TECHNOLOGY PLAN TO ADDRESS THE EM MERCURY CHALLENGE

FEBRUARY 2016

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Technology Plan to Address the EM Mercury Challenge

FEBRUARY 2016

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Summary

Mercury contamination poses a unique, high priority challenge to the cleanup mission of the US Department of Energy's Office of Environmental Management (EM), particularly at the Oak Ridge Reservation (ORR) and Savannah River Site (SRS). This plan identifies mercury-related research and technology development (TD) to resolve key technical uncertainties in three EM mission areas: environmental remediation, facility deactivation and decommissioning (D&D), and tank waste processing. Recommendations for the first two areas include developing rapid screening methods as well as sensitive, quantitative analyses for mercury in environmental and infrastructure samples; assessing decontamination approaches for D&D; developing in situ stabilization for mercury-contaminated soil; refining site-specific environmental mercury models; and mitigating mercury in creek ecosystems through source zone stabilization, water chemistry modification, and ecological management. Recommendations for research related to tank waste include improving capabilities for mercury analysis and species determination in high level waste liquids and sludges; developing processes for the controlled conversion of mercury from one species to another (i.e., between organic, inorganic ionic, and elemental forms); developing mercury sorbents for removing organomercury from alkaline waste solutions; and pursuing fundamental science to improve understanding of mercury speciation and reaction mechanisms in chemically complex radioactive tank waste. Two crosscutting research topics are also recommended: grout formulation for mercury-bearing wastes and alternative assessments of waste form leachability. Finally, EM should form a technical working group to formalize and strengthen synergies and information sharing among agencies, institutions, and industries engaged in mercury research, TD, and operations.

1. Background

Mercury (Hg) is a toxic, persistent element that occurs both naturally and as an anthropogenic pollutant. It is present at more than 3,000 contaminated sites worldwide (Kocman et al. 2003) and is also found globally in environments that may not be discernably polluted. The United Nations Environment Programme (UNEP 2013) recently highlighted the risk of mercury contamination to human and ecological health. Methylmercury (MeHg), an organic form of the element, is especially toxic. It damages the nervous system, is quickly absorbed but slowly excreted from living organisms, and biomagnifies in the food chain. Appendix A provides a summary of mercury's biogeochemistry in the environment.

Mercury is released from a variety of anthropogenic sources, including fossil fuel (e.g., coal-fired power plants); mining, including artisanal and small-scale gold mining; smelting and metal production; cement production; oil refining; and a number of industrial production processes that use mercury as a catalyst. Examples of such industrial processes include the electrolytic Castner–Kellner process, which uses elemental mercury to produce chlorine and alkali hydroxide (UNEP 2013), and the Chisso process, which uses mercury salts to convert acetylene to acetaldehyde (a precursor for plastics) (Othmer et al. 1956). One of the world's most notorious instances of mercury poisoning resulted from methylmercury discharges to Minamata Bay in Japan by an industrial facility using the Chisso process.

Mercury contamination is particularly important at two US Department of Energy (DOE) legacy waste sites that used mercury in industrial-scale processes, namely lithium isotope separations at the ORR and dissolution of spent fuel aluminum cladding at SRS. The unique mercury-related challenges at these two sites are described below.

1.1 OAK RIDGE RESERVATION'S MERCURY CHALLENGE

DOE's ORR in Oak Ridge, Tennessee, houses the Y-12 National Security Complex (Y-12), which used large amounts of mercury from the early 1950s through the 1970s (Brooks and Southworth 2011). During peak usage (1950–63), approximately 11 million kg of mercury were used, and about 3% of this mercury (330,000 kg) was released to the surrounding environment. Ongoing mercury abatement and remediation efforts that began in the 1980s have targeted soil and sediment contamination within Y-12 as well as in and near East Fork Poplar Creek (EFPC), a stream with headwaters at Outfall 200 that flows from Y-12 through the city of Oak Ridge (DOE 2014). These remediation activities have significantly decreased overall mercury releases to the environment, but elevated concentrations remain in infrastructure (e.g., at four former mercury use facilities), water, and soil within Y-12. Mercury concentrations in stream water exiting the Y-12 site boundary at Station 17 continue to exceed the emerging regulatory limit (Tennessee's Ambient Water Quality Criterion for mercury, 51 ng/L) and the interim remediation goal (200 ng/L). Additionally, all major Oak Ridge watersheds exceed the current fish-based water quality criterion for mercury, 0.3 mg/kg in fish tissue. Thus, Y-12 mercury contamination has impacts well beyond the ORR.

The overarching mercury challenges at Oak Ridge include remediation of the large quantity of residual elemental mercury still present in shallow source zones adjacent to and beneath former mercury use facilities, potential mobilization of mercury during planned deactivation and decommissioning (D&D) of large mercury-contaminated facilities and associated infrastructure overlying potential mercury sources, potential mobilization of other contaminants, and the persistence and bioaccumulation of methylmercury in the EFPC watershed despite remediation efforts. The estimated cost for mercury remediation at Y-12 is between $1 billion and $3 billion.

1.2 SAVANNAH RIVER SITE'S MERCURY CHALLENGE

Mercury has been used for decades at SRS as a catalyst in the dissolution of aluminum cladding from irradiated targets in nuclear separation processes in the canyon facilities and as a precipitating agent to remove chlorides. Following cladding dissolution, waste solutions were discharged to the high level waste (HLW) tanks for storage and ultimate disposition. The current estimate of mercury distributed in the Liquid Waste System (LWS) is approximately 60,000 kg. This mercury has been isolated within the LWS process vessels and HLW tanks, with minimal releases to the surrounding environment to date. Recent analytical data from HLW tank samples indicate that mercury currently is being recycled and concentrated back in the HLW tanks as waste sludge is processed into glass at the Defense Waste Processing Facility (DWPF). Consequently, mercury concentrations are increasing in the LWS and in low-temperature waste forms such as saltstone. An overview of recent findings concerning mercury in the LWS is presented in Appendix B.

High level waste containing a significant quantity of mercury is being stored in waste tanks and managed in the LWS. The typical concentration of total mercury in the LWS is orders of magnitude higher than the concentrations that have been studied in aqueous environmental systems. This, coupled with the very complex and concentrated composition of the HLW solutions, results in significant differences in mercury behavior.

Chemical residues from fuel reprocessing operations are made strongly alkaline (pH 13+) before transfer into HLW storage tanks. Under these high pH conditions, almost all of the metallic ions precipitate as metal hydroxides or hydrous metal oxides that settle by gravity into a layer referred to as sludge. HLW supernatants, on the other hand, are high ionic-strength solutions composed principally of sodium salts of oxoanions (such as nitrate, nitrite, sulfate, carbonate, aluminate, and phosphate), as well as other inorganic and organic constituents from fuel reprocessing. Minimization of HLW supernatant volume is achieved by evaporating the liquid and cooling the concentrated supernatant to produce crystalline salts referred to as saltcake. Historically, organic-based antifoaming agents were used during evaporation in the LWS evaporators and in the DWPF, although their use in the evaporators has been discontinued.

Mercury reactions in the complex, alkaline chemical environment of HLW have resulted in the presence or formation of solid phases, liquid (elemental) mercury, and dissolved aqueous species. Inorganic mercury species present in HLW include elemental mercury, mercury oxides and hydroxides, and ionic mercury and complexes. The recent data indicate that some HLW tanks also contain significant levels of organomercury, predominantly methylmercury cation. Organic mercury is the predominant form in Tank 50.

The presence of organomercury species in the system reduces the effectiveness of the mercury removal operations built into the existing flowsheet. As a result, mercury concentrations in the LWS are increasing as the waste sludge is processed into glass at the DWPF. This directly affects the composition of salt batches, which were expected to contain only low levels of mercury (mostly soluble mercury); the concentration of mercury in the salt batches has increased significantly. Furthermore, the data suggest that organomercury species are more leachable than inorganic mercury species are, potentially altering the effectiveness of mercury immobilization in saltstone. Mercury levels in the LWS are projected to continue to increase because of the processing of sludges that originated from operations at SRS's H-Canyon facility, where larger quantities of mercury were used. The complex and dynamic chemistry of tank waste, the limited information on mercury speciation and transformation in this waste, and the rigorous regulatory and schedule requirements for waste processing pose significant challenges for SRS.

Because more mercury than expected is being collected in the LWS evaporator system, and because higher than expected levels of MeHg were discovered in the Tank 50 feed to saltstone in 2014–2015, DOE asked Savannah River Remediation (SRR) to evaluate the movement, monitoring, and collection of mercury through the entire LWS in an integrated, systematic manner (Folk 2015). As part of this effort, mercury speciation activities were performed on the various process streams that feed into Tank 50. Additional mercury speciation activities were performed around the DWPF Chemical Processing Cell (CPC), the Modular Caustic Side Solvent Extraction Unit (MCU), and the 2H and 3H evaporators to understand mercury processing behavior (Jain et al. 2015). Two system engineering evaluations (SEEs) were also performed for DWPF and tank farm systems (Winship et al. 2015a, 2015b).

