Assessing Potential Impacts of Stannous Chloride Based Mercury Treatment on a Receiving Stream Using Real-World Data from Tims Branch, Savannah River Site

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Synopsis: As part of the efforts to develop and implement a comprehensive mercury mitigation strategy for Oak Ridge, the Department of Energy (DOE) is considering deployment of a stannous chloride based treatment technology to decrease the releases of mercury to East Fork Poplar Creek. Since November 2007, Tims Branch, a stream on the DOE Savannah River Site, has been receiving water treated by a full scale system that uses stannous chloride addition and air stripping. Data on fish, water and sediment from Tims Branch are a unique resource that provides the opportunity to rapidly, efficiently and effectively resolve questions and uncertainties about the potential impacts of such treatment systems and to support future environmental management decision-making.

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Executive Summary

Over the past several decades, Oak Ridge has substantially decreased releases of mercury into the surrounding environment. Currently, Oak Ridge is working with regulators and stakeholders to develop a set of actions to further lower mercury releases and mercury impacts. These actions include: facility decommissioning and source removal, decreasing aqueous mercury discharges, stream-based actions to mitigate impacts from residual mercury in bottom and bank sediments, and potential strategies to minimize mercury methylation (or maximize de-methylation) in the ecosystem. As suggested by this list, the Oak Ridge efforts range from basic science, to applied science, to engineering and operations.

With regard to decreasing aqueous mercury discharges, several strategies are being investigated, including stannous chloride addition and air stripping of outfall 200 and/or traditional mercury removal water treatment (e.g., using resins or carbon) for the highest concentration water sources entering the outfall 200 system. Stannous chloride based water treatment is an extension of the chemistry applied in common analytical methods for mercury in which the mercury is chemically reduced to its elemental form and then stripped from the solution with a gas. Initial testing of stannous chloride addition and air stripping in outfall 200 indicated that the technology may be viable and cost effective. A variety of additional tests and engineering optimization studies have been proposed to confirm these initial findings and to prepare the technology for potential deployment. While the results of pilot tests appear favorable for mitigating mercury inputs to the creek, the impacts of long term addition of inorganic tin to fresh water stream systems have not been studied. ORNL scientists have postulated several uncertainties and potential concerns, specifically: tin methylation, tin mediated mercury methylation, and/or the accumulation of tin in sediments.

We propose resolving these issues by studying the Tims Branch system at the Savannah River Site, a stream analog for Upper East Fork Poplar Creek at Oak Ridge. Tims Branch has been receiving water treated by full scale stannous chloride addition and air stripping since November 2007. Measurement of impacts, or lack of impacts, in Tims Branch would provide an efficient and effective approach to study the hypothesized questions and uncertainties related to this treatment technology. In preparation for this effort, a prospective research team organized the baseline data and identified a series of activities that would resolve the scientific topics to a reasonable level of certainty. Water, sediment and fish monitoring data collected over the last 20 years would be supplemented with new, post stannous chloride addition, data to assess real-world tin impacts in the Tims Branch system. State-of-art analytical methods would be developed and applied to specifically elucidate issues of methylation of tin. The proposed work is a collaborative applied research effort that includes the Savannah River National Laboratory (SRNL), Oak Ridge National Laboratory (ORNL), and the University of Georgia Savannah River Ecology Laboratory (SREL) with participation of a postdoctoral student as well as early career scientists and senior researchers in a variety of disciplines.
Background on Mercury in East Fork Poplar Creek

Between 1953 and 1983, over 100,000 kg of mercury were released to the East Fork Poplar Creek during the operation of the lithium isotope separation processes at the Y-12 Plant. Although the process discharge of high concentrations of mercury from the plant stopped in 1963, mercury inputs continue into EFPC from various point and non-point sources of contamination in the Y-12 complex. In response, Oak Ridge has performed numerous and diverse activities to lower the efflux of mercury into its surrounding environment. These efforts included 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 relative impacts of these remedial actions have varied, but the overall result is a significant decrease in mercury release as indicated by the monitoring of aqueous mercury concentration in EFPC.

In the Upper East Fork Poplar Creek (UEFPC) near the effluent discharge location, early actions taken to lower mercury releases resulted in a clear concomitant decrease of mercury concentration 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 \( \approx 1 \, \mu g/L \) (\( \approx 1000 \, \text{ng/L} \)) to \( \approx 0.5 \, \mu g/L \) (\( \approx 500 \, \text{ng/L} \)) and concentrations in the fish tissue decreased from \( \approx 2 \, \mu g/g \) to \( \approx 0.6 \, \mu g/g \). This trend was significant because it demonstrated clear progress toward lowering mercury concentrations in fish tissue to levels that would be protective of humans consuming the fish (i.e., guidelines for fish tissue concentrations have ranged from about 1 \( \mu g/g \) to 0.3 \( \mu g/g \) during this time period). However, at a sampling location a short distance further downstream 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 \( \approx 1 \, \mu g/L \) (\( \approx 1000 \, \text{ng/L} \)) to \( \approx 0.4 \, \mu g/L \) (\( \approx 400 \, \text{ng/L} \))), but concentrations in the fish remained relatively stable (\( \approx 0.8 \, \mu g/g \)). Subsequent 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 as well as continuing release of mercury from the Y-12 complex and inputs from residual mercury sources remaining in stream and bank sediments (see Looney et al., 2008).
These data suggest that a successful strategy for mitigating the impacts of Oak Ridge mercury on the surrounding environment will include a combination of actions that eliminate/remove remaining source mercury (both onsite and throughout the impacted system), decrease releases of mercury into the surrounding ecosystem, and minimize the transformation processes that methylate mercury (or maximize the processes that de-methylate mercury) in streams, lakes and ponds. The overarching goal of such actions is to lessen eventual mercury uptake and mercury exposure. Oak Ridge is currently working with regulators and stakeholders to define such a comprehensive strategy and set realistic goals that will decrease mercury impacts to levels that are “as low as reasonably achievable” (ALARA). Within this emerging framework, example technologies and activities that are being considered or implemented include: removal of contaminated facilities and excavation (or in situ treatment) of contaminated soil, characterization and cleaning (or removal) of contaminated underground sewer lines, activities to remove or eliminate the impacts of residual mercury sources in stream and bank sediments, and expanded treatment of water discharging to UEFPC. Specific water treatment strategies that Oak Ridge is investigating include technologies to treat the composite discharge entering UEFPC at Outfall 200 (using stannous chloride addition and air stripping), and/or technologies to treat high concentration substreams that contribute a substantial portion of the contamination to Outfall 200 (using traditional mercury treatment technologies such as sorbents). Stannous chloride treatment of water entering EFPC was first proposed by Southworth (1997) and later investigations (Southworth et al. 2009 and 2010) confirmed that the technique is potentially viable for this site.
Background on Mercury Treatment Using Stannous Chloride Addition and Air Stripping

