spent elsewhere. This is not deemed to be a viable option.

**Table 4.**
**ZONE IV -- Upper and Lower Reach of Stream**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| **Sediment/Soil Removal** | Excavation and/or dredging to selectively remove soil or sediment with mercury in form(s) that are bioavailable. | Reduce/eliminate release of bioavailable Hg to creek | Permanent remedy but would not focus on total Hg as a trigger for removal action. | Difficult to fully delineate areas with bioavailable Hg. Removal action may temporarily destroy or impair some functionality of target area and access to these areas. Significant transportation and disposal costs. Uncertainty about long-term effectiveness. | Removal actions of this type are widely practiced and there is local EFPC precedent. | Identification and/or development of better tools to define bioavailability. | Viable but not preferred unless hot spots identified |
| **Bank Stabilization** | Identification and stabilization of eroding or erodable stream banks with significant inventory of Hg | Reduce/eliminate inputs of particle-bound Hg in creek | Relatively simple to implement. | Stabilization actions may temporarily destroy or impair some functionality of target areas and access to these areas. Monitoring/maintenance required. | Bank stabilization technology is well-developed | Need to determine whether particle-bound Hg is an important substrate for methylation | Viable and preferred if eroding banks implicated in maintaining fish Hg |
| **Relocate creek channel** | Identify reaches of EFPC that could be abandoned in place and replaced with new reaches to provide clean pathways for water. | Reduce/eliminate channel reaches/features where Hg is being methylated (e.g., oxbow lakes, riparian wetlands) | Permanent remedy. Contaminated soils/sediment to be left in place in former channel thus no disposal cost. | Land may not be available except on ORR. Some uncertainty in identifying key reaches for application. | Precedents with Melton Branch and Bear Cr where streams relocated or reconstructed. | Detailed sampling/analysis to identify and delineate target channels. | Viable, not preferred |

**Table 4. (continued)**

**ZONE IV -- Upper and Lower Reach of Stream**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| **Stabilize floodplain and stream bank soils using native plants** | Plant highly rhizomous native plants along drainage ways and eroded bank areas | Stabilize bank and/or floodplain soils to prevent contaminated soils from entering the creek | In addition to decreasing mercury inputs to stream, also natural resource benefits. Could be implemented by providing technical advice or plant plugs to watershed organizations or public. Less obtrusive than earth moving options. | Uncertain degree to which riparian and floodplains sources are the problem in EFPC; less permanent than structural changes. | Tools well developed. More successful if conducted in conjunction with armoring/earth moving techniques and close collaboration with landowners. | Need to determine role of bank and floodplain sources in LEFPC. | Viable if can work agreements or collaboration with private landowners. Unlikely alone to result in reaching fish reduction targets. |
| **Create wetland system in Lake Reality and return upper EFPC to 1985 conditions** | Establish a highly vegetated retention basin in Lake Reality that acts as an effective sediment trap. Eliminate flow management while allowing potable (chlorinated) water inputs in EFPC above Lake Reality. | Return stream to circa 1985 conditions when there was there was a pronounced decreasing gradient in mercury bioaccumulation with distance downstream | Fish in lower EFPC were near target concentrations in 1985. With a return to similar stream conditions plus the 90% decrease in loading since that time, fish reduction goals could be met. | Upper 1 -2 km of EFPC would be toxic due to residual chlorine inputs. Changes would eliminate ecological and regulatory benefits of flow management. Unlikely to obtain regulatory and public approval. | Shutting off flow management and dechlorination would be easy to implement. Lake Reality changes would take a couple years but vegetation could be established. Success in reaching mercury reduction goals still uncertain. | Limited understand of the role of chlorine on mercury bioaccumulation and how wetland system may affect mercury bioaccumulation in downstream waters. Research needed. | Not viable in its totality. Chlorine toxicity and elimination of flow management not likely to be acceptable. Lake Reality vegetation changes would be viable, but the degree to which the change would limit mercury bioaccumulation is uncertain. |
| **Modify instream physical conditions that affect ecology and bioaccumulation** | Modify flow management and instream/riparian habitat to affect temperature, amount of TSS/sedimentation, amount of sunlight, and algal/vegetation characteristics. | Change instream factors that affect mercury methylation and bioaccumulation. Such changes can help limit high mercury species (e.g., rockbass, shiners) and enhance others (bluegill, rollers) | With facility inputs and flow management at headwaters, stream conditions are more controllable than other systems. | Could be difficult to control stream processes. | Can change flow, stream temperature/chemistry, or put more clean sediment in stream, but affect on mercury bioaccumulation unknown. | Amenable to controlled scientific study | Unlikely successful alone but could be considered in concert with other actions |