2. Approach

A team organized by EM assessed mercury challenges across the DOE complex and developed a plan to identify mercury-related research and technology development to support resolution of key technical uncertainties. These uncertainties are related to remediation of Y-12, environmental restoration of the EFPC watershed, and operational interferences caused by mercury in liquid radioactive waste processing systems at SRS. A workshop on September 1, 2015, examined mercury contamination from a complex-wide perspective and built upon existing site strategies to help EM meet its operational and regulatory objectives more safely, economically, and efficiently. Participating experts from DOE sites, national laboratories, and outside entities (such as DuPont's South River Science Team, the US Army Corps of Engineers, the National Institute of Standards and Technology [NIST], and academic institutions) explored a variety of crosscutting topics and shared technical details to improve knowledge and control of mercury in complex systems. The workshop discourse and subsequent conversations and visits with additional mercury researchers inform this mercury management plan, whose purpose is to guide EM investments over the next 2–5 years.

The challenges associated with mercury remediation at the ORR and SRS differ not only with respect to prevailing mercury concentrations and dominant chemical forms, but also the status of key remediation planning documents. The Oak Ridge Office of Environmental Management (OREM), on the other hand, has been addressing mercury contamination for decades. Consequently, Oak Ridge has a history of conceptual site models for mercury (most recently, Peterson et al. 2011), a detailed mercury remediation strategy (DOE 2013), and mercury technology development plans (DOE 2014, Peterson et al. 2015). This document presents recommendations for the ORR and SRS in two sections, the former in the context of OREM's current technical approach.

3. OREM'S 2014 Technology Development Plan

OREM's mercury technology development plan identified technology needs linked to the remediation objectives in its "Strategic Plan for Mercury Remediation at the Y-12 National Security Complex" (DOE 2014). The technology development plan sought to

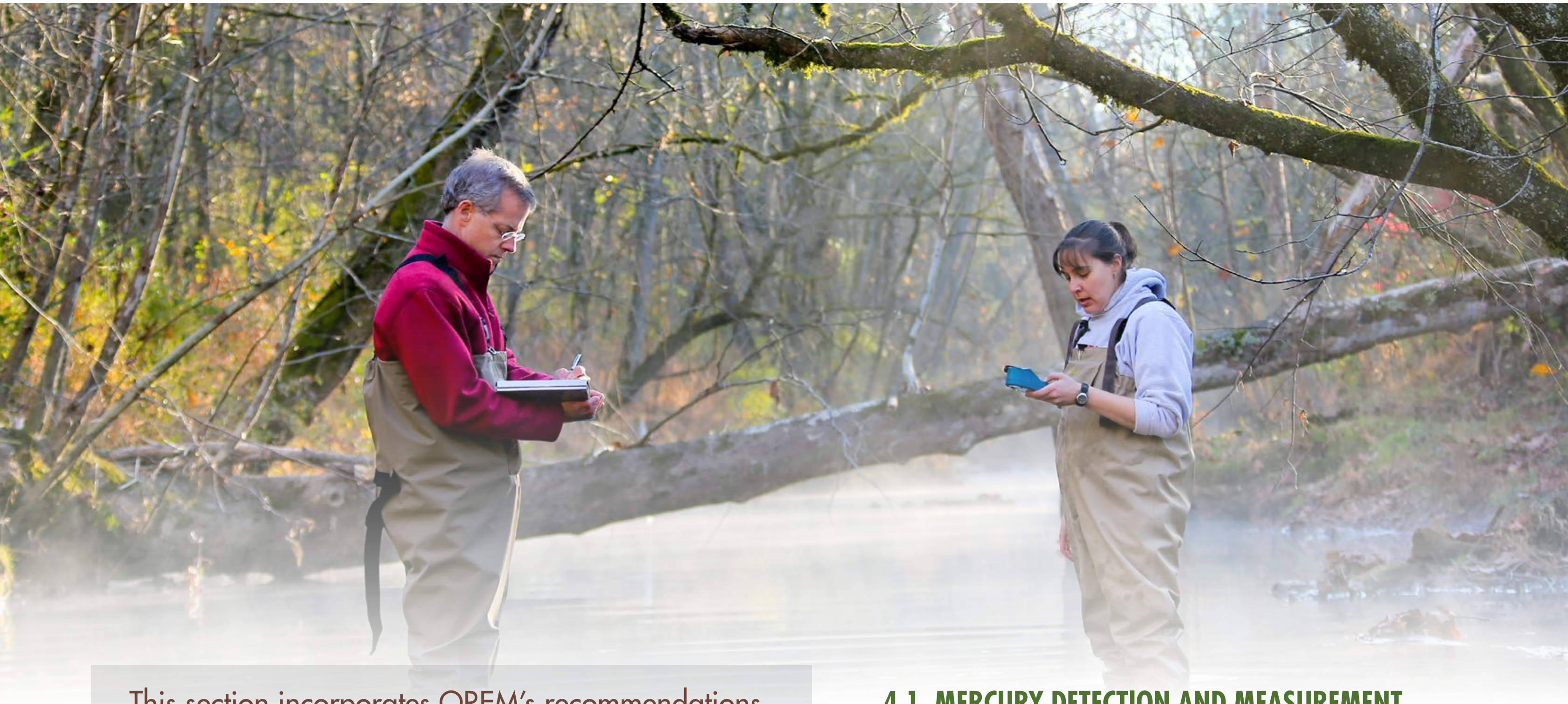
- identify key technology needs for mercury remediation,
- select promising technologies and technical approaches for meeting key needs and assess the readiness of each,
- recommend technology development activities to evaluate and refine the selected technologies and approaches, and
- propose a sequence and preliminary schedule for the recommendations and provide a basis for prioritizing technology development activities.

OREM considered a TD portfolio that encompassed mercury detection and measurement, Y-12 site cleanup, and EFPC in-stream remediation. Technologies and technical processes were evaluated with respect to need, maturity, current usage, and investment recommendations. Table 1 summarizes the results of this evaluation, which identifies the technology categories that OREM is funding or intends to fund. OREM expressed interest in tracking future developments in nearly all of these technology areas, regardless of whether it intends to commit its own TD funding.

Table 1. Summary of Oak Ridge Office of Environmental Management's (OREM's) 2014 technology assessment

	Technology development (TD) needed	OREM TD funding recommended? (✓or no)	Mature technologies
Mercury detection and measurement	Mercury sensor for water analysis	No	Soil gas measurements
	Remote sensing of mercury in equipment, walls, floors	No	Soil mercury probe
			Rapid field analysis of soil, sediment, solid waste
Y-12 National Security Complex site cleanup	Material/debris decontamination	✓	Predemolition
	Material/debris encapsulation	✓	Demolition
	Thermal desorption, in situ	✓	Thermal desorption, ex situ
	Soil washing/mercury extraction, in situ	No	Soil washing, ex situ (immature technology, unsuited for Y-12 application)
	Soil stabilization, in situ	✓	Soil stabilization, ex situ
	Waste disposal	✓	
East Fork Poplar Creek remediation	In-stream soil/sediment source zone stabilization and isolation	✓	
	In-stream water chemistry manipulation	✓	
	In-stream food chain modification	✓	

4. Research and Technology Development Areas for Oak Ridge



This section incorporates OREM's recommendations into a broader set of EM-recommended research and TD activities. It highlights the complementary nature of multiple DOE efforts contributing to mercury research, including OREM-supported programs, EM Headquarters' Applied Field Research Initiative for Remediation of Mercury and Industrial Contaminants, and the Office of Science's Mercury Science Focus Area (SFA). The TD categories include Mercury Detection and Measurement, Y-12 Site Cleanup, EFPC In-stream TD, and Modeling.

4.1 MERCURY DETECTION AND MEASUREMENT

Rapid field analysis in water, soil, sediment, and solid waste. Among the immature technologies OREM identified as necessary, but did not recommend for funding itself, was instrumentation for mercury detection in water. OREM noted that field-deployable instruments that can achieve part-per-trillion level detection limits would be extremely useful, although they are not currently available. A number of entities are conducting development work in this area, including a team funded through the Small Business Innovation Research (SBIR) program. The US Army Corps of Engineers (USACE) also has considerable experience developing rugged sensors and analytical instrumentation for field applications (e.g., at forward operating bases). Continued discussions between EM and USACE are recommended to determine whether a partnership in the area of rapid, highly sensitive mercury detection in water would be beneficial. OREM also surveyed the state of technology for rapid field analysis (i.e., for soil, sediment, and solid waste) and found it to be mature, citing examples of regulator-approved full-scale application of x-ray fluorescence systems and portable atomic absorption instruments (DOE 2014). OREM did not recommend additional TD investments. However, the uniqueness and enormity of OREM's future D&D of mercury-use buildings and infrastructure likely would benefit from tailored screening tools that allow decisions to be made quickly and confidently in the field in support of D&D and remediation activities, particularly in the face of unforeseen obstacles or concerns.