Treating low level mercury contaminated water using tin [stannous, Sn(II)] chloride and air stripping is a straightforward extension of the chemistry embodied in many analytical methods for mercury (e.g., Hatch 1968; EPA 1999). In these methods, stannous chloride is used to reduce inorganic Hg(II) to elemental mercury (Hg(0)), which is volatile and can be removed from water by air-water contact. The volatile Hg(0) is then purged into a detector for analysis. In the lab, a small sparge apparatus is used to strip the mercury. For full-scale treatment, air stripping, water spraying, or sparging are examples of inexpensive air-water contactors for the mercury removal step. Figure 2 is a schematic diagram depicting the simple laboratory and full-scale concept.

Based on the most probable (thermodynamically favored) species in typical outfall and stream water, the overall reaction between stannous chloride and Hg(II) is as follows:

\[
\text{HgCl}_2^0 + \text{Sn}^{+2} + 2\text{H}_2\text{O} \rightarrow \text{Hg}(0) + 2\text{Cl}^- + \text{SnO}_2(s) + 4\text{H}^+
\]

Note that the oxidized tin is predicted to form a relatively stable solid – either the tin(IV) oxide, SnO$_2$(s), or hydroxide, Sn(OH)$_4$(s). Tin in these solid forms would tend to be less available to aquatic biota and less subject to biological transformation (e.g., methylation) than dissolved forms of tin (Hallas and Cooney, 1981).

Figure 2. Schematic diagrams of simple process of mercury removal by means of chemical reduction followed by stripping or sparging in:
(a) laboratory and (b) example full-scale system
When used in analytical methods, the reaction of tin and inorganic mercury is rapid and thermodynamically favored. However, tin-based analytical methods rely on using large excesses of stannous chloride reagent to assure that the reaction is complete. Such high reagent concentrations are incompatible with practical and prudent implementation of this process for large volume water treatment. Research by Southworth et al. (1996, 2009, 2010) suggested that low tin doses (circa 5 times stoichiometry) converted available inorganic mercury to Hg(0) and that the mercury could be sparged. Looney et al. (2003a) and Jackson et al. (2008) generated similar results for groundwater with starting mercury concentrations ranging from approximately 0.15 to 0.25 µg/L (150 to 250 ng/L) and a treated water mercury concentration <0.01 µg/L (<10 ng/L). The data from the various studies indicated that the mercury-tin redox reaction is insensitive to the presence of dissolved oxygen but is sensitive to the presence of strong oxidants such as disinfectants (e.g., chlorine or bromine based biocides). The data also indicated that the mercury-tin redox reaction is relatively specific for Hg(II) and its labile complexes, that the strippability of the resulting Hg(0) is predictable, and that required air-water ratios are favorable (e.g., industry standard air stripper systems with air water ratios of 20 to 30 provide a high level of removal). Tin-based chemical reduction and stripping will not remove recalcitrant mercury species such a covalently bonded organic forms of mercury (e.g., methyl mercury), however, and may not effectively remove strongly bound complexes or particulate mercury.

In general, the results of the early studies suggest that effective treatment of mercury may be possible under appropriate conditions (EPA, 2007) using inorganic tin doses that are within safe levels for both ecological and human health (EPA 2002, ATSDR, 2005). Based on these results, a full scale system was implemented to treat low levels of mercury co-contamination present in solvent contaminated groundwater at the Savannah River Site [Jackson et al. (2008)]. In this system, stannous chloride is added to the groundwater prior treatment in the M-1 air stripper. The treated effluent from this system is released to the headwaters of a tributary to Tims Branch.

**Potential Issues and Uncertainties Associated with Mercury Treatment Using Stannous Chloride and Air Stripping**

Three main scientific issues/uncertainties have been identified related to long term full scale application of mercury treatment using stannous chloride and air stripping. All of these manifest in potential stream impacts: 1) tin methylation (resulting in potential for tin uptake in biota and associated impacts), 2) tin mediated mercury methylation (linked with the first issue, resulting in a potential to increase mercury methylation due to reaction of methyl tin with inorganic mercury species), and 3) deposition and accumulation of tin in sediments (resulting in a build up to levels that might impact sediment ecology). These issues/uncertainties are addressed below individually and in combination where appropriate.
**Issue 1:** Tin is subject to microbial methylation in both aerobic and anaerobic sediments and methyltin compounds have been detected in both fresh and salt water (Ridley et al. 1977, Braman and Tompkins 1979, Gilmour et al. 1985, Chen et al. 2007, Jackson et al. 1982, Craig and Rapsomanikis 1985, Amouroux et al. 2000, Rapsomanikis and Weber 1985, and others). While the fraction of tin that was observed to be methylated by natural processes in many environments was relatively low and the conditions that maximize methylation (e.g., high salinity) are not present in typical freshwater streams, the potential exists for tin methylation in freshwater stream and riparian systems receiving long term discharges from outfalls being treated using stannous chloride and air stripping.

