Controlling Mercury Release from Source Zones to Surface Water: Initial Results of Pilot Tests at the Y-12 National Security Complex

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CONTROLLING MERCURY RELEASE FROM SOURCE ZONES TO SURFACE WATER: INITIAL RESULTS OF PILOT TESTS AT THE Y-12 NATIONAL SECURITY COMPLEX

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LIST OF ACRONYMS

BJC	Bechtel Jacobs Co. LLC
BMAP	Biological Monitoring and Abatement Program
DGM	Dissolved gaseous mercury
DOE	Department of Energy
EM	Environmental Management
EFPC	East Fork Poplar Creek
GPD	Gallons per day
Hg(0)	elemental mercury
Hg(II)	mercury in oxidation state II
NPDES	National Pollutant Discharge Elimination System
OF	Outfall
ORNL	Oak Ridge National Laboratory
SFA	Science Focus Area
RMPE	Reduction of Mercury in Plant Effluent
SRS	Savannah River Site
TDEC	Tennessee Department of Environment and Conservation
TRC	Total residual chlorine
UEFPC	Upper East Fork Poplar Creek
WRRP	Water Resources Restoration Program
Y-12 NSC	Y-12 National Security Complex

ACKNOWLEDGMENTS

EXECUTIVE SUMMARY

This report presents initial results obtained during year 2008 and satisfies a deliverable listed in the work breakdown structure (WBS) element OR081301.

Mercury (Hg) is a pervasive environmental contaminant within the DOE complex, including the Oak Ridge Y-12 National Security Complex (Y-12 NSC), Oak Ridge National Laboratory (ORNL) site, Savannah River site (SRS), Hanford, and other sites. At Y-12 NSC, the major concern is mercury contamination in East Fork Poplar Creek (EFPC), originating primarily from a point source. Field activities have focused on flow diversion and chemical treatment tests near the headwaters of upper East Fork Poplar Creek (UEFPC). Broad objectives of the multi-year project are: 1) evaluation of remediation technologies for waterborne mercury, 2) development of treatment methods for soil mercury, and 3) source identification, characterization and analyses to improve mass balance on mercury estimates.

This report presents the results of pilot tests, conducted in summer and fall 2008, which focused on remediation of waterborne mercury. The goal of this task is to develop strategies and treatment technologies that reduce the concentration and loading of waterborne mercury discharges to the UEFPC, thus minimizing mercury uptake by fish. The two specific studies are:

- Reducing flow augmentation in UEFPC to lessen mercury mobilization from contaminated stream sediments, and
- Treatment of contaminated source waters with a chemical reductant to convert dissolved mercury to a volatile form that can be removed by air stripping or natural evasion.

Diversion of 50% of the flow currently added to UEFPC by the flow management system appeared to reduce mercury inputs from a localized, highly contaminated streambed by 0.6–1.5 grams per day (g/d). A reduction of 0.6 g/d represents ~7-10% decrease in mercury input to UEFPC. Mercury concentrations within UEFPC did not rise proportionately with the loss of dilution, in part because of the reduction in input from the streambed source and in part because of reduced flow from the Y-12 NSC storm drain system. A longer-term test that includes seasonal variability will be the next step to validate these initial field observations of the flow diversion experiment.

Preliminary laboratory experiments show that a large fraction (~90%) of the mercury can be chemically reduced to Hg(0) by addition of low concentrations of tin, Sn(II). Conversion of mercury to volatile Hg(0) in UEFPC was also demonstrated in the field by in-situ addition of low levels of Sn(II) in the headwaters. A substantial fraction (~30% of baseline mercury levels by the end of the experiment) of the mercury was converted from oxidation state II to 0. The addition of the dechlorinating agent sodium thiosulfate mobilized a small amount of additional mercury from the pipe through which EFPC flowed, but the excess Hg largely disappeared by the end of the chemical addition period. No excess tin was observed at the regulatory monitoring point, mercury levels in air were low, and no in-stream toxicity was observed. At a Hg(II) reduction efficiency of ~30%, in-situ reduction coupled with air stripping has the potential to remove large quantities of mercury from the UEFPC flow. Air stripping has not been implemented, but a demonstration is planned for the next phase of field experiments.

The initial results from this 2008 study suggest a combination of reducing augmented flow volume and chemical reduction using stannous chloride will produce at least a 35% reduction in baseflow mercury loading to UEFPC, from approximately 8 g/d to 5 g/d. The goal of research in 2009 and beyond will be to gain further improvements in each of these approaches.

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1. INTRODUCTION

1.1 PROJECT OBJECTIVE

This project has an overall goal of developing a remediation and monitoring strategy for controlling mercury (Hg) release from source zones to surface water. Using Y-12 National Security Complex (Y-12 NSC) as a field site, the project aims to demonstrate treatment technologies that reduce the concentration and loading of waterborne mercury discharges to the upper East Fork Poplar Creek (UEFPC), thus minimizing mercury uptake by fish. This is a multi-year project with the following specific objectives: 1) evaluate remediation technologies for waterborne mercury, 2) develop treatment methods for mercury in soil, and 3) identify and characterize mercury sources with quantitative analysis to improve mass balance. In year 2008, specific aim was to field test flow diversion and chemical reduction as a means of remediation of waterborne mercury discharged to UEFPC.

1.2 BACKGROUND

Mercury is a dominant environmental contaminant within the DOE complex, including the Oak Ridge Y-12 NSC, Oak Ridge National Laboratory (ORNL) site, Savannah River site (SRS), Hanford, and other sites. At the Y-12 NSC, the release of large quantities of mercury during the 1950s and early 1960s resulted in soil and groundwater contamination in source areas and subsequent transport of mercury into the headwaters of the East Fork Poplar Creek (EFPC, Figure 1). Many of those sources remain today with continued high mercury concentrations in creek water, sediment, and biota. Although the primary focus of this project is on mercury contamination within the DOE facilities on the Oak Ridge Reservation (Y-12), research and development results will also be relevant to other DOE sites where mercury is a contaminant of concern (e.g., SRS, Hanford). This is a national technology development and deployment (TDD) project that is established under the Strategic Initiatives identified in the EM Engineering and Technology Roadmap targeting on mercury stabilization. The project specifically addresses EM-22 Groundwater and Soil Remediation Program needs related to Oak Ridge Site priorities for in-situ mercury treatment systems.

This project was initiated in summer 2008 following completion of a mercury focused Technical Assistance Project held in January 2008, sponsored by DOE EM-22. A team of experts discussed issues related to mercury contamination at the Y-12 NSC, the impact on the Upper East Fork Poplar Creek (UEFPC), and remedial approaches using existing and emerging technologies (Looney et al. 2008). Subsequent discussions were held with Y-12 NSC managers regarding their priorities and the list of technologies recommended for field testing. The scope of work for FY2008 included implementation of two "quick win" field activities as the initial phase of this project. These activities are:

- Flow management actions in UEFPC to reduce mercury mobilization from contaminated stream sediments; and

- Treatment of waterborne mercury (in contaminated source water) with stannous chloride ($SnCl_2$) to reduce mercury discharge to UEFPC.