Mercury isotope analysis. EM and national laboratory representatives held a preliminary discussion with mercury subject matter experts from NIST on September 23, 2015, to learn about NIST's capabilities in mercury analysis. NIST is a scientific leader in using isotopic analysis and isotope fractionation measurements to elucidate mercury transformation processes and sources and to support environmental compliance. Additional discussions with NIST are recommended to determine whether a partnership in this area would be beneficial.

Mercury detection in soil gas and soil. From 2009 to 2014, EM Headquarters and OREM supported the development of methods for detecting elemental mercury in soil gas and soil, resulting in successful technology demonstrations at Y-12. Shallow soil gas surveys developed and conducted by Oak Ridge National Laboratory (ORNL) were used to locate and delineate subsurface sources of elemental mercury at Y-12 (Watson et al. 2014). A cone penetrometer-deployed membrane interface probe (MIP), developed from commercially available technology by Savannah River National Laboratory (SRNL), also was tested successfully at Y-12 by SRNL and ORNL. The heated MIP desorbs and volatilizes elemental mercury from the solid phase (Jackson et al. 2013). Both technologies are available to OREM and its contractors and can be used to delineate mercury source zones and reduce uncertainty in estimates of mercury-contaminated debris that will require treatment and disposal. Given the successful demonstration of these applications at field scale, additional TD funding in this area is not recommended. On the other hand, remote detection of elemental mercury in the subsurface using geophysical techniques, particularly in inaccessible locations, has not been pursued and may be a worthwhile topic for applied research at ORR.

Remote sensing of mercury in equipment, walls, and floors. Remote sensing and quantification of mercury in infrastructure has potential applicability for D&D of former mercury use buildings at Y-12. However, OREM noted the lack of literature or ongoing research on this topic and recommended monitoring developments and funding field trials if they become feasible. This plan additionally recommends that EM's Robotics Initiative be followed for potential partnership and development opportunities in remote sensing.

4.2 Y-12 SITE CLEANUP

OREM's 2013 Mercury Remediation Strategy assumes that most of the low-level and mixed (low-level and hazardous) waste from Y-12 D&D activities will be disposed of at the on-site Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) facility, the Environmental Management Waste Management Facility (EMWMF), provided waste acceptance criteria (WAC) are met. The EMWMF is projected to reach capacity in fiscal years 2020–21, after which wastes will be disposed of in a future CERCLA facility. WACs (concentrations of mercury and other contaminants, debris size, and waste forms) and other characteristics of this future landfill have not yet been established by OREM and its regulators.

Handling and disposing of D&D materials as nonhazardous waste is often preferred to reduce costs and consume less space in CERCLA facilities. Nonhazardous, nonradioactive waste generated during Y-12 D&D and remediation activities will be disposed of at ORR industrial landfills, which should have sufficient capacity for Y-12 cleanup efforts. ORR landfills are OREM's preferred disposal pathway for non-LLW mercury-contaminated wastes (debris and soil) that have been treated to meet land disposal restrictions and the landfills' WAC.

Predemolition and demolition. Predemolition includes contaminant characterization, identification and removal of hazardous materials, and targeted decontamination or stabilization of materials. OREM recently assessed demolition practices for mercury-contaminated infrastructure (e.g., in the chloralkali industry) and anticipates that its demolition of mercury-contaminated facilities will be conducted appropriately using conventional methods. Decommissioning experience in the chloralkali industry has shown that volatile elemental mercury permeates many types of material, from steel to concrete. Thus, segregation and disposal of noncontaminated materials will depend on the availability of mercury detection methods that are demonstrably rapid and field-applicable and that produce results commensurate with the Toxicity Characteristic Leaching Procedure (TCLP) for distinguishing hazardous waste.

Material/debris decontamination. Decontamination of D&D debris permits handling and disposal of materials as non-hazardous waste, reducing the capacity consumed in CERCLA disposal cells. Rigorous cost-benefit analysis can show whether decontamination offers economic and worker safety advantages compared with hazardous waste disposal, particularly at sites with existing CERCLA cell space. Such an analysis is recommended for the ORR to assess the need for decontamination TD. Decontamination methods vary widely and include, for example, strippable coatings, abrasives, and thermal and chemical technologies. OREM recently sponsored a review of mercury decontamination methods, and OREM's contractor, URS | CH2M Oak Ridge LLC (UCOR), stated at EM's mercury workshop on September 1, 2015, that new field-based technologies would be needed to remove mercury more effectively both surficially and at depth from a variety of materials, including porous materials (concrete, transite), nonporous nonmetal materials, steel, and other metals. Ideally, removal would achieve the mercury land disposal restriction concentration of 0.2 mg/L in TCLP tests. EM Headquarters is funding a project through the SBIR program on strippable coatings for removing mercury and other contaminants of concern. UCOR has proposed to use the West COLEX area of the Alpha 4 building at Y-12 as a site to evaluate elemental mercury removal from equipment and building structures under realistic working conditions and for the evaluation of sampling and characterization technologies.

Material and debris encapsulation/waste disposal. Encapsulation of debris from D&D activities allows for safe disposal of contaminated materials and mitigates dust and vapors during handling. OREM cited evaluation of in-cell macroencapsulation for disposal of mercury-contaminated debris as an Oak Ridge need in its 2014 TD plan and during the mercury meeting at EM Headquarters on September 1, 2015. OREM plans to support a review of available encapsulation technologies for large quantities of D&D materials and to perform encapsulation tests at the West COLEX area of Y-12. In-cell macroencapsulation should be evaluated as a TD effort to support the disposal of mercury-contaminated materials. This should include formulation and testing of new grout mixtures for stabilizing mercury-bearing material. These activities may benefit from collaboration with USACE.

Thermal desorption. Ex situ thermal desorption is the US Environmental Protection Agency's (EPA's) preferred or mandated treatment technology for mercury at TCLP levels greater than 260 parts per million. This mature technology is thought to be inappropriate for large-scale application at Y-12 because of its expense and licensing requirements. However, France-based AREVA recently completed removal of mercury in soil at a decommissioned lithium production facility in Spain using thermal desorption combined with other processing methods. It is recommended that OREM consult with AREVA regarding its recent implementation of thermal desorption. A related immature technology, in situ thermal desorption combined with soil vapor extraction, may have limited application within Y-12. OREM recommended that related technology development be included in its program.

Ex situ soil washing. This technology was determined to be inappropriate for ORR waste types. Technology development is not recommended.

Ex situ soil stabilization. This technology was deemed by OREM to be mature. Two vendors and Brookhaven National Laboratory tested three different stabilization approaches using mercury-spiked Y-12 soils in 2012. All three met the TCLP target for mercury. OREM did not recommend further technology development.

In situ soil washing or mercury extraction. In situ soil washing is an immature technology with technical considerations that likely preclude its field-scale use at Y-12. Mercury sulfide found in contaminated Y-12 soil has low solubility and would require the use of strong lixiviants for in situ extraction. Uncontrolled flushing or incomplete recovery of mobilized mercury in the heterogeneous subsurface could increase rather than mitigate mercury transport. This technology is therefore not recommended for future TD funding.

In situ soil stabilization. If successfully immobilized in situ, mercury is not subject to land disposal restrictions, thus reducing the need for soil excavation, ex situ treatment, and disposal in landfills. Given the significant potential cost savings offered by in situ stabilization, OREM identified TD support in this area as key. Past research efforts reported in the literature focused on immobilization amendments such as iron sulfide nanoparticles, elemental sulfur, or heated sulfur vapor. EM Headquarters is currently funding ORNL's development, testing, and upscaling of calcium polysulfide-based in situ stabilization methods for mercury-contaminated soil. This effort is recommended for continuation in fiscal year 2017. Future work must address the presence of commingled mercury species (elemental, ionic, and organic-bound) and effective subsurface delivery methods to ensure that amendments access and react completely with mercury contamination. Testing and verification of the long-term stability of resulting in situ waste forms also will be required; this ties into the assessment of appropriate methods of leachability testing as described in the "Recommendations" section under "Crosscutting Topics."

4.3 EAST FORK POPLAR CREEK REMEDIATION

The in-stream remediation approaches identified below aid in avoiding large-scale excavation of stream sediments and contaminated floodplain soils, which would be costly, environmentally disruptive, and possibly ineffective in meeting remediation objectives. Upper EFPC (UEFPC) is defined as the 2-km stretch of the creek that originates at Y-12 and ends at Station 17, a monitoring station at the ORR boundary. Lower EFPC (LEFPC) is the stretch of creek extending for approximately 23 km downstream of Station 17. LEFPC flows outside of the ORR boundary for about 15 km and passes through the city of Oak Ridge before reentering the ORR.