**Issue 2:** Abiotic methylation of dissolved Hg(II) by methyltin species was investigated in a series of detailed kinetic studies by Celo et al. 2006. They found monomethyltin to be the most effective reactant, and measured reaction kinetics at 20°C using 0.02 mM (4 mg/L) Hg(II) and 0.2mM monomethyltin (24 mg/L as Sn). The reaction was found to be sensitive to pH (increasing with increasing pH) and chloride concentration. Celo et al. then used the kinetic data from their study to estimate how fast the reaction of monomethyltin with Hg(II) would proceed in seawater at pH 8, 20°C using 1200 ng/L as the concentration of monomethyltin and 1 ng/L as the concentration of dissolved Hg(II). They estimated a reaction half-life under these conditions of 4.5 years.

**Issues 1 & 2:** Gilmour et al. 1985 added high concentrations (10 mg/L) of Sn(IV) to anaerobic estuarine sediments, and found a maximum concentration of 3 ng/g monomethyltin after incubation for 21 days. Virtually all (95%) of the organotin produced in that study was monomethyltin. Note that the concentration of Sn(IV) used in the Gilmour study was three orders of magnitude higher than the maximum concentrations released from stannous chloride based mercury treatment systems and the formation of methyltin would be expected to be facilitated by the salinity of estuarine water. Nonetheless, the demonstration that Sn(IV) is subject to methylation in aquatic sediment systems (e.g., Gilmour et al 1985) combined with studies that demonstrate that methyltin is capable of slow reaction with inorganic mercury to form methyl mercury (e.g., Celo, 2007), generates potential scientific uncertainty. Additional review of the scientific literature, combined with field and supporting laboratory studies, as needed, would assist in determining if the various methyltin concerns are credible or significant.

**Issue 3:** Accumulation of tin in a small-stream sediment ecosystem has the potential to impact the local microbiology and the macro-fauna. Hallas and Cooney (1981) showed that high levels of tin(IV) added to Chesapeake Bay sediment and various culture media decreased the viability of natural microbial populations. Importantly, they also demonstrated that tin(IV) toxicity “depends more on chemical species than on the metal concentration in the medium” and that tin(IV) that precipitated “did not participate in the metal’s toxicity.” Thus, the potential impacts of tin accumulation hinge on the amount of tin that builds up under representative conditions, the chemical form of this tin and whether it is primarily present as an oxide/hydroxide precipitate, physical habitat alterations from long-term application in small stream systems, and the relative levels of added tin versus natural tin in the system.
Description of Tims Branch and Example Baseline Data

As shown in Figure 3, Tims Branch is located in the A/M Areas of the Department of Energy Savannah River Site (SRS). SRS is underlain by the layered and interbedded geology of the Southeastern Coastal Plain. Tims Branch is a second-order stream system flowing into Upper Three Runs, a tributary of the Savannah River. The headwaters of Tims Branch originate from facility outfalls in two areas – the Savannah River National Laboratory (formerly the Savannah River Laboratory) to the north and the fuel and target manufacturing facility (“M Area”) to the west. In the headwater areas, the Tims Branch system is a “losing stream” (its base is above the water table and water seeps into the ground). As Tims Branch flows toward the confluence with Upper Three Runs, the stream elevation intersects the groundwater and it transitions to a “gaining stream” (water flows into the stream from the groundwater).

Key morphological features relevant to potential studies in this stream include: 1) a rip-rap stabilized streambed “drop” followed by a catch basin, drain and overflow weir in the M Area outfall tributary (“outfall ditch”), 2) Steed’s Pond (a former farm pond located approximately midway along Tims Branch which served as a sediment trap in the past but the dam has been removed), and 3) several beaver dams and associated pools.

Discharge of process wastewater from M Area and SRNL resulted in contamination of the Tims Branch riparian ecosystem and underlying groundwater. Early M Area operations (1950s) discharged high-strength process wastes (such as aluminum forming and metal plating wastewater and spent solvents), directly into the headwaters of the outfall tributary shown in Figure 3. Later M-Area operations discharged the most contaminated wastewater to the M-Area settling basin and sent less concentrated waste streams to the outfall. All M-Area process waste discharges into the Tim’s Branch system ceased in 1982 and subsequent discharges to the outfall primarily contain noncontact cooling water, treated groundwater, and facility runoff. SRNL discharged dilute laboratory and facility wastewater and runoff to the Tims Branch system in the northern headwaters beginning in the 1950s. In 2001, a wetland treatment system was installed (Figure 3) to mitigate the impacts of SRNL discharges and to lower the concentration of several metals in the stream system. The performance of the wetland treatment and its potential impact on baseline data for the proposed mercury study are discussed below.

Key Points:

Tims Branch represents an interesting and important environment in which a small stream ecosystem has been influenced by an extended period with inputs of water containing oxidized inorganic tin associated with full-scale mercury treatment using stannous chloride addition and air stripping. Based on its characteristics, it is a reasonable analog for UEFPC at Oak Ridge.
Figure 3. Tims Branch stream system in the A/M Areas of the Savannah River Site (SRS)
Tims Branch has been the subject of a large number of ecological and geochemical research studies (Looney et al., 2003b). Of these studies, the following datasets provide the most relevant baseline data to assess the impacts, or lack of impacts, of receiving large scale input of water that has been treated to remove mercury using stannous chloride addition and air stripping.