The rationale, methods, results, and preliminary conclusions for each of the above activities are provided in Section 2, focused on flow management, and Section 3, focused on in situ chemical reduction by reduced tin, i.e., stannous chloride. A short project summary in Section 4 highlights the relevance of the 2008 results and the proposed plans for further testing in 2009.
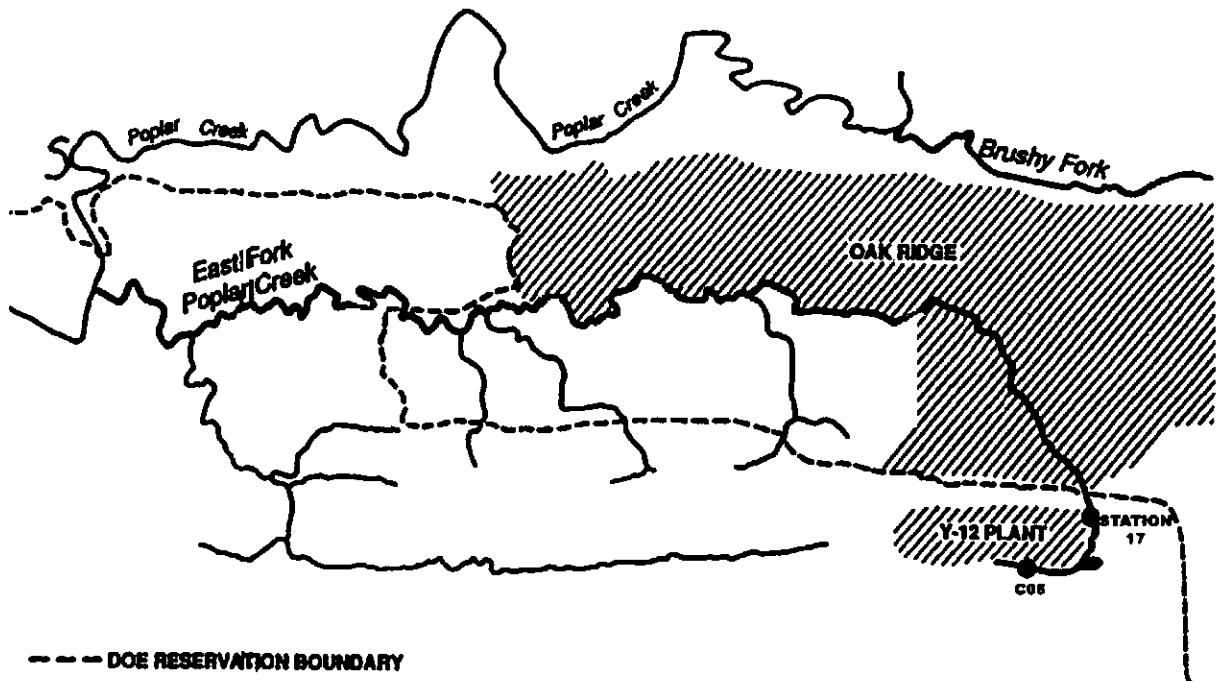
Fig. 1. Site vicinity map showing location of East Fork Poplar Creek in relationship to Y-12 National Security Complex and the City of Oak Ridge. Upper East Fork Poplar Creek is generally regarded as the stream from the headwater to Station 17.

2. EFFECTS OF FLOW MANAGEMENT DIVERSION ON WATERBORNE MERCURY FLUX IN UPPER EAST FORK POPLAR CREEK

2.1 BACKGROUND

Decreased water usage within the Y-12 NSC in the early 1990s resulted in a substantial reduction in flow in Upper East Fork Poplar Creek (UEFPC, Figure 2). Restoration of minimum flow to levels typical of the late 1980s was viewed as an action beneficial to the ecology of the stream, lessening effects of Y-12 discharges and groundwater inputs on water quality. In a negotiated agreement with the Tennessee Department of Environment and Conservation (TDEC), a flow augmentation system (referred to as 'flow management') was emplaced in late 1996. That system added approximately 17,000 m^3/d of water from Melton Hill Reservoir on the Clinch River to UEFPC at the stream head (also known as Outfall 200), where the subsurface storm drain emerges within the Y-12 facility (Figure 2). The added water mixed with the storm drain flow discharged at Outfall 200, was expected to dilute waterborne mercury concentrations in UEFPC and produce a concomitant decrease in mercury in fish in the stream.

After flow management was implemented in August 1996, total mercury (dissolved plus particle-associated) concentration and loading in UEFPC increased as result of resuspension of mercury-laden fine particulates. This increase in mercury was thought to be temporary. A new steady state was anticipated to establish between suspended load and bed sediments. When the increased mercury loading did not decrease as expected, follow-up studies were carried out to determine the nature of the problem.

Those studies found that a gradual increase in waterborne mercury concentration occurred across a 250-m reach of stream at approximately 100 m (roughly bounded by C11 to Outfall109 in Figure 2) from the headwater at Outfall 200 (BJC 1998). The streambed pore water within that reach contains very high concentrations of dissolved mercury, often exceeding 20 µg/L (approximately 30 to 50 times of the concentration in overlying surface water). Metallic mercury was observed during emplacement of piezometers in the streambed. With respect to the surface flow, equal or lower hydraulic heads were recorded in the streambed; thus, surface flow was likely entering the streambed, flowing within it, and eventually re-entering the surface flow (Figure 3). A relatively small flow through the highly contaminated sediments could easily account for the observed mercury input across the reach. In 1998, the flow management system was shut off temporarily to identify mercury inputs experimentally, but each time operational problems were encountered. A complete shutoff of the flow management system appeared to have reduced mercury loading in the sediment source from 8 g/d to about 3 g/d (BJC 1999).

Erosion of contaminated stream-bank soils was also found to contribute to mercury loading across the source reach, and an action was taken in late 1999 to protect eroding stream banks with sand-filled geotextile tubes (USDOE 2001). That effort appeared to reduce storm flow transport of mercury from UEFPC, but did not have a discernible effect on mercury inputs from the base flow in the treated reach.

In the period between 2000 and the present time, the magnitude of the streambed mercury source in UEFPC appears to have decreased. Measurements of mercury concentration in the source reach made in 2007 and 2008 indicated that the streambed now adds about 1.5 - 2 g/d of mercury to EFPC (versus ~8 g/d in the late 1990s). In a December 2007 study of mercury fluxes throughout the length of EFPC, the streambed source added 1.9 g/d mercury. In the same study, mercury flux from the headwater was 5.2 g/d. Although mercury input from the streambed source has declined over the past decade, it remains a significant fraction of the total mercury input to EFPC. Thus, reducing the magnitude of the flow management input could lead to a proportional decrease in mercury input from the streambed source. For example, cutting the augmented flow volume by 50% could reduce mercury flux by 0.5 to 1 g/d while