**Table 4. (continued)**

**ZONE IV -- Upper and Lower Reach of Stream**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| **Se Amendment to stream water** | Addition of a selenium compound in soluble or sparingly soluble form at low levels. | Reduction of methylation or bioaccumulation of mercury by biota | Avoids potentially destructive aspects of physical remedies. Relatively low cost to implement. | Risk of toxic response if dosing is not carefully controlled. Long-term maintenance and monitoring required. Regulatory approval may be difficult to obtain | Practiced successfully in Sweden for some lakes and reservoirs but no applications thus for to flowing systems | Trial application in a mesocosm or artificial stream. Development of suitable Se-bearing matrix (mineral form) for use in long-term dosing. | Viable and preferred assuming successful demonstration in flowing system and acceptability by regulators and stakeholders. |
| **Addition of photochemical inhibitors to UEFPC** | Photochemical processes (both reduction and oxidation) drive the rapid cycling of waterborne Hg (including particle-associated Hg) between Hg(0) and Hg(II), possibly generating reactive Hg species that are key precursors for MeHg generation. Chemical inhibitors may interfere with this process | Add trace concentrations of photochemical inhibitors (probably dyes) to EFPC to prevent generation of ephemeral reactive precursor Hg species, reducing formation of methylmercury in system | Potential inexpensive way to reduce Hg bioaccumulation with little ecological effects, possible aesthetic improvement (to some). | Totally speculative, untested theory. May be regulatory blocks to adding photochemical inhibitors to public waters | Dyes are commonly added to privately controlled ponds to inhibit weed control and improve appearance. Their affect on Hg bioaccumulation has not been investigated. | An unexplored area for research that could be easily and inexpensively pursued in microcosm studies and by sampling fish from ponds treated with photochemical inhibitors such as Aquashade. | Not presently viable, not recommended. |
| **Increase demethylation by bioaugmentation** | Add bacteria that have been isolated from the environment with lower threshold for induction of mer genes | Reduce methymercury in water and sediments to reduce concentrations in fish | Could reduce both total and methylmercury in water and in fish, cost could be low | Right bacteria need to be found and it is unknown if they would they survive in competition in the environment, potential effectiveness is unknown | Never tried | Fundamental Research needed | Not viable until much future research is done |

**Table 4. (continued)**

**ZONE IV -- Upper and Lower Reach of Stream**

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| **Increase demethylation by GMO bacteria** | Add GMO bacteria that constitutively express mer genes | Reduce methymercury in water and sediments to reduce concentrations in fish | Could reduce both total and methylmercury in water and in fish, cost to deploy could be low. | GMO would have to be constructed, would they survive in competition in the environment, would they be acceptable to public, potential effectiveness is unknown. | Immature, Never tried. | Fundamental Research needed. | Not viable until much future research, may not be viable due to acceptability even if technical challenges are met. |
| **Increase Demethylation by geochemical manipulation** | Addition of removal of chemicals such as sulfate, organic carbon, humics, molybdate, etc. that could reduce mercury methylation. | Reduce methylmercury in water and sediments to reduce concentrations in fish. | Could reduce both total and methylmercury in water and in fish, cost to deploy could be low. | Don't know which additions will work, may require constant additions, would additions be acceptable (e.g., sulfate). | Immature, Never tried | Fundamental Research needed. | Not viable until further research is done. |
| **Decrease methylation by geochemical manipulation** | Addition of removal of chemicals such as sulfate, organic carbon, humics, molybdate, etc that could reduce mercury methylation. | Reduce methylmercury in water and sediments to reduce concentrations in fish. | Should reduce methylmercury in water and in fish, cost to deploy could be low. | Don't know which additions will work, may require constant additions, would additions be acceptable (e.g., sulfate). | Immature, Never tried | Fundamental Research needed. | Not viable until further research is done. |
| **Decrease methylation by bioaugmentation** | Add iron reducers or (No Suggestions) that do not have methylation capacity. | Reduce methylmercury in water and sediments to reduce concentrations in fish. | Should reduce methylmercury in water and in fish, cost to deploy could be low more acceptable than GMO. | Unknown if they would they survive in competition in the environment, effectiveness is unknown. | Immature, Never tried | Fundamental Research needed. | Not viable until further research is done. |

## Table 4. (continued)
### ZONE IV -- Upper and Lower Reach of Stream

| Technology/Approach | Description | Objective | Positives | Negatives | Technical Maturity | Research Needs | OVERALL |
|---|---|---|---|---|---|---|---|
| **Remove highly contaminated fish** | Selective removal of game fish from contaminated EFPC waters using electrofishing techniques | Remove source of risk to humans by removing most if not all edible game fish containing high mercury levels. | Immediate risk reduction. Changing the fish population in the upper EFPC is relatively simple upstream of LR/bypass weirs. Independent of source control. | Less manageable with distance downstream and open system. Unless a weir/dam created downstream, requires continued fish management control long-term. Some public sensitivity to killing fish. | Fish management tools are off the shelf, but application of these tools for bioaccumulation reduction limited. Recent regulatory-approved remediation option in Oak Ridge | Need better understanding of unintended consequences of food chain manipulation on mercury processes. | Viable especially in uppermost EFPC. Could be conducted in concert with other actions such as flow management changes |
| **Add fish with low bioaccumulation potential** | Stock or enhance fish populations that accumulate low levels of methylmercury (e.g., bluegill, trout). | Change fish community to shorter and more terrestrial food chain, thus limiting biomagnification. | Doesn't require instream fish management, only stocking (addition) of fish. Independent of source control. | Depends on successful species competition (i.e., stocked fish replace existing species), when species interactions uncertain. Will take time (years) to see benefits. | Fish culture and stocking tools are off the shelf, but application of these tools for bioaccumulation reduction limited. Recent regulatory-approved remediation option at ETTP | Need better understanding of unintended consequences of food chain manipulation on mercury processes. Ideally suited for a pilot experimental study. | Viable especially in uppermost EFPC. Could be conducted in concert with other actions such as flow management changes. |
| **Add uncontaminated food for fish** | Provide fish feeders near stream that provided uncontaminated food pellets for fish. | Reduce uptake of mercury in fish by replacing the instream food sources with uncontaminated food. | Likely to reduce mercury concentrations in fish that do eat the food. | May reach small part of population without significant effort. Will need to train fish to eat food. Could increase risks by having larger fish population or bigger fish. | Never before done to reduce contaminant bioaccumulation. | Field scale effort could be conducted, but research effort probably better spent elsewhere. | Not viable. |