- Data on mercury concentrations in Tims Branch fish collected by the SREL for basic science and for EM operations – these data were collected at various times and are archived in SRS and SREL environmental databases. The most important Tims Branch data are from 2006. This sampling occurred approximately 5 years after the installation of the wetland treatment system in the northern headwaters (allowing a period of equilibration to the altered inputs) and approximately one year before the startup of the stannous chloride treatment process.

- Data on total and methyl mercury in water – these data were collected at various times -- in this case the most important data were collected as part of a sitewide special study between 1999 and 2001 (Halverson et al. 2008).

- Data on metals concentrations in Tims Branch sediments – these data were collected at various times (e.g., Pickett, 1990).

To demonstrate the type of available baseline data for Times Branch, 2006 fish data were organized for this document and are summarized and presented graphically in Figure 4. In this figure, the data are organized on the x axis according to “northing” coordinate; thus (from left to right) the graph depicts the stations starting near the northern headwaters and ending near the confluence with Upper Three Runs. This was a relatively robust study, performed by SREL, in which suite of metals concentrations in a total of 585 individual fish were measured. A striking feature of this graph is the significant difference (increase) in mercury concentration in fish downstream of the influence of the M Area outfall tributary. Note that this general pattern is also evident in other datasets such as metal concentration and radionuclide activity in sediments (Pickett et al., 1990).

Importantly, if the tin based mercury treatment is having a positive impact due to decreased mercury inputs, or a negative impact due to the hypothesized tin methylation or tin mediated mercury methylation, then changes in the mercury and tin levels in Tims Branch fish collected in 2010/2011 (after two or three years of continuous treatment system operation) should provide a relatively sensitive and diagnostic metric.

Key Points:

To address the applied science needs, the principal tasks focus on generating a post exposure datasets that are roughly equivalent (correlatable) to the pre-exposure data and that directly test hypotheses about potential impacts of the added tin. For example, if tin methylation is significant, it will be detected in water and fish, if tin mediated mercury methylation is significant, mercury concentrations in fish will increase relative to the baseline, if tin accumulation in sediment is significant, it will be detected in the streambed samples.
Figure 4. Example of baseline (2006) fish data from several sampling areas along Tims Branch. Note that this graph includes all species. While similar species were collected at all stations, a more detailed analysis, separating the data by species and/or trophic classification and other potential influencing factors would be included as part of any research effort.

The baseline (1999-2001) water data from a special study at the Savannah River Site (Halverson et al. 2008) were organized for this document and are presented in Figure 5. It is clear from this graph that surface water has generally lower total mercury concentration and higher methyl mercury concentration than rainfall. Further, small streams and tributaries which would tend to have more “wetlands” influences exhibit a higher methyl mercury fraction than the Savannah River. The water samples from Tims Branch in this study were similar to other streams on the Savannah River Site. These data suggest that measurements of mercury and tin speciation in this water are feasible and these data will be potentially diagnostic, particularly if expanded to elucidate dissolved versus particulate forms and when carefully matched to fish and sediment collections.
Figure 5. Example baseline (1999-2001) water data for mercury in surface waters and rainfall near the DOE Savannah River Site

The various solid lines indicate the relationship between methyl and total mercury for (from bottom to top) the Savannah River (median), on site streams (median) and on site stream (upper bound of the data). The dashed lines indicate median rainfall from the National Atmospheric Mercury Deposition Program collection station located at the Savannah River Site. All data from Halverson et al., 2008.

Key weaknesses in the pretreatment baseline information include: 1) little/no pretreatment tin concentration data on any media (except associated with the treatment system startup in the near-field and outfall), 2) no pretreatment tin speciation data at any location, 3) no baseline data on the biofilm / iron floc and limited soil core information (with no tin data), and 4) startup of the wetland treatment system in the northern headwaters after the collection of the water baseline in 1999-2001. Each of the task descriptions below was formulated to mitigate these weaknesses. For example, local water concentrations from the detailed five year study of the performance the wetland treatment system (Nelson and Gladden 2007), when combined with the 1999-2001 data for all of the Tims Branch system (Halverson et al. 2008) will allow the team to generate a reasonable composite baseline for water. Similarly, we have access to some of the previously collected fish tissue samples and some of the missing information (e.g., baseline tin levels) may be able to be filled in.

Figure 6 summarizes graphically depicts the background information described above -- the historical inputs from SRNL and M Area and the available environmental data/samples from the Tims Branch system -- and highlights the start-up of stannous chloride treatment.
Figure 6. Graphical summary of the history of discharges to the Tims Branch System and available environmental data.
Recent Data Collections Associated with Stannous Chloride and Air Stripping System Operation

The M1 air-stripper system has operated since 1985 to treat groundwater containing chlorinated solvent, primarily tetrachloroethene (PCE) and trichloroethene (TCE). The groundwater treatment system consists of a series of groundwater recovery wells and the air-stripper that operates at a nominal 460 gallons per minute (gpm). Mercury concentrations in the groundwater entering the air-stripper are on the order of 0.25 µg/L (250 ng/L). The mercury level at the outfall downstream of the stripper discharge exceeded a 0.051 µg/L (51 ng/L) limit (to be met by December 2007) set by a National Pollutant Discharge Elimination System (NPDES) permit.

Since November of 2007 a stannous chloride injection system has been operating as an integral component of the M1 Air Stripper at the Savannah River Site. The reagent converts the aqueous mercury to a volatile Hg(0) species which can be removed by the existing air stripper. The process removes almost 95% of the mercury via the combination of chemical reduction and air stripping (Figure 7). Initial capital costs for the system were less than $5000 and the increase in operating costs were less than $0.17 per thousand gallons. Prior to the injection of stannous chloride, the air-stripper was ineffective in removing the mercury from the groundwater. Some key early mercury and tin data are summarized below. A more detailed description of the system and the early tin-related data collections are provided in Jackson and Looney (Appendix A).