Soil/sediment source zone stabilization and isolation. Erosion, scouring, and other disruptions to the floodplains, banks, and sediments of UEFPC and LEFPC contribute to the elevated mercury concentrations found in stream water and biota. Cost-effective methods to stabilize contaminated stream banks and beds are desirable to decrease mercury flux into the waterway. OREM and its collaborators have looked to the analogous South River system in southwest Virginia for examples of research and remediation approaches that may have application at the ORR. DuPont used mercury at its rayon production facility in Waynesboro, Virginia, from 1929 to 1950. The company discovered mercury in soil at the site in 1976 and shortly thereafter began examining mercury impacts to nearby river systems. Fish of the South River, South Fork Shenandoah River, and part of the Shenandoah River continue to exhibit elevated mercury levels, much as they do at the ORR.

DuPont established the South River Science Team (http://southriverscienceteam.org/) in 2001 with partners in local, state, and federal governments; academic institutions; and stakeholder organizations to elucidate mercury's persistence in biota and to develop remediation approaches for this ecosystem. The team's work has been documented in more than 100 research publications. OREM and ORNL are actively leveraging the team's research and TD outcomes to improve knowledge of and environmental management for the EFPC watershed.

The South River Science Team identified four mechanisms responsible for mercury's persistence in South River fish:

- Continued small mercury releases from the former DuPont facility
- Erosion of legacy mercury from riverbanks into the river
- Mercury flux from deep riverbed sediment into the overlying water column
- Rates of fresh sediment deposition that are insufficient to bury legacy mercury and thus reduce exposure

DuPont has attempted to address the last three phenomena by using bank stabilization and sediment amendments along sections of the South River to limit erosion and mercury flux. OREM has recommended similar approaches and complementary technology development for the ORR because effective isolation or in situ treatment strategies can offer major cost benefits over baseline excavation and disposal options. Research and TD should, for example, address the long-term effectiveness of sediment amendments; develop and demonstrate new materials for in situ reactive caps, liners, mats, and sorbents; and improve understanding of the spatial and temporal variability of stream erosion (including during storm events) and groundwater seeps and their associated mercury releases.

Water chemistry manipulation. The headwaters of UEFPC are located at Outfall 200, where cooling water originating from Y-12 dominates creek influent during dry weather. Cooling water discharges contain the dechlorination agent bisulfite as well as corrosion inhibitors. Research is needed to understand any impacts these additives have on mercury methylation in the creek and whether other water additives could be used safely to mitigate mercury methylation and bioaccumulation. OREM-supported water chemistry manipulation research will be conducted under realistic field conditions at the planned LEFPC Field Research Station, a test bed site. Complementary research is being conducted through the Mercury SFA to identify natural biogeochemical factors that affect mercury methylation in EFPC.

Food chain modification. Mercury methylation and bioaccumulation in EFPC are complex and depend on physical, chemical, and biological processes as well as on the total quantity of mercury present in the stream. OREM currently is using its own technology development funds to support investigation and implementation of ecosystem management actions that reduce mercury bioaccumulation or physically remove mercury. Proposed actions include (1) replacing current fish populations with species that bioaccumulate mercury to a lesser extent and (2) cultivating and harvesting mussels that consume methylmercury-accumulating periphyton to reduce mercury that is bioavailable to fish. These activities would constitute only one aspect of OREM's "adaptive management" approach to mercury remediation and would require careful monitoring to establish their overall contribution to mercury mitigation in LEFPC. Collaboration with USACE may be beneficial in this area.

4.4 MODELING

Conceptual models or industrial flowsheets enable consolidation of complex data and knowledge of system behavior into structured, accessible forms that highlight key processes and relationships. Such models should be treated as dynamic and should be updated or expanded as new information becomes available from research advancements and data collected during system operation, testing, characterization, and monitoring. Comprehensive conceptual models can support the development of powerful and intuitive insights useful for informing critical decisions. They also can guide research direction and the development and application of predictive numerical models. OREM has used such models to represent mercury-contaminated Oak Ridge facilities and source areas, as well as downstream impacts, for many years (Peterson et al. 2011).

OREM's models are supported by its investigations of the relative contributions of mercury from ongoing facility discharges, contaminated streambank soil and sediment, floodplain surface soils, and other sources. A recently developed conceptual model was used to identify major mercury sources, transport pathways, and flux at the Y-12 facility and UEFPC (Peterson et al. 2011). OREM used this model to inform its 2013 mercury remediation strategy and 2014 technology development plans. Concurrently over 2013–2016, a CERCLA Five Year Review (FYR) Action Plan study was conducted to assess the role of downstream mercury sources and the entire hydrologic system. As part of that study, conceptual modeling was used to define field, laboratory, and quantitative modeling needs in the LEFPC system.

During fiscal year 2016, the conceptual model for LEFPC will be refined further by the OREM FYR project and EM's Applied Field Research Initiative for the Remediation of Mercury and Industrial Contaminants, with the goal of incorporating new data from compliance monitoring efforts, mercury technology development studies, and other fundamental and applied research. Conceptual models will need to be updated continually as knowledge of key mercury fate and transport processes changes.

Robust numerical models also are essential to represent, select, and optimize remediation actions and to identify expected outcomes. This is particularly important for OREM's adaptive management approach to mercury remediation, which depends on evaluating environmental responses to sequential actions. Recently a greater emphasis has been placed on creating a preliminary semiquantitative model of mercury uptake through the aquatic food chain culminating in fish tissue. A multicompartmental watershed scale model of mercury transport and bioaccumulation was developed for the LEFPC watershed as part of the FYR study. Critical modeling components included surface water flow, mercury transport (e.g., sedimentation, storm flux, groundwater–surface water interactions); reactivity (e.g., methylation); and trophic transfer. Next steps for the OREM model will improve representations of flow and sediment transport in the EFPC floodway, which to date have been hampered by the lack of high accuracy terrain and channel morphology models. Recently the US Geological Survey acquired LIDAR data for the ORR as part of a regional mapping program. When the processed data from that mapping become available, it may be feasible to create a more quantitative flow and sediment transport module for LEFPC.

OREM recognizes the benefit of continuing tandem support for its applied site model and the basic research model being developed by the Mercury SFA program. During the next 3 years, SFA model development will center on obtaining a detailed mechanistic, biogeochemical understanding of mercury stream processes. This "bottom-up" approach, which in the future could be used in conjunction with other models including OREM decision-support modeling tools (e.g., the FYR model), can aid OREM in gaining a multiscale understanding of mercury fate and transport.

5. Research and Technology Development Areas for the Savannah River Site

Inadequate understanding of mercury speciation in the SRS liquid waste system poses a significant operational challenge to effective and efficient mercury management at SRS. It is believed that organomercury reduces the effectiveness of the mercury removal system in the DWPF, limits the quantity of mercury removed in the LWS system evaporators, and increases the leachability of mercury from saltstone. Focused basic and applied science investments are needed to understand solution and vapor phase mercury chemistry and to develop the technical basis for practical and cost-effective strategies to address mercury in the LWS sustainably. Target strategies should provide quantifiable and controlled mercury removal from the LWS; generate acceptable mercury waste forms that do not adversely affect the surrounding environment; and support timely processing of HLW into glass and cementitious waste forms.

The data that signaled the urgency and significance of the mercury challenge at SRS were generated during the past few years, particularly in 2015 when additional mercury speciation activities were initiated around specific flowsheet operations (e.g., DWPF CPC sludge preparation unit operations, MCU processing, salt batch feed preparation, and 2H/3H evaporator operations) to understand mercury behavior (Jain et al. 2015). DOE, along with its operating contractor at SRS, SRR, and its technical support organization, SRNL, are responding to the emerging information with a number of strategic planning activities. Along with mercury speciation around the different processes, two SEEs were performed for DWPF (Winship et al. 2015b) and for the remainder of the LWS for mercury removal or mitigation (Winship et al. 2015a). The SEEs were established to elicit creative ideas from a diverse group of experts and to identify potential process modifications and solutions.

Key emerging themes from these reviews will form the basis of the SRS mercury strategic plan.

Both SEE teams investigated cost-effective opportunities in three areas: removal of mercury (any form) from the liquid waste system at a rate that would maintain or reduce mercury concentrations in the LWS, alteration of mercury speciation to control its behavior, and improvement in the ability of saltstone to sequester mercury and limit the potential for leaching. The teams identified target tanks within the LWS/DWPF and potentially applicable technologies. They also considered the quantity and characteristics of mercury-containing wastes, taking into account waste streams that are protective of the environment and those that are already permitted with existing disposal paths. The results will assist DOE and SRR in planning and executing the processing of HLW into stable and environmentally protective waste forms.

The emerging plan to address mercury in the LWS includes currently funded or future baseline operational scope, near-term to midterm applied science activities, and relevant basic science topics, as shown in Table 2. Basic science needs include understanding the mechanism and kinetics of the transformation of inorganic mercury species into organomercury compounds, conversion of organomercury compounds into inorganic mercury, and vapor phase mercury chemistry as it relates to corrosion of tank farm and processing facilities. The proposed applied science activities highlighted in the table are described below.