## 4.0 Recommendations

One of the requested deliverables of the mercury workshop was a prioritized list of recommendations (Quick Wins) for applied science and technology support from EM-22 for mercury issues at Y-12 and Oak Ridge facility. At the January workshop, the team divided the Y-12 area and East Fork Poplar Creek watershed site into four subdomains and then evaluated these based on a site specific conceptual model. This resulted in specific technology recommendations for each of these areas. The four subdomains were: I) buildings and rubble piles, II) shallow source zone soil, III) the Outfall 200 area, and IV) the upper and lower reaches of the East Fork Popular Creek. A technology matrix was prepared for each of the areas that identified potentially applicable technologies/strategies. The consensus of the team was documented for each concept using terminology such as "viable-preferred", conditionally viable, viable but not preferred, or not viable. The following list is a compilation of the technologies that were identified as preferred and viable and a summary of the results from each of the matrices.

**Subdomain I: Buildings Rubble and Shallow Soil <u>and</u> Subdomain II Surface Soil and Shallow Subsurface Contamination**

- No Quick Wins Identified
- The primary challenge in these zones is the linkage of achieving site wide Remedial Objectives to the decisions and actions.
- Beneficial technologies such as field screening tools and sensors would be useful in these subdomains and these might be available through programs such as SBIR.

The team recommended that Office of Science consider investments in basic research to linkage actions taken to decommission building and to remediate soil to the broader goal of limiting uptake of mercury in the food chain (e.g., though development of models).

**Subdomain III (Outfall 200 Area)**

- Identified as an area of opportunity for several Quick Wins
    - Stannous Chloride – Treatment of water in the NS pipe – Confirm effectiveness under current conditions
    - Addition of mercury sequestrants at Outfall 200
    - Use sodium thiosulfate as dechlorinating agent at Outfall 200
- Mercury inputs to surface water in this subdomain are somewhat unique in they are accessible and are comprised primarily of dissolved reactive forms of mercury.
- This combination of access and chemistry provides opportunities for alternative strategies to reduce the accumulation of methylmercury in fish throughout the entire stream system.

**Subdomain IV (Creeks and Streams)**

- Identified as an area of opportunity for Quick Wins
    - Addition of trace Se to reduce methylation and/or uptake and maintain low fish tissue levels

Identified other viable and preferred technologies that involve selective physical modifications at areas of methylation (bank stabilization, channel relocation)

- Identified promising ideas that need more research (manipulation of microbial ecology)

As noted above, several of the viable and preferred alternatives were designated as potential "Quick Wins." Quick Win ideas tend to be more mature, have relatively low risks and potentially significant impacts, and may need relatively small levels of funding for bench or field studies to support implementation.

In order to select and prioritize the near-term technology options, several considerations must be taken into account. First, it must be recognized that the concentrations of mercury and methylmercury in East Fork Popular Creek result from a series of complex and variable chemical processes that are not completely understood. Second, some of the technical recommendations on the Quick Win list may be in conflict especially if they are not properly coordinated and sequenced. As an example, some of recommended chemical modifications are incompatible with each other and/or need to be assessed to make sure that there are no downstream impacts to fish.

The technical working group recommends that development of a specific proposal to move forward and implement a defensible selection of the quick win ideas. This would involve developing a plan that logically integrates some of the recommendations into a coordinated technical approach. This process will require the participation of the relevant Oak Ridge organizations, state and federal regulators and stakeholders. We anticipate that a logical and robust "Quick Win" portfolio will incorporate some type of fisheries management and ecosystem controls, some action(s) near Outfall 200, and possibly some related lab screening studies for promising amendments. Another very important consideration is that although some of the technologies may be technically viable, they may not be acceptable to site regulators, stakeholders, and site problem holders. Participation of these groups in the decision-making and selection process is crucial.

At this point, it is not appropriate for the technical working group to select the preferred technology portfolio. We recommend that the next steps will be best performed in two stages: The first stage consists of assembling a local mercury "Creative Solutions Team" to consider the identified Quick Win ideas. This team, through a period of focused and intense effort, would identify and develop a detailed recommendation for consideration by DOE. The resulting plan would lay out a specific set of actions for implementation along with the priority, schedule and resources. The team should include key individuals from the diverse groups identified above. For perspective, we believe that the process should be performed rapidly and with minimal cost. The goal is to develop local consensus and to determine which combination of options provides the most potential benefits within the real-world constraints of the site. Based on the recommendations, DOE should consider moving forward on key Quick Win activities as part of a second stage

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## 6.0 Appendices

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**Areas of Expertise:**
*Dr. Looney* (Ph.D. Environmental Engineering) is a senior fellow at the Department of Energy Savannah River National Laboratory in Aiken SC. For the past 23 years, he has coordinated development and deployment of environmental characterization and clean-up methods based on the fundamental principles of geochemistry, geohydrology and engineering. His efforts resulted in the successful development or application of improved subsurface access methods (environmental horizontal drilling and cone penetrometer), improved remediation (e.g., sparging, bioremediation and thermal methods), and improved characterization (e.g., tracer testing, soil gas methods and geophysics). Dr. Looney has conducted research targeting clean up of source zone contamination using destruction, stabilization and/or enhanced removal methods. He has also conducted research on methods for dilute fringe contamination using barometric pumping, phytoremediation and the like. Dr. Looney has authored and edited many publications including the recent book, *Vadose Zone Science and Technology Solutions*. He currently holds ten U.S. and one foreign patent for environmental technologies. Dr. Looney received the 2006 National Groundwater Association Technology Award, 2005 American Chemical Society Industrial Innovation Award, 1996 and 2000 Federal Laboratory Award of Excellence in Technology Transfer, 2004 Worlds Best Technology Award, and 2000 Energy 100 Award.