![Removal of Mercury via Chemical Reduction at Savannah River Site](image)

**Figure 7.** Mercury concentrations at the outfall downstream of the M-1 Air Stripper.
Tin data were collected during feasibility testing (six hour test), dose response testing (over a two day period), and during system start-up and initial operations. All data are for total tin so they do not explicitly distinguish dissolved and particulate forms. The various data collected indicated: 1) small increases in tin concentration in the air stripper effluent were discernable in the short term studies, 2) tin concentrations in the air stripper effluent (Figure 8) increased over the first several months of operations and ultimately reached a pseudo-steady state (i.e., the tin leaving the air stripper approximately matches the tin entering the air stripper), 3) the variability in tin concentrations and periodic “pulses” in concentration are consistent with a hypothesis that the tin has precipitated and is in the form of a particulate, and 4) concentrations of total tin at a downstream outfall (located on the M Area outfall tributary near the entry into Tims branch) increased over the first several months of operation from a baseline of 1 to 2 µg/L up to approximately 4 to 6 µg/L.

![Figure 8. Concentration of total tin in the effluent of the M1 Air Stripper during the development and implementation of stannous chloride based mercury treatment.](image)

The dashed line is the predicted “steady-state” discharge.
Research Concept to Leverage Tims Branch to Resolve Scientific Issues and Uncertainties Related to Stannous Chloride Based Mercury Treatment

A team of researchers from SRNL, ORNL and SREL has evaluated the historical data and developed a focused research concept/plan to efficiently and effectively resolve the issues and uncertainties that have been identified related to stannous chloride based water treatment. As described above, the research concept considers Tims branch to be a reasonable analog for East Fork Poplar Creek (Figure 9) but Tims Branch has been influenced by several years of water input from a full scale stannous chloride treatment system. The proposed research consists of three major tasks:

1) Biological Monitoring: Measurement of mercury and tin in fish and assessment of changes relative to the 2006 baseline data. The initial objective of this task is to resolve if the impacts of the treatment are measurable in a key ecological compartment and regulatory endpoint (fish tissue). If differences are observed, they will provide relatively definitive information about the benefit of lowering mercury inputs and the potential significance of the hypothesized adverse collateral impacts (tin methylation and tin mediated mercury methylation). We propose collection and processing the fish using methods that are equivalent to the 2006 sample set. This task includes a primary collection and analysis effort, as well as a few supplementary studies to help resolve uncertainties associated with unpurged whole body samples versus tissue samples. Further, the availability of “left-over” sample materials from many of the 2006 fish provides the opportunity to forensically fill in the baseline fish data for tin (which was not included in the original analytical runs).

2) Treatment Process Characterization: Geochemical characterization of tin in the air stripper and in the air stripper effluent. The principal objective of this task is to identify/confirm the form of tin exiting the process using measurements of dissolved and particulate tin, characterization of coatings on the stripper packing, chemical/thermodynamic modeling, and state-of-art imaging and elemental analysis of solid phases.

3) Geochemical Monitoring: Measurements of concentrations and speciation of tin and mercury in water and sediments. The principal objectives of this task focus on tin fate and distribution in the receiving stream system (i.e., tin methylation and tin mediated mercury methylation) and whether tin is accumulating or focusing in such a manner that it might build up to adverse levels in sediments. A semiquantitative sediment/substrate habitat assessment will be conducted to evaluate physical impacts. Aqueous samples would be evaluated for dissolved versus particulate and inorganic versus methyl species using methods developed during this project. The sediment and bio/iron film samples would be extracted and analyzed using the same methods as task 1.

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1 Measure length in the field and put on ice, weigh in the lab and freeze until further processing, freeze dry and grind, store in whirlpak bags prior to extraction and analysis. Total samples are extracted using a nitric acid microwave sequence followed by oxidant microwave sequence prior to analysis by ICP. Methods for tin and mercury speciation of the dry ground samples will be developed as part of this research.
Photographs of a natural downstream reach of EFPC and a similar reach in a potential analog stream, Tims Branch, at the Savannah River Site. Base flow in EFPC (e.g., near Station 17, including flow augmentation) is approximately 13,000 to 18,000 m³/day and base flow in Tims Branch is approximately 4,000 to 8,000 m³/day downstream of the M Area outfall tributary.

Figure 9.

Figures 10-12 provide flowchart summaries of the three tasks. The proposed work is a collaborative applied research effort that includes SRNL, ORNL, and SREL. In addition to cost effectively addressing high priority applied science needs, this research would provide additional benefits for DOE and the participants as the proposed research team would consist of a postdoctoral student (one year appointment split between ORNL 80% and SRNL/SREL 20%) as well as early career scientists and senior researchers in a variety of disciplines.
**TASK 1: Biological Monitoring**

- **Fish Collection**: 4 sites, 60 fish/site (approx). Sites located upstream and downstream of stannous chloride input.
- **Fish Processing**: 80% of the fish (weigh, dry, and grind).
- **Fish Purging**: 20% of the fish (weigh, dry, and grind).
- **Fish Splitting**: Samples split and analyzed for total metals in all whole body and purged fish samples (mercury, tin, and other elements by ICP).
- **Composite Analysis**: If needed, composite samples analyzed for mercury and tin species.
- **Forensic Evaluation**: Analyze total tin in all available fish samples collected in 2006. Composite 2006 samples (as needed) and analyze mercury and perhaps tin species.

**Figure 10.** Graphical depiction of the proposed biological monitoring activities in Task 1.
TASK 2: Treatment Process Characterization

- collect water (filtered and unfiltered), as well as air stripper packing coatings, and solids for detailed studies
- analyze total metals in all water samples (mercury, tin, and other elements by ICP)
- analyze mercury and tin speciation in water samples (as needed)
- Detailed study of solids (as needed) using SEM, and micro-analytical methods
- prepare and digest solid samples
- analyze total metals
- analyze mercury and tin speciation (as needed)

Assess specific topics associated with tin and mercury behavior in the treatment process. Confirm that tin(IV) is primarily in the form of oxide when discharged and is a solid (or particulate) phase.