The results of the LWS evaluation were documented recently (Winship et al. 2015). Twenty potential options to remove or mitigate mercury in the LWS were identified. The 20 options subsequently were reduced to 13 through a screening process. Based on evaluation of the 13 options, the team made three recommendations: (1) deploy methods to remove elemental mercury mechanically from process tanks in the LWS, (2) deploy technology to enhance removal of ionic mercury in the H-area evaporators by the addition of a reducing agent to convert ionic mercury to elemental mercury, and (3) pursue conversion of the organomercury cation (HgR^+) in Tank 50 (feed to saltstone) to ionic and elemental mercury using ultraviolet light and maturing the technology for deployment. Parallel tests were recommended to enhance retention of mercury in saltstone. These recommendations align very closely with the strategic components listed in Table 2 under the heading "applied science and technology development."

More complete descriptions of the applied science and technology components are provided below.

Develop a process to convert organomercury to inorganic mercury. This work would focus initially on the chemical conditions of Tank 50, the low-activity waste feed to the saltstone process. Converting organomercury to inorganic species in this low-activity solution would reduce mercury leachability from the resulting saltstone grout. Sampling results indicate that methyl- and ethylmercury are the main mercury species that leach from the saltstone grout matrix. Previous testing (Langton 1988) showed acceptable performance of grout materials containing nearly 500 mg/L inorganic mercury, such as mercuric ion. Studies would examine potential technologies to oxidize the organic fragment of the organomercury species (e.g., ultraviolet-C photoreactors) to mercuric ions. One or two likely technologies would be selected for initial testing with the goal of selecting one technology for pilot-scale development and demonstration. The technology development activities for Tank 50, if successful, could be considered for other locations in the LWS system (e.g., in the tanks feeding the evaporators) to maximize mercury removal by the evaporators.

Table 2. Key components of the strategic plan for mercury in the Savannah River Site Liquid Waste System (LWS)

Funded baseline operations activities	• Develop standards, practices, and capabilities for analysis of mercury species in high level waste (HLW) liquids and sludges • Conduct detailed characterization and monitoring of mercury in the LWS • Implement technical modifications to mercury recovery system in the Defense Waste Processing Facility • Develop organic mercury waste acceptance criteria for saltstone grout
High-priority future operations activities	• Develop improved mercury removal or mercury control flowsheet based on applied science results. Install required systems and infrastructure
Applied science and technology development	• Develop process to convert organomercury to inorganic ionic mercury (e.g., ozone or ultraviolet-C photoreactor) • Develop process that reduces inorganic ionic mercury to elemental mercury • Develop mercury "getters" as additives for grout formulations • Develop mercury sorbents focused on removal of organomercury from alkaline waste solutions • Elucidate mercury speciation in sludge solids
Basic science topics	• Understand chemical speciation and transformation of mercury (mechanisms and kinetics) in complex, high-ionic-strength alkaline solutions • Identify vapor phase mercury chemistry (reactions and species) under appropriate HLW tank conditions • Elucidate reaction mechanisms during conversion of organomercury to inorganic mercury (photoreactions, ozone reactions, free radicals, etc.) • Develop information on critical mercury chemistry in HLW (such as organomercury solubility in various HLW matrices)

Develop a process that converts inorganic mercury to elemental mercury. Sampling results indicate that 2H/3H evaporator feed/drop tanks contain substantial quantities of inorganic mercury. Conversion of this ionic species to elemental mercury would improve the performance of the evaporator's built-in mercury removal system. Mercury would be removed in flasks from the LWS as liquid mercury, a currently recognized waste form. Studies examining chemistries or technical approaches to convert ionic mercury species to elemental mercury in alkaline waste liquids would enable selection of one or two chemical additives (such as $SnCl_2$ or borates). An initial round of testing would then be conducted with the goal of selecting one additive for development and demonstration.

Develop mercury "getters" as additives for grout formulations. Organomercury species are far more soluble than ionic mercury species. The use of mercury getters should be explored to enhance organomercury species retention in the saltstone grout matrix. This could offer an alternative or supplementary technology to improve saltstone grout performance without chemically converting organomercury to inorganic mercury. Candidate additives for improving mercury retention must be tested to ensure no harm to other important properties of grout, such as set time and compressive strength. Once additives are shown to improve mercury retention during TCLP testing, testing with actual Tank 50 waste would be conducted.

Refine previous studies on mercury ion exchange in light of organomercury's presence. Previous studies demonstrated that various sorbents or ion exchangers (e.g., GT-73 resin) are stable in alkaline tank wastes and are effective at removing mercury in the form of mercuric ion from a simulated waste matrix. This task would develop the basic data needed to support the design of a mercury removal system that could be deployable at selected locations in the tank farm. Adsorption isotherms would be developed for mixed organomercury species and bench-top ion exchange column testing. Additionally, testing would be conducted to characterize the hazardousness of spent, loaded resin to aid in determining disposal options. Testing with real waste samples would confirm that the isotherms developed with chemical simulants depict the same or nearly the same performance as tank waste supernatants.

Mercury speciation in sludge. Mercury is believed to be in the form of mercury oxide in sludge; however, it is not known whether all mercury is in this form. Elemental mercury, mercuric sulfide, or other species also may be present, each potentially exhibiting different behavior across the DWPF flowsheet. It is proposed that sludge be sequentially extracted to identify specific mercury species. The extraction of as many as 10 different mercury species would be quantified.

6. Recommendations

EM should create a technical working group to formalize and strengthen the synergies among agencies, organizations, and industries engaged in mercury-related research, TD, and operations. This group would advocate the sharing of knowledge and technical advancements, reach out to subject matter experts, identify opportunities and investments to ensure robust responses to EM's mercury challenges, and offer recommendations to EM's managers and technical advisors as requested. EM's leadership through this group must be visible and proactive.

EM also should track the progress and outcomes of its partnership with the DOE Office of Science to address EM's basic research needs. A report on these needs (DOE 2016) recommended fundamental research focused on contaminant fate and transport in geologic environments, waste stream characterization and separations, non-equilibrium speciation and reactivity in complex radioactive wastes, and mechanisms of material degradation in harsh environments, among other areas. Although mercury is not a target for the suggested research, it is reasonable to anticipate that resulting discoveries may be pertinent to EM's mercury management mission.

Additional site-specific and crosscutting recommendations are given below.

Oak Ridge Reservation. The applied research and technology development activities recommended for the ORR in this report are informed by OREM's mercury remediation strategy (DOE 2013); its mercury TD plan (DOE 2014); and the gaps between the technical requirements of EM's cleanup mission and the capabilities of current commercially available technologies. TD topics cover mercury characterization, Y-12 remediation, and offsite restoration of LEFPC, as discussed below.

Remediation of mercury contamination at Oak Ridge will require a multipronged approach that includes (1) constructing and operating the Outfall 200 Mercury Treatment Facility (MTF), (2) enabling disposal of mercury contaminated debris, (3) treating discrete soil source zones in Y-12, and (4) mitigating residual mercury sources in LEFPC. Regarding the first point, the MTF is not a TD activity but rather is a capital project intended to limit future mercury releases. Concerning the second point, the challenges associated with mercury contaminated debris would benefit from applied research and TD focused on developing robust, easily deployable field instruments as well as macroencapsulation to facilitate on-site disposal of debris; off-site waste disposal would be excessively costly. EM should leverage USACE's expertise in developing tools to facilitate real-time mercury detection and quantification. Regarding the third point, EM's current TD focused on Y-12 in situ chemical treatment/stabilization is intended ultimately to reduce waste volumes requiring disposal and minimize the potential for additional mercury releases caused by excavation. The fourth point is being pursued by OREM's TD program and is key to decreasing methylmercury production and bioaccumulation as well as the risks to ecosystem and human health. OREM also has proposed construction of a small research facility along LEFPC as a test bed for other stream-related TD topics, including manipulation of water chemistry and of prevailing aquatic species to mitigate mercury bioaccumulation. All of these efforts will continue to benefit from engaging outside expertise, such as the South River Science Team and various universities. A number of university collaborations are ongoing through EM's Minority Serving Institutions Partnership Program and the Mercury SFA.

Savannah River Site. Research and TD recommended for Savannah River will improve understanding of mercury chemistry and speciation in the Liquid Waste System and will lead to mercury removal methods that support the site's baseline operations. Treatments that convert organomercury to inorganic mercury, and inorganic mercury to elemental mercury, are needed to reduce mercury leachability in saltstone and to improve mercury removal in the 2H/3H evaporator, respectively. Additionally, sorbents or ion exchangers for removing ionic mercury in the presence of organomercury should be tested for removal efficacy and for the hazardousness of the resulting spent material. Finally, studies elucidating the speciation of mercury in sludge are needed to reduce uncertainties about mercury behavior across the DWPF flowsheet.