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**Areas of Expertise:**
*Dr. Palumbo* is the Deputy Director of the Biosciences Division of ORNL and the Group Leader for the Microbial Ecology and Physiology group. In this position he has developed and directed numerous research projects focused on understanding the functioning of microbial communities in natural and contaminated environments and the bioremediation of metals and organic pollutants including TCE and PCE. Among those is the project "Geochemical, Genetic, and Community Controls on Mercury Methylation" which focuses on understanding the genetic basis for mercury methylation in Desulfovibrio. Dr. Palumbo holds two patents related to environmental technologies and is an author of over 110 papers on environmental microbiology, remediation, and microbial ecology. He is a Fellow of the American Academy of Microbiology.

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**Areas of Expertise:**

Mr. Peterson (M.S., Biological Sciences) is the Leader of the Ecological Assessment Group in the Environmental Sciences Division at Oak Ridge National Laboratory, and the program manager of the Biological Monitoring and Abatement Program – a long-term multidisciplinary monitoring program implemented primarily in Oak Ridge, Tennessee. As both a principal investigator and program manager, he has evaluated the aquatic environment near the Y-12 Plant since 1988, including assessment of changes in mercury contamination in fish. He has over 25 years of environmental assessment experience with the last twenty years focused on the bioaccumulation of contaminants near Department of Energy and Department of Defense sites. In addition to contaminant-related evaluations, he has extensive experience working with engineering and construction staff in the design, implementation, and performance of stream and wetland restoration projects. Projects include stream-rerouting, bank stabilization, and hydrologic isolation actions designed to reduce contaminant concentrations in surface waters and fish, while maintaining or enhancing long-term habitat value. Related to mercury, he provided multi-year technical support to the Lower East Fork Poplar Creek (LEFPC) Remedial Action Project, the Reduction of Mercury in Plant Effluent (RMPE) Program (both in Oak Ridge), the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) in Ontario, Canada, and the Barrow Arctic Mercury Study (BAMS) in Alaska. Mr. Peterson has led the development of an innovative remediation strategy, the first of its kind to be approved by EPA, which uses ecological management and enhancement tools to reduce human and ecological risks associated with sediment contaminated ponds. Scheduled for a fall 2008 start, this Non-time critical (NTC) removal action is estimated to save DOE 23 million over the conventional sediment removal alternative. Mr. Peterson has authored over 100 scientific articles and reports, most of which focus on the effects of Department of Energy missions on aquatic ecosystems.

**GEORGE SOUTHWORTH**

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**Areas of Expertise:**

*George Southworth* has worked as a researcher in environmental chemistry and toxicology at ORNL since 1974, and is presently a Senior Research and Development Staff member in the Environmental Sciences Division. His research background is in the environmental transport and transformation of chemicals in surface waters and groundwater, and studies of the toxicological and ecological effects of chemicals on aquatic organisms and communities. He has worked in the Biological Monitoring and Abatement Program at ORNL since 1985 as Principal Investigator and Group Leader, with primary emphasis on the bioaccumulation of mercury, PCBs and other metals and organic chemicals. In 1997, he became lead scientist in the Reduction in Mercury in Plant Effluent (RMPE) program at the Y-12 Plant. In this role, he participated in studies of new treatment technologies (chemical reduction/air stripping) and helped identify previously unrecognized sources of mercury contamination to East Fork Poplar Creek (metallic mercury in streambed sediments). In 1999, he began working on several EPA and DOE-funded studies of mercury cycling between the atmosphere and aquatic and terrestrial systems, in field studies of Hg sources and cycling at sites in Alaska, Canada, Florida and the upper Midwest. Most recently, he has become a participant in the DOE Subsurface Focus Area research on the environmental behavior of Hg on the Oak Ridge Reservation.

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**Areas of Expertise:**
*Dr. Turner* has diverse experience spanning more than 30 years in the field of biogeochemistry of terrestrial and aquatic ecosystems. In 1975, Dr. Turner became a researcher in the Environmental Sciences Division of Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee. During his tenure at ORNL he conducted extensive research and characterization at two large mercury-contaminated sites: a defunct chloralkali plant in Virginia and a nuclear weapons plant (Oak RidgeY-12). Among other innovative achievements related to mercury he developed a rapid field method for the determination of mercury in water and soils that saved significant cost in site characterization costs for his sponsors. He also initiated and supervised Hg speciation and bioavailability investigations that resulted in a much higher residential soil cleanup level (400 ppm) than derived in the absence of these investigations. In 1996 he spent a year as a National Research Council Senior Associate working at the U.S. Environmental Protection Agency[1]s Gulf Breeze Research Laboratory in Florida. During this period he helped to refine a novel luminescent biosensor for application in estimating the bioavailability of mercury in natural media. While at EPA he also wrote two review chapters for a book on mercury-contaminated sites. In February 1997, after retiring from ORNL, he joined Frontier Geosciences, a specialty research and analytical services company in Seattle, Washington, where he held the position of Senior Scientist in the Research and Consulting Group. Prior to this position he managed the Aquatic Mercury Group, which performed laboratory analyses of mercury and mercury speciation for client-supplied samples and acted as scientific consultant to certain clients, including several representing chloralkali and Hg-mining sites. In February 2000, he formed his own company, RT Geosciences Inc., in Squamish, British Columbia. Consultant activities have included project planning (mainly sampling and analysis), conduct of special field and laboratory projects (e.g., Hg treatability studies, measurement of soil fluxes of Hg vapor, sediment pore water extraction and analysis, dendrochemistry to reconstruct historic atmospheric Hg releases, building decontamination, Hg immobilization studies, in situ and ex situ groundwater treatment R&D, soil/sediment Hg speciation studies, thermodynamic modeling of Hg behavior, design and supervision of post-remediation monitoring programs). He serves, or has served, on several [3]mercury expert panels[2] for private industry as well as government agencies. Since 2001 he has