Figure 11. Graphical depiction of the proposed treatment process characterization activities in Task 2
TASK 3: Geochemical Monitoring

- collect water (filtered and unfiltered), biofilm/floc, and surface sediment (8 to 10 locations)
- analyze total metals in all water samples (mercury, tin, and other elements by ICP)
- analyze mercury and tin speciation in water samples (as needed)
- Detailed study of solids (as needed) using SEM, and micro-analytical methods
- prepare and digest solid samples
- analyze total metals
- analyze mercury and tin speciation (as needed)

Assess overall pattern of tin distribution and potential impacts in the system using total concentrations, mercury and tin speciation data, concentration patterns and profiles. Estimate tin accumulation patterns and areas and potential for adverse impacts to sediment ecosystem.

Figure 12. Graphical depiction of the proposed geochemical monitoring activities in Task 3
References


Environmental Protection Agency (EPA), 2002. “ECOTOXicology database (ECOTOX).” Office of Research and Development (ORD), and the National Health and Environmental Effects Research Laboratory’s (NHEERL’s!) Mid-Continent Ecology Division. Available at http://www.epa.gov/ecotox.


Appendix A

Levels of Tin Observed While Implementing a Mercury Removal System based upon Stannous Chloride

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Introduction & Background: Since November of 2007 a stannous chloride injection system has been operating as an integral component of the M1 Air Stripper at the Savannah River Site. The purpose of the injection system is to promote the chemical reduction of Hg(II) that is present in the entering wastewater to the volatile Hg(0) species. The process removes almost 95% of the mercury via the combination of chemical reduction and air stripping. Initial capital costs for the system were less than $5000 and the increase in operating costs were $0.17 per thousand gallons.

The M1 air-stripper system has operated since 1985 to treat groundwater containing chlorinated solvent, primarily tetrachloroethene (PCE) and trichloroethene (TCE). The groundwater treatment system consists of a series of groundwater recovery wells and the air-stripper that operates at 460 gallons per minute (gpm). Mercury concentrations in the groundwater entering the air-stripper are on the order of 0.25 micrograms per liter (µg/L). The mercury level exceeded a 0.051 µg/L limit that was promulgated in December of 2007 by the State of South Carolina for the receiving outfall under a National Pollutant Discharge Elimination System (NPDES) permit. Prior to the injection of stannous chloride, the air-stripper was ineffective in removing the mercury from the groundwater.

In 2003 SRNL performed a pilot study of a stannous chloride treatment modality specific to SRS. This study was based upon previous work performed by ORNL in support of mercury contamination associated with the Oak Ridge facility. In November of 2007 a treatment system was in-place that reduced concentrations to satisfy forthcoming NPDES limits. A synopsis of the activities specific to SRS is highlighted in Figure 1 along with the historical mercury concentration at the affected outfall, which receives treated wastewater from the M1 system. The data collected from the laboratory, full scale field testing, and implementation indicate that mercury can be effectively removed from wastewater using chemical reduction followed by volatilization using a conventional air-stripper.

Scientists from ORNL have identified uncertainties related to stannous chloride treatment and air stripping. These questions and uncertainties center on stream impacts such as tin methylation, tin mediated mercury methylation, and the accumulation of tin in stream sediments. The following discussion provides a synopsis of tin monitoring associated with the development and implementation of the treatment scheme at the Savannah River Site.
Removal of Mercury via Chemical Reduction at Savannah River Site
Objective to Reduce Mercury at Outfall to satisfy New NPDES Limits.

12/01/2007 - NPDES Limit
- Daily Max: 141 ng/L
- Monthly Ave: 51 ng/L

Implementation Timeline:
2001-2005: SRS Monitor & Report on Total Hg
2003: SRNL Pilot Study on Treatment Method
07/10/2007: SRNL Performs 6-hr Full Scale Feasibility Test
08/21-22/2007: SRNL Directs a 48-hr Dose Response Test
11/05/2007: SRNL & SRS Operations Implement Hg Removal Process
11/15-30/2007: Dose Optimized for Competing Electron Acceptors in Wastewater
12/01/2007: New NPDES Limits Become effective - 141 ng/L Total & 51 ng/L Average
03-06/2008: Refine Operations & Equipment for Long-Term Reliability

Figure 1: Development and Implementation of a Mercury Removal System based upon Chemical Reduction using Stannous Chloride at the Savannah River Site.

Feasibility Testing: Initial testing of the treatment scheme was performed on July 10, 2007 utilizing the M-1 air stripper that is located at the Savannah River Site. During this test reagent was injected into the influent wastewater (Q = 460 gpm) at a rate of 11.8 mg/min, representing 25X the stoichiometric requirement necessary to promote the reduction of mercury. During the injection period mercury concentrations in the effluent decreased approximately 94%, from 0.248 µg/L at the inlet of the air stripper to 0.014 µg/L at the outlet.