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maintaining the beneficial aspects of stable minimum flow. An experiment to test whether such a change would decrease mercury loading was carried out in July–August 2008.
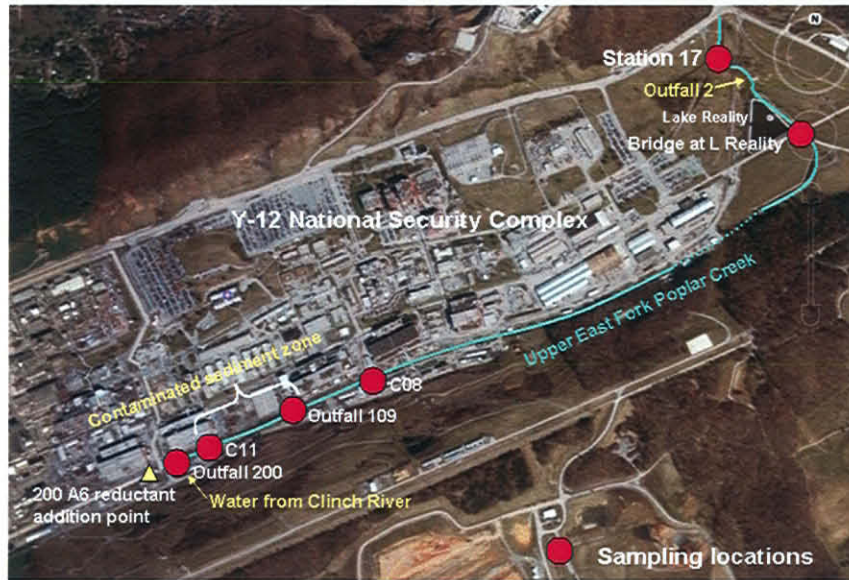
Fig. 2. Key surface water sampling locations for flow management diversion and chemical reduction (using reduced tin) tests conducted in year 2008 at Y-12 National Security Complex. Location at which Clinch River water is added via flow management system is shown.
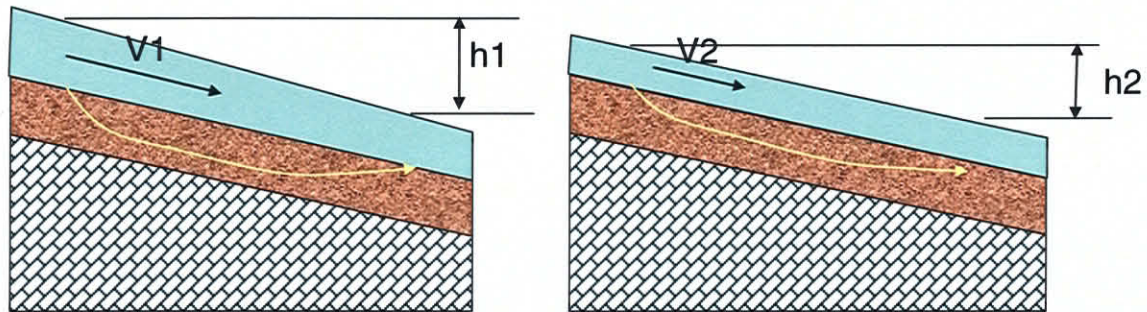
Fig. 3. Schematic illustration of potential effect of flow reduction on sediment bound mercury release in UEFPC: with full flow augmentation (left diagram) and reduced flow condition (right). Note, total dissolved mercury in water is averaged at ~1400 ng/L, whereas, in the sediment, the level is greater than 30,000 ng/L. Lowering hydraulic head on streambed ($h2 < h1$) could result in less subsurface flow. Additionally, lowering surface flow can lead to less erosion (i.e., $V2 < V1$, lower velocity causes less shearing stresses on stream bed).

2.2   METHODS

The experiment was conducted by reducing 50% augmented flow volume at Outfall 200, and reroute this volume of water at a downstream location at Outfall 2 (Figure 2). The impact of the altered flow on baseflow mercury fluxes to UEFPC was evaluated by monitoring surface water flow characteristics and chemical parameters as follows:

1. Pre-diversion phase (July 14 to July 25, 2008), 100% augmented water input (from Clinch River) was present near Outfall 200;

2. Flow diversion (August 5 to August 15, 2008), water input was reduced by approximately 50% at Outfall 200 (Figure 2). Clinch River input was diverted to Outfall 2 by increasing water input to near maximum capacity at the outfall. This effort was aided by Y-12 Utilities personnel who operated the valves and pipelines based on the capacities of the system; and

3. Post diversion phase (August 16 to August 29, 2008), 100% water augmentation at the headwater was resumed near Outfall 200.

The field test was initiated on July 14, 2008 and lasted for approximately 6 weeks. Monitoring consisted of measuring in-situ water quality parameters, such as pH, temperature, and electric conductivity. Measuring flow rates and collecting duplicates of water samples occurred daily throughout the duration of the field test from most of the sampling/monitoring locations shown in Figure 2. Selected outfalls between Outfall 200 and Station 17 were also periodically sampled.

Stream flow was monitored at gauging stations (Station 17, Station C08, and Station C11; Figure 2) by Y-12 NSC staff. Duplicate water samples were collected daily from each of six locations in UEFPC: Outfall 200, the Clinch River (i.e., raw) water input point, C11, Station C08, Station 17 and the main channel of UEFPC immediately upstream from Outfall 109. Samples were immediately preserved and digested using bromine monochloride/HCl solution according to EPA procedure 1631. Water samples were subsequently treated with hydroxylamine and stannous chloride, to reduce mercury to Hg(0), and analyzed for total mercury by cold vapor atomic absorption spectrometry using a Lumex RA915+ Zeeman effect mercury analyzer. Mercury fluxes were calculated by using gauged stream flow rate at the time of sampling multiplied by the mean values of duplicate mercury measurements at each sampling location.

The Oak Ridge National Laboratory Science Focus Area (ORNL-SFA) Project funded by the Office of Science (BER ERSP program) conducted additional sampling during the experiment to investigate the effects of flow reduction on the chemistry of subsurface mercury sources. That study sampled effluents, groundwater, and mainstream surface flow twice weekly and analyzed samples for a wide range of constituents and parameters, including dissolved and total mercury, anions, cations, suspended solids, pH, conductivity and soluble reactive phosphorus.

2.3   RESULTS

2.3.1   Change in Flow

Baseline monitoring for changes in volumetric flow in UEFPC was initiated on July 14, 2008 and continued through July 25, 2008. Mean flow and the standard deviation at monitoring station C11 (Figure 2) was $20,700 \pm 950$ m^3/d over that period. Clinch River water input from the flow management system at Outfall 200 was reduced approximately 50% on August 5, 2008. A volume of water approximately equivalent to that removed from the headwater was added at Outfall 2 (Figure 2), maintaining an

unchanged volumetric flow at the downstream monitoring station (Station 17). Flow at monitoring station C11 averaged 12,230 ± 807 m³/d for the period when flow management input was reduced. Flow at Station 17 averaged 27,963 ± 727 m³/d in the pre-diversion period and 24,014 ± 3714 in the period of reduced headwater flow. River water input to UEFPC was restored to pre-diversion levels on August 15, 2008, but several days were required to get the system adjusted properly, and flows before 8/20/2008 were lower than targeted (see Figure 4). The following week (8/25-8/30), heavy rain elevated flows throughout the creek (Figure 4). Thus, although post-flow restoration sampling continued for two weeks following the flow diversion phase, flow variability during that period complicates its use as an example of baseline conditions. As can be seen in Figure 4, rainfall events can increase base flow by several times the average flow volumes.
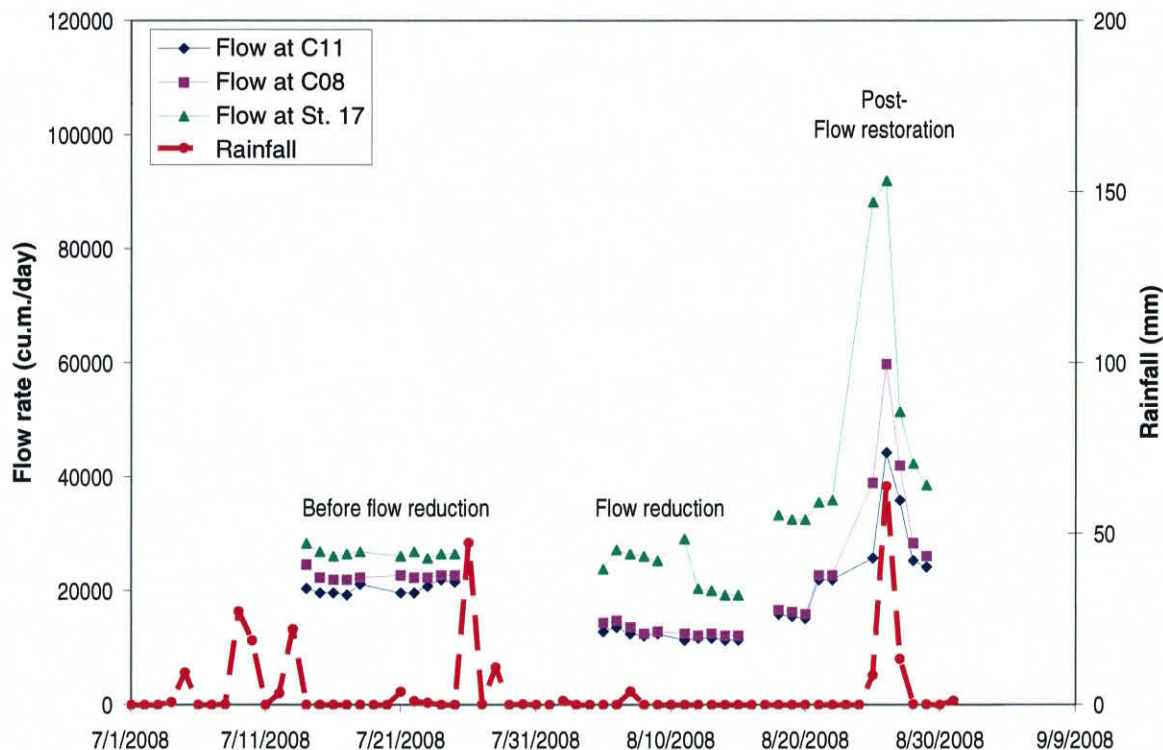
Fig. 4. Volumetric flow rates monitored at UEFPC locations, C11, C08 and Station 17, and rainfall during the 2-month flow diversion study period.