been a member of the Expert Panel for the South River Science Team, a consortium of scientists, engineers, NGOs, state and federal regulators and industry (Dupont) managers formed to address legacy mercury issues in the South River and South Fork Shenandoah River in Virginia.

## APPENDIX C Conceptual model for mercury in soil, groundwater and streams

Mercury exhibits especially complex biogeochemical behaviour in the environment (Figure C1) and may persist in different forms for a significant amount of time after removal of the source. Mercury may be transformed by natural processes to relatively stable forms (e.g., mercuric sulphide) or converted into more mobile volatile and soluble forms that can potentially spread through the environment and bioaccumulate (e.g., methylmercury) in terrestrial and aquatic food chains. The actual environmental fate and transport (and in turn toxicity) of mercury at a given location is highly dependent on the physical, chemical, and biological conditions that predominate at that specific area.

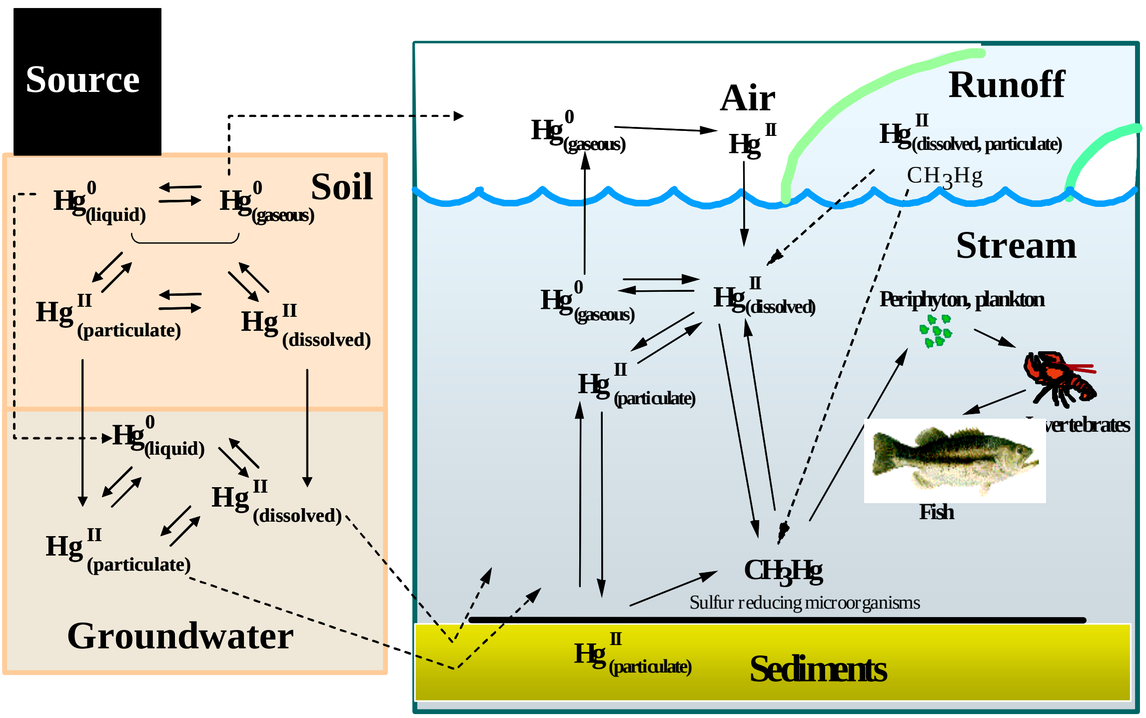


Figure C1. Biogeochemical Cycle of Mercury

<u>**General Speciation and Biogeochemical Behavior of Mercury**</u> - Speciation of mercury in the environment is governed by such factors as pH, redox potential, sulphide content, halide content, organic matter concentration, and microbial activity. Mercury occurs in three oxidation states, elemental ($Hg^0$), mercurous ($Hg_2^{2+}$) and mercuric ($Hg^{2+}$). Mercury released to aquatic and terrestrial environments can exist as a number of mercuric ($Hg^{+2}$) and mercurous ($Hg^+$) complexes or simply as elemental mercury either in dissolved gaseous form or adsorbed to organic and inorganic matrices. Microbial, as well as chemical and photochemical reduction of mercuric and mercurous complexes to elemental mercury may promote re-emission of mercury to the atmosphere from both water and soil surfaces. The general lack of significant concentrations of mercury in groundwater (Krabbenhoft and Babiarz 1992) outside of some industrially-contaminated sites, and typical vertical profiles in soil showing strong enrichment in the organic horizon, suggests that mercury compounds in soil remain strongly sorbed to organic

matter and are not readily leachable (Andersson 1979). This has been supported by numerous laboratory and field studies on mercury leachability. Relatively insoluble forms of organic mercury (e.g., methylmercury) and inorganic mercury complexes in soils and sediments can, however, be transported by surface runoff and groundwater and deposited into distant bodies of surface water, where further changes in speciation may take place. In particular, wetlands are now recognized as important net sources of methylmercury to lakes and downstream aquatic systems (Zillioux et al 1993, St Louis et al 1994).