Crosscutting topics. Mercury-related interests at the ORR and SRS intersect in two main areas: grout formulation and alternative tests for waste form leachability. TD investments are recommended for both, as noted below.

Development and demonstration of grouts that retain predominant mercury species and maintain waste form integrity over expected concentrations and time are important for sequestering organomercury in saltstone at SRS and for encapsulating mercury-bearing soil and debris for on-site disposal at the ORR. As new grouts are developed and tested, information should be shared between sites. The Mercury Issues Coordination Team already formed by the site contractors at Oak Ridge (UCOR) and Savannah River (SRR) is one mechanism by which lessons and information can be exchanged (Weapons Complex Monitor 2016). EM's Cementitious Barriers Partnership is another.

When TCLP is not a regulatory requirement and does not reflect expected disposal conditions (it was developed for municipal solid waste), it may not provide an appropriate technical foundation for waste acceptance criteria or treatment and disposal evaluation and decision-making. Alternative leaching assessments may be more appropriate for mercury species in saltstone or for macroencapsulated mercury-bearing debris from D&D activities. A review of available leaching protocols and possibly development of new protocols for mercury-contaminated wastes under relevant disposal conditions are recommended.

7. Schedule

	FY 2015	FY 2016	FY 2017	FY 2018	FY 2019	FY 2020	FY 2021	FY 2022	FY 2023	FY 2024	FY 2025	FY 2026	FY 2027–43	DOE funding source
Y-12 National Security Complex cleanup activity timeline														
Y-12 process facility D&D							■	■	■	■	■	■	■	OREM
Y-12 soil remediation												■	■	OREM
Outfall 200 Mercury Treatment Facility design and construction	■	■	■	■	■	■								OREM
Outfall 200 Mercury Treatment Facility operations							■	■	■	■	■	■	■	OREM
Analysis of alternatives for interim remedial action in EFPC							■	■						OREM
EFPC interim remedial action (if determined to be necessary)									■	■	■	■		OREM
EFPC possible long-term remedy													■	OREM
Research and technology development—Oak Ridge														
Mercury detection and measurement														
Mercury detection in water, soil, sediment, and debris (with USACE)			■	■	■									HQ
Mercury isotope analysis (with NIST)			■	■	■									HQ, SC
Remote sensing of mercury in equipment, walls, and floors			■	■	■									HQ
Y-12 remediation														
Predemolition and demolition: Assessment of efficacy of debris sorting to segregate mercury-bearing waste			■	■										OREM
Material/debris decontamination			■	■	■									OREM
Material/debris encapsulation, in-cell macroencapsulation (pilot to engineering scale)		■	■	■	■	■	■							OREM
Development of caps, reactive liners, and chemical amendments for mercury disposal cells		■	■	■										OREM
In situ thermal desorption with soil vapor extraction				■	■	■	■							OREM
In situ soil stabilization (lab to field tests)	■	■	■	■	■	■	■							HQ
Grout formulation for in-cell macroencapsulation—*Pertinent to Savannah River Liquid Waste System (with USACE)*			■	■	■	■								HQ

	FY 2015	FY 2016	FY 2017	FY 2018	FY 2019	FY 2020	FY 2021	FY 2022	FY 2023	FY 2024	FY 2025	FY 2026	FY 2027–43	DOE funding source
Development of leaching test alternatives—*Pertinent to Savannah River Liquid Waste System*			■	■	■									HQ
East Fork Poplar Creek remediation														
Soil/sediment source zone stabilization and isolation	■	■	■	■	■	■	■							OREM
Water chemistry manipulation		■	■	■	■	■	■							OREM
Food chain modification	■	■	■	■	■	■	■							OREM
Modeling														
Refinement of ORR conceptual model for mercury sources, transport, flux		■				■				■				HQ, OREM, SC
Development of site-specific model components for mercury biogeochemistry and multiscale transport	■	■	■	■										SC
Research and technology development—Savannah River														
Develop a process to convert organomercury to inorganic ionic mercury		■	■	■										HQ
Develop a process to convert inorganic ionic mercury to elemental mercury		■	■	■										HQ
Develop mercury getters as additives for grout formulations		■	■	■										HQ
Develop mercury sorbents to remove organomercury from alkaline waste solutions		■	■	■										HQ
Develop methods to measure mercury species in sludge		■	■	■										HQ, SRR
Elucidate the mechanism and kinetics of the transformation of ionic mercury into organomercury compounds in complex waste solutions			■	■	■	■	■							HQ, possibly SC
Elucidate vapor phase reaction chemistry of mercury			■	■	■	■	■							HQ, possibly SC
Elucidate mechanism and kinetics of the conversion of organomercury into inorganic mercury in complex waste solutions			■	■	■	■	■							HQ, possibly SC

Notes: DOE = US Department of Energy; D&D = deactivation and decommissioning; EFPC = East Fork Poplar Creek; FY = fiscal year; HQ = Office of Environmental Management Headquarters; NIST = National Institute of Standards and Technology; OREM = Oak Ridge Office of Environmental Management; SC = US Department of Energy Office of Science; SRR = Savannah River Remediation; USACE = US Army Corps of Engineers; Y-12 = Y-12 National Security Complex.

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APPENDIX A: ENVIRONMENTAL MERCURY BIOGEOCHEMISTRY

Mercury (Hg) is a persistent and chemically complex global pollutant. Because of its unique physicochemical characteristics, mercury is one of the most challenging contaminants in the environment to remediate. The distinctive physicochemical properties of mercury include its liquid state as elemental mercury, Hg(0), at ambient temperature and pressure and its status as one of the few metals that is transported under environmental conditions as a cation, Hg(II), and/or as dissolved or gaseous elemental metal, Hg_{DG}, similar to an organic solvent (Fig. A1). Most importantly, mercury undergoes biogeochemical transformation processes, including aqueous and surface complexation, redox reactions, and atypical methylation reactions, producing the potent neurotoxin methylmercury (Dong et al. 2010, Gu et al. 2011). Mercury exhibits all of the aforementioned characteristics in the heterogeneous, dynamic watershed-scale system of Oak Ridge, which includes the Y-12 National Security Complex boundary and the 23 km of contaminated creek and floodplain downstream.

The high toxicity of methylmercury (MeHg) endangers human health, primarily via fish consumption. Although it is well known that inorganic Hg(II) is transformed into MeHg by natural processes that mostly result from microbial activity in the environment, the environmental drivers for mercury methylation remain poorly understood. Mercury is extremely reactive and readily undergoes chemical, photochemical, and biochemical transformations (He et al. 2014; Morel et al. 1998; Qian et al. 2014; Barkay et al. 2005a, 2005b). As a soft Lewis acid, Hg(II) prefers sulfur atoms (Riccardi et al. 2013a, 2013b), forming strong complexes with both organic thiol groups (e.g., those in dissolved organic matter

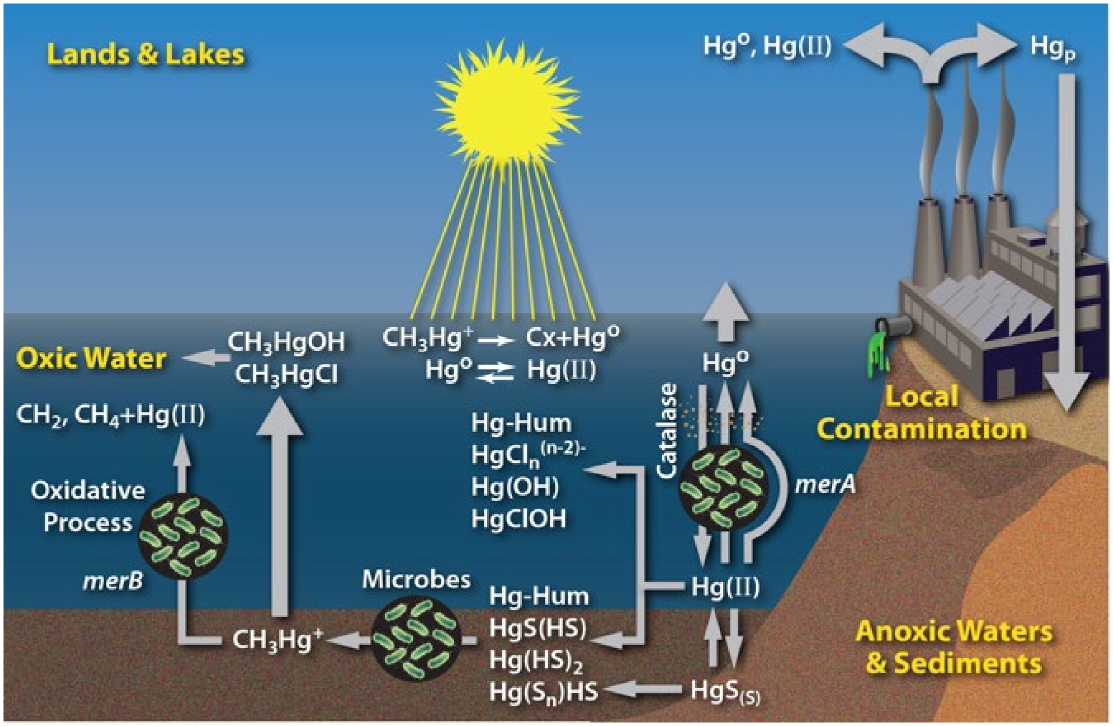

Fig. A1. Mercury sources and biogeochemical cycle in environmental systems. Figure adapted from: Barkay, T., S. M. Miller, and A. O. Summers. 2003. "Bacterial Mercury Resistance from Atoms to Ecosystems." FEMS Microbiol. Rev. 27 (2–3):355–84. doi: 10.1016/S0168-6445(03)00046-9.