A total of 24 wastewater samples were collected and analyzed for total tin. Total tin analysis was performed by contract laboratory using EPA Method 6020 on unfiltered samples. The analytical results for total tin in the wastewater are presented in Table 1 below. The concentration of total tin in all of the samples was below the detectable limit (2 µg/L) of the analytical method. Some of the samples were coded by the laboratory with a usage code of “J”, indicating a positive response for the analyte at a concentration less the detectable limit. The only definitive statement regarding the concentration of tin during this test is that the level was less than 2 µg/L. At the wastewater flow rate of 460 gpm, the injection of 11.8 mg/min of reagent would have contributed 2.97 µg/L of total tin to the wastewater, a level that is above the method detection limit of 2 µg/L. If the tin was in the aqueous phase it should have been detected in the effluent during the injection period. We hypothesis that once the tin is oxidized to tin(IV) it combines with abundant oxygen to form tin(IV) oxide which have a very low solubility and likely form

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1 All data on the reagent delivery rate are presented in terms of the mass (e.g., mg) of the reagent salt, tin(II) chloride dehydrate, and not in terms of tin metal or anhydrous reagent.
a precipitate under these wastewater conditions, pH in the 5.0 to 5.5 range. Even though the concentrations are below the method detection limit, the data suggest that the estimated total tin concentration in the outlet increases slightly during the injection period and subsequently decreases following injection.

Table 1: Concentration of Total Tin in the Inlet and Outlet of the M-1 Air Stripper During the Initial Evaluation of Stannous Chloride Treatment System (July 10, 2007).

<table>
<thead>
<tr>
<th>Period</th>
<th>Time</th>
<th>Total Tin Inlet (µg/L)</th>
<th>Total Tin Outlet (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Injection</td>
<td>-24 Hours</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
</tr>
<tr>
<td></td>
<td>7:30</td>
<td>&lt; 2</td>
<td>0.41 (J)</td>
</tr>
<tr>
<td></td>
<td>8:30</td>
<td>&lt; 2</td>
<td>0.42 (J)</td>
</tr>
<tr>
<td>Injection</td>
<td>9:30</td>
<td>&lt; 2</td>
<td>0.57 (J)</td>
</tr>
<tr>
<td></td>
<td>10:30</td>
<td>&lt; 2</td>
<td>0.56 (J)</td>
</tr>
<tr>
<td></td>
<td>11:30</td>
<td>&lt; 2</td>
<td>0.46 (J)</td>
</tr>
<tr>
<td></td>
<td>12:30</td>
<td>&lt; 2</td>
<td>0.55 (J)</td>
</tr>
<tr>
<td></td>
<td>13:30</td>
<td>&lt; 2</td>
<td>0.52 (J)</td>
</tr>
<tr>
<td></td>
<td>14:30</td>
<td>&lt; 2</td>
<td>0.57 (J)</td>
</tr>
<tr>
<td>Post Injection</td>
<td>15:15</td>
<td>&lt; 2</td>
<td>0.34 (J)</td>
</tr>
<tr>
<td></td>
<td>15:45</td>
<td>&lt; 2</td>
<td>0.26 (J)</td>
</tr>
<tr>
<td></td>
<td>+24 Hours</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
</tr>
</tbody>
</table>

**Dose Evaluation:** Dose response testing of the treatment mechanism was performed on August 21 and 22, 2007. During this testing the dose rate of the reducing agent (tin(II) chloride dihydrate CAS #10025-69-1) was adjusted to examine the effectiveness of the treatment method at various doses. During the test, the dose rate of the reagent was incrementally increased from 0.27 mg/min to 133 mg/min. A total of nine (9) different dose rates were investigated. Results indicate that a minimum dose rate of 6.6 mg/min of reagent (16X the required stoichiometry) is necessary to promote the removal of mercury (91%) from the entering wastewater. An increase in the dose rate to 13.3 mg/min (30X the required stoichiometry) resulted in removal of 95% of the mercury in the associated wastewater.

During this testing campaign a total of nine (9) wastewater samples from the discharge of the stripper were collected and analyzed for total tin. Total tin analysis was performed by contract laboratory using Method 6020. The theoretical (based upon applied dose) and observed (analytical results from unfiltered samples) for total tin in the wastewater are presented in Table 2. As shown in this table eight of the nine samples are coded with a usage code of “J” indicating a positive response for the analyte at a concentration less the detectable limit. The only definitive statement regarding the concentration of tin during these treatments is that the level was less than 2 µg/L. The treatment level that resulted in a detectable quantity of tin in the effluent was associated with an applied dose rate of 133 mg/L of reagent. At this treatment level total tin in the effluent was observed to be 3.8 µg/L, 89% less than the amount injected. This decrease provides additional evidence supporting the hypothesis that the tin(IV) combines with available oxygen to form tin(IV) oxides (or hydroxides) which precipitate out of the aqueous phase.
Table 2: Concentration of Total Tin in the Effluent of the M-1 Air Stripper During the Dose Evaluation Testing of the Stannous Chloride Treatment System (August 21-22, 2007).

<table>
<thead>
<tr>
<th>Test</th>
<th>Dose (mg/min)</th>
<th>Sn – Based on Dose (µg/L)</th>
<th>Total Sn – Observed (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.27</td>
<td>0.07</td>
<td>0.42 (J)</td>
</tr>
<tr>
<td>#2</td>
<td>0.53</td>
<td>0.13</td>
<td>0.44 (J)</td>
</tr>
<tr>
<td>#3</td>
<td>1.33</td>
<td>0.34</td>
<td>0.69 (J)</td>
</tr>
<tr>
<td>#4</td>
<td>2.66</td>
<td>0.67</td>
<td>0.65 (J)</td>
</tr>
<tr>
<td>#5</td>
<td>6.65</td>
<td>1.68</td>
<td>0.49 (J)</td>
</tr>
<tr>
<td>#6</td>
<td>13.3</td>
<td>3.35</td>
<td>0.71 (J)</td>
</tr>
<tr>
<td>#7</td>
<td>26.6</td>
<td>6.70</td>
<td>1.1 (J)</td>
</tr>
<tr>
<td>#8</td>
<td>53</td>
<td>13.40</td>
<td>0.93 (J)</td>
</tr>
<tr>
<td>#9</td>
<td>133</td>
<td>33.50</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Start-Up & Initial Operations: Based upon the effectiveness demonstrated during the Feasibility and Dose Response testing, a full scale system was designed and installed. The system was placed into service on November 5, 2007 and provided an applied dose of 16.5 mg/min of reagent. The reagent solution contains 10% (w/v) stannous chloride dihydrate [CAS #10025-69-1] in a 20% (v/v) hydrochloric acid [CAS #7647-01-0] solution. Initial monitoring of the system involved the daily collection of samples at the inlet, outlet, and outfall locations, with weekly analysis of all the samples performed by a contract laboratory using EPA Method 6020. All samples were unfiltered and monitoring was performed for the first 4-months of operation (through 2/28/2008). Results of this monitoring are presented in Figure 2 along with the theoretical concentration (based upon injected mass) if all of the tin was present in the aqueous phase. Note that in late November the reagent dose was increased to overcome competing electron acceptors associated with seasonal variations in the inlet wastewater.