Mercury is most commonly found in surface waters as mercuric complexes (such as $Hg(OH)_2$ and $HgCl_2$), incorporated into dissolved organic matter (e.g., fulvic acid), and to a lesser extent as dissolved gaseous ($Hg^o$) mercury. Microbial and abiotic reduction of mercuric mercury promotes the formation of elemental mercury and the possibility of its subsequent emission to the atmosphere (Figure D1). Elemental mercury, that is relatively insoluble in water at about 60 g/L, can also be oxidized to far more soluble forms (HgO). Typically methylmercury accounts for a small fraction (5 to 20%) of total mercury in surface waters with the fraction increasing in suboxic and anoxic zones, such as the hypolimnion of lakes, sediment pore water and hyporheic waters. The speciation of mercury in anoxic pore water is dominated by mercury-suphide complexes, some of which are hypothesized to be the key bioavailable species for methylating bacteria (Benoit et al 1999, 2001).

Methylmercury in surface waters may occur as either monomethylmercury (e.g., $CH_3HgCl$) or dimethylmercury, $(CH3)_2Hg$. Dimethylmercury ($[CH_3]_2Hg$) has also been found in the environment in the mid-depths of the ocean (Mason and Fitzgerald 1991) and in floodplain soils of a large river (Wallschlaeger et al 1995). Ionic and neutral forms (Hg(II) compounds) of mercury can be transformed to mono- (and di-) methylmercury by biotic and abiotic processes. The concentration of total mercury in the environment and particularly in aquatic ecosystems has, however, generally not been found to be a good predictor of the concentration of methylmercury present (Kelly et al 1995). This is due to the complex interaction of factors that control the production, nature and behaviour of methylmercury.

Seasonal fluctuations in such parameters as temperature, light, nutrient supply, oxygen supply and hydrodynamics also play a significant role in the rate and nature of mercury methylation. For example, studies in Lavaca Bay (Bloom et al 1999) demonstrated that concentrations of methylmercury in sediments and sediment pore water reached maximum values in early spring and then decreased throughout the balance of the year. Similarly, methylmercury concentrations are commonly observed to increase through the summer and early fall in anoxic hypolimnetic waters of thermally-stratified lakes and then decrease sharply after the fall mixing of bottom and surface waters. Detailed studies in the South River in Virginia have also documented a strong seasonal cycle in methylmercury production. Total mercury in the water column may also vary due to such factors as resuspension of bottom sediment during seasonal storms. Other factors that can control the presence of methylmercury in an aquatic system include the type of system (lake, river, estuary, ocean, etc.), water circulation patterns, catchment type, rainfall and water level fluctuations (e.g., artificial reservoirs).

All compounds of mercury, including methylmercury, can become strongly bound to suspended matter in surface water and effectively removed from the water column by sedimentation. Methylmercury has lower affinity for suspended matter (log $K_d$s 2 to 4) than inorganic mercury (log $K_d$s 5 to 7) and thus tends to be somewhat more mobile in soluble form. As discussed below, however, methylmercury and other mercury compounds may also be taken up by aquatic organisms and, over time, gradually bioaccumulate in the food chain.

Mercury in sediment is generally found in association with organic matter, sulphide or both. Where industrial releases have occurred mercury may sometimes be found in its elemental form as beads or amalgamated with other metals. The physicochemical behaviour of mercury in sediments is principally controlled by the pH, redox potential and free sulphide content of the sediment. In anaerobic conditions, mercury binds with sulphides to form highly insoluble mercuric sulphide (HgS) (e.g., Barnett et al 1997) but the solubility of this compound increases with increasing pH and increasing concentration of free sulphide in sediment pore water. Mercury readily replaces (substitutes for) other metals in metal sulphides in the acid volatile sulphide fraction of sediments, and is not released with other metals when sediments are acidified. Under aerobic conditions, mercury sulphide may be oxidized to mercury sulphate and thus released in soluble form. However, studies (Burkstaller et al 1975; Barnett et al 2001) have shown that the release of soluble mercury from mercuric sulphide undergoing oxidation is not proportional to the release of sulphate due to readsorption of the mercury.

**<u>Methylation/Demethylation</u>** - Methylation of mercury appears to be a co-metabolic reaction with no specific gene control (Summers 1986). In many aquatic systems biotic methylation appears to produce almost all the methylmercury and sulphate-reducing bacteria (SRBs) appear to be important mediators of the methylation process, although not all SRBs are known to methylate. Where SRBs are implicated as methylators there appears to be an optimal range of sulphate concentration (10 to 300 M) associated with maximum production of methylmercury while optimal sulphide concentration is quite low (10 M) (Gilmour et al 1992,1998;Benoit et al 2001) other factor being equal. Some recent work has also implicated some iron reducing bacteria (IRBs) as methylators (Fleming et al 2006).