2.3.2 Aqueous Mercury Concentrations

The flow reduction–diversion experiments are designed to demonstrate the decreased flux of mercury downstream of the sediment contaminated zone. However, interpretation of change at the downstream locations is influenced not only by the change in flow augmentation but also changes associated with Y-12 operations and flow from Outfall 200. This is not unexpected, but does highlight the difficulties relative to data variability at field sites and the desirability of getting enough samples for a long enough time period to ensure that measured changes are primarily due to the test manipulations. For example, the mercury concentrations in Outfall 200 varied from a low of 940 ng/L to a high of 2000 ng/L, with an average of 1400 ± 240 ng/L during the entire experimental period (Figure 6). The flow reduction-diversion experiments were carried out downstream of Outfall 200 and should not affect the concentrations of waterborne mercury at this upstream location. The fact is mercury concentrations in Outfall 200 during the pre-, during- and post flow diversion phases did vary (Figures 5 and 6) and this needs to be considered in subsequent analysis of mercury load change in downstream locations.

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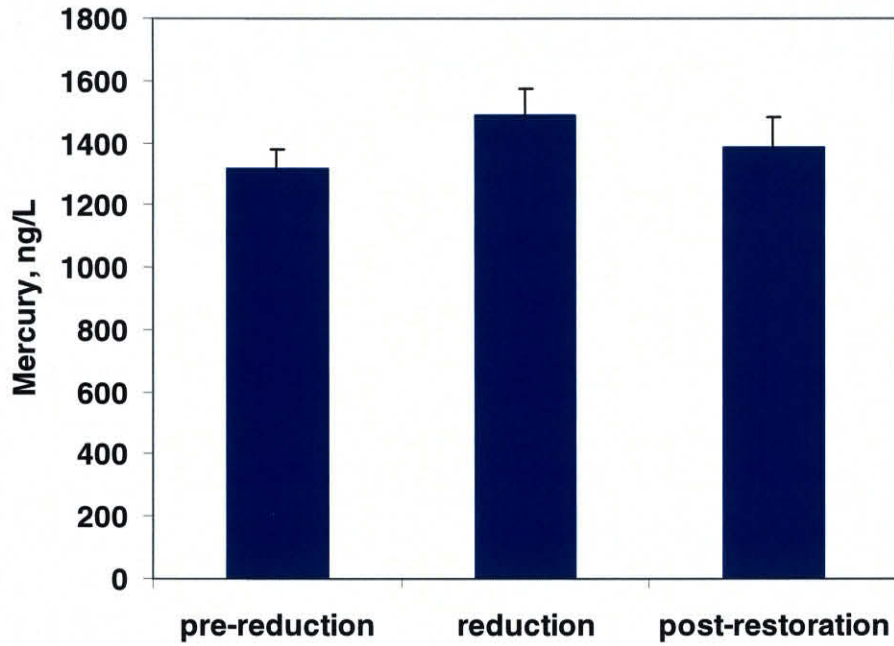
Fig. 5. Mean total mercury concentration measured in Outfall 200 (primary mercury source to UEFPC) before, during, and after reduction and diversion of 50% of the flow management input.
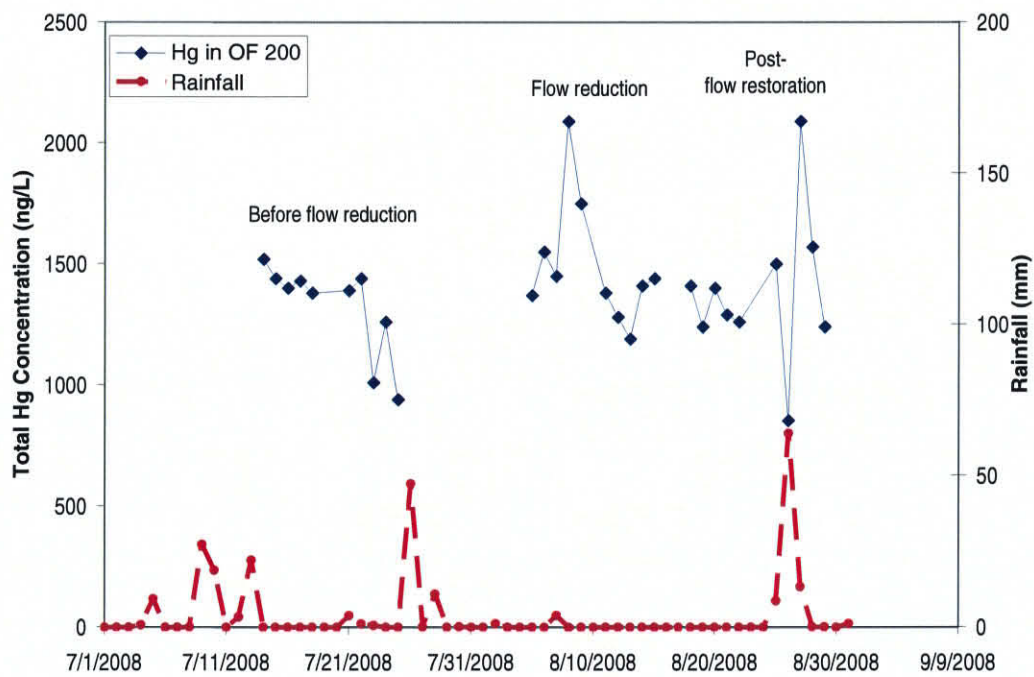
Fig. 6. Time-series graph showing total mercury concentration variability at Outfall 200 and rainfall during the flow management diversion study.