[DOM]) and inorganic S(II) ligands (Gu et al. 2011, Dong et al. 2010, Zheng et al. 2012). At the sediment–water interface in streams such as East Fork Poplar Creek (EFPC), chemical and microbiological properties can change significantly, affecting mercury redox transformation and the potential for mercury methylation. These processes are complicated further by the degradation of MeHg (He et al. 2014, Qian et al. 2014), mass transfer, and/or accumulation following downgradient transport along flow paths. As a result, aqueous MeHg concentrations often do not reflect the ecosystem compartments in which the MeHg was produced. The interplay of abiotic mercury reactions that remove or produce mercury species for methylation, the relative rates of methylation and demethylation, and mass transfer all influence MeHg levels in stream systems.

Previous studies have generated extensive data on the relationship between MeHg and dissolved mercury concentrations in lakes, rivers, and water bodies at mining and industrial sites (Brooks and Southworth 2011 and references therein). In general, the total mercury concentration is not a good indicator of MeHg in water, including at EFPC, where the sources of MeHg are not identified clearly. Both field manipulation and laboratory incubation studies suggest that MeHg production is positively linked to certain groups of microorganisms, their activity, and bioavailable Hg(II) (Parks et al. 2013, Gilmour et al. 2013, Hu et al. 2013, Marvin-DiPasquale et al. 2008) as well as to site-specific factors such as hydrology and water chemistry (Hintelmann 2010). For example, recent studies revealed that microorganisms that possess *hgcAB* genes are capable of methylating Hg(II), although their ability to do so can vary widely across microbial groups (Parks et al. 2013, Gilmour et al. 2013). Furthermore, the bioavailability of Hg(II) for uptake and microbial methylation can be affected by many geochemical factors, including suspended particles and water chemistry parameters such as pH, Eh, complexing ligands such as DOM, ionic composition and strength (Gu et al. 2011; Dong et al. 2010; Schaefer et al. 2011; He et al. 2014, 2012; Zheng et al. 2012), and the surface chemistry and biochemistry of microbial cells (Hu et al. 2013; Lin et al. 2014a, 2014b).

Aside from DOM and other geochemical factors, particulate organic matter and minerals also influence mercury partitioning in stream systems (Brooks and Southworth 2011, Gu et al. 2014). Field monitoring and analyses indicate that a large fraction of total mercury is particle-bound. Whether particle-bound mercury is a source for methylation or a sink for dissolved mercury in streams is presently unknown. Furthermore, most studies to date have focused on the chemical or photochemical transformation of mercury and MeHg in homogeneous solutions, whereas reactions on heterogeneous surfaces or suspended particles have been largely overlooked.

Many factors affect mercury speciation in soil/sediment systems, including soil pH, redox potential, soil properties, microbial activity, and the presence of other ligands (Boszke et al. 2003). Mercury species commonly found in contaminated soil and sediment include Hg(0), cinnabar and meta-cinnabar (HgS), mercuric chloride ($HgCl_2$), mercuric oxide (HgO), and methylated compounds (CH_3HgCl and CH_3HgOH) (USEPA 2007). Each species has a different solubility that affects its potential for mercury release. HgS is the least soluble form (4.65×10^{-25} g/L at 25°C), followed by meta-cinnabar (1.04×10^{-24} g/L at 25°C), whereas HgO is one of the most soluble forms (69 g/L at 20°C).

Given the complexities discussed above, cost-effective and sustainable solutions for reducing mercury flux from various primary and secondary contamination sources at Oak Ridge will require focused investments that incorporate fundamental knowledge into applied research to advance EM's capabilities in remediation, characterization, monitoring, and modeling.

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APPENDIX B: MERCURY IN DOE LIQUID WASTE SYSTEMS—OVERVIEW OF RECENT FINDINGS AT THE SAVANNAH RIVER SITE

Mercury in the Savannah River Site (SRS) Liquid Waste System (LWS) originated from decades of radiochemical processing in the "canyon" buildings, where mercury was used to aid reactor fuel dissolution. The resulting mercury is present in a number of chemical forms and is distributed throughout the LWS. The current inventory of mercury in the LWS is approximately 60 metric tons. Mercury has long been a consideration in the LWS, both as a biological hazard and for its impact on processing operations. Occupational exposures and environmental releases to date have been below applicable standards, and waste treatment systems and waste forms have complied with regulatory requirements. Recent data indicate that the mercury removal processes associated with the Defense Waste Processing Facility (DWPF) are underperforming. As a result, a significant fraction of mercury is returned to the LWS as waste is processed into stabilized waste forms such as glass. The net result of recycling mercury while total waste volume is decreasing is an increase in mercury concentrations throughout the LWS. A technical basis for the observed mercury behaviors and trends has been generally identified (complex mercury speciation), along with a number of uncertainties, engineering/process improvement actions, and applied science opportunities.

Figure B1 shows the core functions and objectives of the SRS LWS, DWPF, the Saltstone Production Facility, and the Saltstone Disposal Facility (SDF). The primary mission of these facilities and processes is to convert the legacy high-level radioactive wastes currently being stored in 43[1] waste tanks (each with a capacity of approximately 3.5 million L) into stable and protective waste forms and to safely decommission the tanks. To meet the objectives, the solids (e.g., sludge) and separated radionuclides are vitrified (see [a] in Fig. B1). The resulting glass is sealed in stainless steel canisters that ultimately will contain almost all of the radionuclides from the waste tanks. Contaminated liquids (e.g., salt solutions or "supernates") are concentrated in evaporators, treated to remove radionuclides, and then converted into a solid waste form known as saltstone (see [b] in Fig. B1). Saltstone ultimately will contain <<1% of the radionuclides from the waste tanks. As the waste is processed and waste tanks are emptied, the tanks are cleaned and filled with specialized solid grout mixtures to stabilize the tanks in place and to limit the release of residual

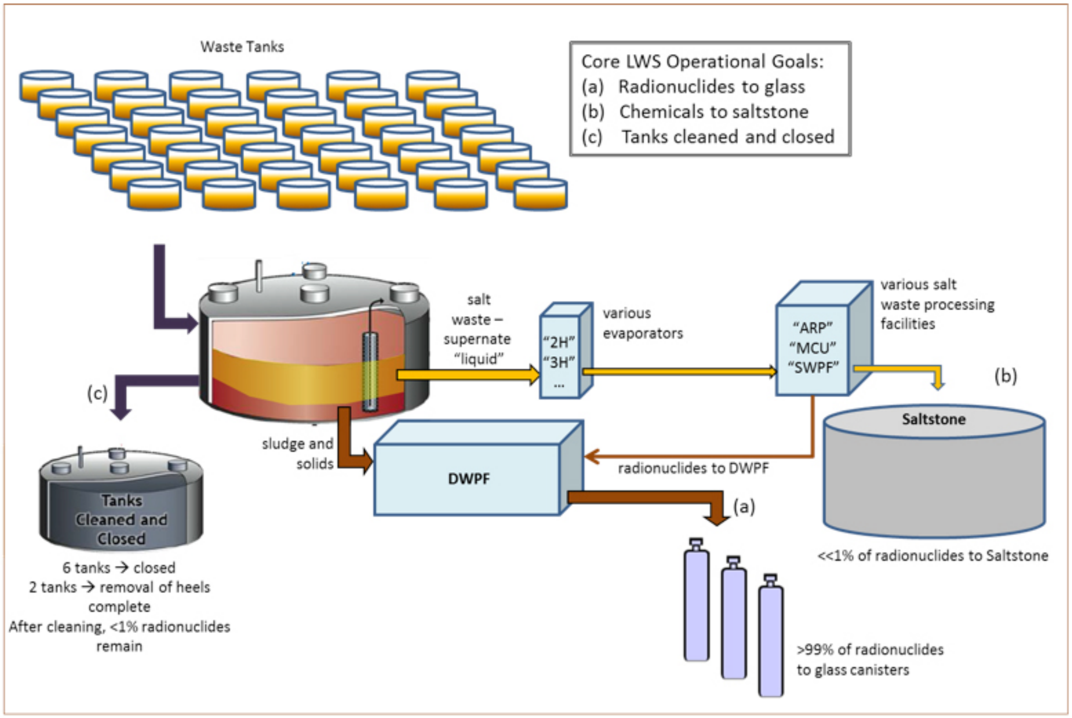

Fig. B1. Simplified depiction of the core functions and processes in the Savannah River Liquid Waste System (LWS), Defense Waste Processing Facility (DWPF), and saltstone systems.