Degradation (demethylation) of methylmercury is also controlled by microbial processes but photodegradation is also important within the photic zones of aquatic systems (Sellars et al. 1996). The production (and degradation) of methylmercury depends on such factors as the availability of Hg (II), oxygen concentration, pH, redox potential, presence of sulphate and sulphide, salinity, sunlight, and the nature and presence of organic carbon and other organic and inorganic agents. Additions of sulphates to freshwater sediments are generally stimulatory to production of methylmercury while the high sulphate concentrations of seawater limits methylation in estuarine sediments presumably due to complexation and precipitation as mercuric sulphide (King et al 1999). Certain oxyanions (e.g., molybdate) are known to inhibit methylation by suppressing the activities of SRBs (Chen et al 1997).

In spite of the complex nature of methylmercury, general conclusions can be made in regards to environmental conditions that promote or inhibit the formation of this compound. As discussed above, inorganic mercury may be converted to methylmercury by sulphate reducing bacteria. Methylation of mercury is most favourable under moderate pH and Eh conditions in anaerobic/reducing environments, or near interfaces between oxic/anoxic conditions. Methylation of mercury is most significant at the sediment-water interface (e.g., Bloom et all 1999) but can also occur within the water column. High concentrations of nutrients enhance microbial activity as well as anaerobic conditions. High pH and/or low Eh enhances sulphide activity and can cause mercury to be precipitated as insoluble mercuric sulphide. Exposure of the sediment to oxidizing conditions, however, promotes the conversion of sulphide to sulphate and potential availability of mercury for methylation. This could occur either naturally, through a decrease in the organic load or seasonal turnover, or to disturbance and re-suspension of the sediment through activities such as dredging.

Mercury complexes strongly with sulphur compounds (HS-, S2-, and organosulphides) but also undergoes both biotic and abiotic pathways to methylmercury. A significant positive correlation (r=0.94) between AVS and methylmercury concentrations has been found in sediments from the Elbe River (Hintelmann and Wilken, 1995). In that study, it was suggested that the strong binding of $CH_3Hg^+$ to sulphide in sediments may be an important factor controlling the transformation and accumulation of methylmercury. However, Benoit et al (2001) recently reported that mercury methylation rates were linearly related to the calculated concentration of the dominant neutral complex in solution, $HgS^0$.

**Bioavailability** – The bioavailability of mercury to an organism is dependent on its speciation, the physical and chemical nature of the environmental media (e.g., water, sediment, prey) and the ecological habits (e.g., feeding) and physiological characteristics of the organism (e.g., physiological aspects that promote bioaccumulation). The same geochemical factors that govern the fate and transport of mercury in the environment affect bioavailability to organisms. Characteristics of soil, sediment or water that promote the bioavailability of mercury in organisms include high concentrations of methylmercury, low concentration of organic carbon (both dissolved and particulate) available for binding, low capacity to form charged inorganic complexes, and moderate redox conditions. Recent research by Mason and Lawrence (1999) in Baltimore Harbour highlighted the likelihood of increased bioavailability of methylmercury in sediments following general water quality improvements that typically result in lower organic content of sediments. Barkay et al (1997) also demonstrated that higher concentrations of dissolved organic carbon in the aqueous phase reduced the bioavailability of inorganic mercury to bacteria.

Bioavailability can also be evaluated in terms of potential complexation of mercury with available sulphide in sediment. In a manner analogous to the binding of organic chemicals with organic carbon, certain divalent metal ions ("simultaneously extracted metals", SEM) can react with $H_2S$ released from the breakdown of amorphous iron and manganese sulphides ("acid-volatile sulphides", AVS) to form insoluble metal sulphides. When sufficient AVS is available, the bioavailability of these potentially toxic metals can therefore be significantly reduced. When concentrations (molar basis) of the SEM metals exceed concentrations (molar basis) of AVS, the remaining, uncomplexed metals is considered to be bioavailable. However, mercury sulphide is by far the least soluble metal sulphide and is not extracted from soils and sediments with the other AVS-associated metals (Cooper and Morse 1998). In addition, Mikac et al (2000) showed that mercury initially extracted from sediment in the typical AVS protocol may react with $H_2S$ released from AVS phases and actually form mercuric sulfide during the extraction. Thus, AVS/SEM has not been a very useful tool to characterize the bioavailability of total mercury in sediments. Nonetheless, mercury in sediments with significant AVS is likely to be bound to sulphide and not be very bioavailable.

Sulphide concentrations increase as the sediment environment becomes more reducing and decrease in oxidizing environments. In highly oxidized environments, complexing agents other than AVS can decrease mercury bioavailability. For example, bioavailability of mercury in sediments has been demonstrated to decrease with increasing organic carbon content (Mason and Lawrence 1999; Hammerschmidt and Fitzgerald 2004). Other agents that may reduce the bioavailability of mercury include chloride, carbonates and hydroxides (Sadiq 1992). Selenium may also reduce the bioavailability of mercury, although the exact mechanism remains unresolved (Belzile et al 2006).

**Bioaccumulation** - Bioaccumulation of mercury has been shown to occur in aquatic plants, invertebrates, insects, scavengers, fish and mammals. Benthic organisms are particularly susceptible to bioaccumulation of mercury (especially methylmercury) due to their close ties to the geochemistry of the sediments that they live on and in. Uptake occurs primarily via dissolved-phase mercury in interstitial pore waters, with the mass of mercury bound in the sediment serving as a source. Studies have shown that bioaccumulation of mercury in invertebrate benthic organisms is relatively low in comparison to higher trophic level organisms such as mussels, shrimp, crabs and fish. This is due in part to the ability of the different organisms to eliminate mercury from their systems following initial uptake.