The mercury concentrations at locations upstream of Outfall 2, however, were expected to increase during the flow diversion period because decreasing the volumetric flow from flow augmentation should result in an immediate loss of dilution. This was indeed demonstrated. Figures 7 and 8, illustrate mercury concentrations in stream water at C11, near Outfall 109, and at C08. Due to variability in mercury source levels (Figures 5 and 6) and volumetric flow rates (Figure 4), mercury concentrations in the stream can vary considerably on a daily basis (Figures 7 and 8). Despite the variability observed in the concentration at a given location, discernable differences between locations can be calculated for before and during the flow diversion experiments. To facilitate the discussion we used the average values (Figure 7) as well as a time-series (Figure 8).

The magnitude of increase in aqueous mercury concentration at sampling locations (i.e., Outfall 109, Stations C11 and C08) was proportionally small compared to flow rate reduction. For example, at C08, average values of waterborne mercury increased by only 12 ng/L (from 349 to 361 ng/L) following the reduction in flow management augmentation. At C11, the flow rates showed a 40% volumetric reduction, but the average mercury concentration increased by about 25%. The lack of a large increase in mercury concentration associated with decreased dilution generally meets our expectation as illustrated in Figure 3. The reduced hydraulic head leads to less subsurface flow, which in turn results in less sediment bound mercury release to surface water. However a quantitative analysis is difficult because the variability in the daily mercury concentrations and flow rates. Additionally, in-stream removal of mercury may occur during the experiment. A longer period of experiments should be conducted to include daily, weekly and seasonal variability to improve data interpretation.

The diverted volume of flow added at Outfall 2 maintained the flow discharge at Station 17 at its normal range throughout the flow diversion experiment. Thus, a reduced sediment load at upstream locations was anticipated to result in a decrease in waterborne mercury concentration at Station 17. Figure 9 shows the mean mercury concentration at Station 17 before, during and after the flow diversion experiment. A small decrease, 14 ng/L, in average total mercury concentration at Station 17 was observed after reducing the flow management input in the headwater near Outfall 200. At a typical Station 17 discharge rate of 27,000 m^3/d, this represents a 0.4 g/d reduction in mercury inputs at this location. As noted earlier, because of rainfall and the resulting high flows (Figure 10), as well as other complications during the post-flow diversion phase, the mercury data collected during the post-flow diversion period was not used as a baseline number in the discussion.