[1] *Originally, the Savannah River Site built and operated 51 waste tanks. As of January 2016, seven of the tanks have been closed, and one tank has been emptied and is being prepared for closure.*

radioactivity (see [c] in Fig. B1). After cleaning and closure, each waste tank will contain <<1% of the original inventory of radionuclides. The operational plan is to continue to treat the waste and clean/close waste tanks until all of the remaining waste tanks have been emptied. Note that Fig. B1 is a highly simplified schematic diagram.

In practice, some of the waste tanks are used to transfer and store liquids as they move from one process to another or to serve as feed and collection tanks for unit operations such as evaporators. The waste chemistry varies somewhat from tank to tank and from area to area (i.e., the wastes in the tanks in F Area are somewhat different from the wastes in the tanks in H Area because of differences in the chemical separation processes). Nonetheless, Fig. B1 provides a synopsis of the core function of the LWS, DWPF, and saltstone facilities toward "closing the circle" on more than a half-century of nuclear materials production at the Savannah River Site.

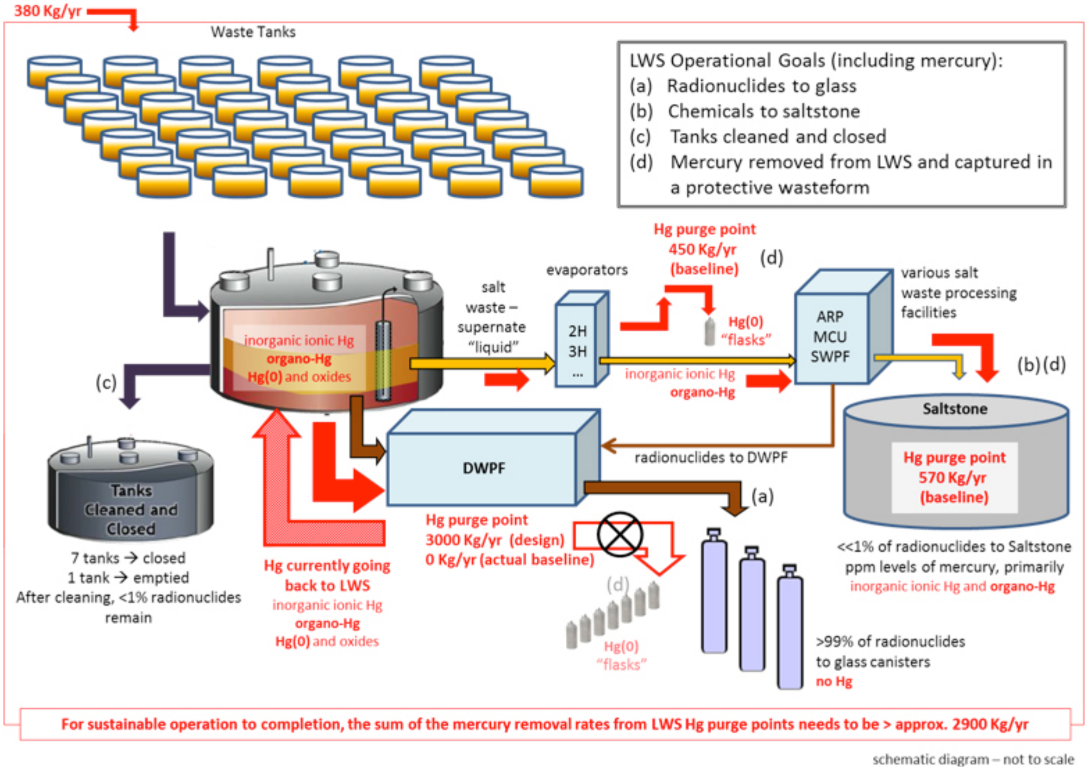

Fig. B2. Simplified depiction of the Savannah River Liquid Waste System (LWS) and Defense Waste Processing Facility (DWPF) showing the general flow of mercury (red) and radionuclides (brown).

Figure B2 augments the diagram of the LWS, DWPF, and saltstone systems to include mercury. This figure summarizes mercury treatment goals, identifies mercury fluxes and speciation, indicates the designed locations for mercury removal (i.e., mercury "purge points"), and recaps the baseline data on how these purge points are performing (see [d] in Fig. B2). Mercury information on this diagram is shown in red. The flux arrows provide a rough idea of how much mercury is moving through the system. The dominant mercury specie(s) are shown in bold in each location. Speciation data, recently generated using emerging analytical methods, indicate that organomercury species are dominant in many locations throughout LWS, DWPF, and saltstone facilities, and the primary organomercury species is methylmercury ($HgCH_3^+$).

The complex chemical compositions in high level waste liquids and sludges and the resulting speciation of mercury affect the performance of the designed mercury purge points. Two of the mercury purge points (the evaporators and saltstone) are removing mercury at the anticipated rates. However, these two purge points remove a relatively small amount of mercury (450 kg/year and 570 kg/year, respectively). As indicated by the largest flux arrows, the primary "designed" mercury purge point is located in the DWPF. This mercury removal system was anticipated to collect approximately 3,000 kg/year, but instead, it removes a minimal amount of mercury, and the bulk of the mercury entering DWPF is "recycled" back to the LWS.

The underperformance of the mercury removal systems in DWPF results in a trend of increasing mercury concentration in the LWS as the total volume of waste is reduced at a rate faster than that of mercury. In response to this emerging information, DOE along with its support contractor and applied research laboratory (Savannah River Remediation and Savannah River National Laboratory) have initiated activities to (1) re-establish the performance of the mercury removal systems in DWPF to the extent practicable, (2) increase the amount of mercury removed in the LWS purge points (e.g., collect more mercury in the evaporators by altering the speciation of the feed liquids), and (3) identify opportunities for additional mercury purge points or protective actions (e.g., altering speciation to limit the release of mercury from saltstone).

The current strategy seeks to ensure that mercury removal from the LWS and DWPF exceeds 2,900 kg/year. The separated/captured mercury needs to be in waste forms that protect people and environment, that are acceptable to regulators and stakeholders, and that have a disposal path. Resolving technical unknowns and uncertainties will play a key role in the success of these planned activities.

In summary, chemical speciation of mercury has emerged as one of the most important factors controlling its distribution in the LWS, DWPF, and SDF. Organic mercury reduces the effectiveness of the baseline mercury removal systems, limits the quantity of mercury removed in LWS system evaporators, and increases the leachability of mercury from saltstone. The data that signaled the urgency and significance of the mercury challenge at SRS were generated during the past few years with recently developed chemical speciation methods. DOE is responding to the data by developing cost-effective actions to (1) remove mercury from the LWS, providing for sustainable processing of the waste through completion of tank emptying and cleaning, and (2) characterize and control mercury speciation to improve system performance. The overarching functional objective of these efforts is to enhance system safety and robustness by providing reliable purge point(s) for mercury from the LWS and by implementing supplemental actions to reduce flowsheet/personnel risks.

ACRONYMS AND ABBREVIATIONS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CPC	Chemical Processing Cell
D&D	deactivation and decommissioning
DOE	US Department of Energy
DOM	dissolved organic matter
DWPF	Defense Waste Processing Facility
EFPC	East Fork Poplar Creek
EM	Office of Environmental Management
EMWMF	Environmental Management Waste Management Facility
EPA	US Environmental Protection Agency
FYR	Five Year Review
Hg	mercury
Hg(0)	elemental mercury
Hg(II)	mercury cation
Hg_{DG}	dissolved, gaseous elemental mercury
HgO	mercuric oxide
HgS	mercuric sulfide (cinnabar and meta-cinnabar)
HLW	high level waste
LEFPC	lower East Fork Poplar Creek
LLW	low-level waste
LWS	Liquid Waste System
MCU	Modular Caustic Side Solvent Extraction Unit
MeHg	methylmercury
MIP	membrane interface probe
MTF	Mercury Treatment Facility
NIST	National Institute of Standards and Technology
OREM	Oak Ridge Office of Environmental Management
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
SBIR	Small Business Innovation Research
SEE	system engineering evaluation

ACRONYMS AND ABBREVIATIONS *(continued)*

SDF	Saltstone Disposal Facility
SFA	Mercury Science Focus Area of the Office of Science
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
TD	technology development
UCOR	URS I CH2M Oak Ridge LLC
UEFPC	upper East Fork Poplar Creek
USACE	US Army Corps of Engineers
WAC	waste acceptance criteria
Y-12	Y-12 National Security Complex

Oak Ridge
National Laboratory