Methylmercury is preferentially bioaccumulated in organisms, although bioaccumulation of mercury in the inorganic forms (neutral and charged aqueous complexes, e.g., $Hg(OH)_2$, $HgCl_2$) has also been documented. Preferential uptake of methylmercury is due in part to its greater solubility in biological fluids and its lower rate of elimination in comparison to other organic and inorganic mercury complexes. In particular, methylmercury has a very high affinity for sulfhydryl groups in proteins and is absorbed much more efficiently by organisms than inorganic mercury forms. Except at the base of foodwebs uptake and accumulation of mercury in the water column takes place primarily via food. Mercury is later redistributed throughout other tissues in the organism and retained for long periods of time. Inorganic mercury complexes may be initially taken up within digestive tract of fish but the majority of mercury is soon excreted. Biomagnification of mercury through the food chain as methylmercury has been demonstrated in high-trophic-level piscivorous fish and can be especially significant in marine mammals that feed on these fish, although this varies widely between species.

**Biomagnification** - The term biomagnification refers to the progressive build up of a substances (e.g., methylmercury, PCBs, DDT) by successive trophic levels in a food chain. It relates to the concentration ratio in a tissue of a predator organism as compared to that in its prey. For methylmercury this ratio always exceeds unity. As a consequence, there is a selective enrichment of methylmercury (relative to inorganic mercury) as one moves from one trophic level to the next higher trophic level within a food chain.

**Mercury in Fish** - The predominant form of mercury in fish is methylmercury (MeHg) and is most often derived, as discussed above, from microbial processes in the environment that convert inorganic mercury forms to methylated forms that are accumulated and "magnified" within food chains leading to fish and other organisms that consume fish. Thus, for example, some sulfate reducing bacteria (SRBs) are capable of transforming inorganic mercury to methylmercury that is in turn absorbed by primary producers (phytoplankton-periphyton) at the base of a food chain and passed on to secondary (e.g., zooplankton-grazers) and higher consumers with very high efficiency. There are also some rare circumstances where methylmercury was an accidental industrial by-product (e.g., acetaldehyde production, Minamata, Japan, Kudo and Turner 1999), or produced abiotically by interaction of inorganic mercury with natural and anthropogenic methyl donors in the receiving environment, with the result that fish and wildlife was contaminated with methylmercury.

**Recovery of Hg-Contaminated Fisheries** – The discharge of inorganic mercury to water bodies as a cause of fish contamination with methylmercury was first recognized in the late 1960s and efforts to reduce loading, at least from point sources, began in the early 1970s. Thus there are now numerous sites around the world where long-term monitoring data is documenting the recovery of Hg-contaminated fisheries. A common temporal trend observed at sites where point source loading was initially high (e.g., kg/day) and then sharply reduced or eliminated is a rapid decline in mercury in fish in the receiving water bodies (see reviews by Turner and Southworth 1999; Munthe et al 2007). Mercury in fish at very few river and lake sites that experienced early high Hg loadings have fully recovered even after more than 30 years (e.g., South River in Virginia, Onondaga Lake in New York). The reasons for failure of fish to fully recover vary somewhat from site to site but typically include: 1) continued residual loading from the point source(s) and 2) accumulation of mercury within the receiving water body and/or riparian terrestrial system that is continuing to feed mercury back to the water column and biota for long periods after the original source of contamination is curtailed.

Many factors can affect recovery of Hg-contaminated fisheries. Munthe et al (2007) review these factors as they pertain to both point and non-point sources of mercury. These factors can be divided between those affecting net methylation and those affecting the uptake of methylmercury by the food web. For inputs of mercury to a water body to result in methylmercury in biota inorganic mercury must be converted to methylmercury. Net methylmercury production is affected by the concentration of bioavailable mercury and by a complex system of environmental factors that include 1) the areal extent and connectivity of methylating and demethylating zones within the water body and 2) the bioavailability of mercury and methylmercury to methylating and demethylating bacteria and the relative activities of those organisms. As noted previously methylation is favored by reducing conditions and thus the presence and spatial distribution of such conditions within a receiving system determines where and how much methylmercury can be produced.

Recovery of a Hg-contaminated fishery may be affected by changes in the food chain that occur as loading of mercury is decreased by remedial activities. Such changes are unlikely to be related directly to mercury loading but to other changes in water quality and nutrient loading. For example, mercury concentrations in top level predators within a system depend in part on the number of steps in the food chain leading to the predator. Thus a "short" food chain may produce lower predator mercury levels compared to a "longer" food chain. Differences in feeding behavior among several top predators can also be significant if the dominant predator is replaced by another over time.

One novel hypothesis concerning recovery of Hg-contaminated implicates mercury-resistant bacteria in suppressing production and persistence of methylmercury where water concentrations of inorganic mercury are sufficiently high to stimulate and maintain resistance mechanisms in indigenous bacteria. These mechanisms include MerA-mediated reduction of mercuric ion and MerB-mediated demethylation (Schaefer et al 2004) and can significantly affect the amount of methylmercury that is available for entry into the aquatic food web. According to this hypothesis successful efforts to reduce loading of inorganic mercury may ultimately deactivate these mechanisms and cause unexpected spatial and temporal trends in mercury in fish. For example, fish mercury concentrations may increase downstream from a point source even as total mercury is decreasing over the same distance.

{References in Main Document}