2.3.3 Effect of Flow Reduction on Mercury Flux from the Streambed Between C11 and Outfall 109

The most straightforward measure of net mercury flux from the UEFPC streambed is the change in waterborne total mercury concentration between monitoring station C11 and the bridge at Outfall 109, 250 meters downstream (See Figure 2). There are no known substantial discharges adding to the flow between those points, and thus it is assumed that the concentration change is a direct measure of the change in mercury flux from the sediments due to streambed through-flow (See Figure 3). The amount of mercury gained from the streambed is calculated using the flow at C11 multiplied by the change in total mercury concentration between the two locations. Results of that analysis for the experimental reduction in flow are depicted in Figure 11.
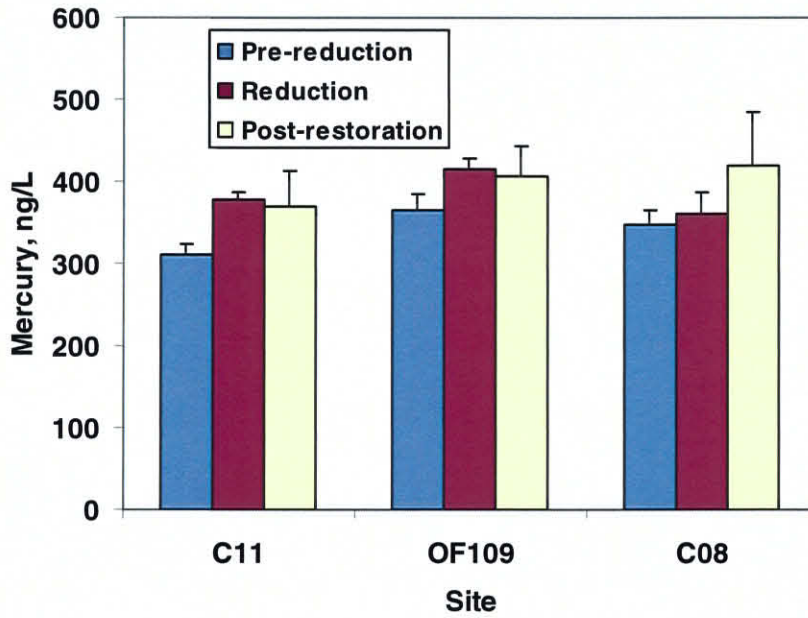
Fig. 7. Mean total mercury concentrations at surface water sampling locations in UEFPC, including C11, at Outfall 109 (labeled as OF109) and C08. Data are average of each 2-week period before, during, and after flow reduction-diversion of approximately 50% volume of water from flow management system.
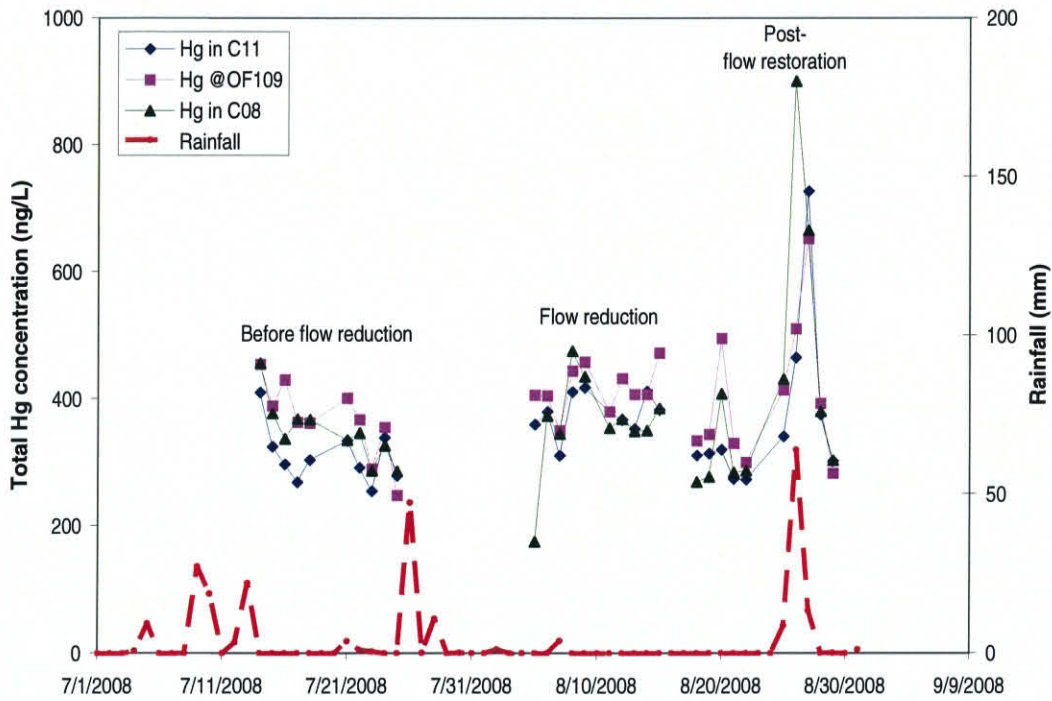
Fig. 8. Time-series of total mercury concentration at surface water sampling locations in UEFPC, including C11, at Outfall 109 (labeled as OF109) and C08. Rainfall data during the flow diversion study are shown.
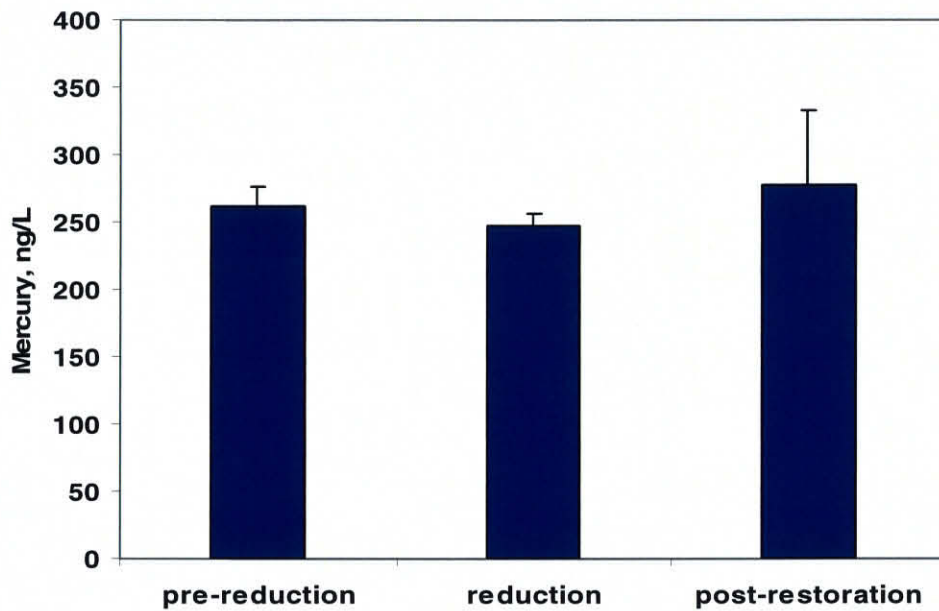
Fig. 9. Mean total mercury concentration in UEFPC at Station 17 in the three 2-week periods before, during, and after an approximately 50% reduction in flow management input near the headwater of UEFPC.
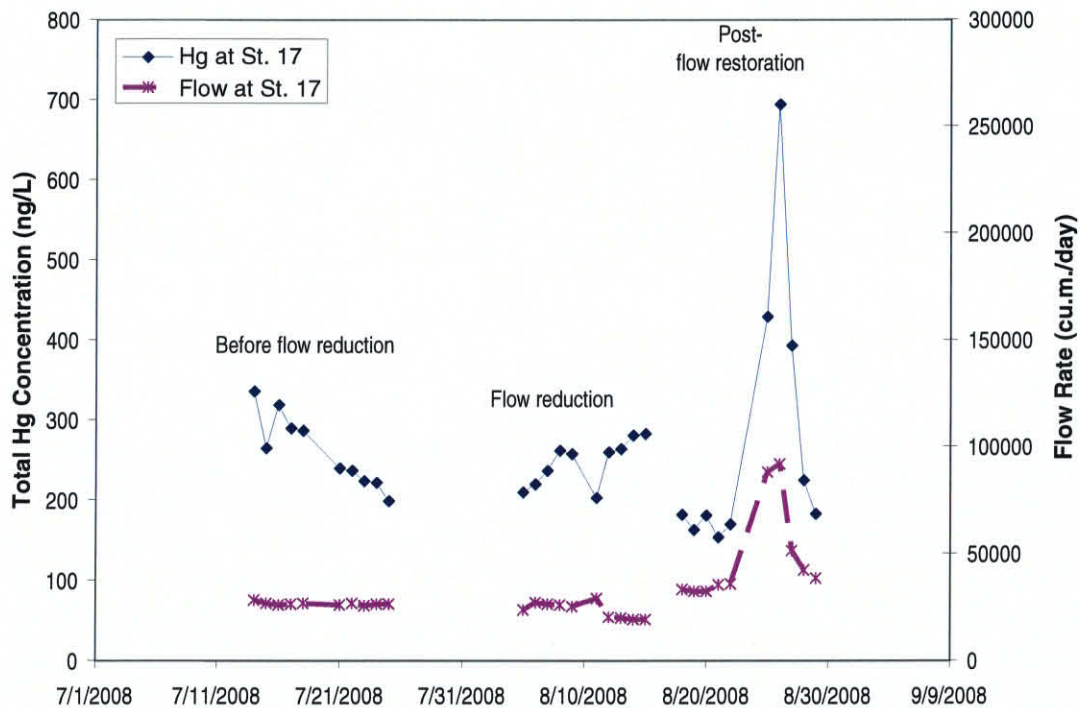
Fig. 10. Time-series graph of total mercury concentration and flow at Station 17 during the flow management diversion study.
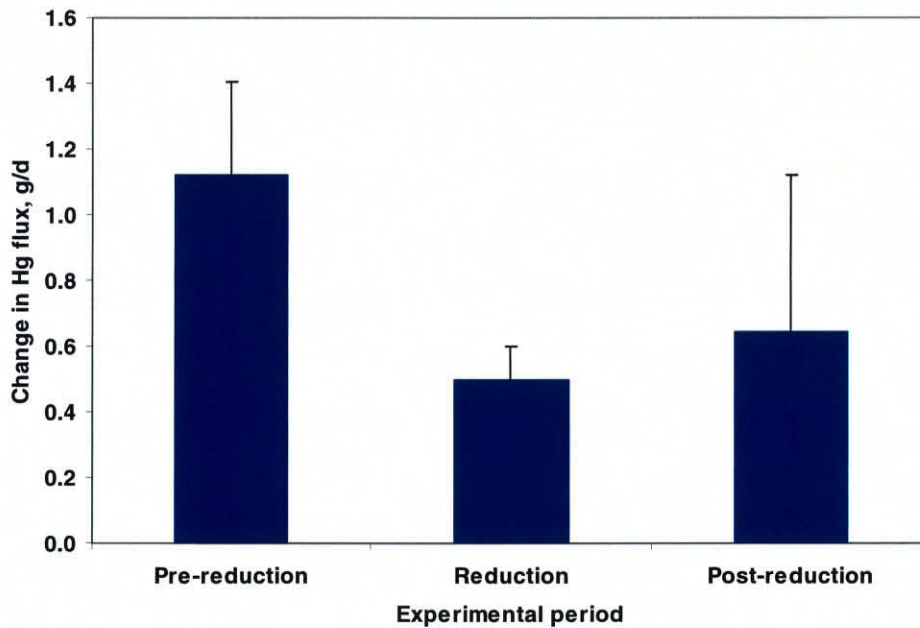
Fig. 11. Mean change in mercury flux across the stream section between Outfall 109 and C11 in two-week periods before, during, and after a 50% reduction in flow augmentation at the headwater of UEFPC.

In the two week period prior to flow reduction, the average input of mercury to the surface flow of UEFPC in the reach between monitoring station C11 and Outfall 109 was 1.1 ± 0.28 grams per day (mean ± SE, n = 10). Following reduction in flow, the mercury input decreased to 0.50 ± 0.10 g/d, and rebounded to 0.64 ± 0.48 g/d in the two-week period after flow was restored Figure 11). Statistical comparison of the pre-reduction flux with flux under reduced flow (one-tailed T test, assumption of unequal variances) indicated a statistically significant difference (P = 0.03). The comparison between reduced flow conditions and post-flow restoration period was not statistically significant. However, the post-flow restoration period was complicated by difficulties in restoring flow to its original magnitude and by high flows associated with heavy rainfall (Figure 4). The high variability (large SE) in added flux over this period was a result of these conditions. Thus, the comparison of the two-week period of stable decreased flow with the two-week post-restoration period is not a valid measure of changes in mercury flux associated with flow reduction.