As indicated by the data in Table 3, the concentration of total tin in the effluent was variable and is poorly correlated (linear relationship, $R^2 = 0.0694$) with the theoretical concentration based upon injected dose. The poor correlation is considered to be associated with collection and analysis of unfiltered samples and variation of operational parameters. During this period the concentration of total tin at the outfall, which is located several hundred meters downstream of the discharge of the stripper, was consistently at or below the method detection limit.

Table 3: Concentration of Total Tin in the Effluent of the M-1 Air Stripper Associated with the Initial Operation of the Stannous Chloride Treatment System.

<table>
<thead>
<tr>
<th>Date</th>
<th>Wastewater (gpm)</th>
<th>Reagent Dose (mg/min)</th>
<th>Total Sn - Stripper Effluent (µg/L)</th>
<th>Total Sn – Outfall (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Theoretical Observed</td>
<td></td>
</tr>
<tr>
<td>11/08/07</td>
<td>525</td>
<td>16.5</td>
<td>3.64 5.59 (U)</td>
<td>1.89 (U)</td>
</tr>
<tr>
<td>11/15/07</td>
<td>525</td>
<td>16.5</td>
<td>3.64 7.59</td>
<td>1.58 (J)</td>
</tr>
<tr>
<td>11/20/07</td>
<td>526</td>
<td>16.5</td>
<td>3.63 4.98 (J)</td>
<td>1.82 (J)</td>
</tr>
<tr>
<td>11/29/07</td>
<td>526</td>
<td>50</td>
<td>11.01 7.47</td>
<td>n/a</td>
</tr>
<tr>
<td>12/11/07</td>
<td>459</td>
<td>50</td>
<td>12.62 14.6</td>
<td>1.56 (J)</td>
</tr>
</tbody>
</table>
System Operations: Following the initial sampling campaign, routine monitoring of tin has been limited. In late 2008 through 2009, SRS initiated a campaign to monitor and report on zinc associated with this system. Wastewater samples were collected from the inlet and outlet of the system and analyzed using EPA Method 6010 (ICP-AA), which provides information on tin. For tin, this method has a higher quantitation limit than analytical techniques (Method 6020, ICP-MS) used in previous analysis (50 μg/L versus 2 μg/L). In April of 2010 SRS initiated monthly sampling and analysis for total tin using EPA Method 6020. Analytical results from these sampling events are presented in Table 4. Since all of these samples were unfiltered, the results from 02/02/2009 and 08/03/2009 events are suspect and believed to have contained particulate material. Overall the values that were estimated from ICP-AA analysis are consistent with results from ICP-MS analysis.

Table 4: Concentration of Total Tin in the Effluent of the M-1 Air Stripper Associated with the Continuous Operation of the Stannous Chloride Treatment System.

<table>
<thead>
<tr>
<th>Date</th>
<th>Total Tin Inlet (µg/L)</th>
<th>Total Tin Outlet (µg/L)</th>
<th>Method - EQL</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/06/08</td>
<td>n/a</td>
<td>6.69 (J)</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>12/01/08</td>
<td>n/a</td>
<td>8.84 (J)</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>02/02/09</td>
<td>n/a</td>
<td>170</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>05/11/09</td>
<td>n/a</td>
<td>14.1 (J)</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>07/08/09</td>
<td>50 (U)</td>
<td>20.1 (J)</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>08/03/09</td>
<td>50 (U)</td>
<td>1980</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>09/08/09</td>
<td>50 (U)</td>
<td>13.5 (J)</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>11/30/09</td>
<td>n/a</td>
<td>16.7 (J)</td>
<td>EPA 6010 - 50</td>
</tr>
<tr>
<td>04/05/10</td>
<td>2.4</td>
<td>14.3</td>
<td>EPA 6020 – 2</td>
</tr>
<tr>
<td>05/04/10</td>
<td>1.3 (J)</td>
<td>10.2</td>
<td>EPA 6020 – 2</td>
</tr>
</tbody>
</table>
Figure 2 compiles the observations of total tin in the effluent of the M1 stripper system during evaluation, installation, initial and continuous operations (Tables 1, 2, 3, and 4). Since November 11, 2007 stannous chloride has been continuously injected into the system. The rate of injection has varied as issues with competing electron donors and equipment (injection pump) compatibility have been identified and resolved. Since the summer of 2008 a continuous reagent dose of 50 mg/min has been applied using a pulse-injection pump. This dose would produce a total tin concentration in the effluent of 12.88 µg/l. With two exceptions, the monitoring of tin in the effluent using unfiltered sampling techniques is consistent with this steady-state condition. The two exceptions (identified in Figure 2) are considered to be associated with particulate material in the effluent. SRS continues to monitor mercury and total tin in the effluent of this system.

![Figure 2: Concentration of Total Tin in the Effluent of the M1 Air Stripper during the Development and Implementation of a Mercury Removal System based upon Chemical Reduction using Stannous Chloride.](image-url)