Figure 12 shows the change in mercury flux and flow rate between stations C11 and C08 (located downstream of Outfall 109). Both mercury flux and flow rate changes between stations are lower during flow diversion compared to pre-diversion conditions, which confirms our hypothesis that reduced hydraulic head at Outfall 200 (by flow reduction) would reduce the amount of sediment bound mercury release. The impact of the rainfall is apparent during the post-diversion period; there was a significant influx of water as well as mercury between the stations probably from outfalls (e.g., Outfall 109), upwelling streamed flow and groundwater between these two monitoring stations.

Statistical comparison of pre- and post-flow alteration periods entails the assumption that the flux of mercury from the streambed to overlying water in the source reach was a random variable (thus, the flux observed one day was not related to that seen the previous day). Mercury inputs from the reach between C11 and C08 appeared to trend downward in the two-week pre-flow alteration period. While an apparent downward trend is certainly possible within a random assortment of a relatively small number of data points such as this, it nevertheless does add a degree of uncertainty to the conclusions and reinforces the need for evaluation of the effect of flow alteration over a much longer period of time.

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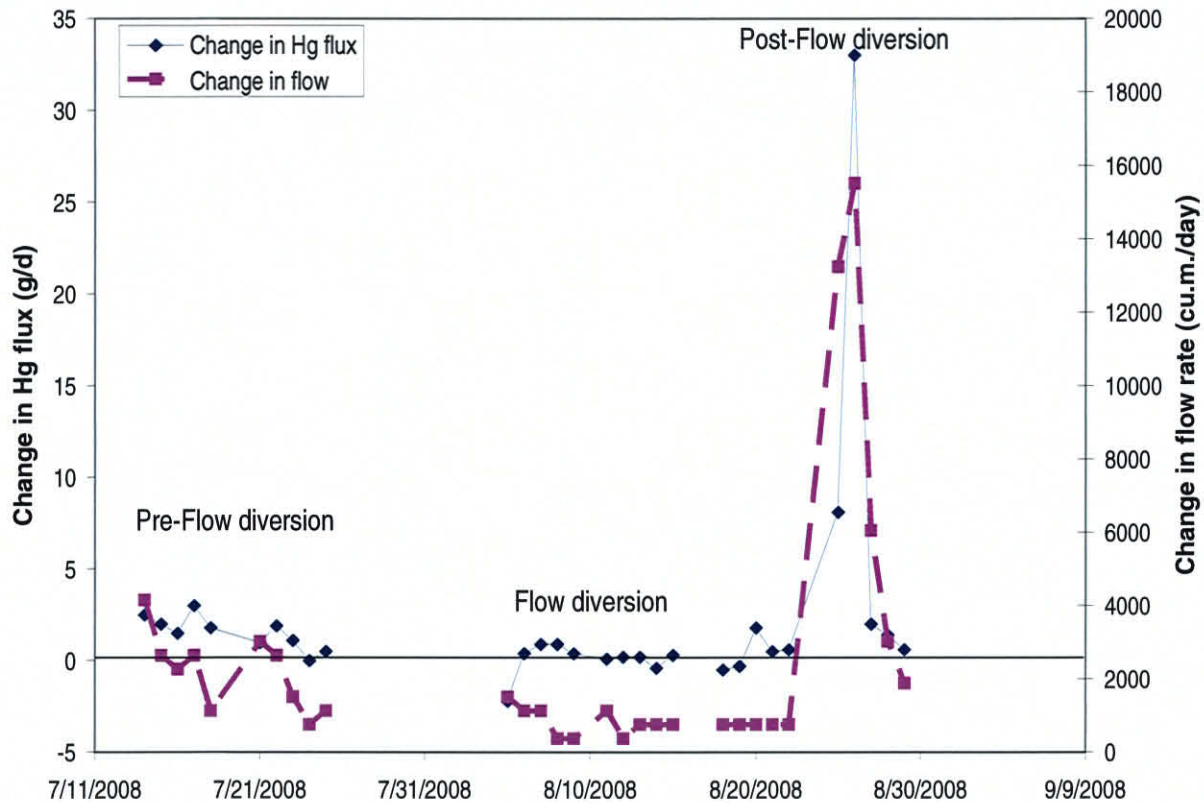
Fig. 12. Change of mercury flux (grams per day) in stream water between C11 and C08, which includes the suspected mercury contaminated reach of UEFPC.

2.3.4 Effect of Flow Reduction on Mercury at Monitoring Stations C11, C08, and Station 17

Both flow rates and mercury concentrations were measured at three sampling locations in UEFPC: C11, C08, and Station 17. Mercury flux can thus be computed at each location from the product of total mercury concentration and volumetric flow rates. Comparisons among these three sampling locations are subject to confounding factors such as streambed uptake of mercury, other outfall discharges between C11 and downstream sampling locations, and inconsistent methods of measuring flow rates using different stream-flow gauges. Nevertheless they provide data with which to evaluate the effects of flow reduction. The data are depicted in Figures 13 and 14.

Monitoring station C08 is located a short distance downstream from the Outfall 109 location (Figure 2) and is used to measure streambed fluxes (discussed in the previous section). The difference in mercury flux at the gauged monitoring stations C11 and C08 represents inputs from the streambed source and inputs and losses that occur between Outfall 109 and C08. During the pre-flow reduction phase, average mercury flux increased from 6.4 ± 0.30 g/d at C11 to 8.0 ± 0.43 g/d at C08, a net increase of 1.6 g/d (Figure 13). In the two weeks of reduced flow, the mean fluxes at the two sampling locations were 4.6 ± 0.15 g/d at C11 and 4.7 ± 0.3 g/d at C08, a net increase of 0.1 g/d (Figure 13). In the post-reduction period, fluxes were 10.0 ± 2.4 and 14.7 ± 5.0 g/d at those locations, respectively (Figure 13). The 4.7 g/d increase observed between C11 and C08 during the flow restoration period was heavily influenced by increased flow between the sampling locations during wet weather (Figure 14), much of which entered via Outfall 109.

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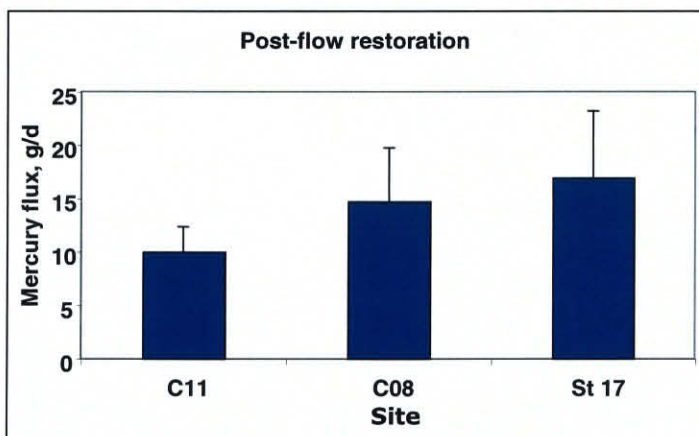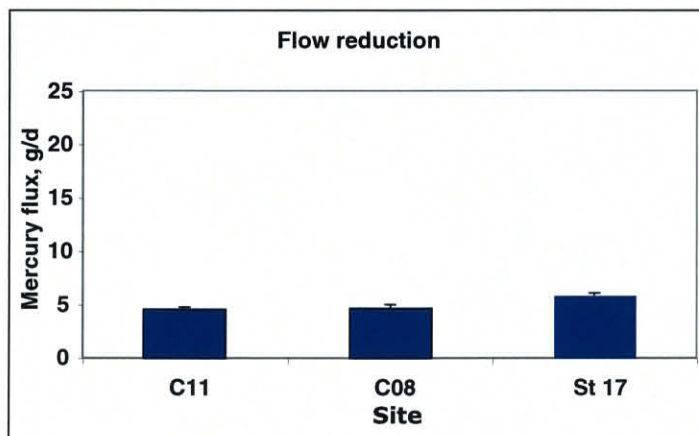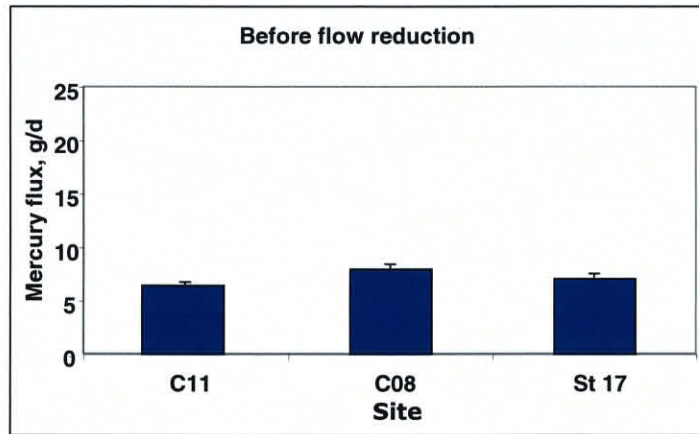
Fig. 13. Mean mercury flux (grams per day, ± SE, n = 10) at gauged monitoring stations in Upper East Fork Poplar Creek in the two-week periods before, during, and after a 50% reduction in flow augmentation at the headwater of UEFPC.
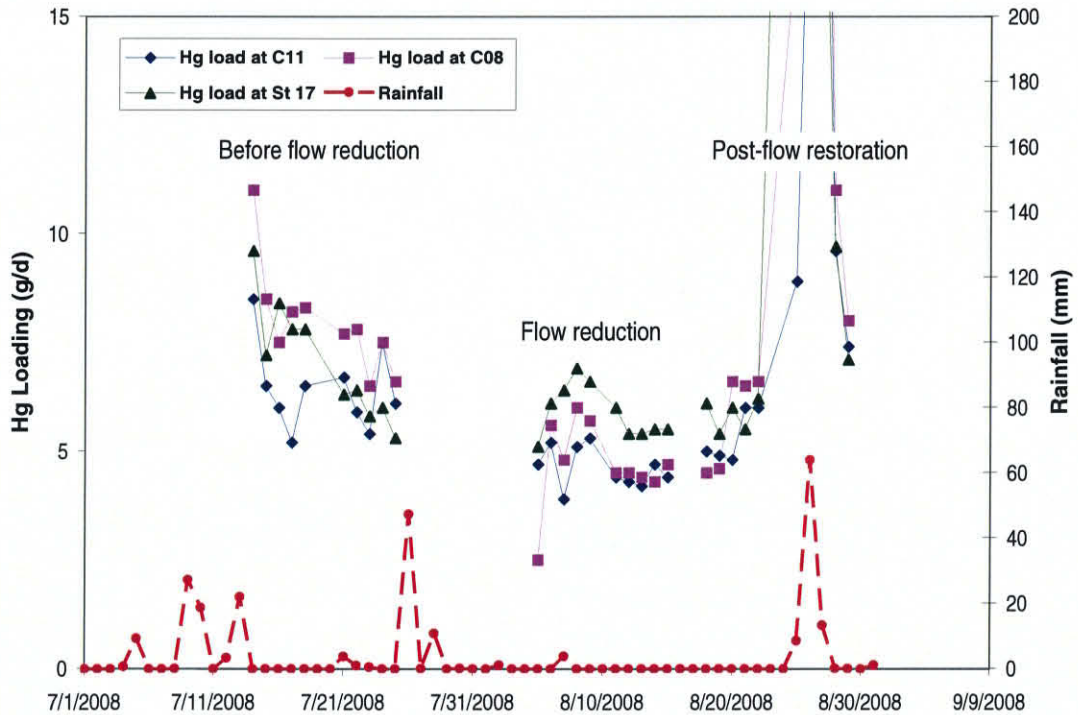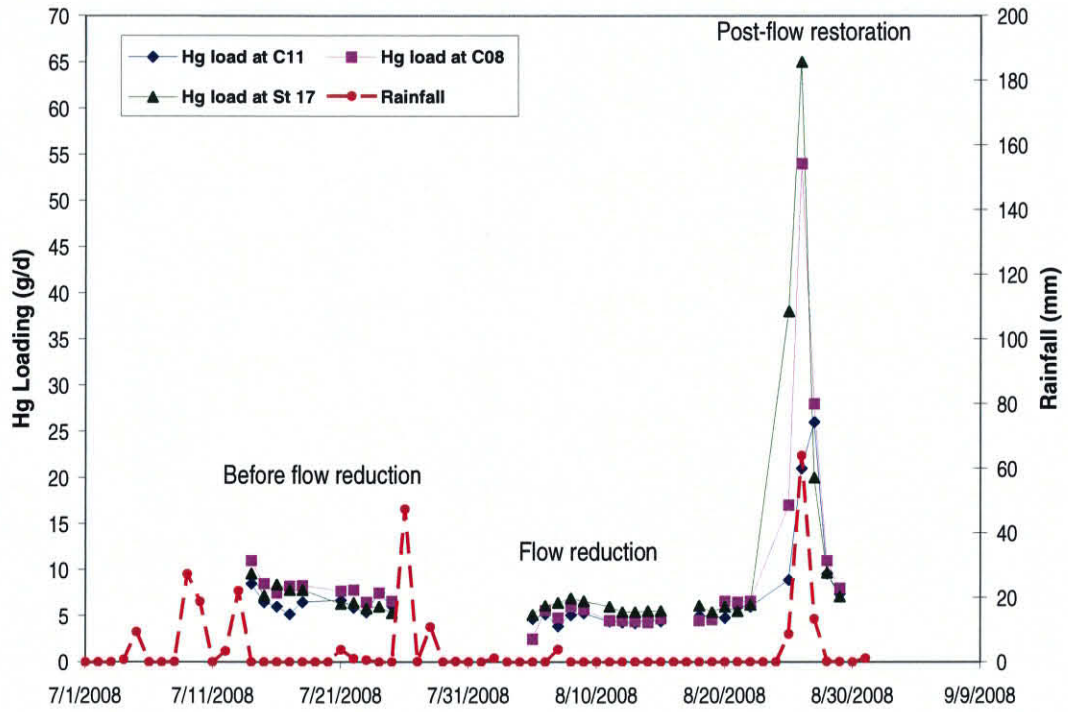
Fig. 14. Time series of mercury flux (grams per day) at monitoring stations (C11, C08 and Station 17) in the UEFPC before, during, and after a 50% reduction in flow augmentation at the headwater of UEFPC. The graphs show the same set of data; the y-scale in the lower graph was chosen to show details in the monitoring period before the significant rainfall that occurred during the post-flow diversion monitoring.

Station 17 is the long-term monitoring site for the Y-12 NPDES permit, where mercury bioaccumulation in fish has been monitored since 1985. Mean mercury flux at this location was 7.1 ± 0.43 g/d in the pre-reduction period and decreased to 5.9 ± 0.19 g/d during the period when headwater flow was reduced. During the wet weather-influenced period after flow restoration, mercury flux averaged 16.9 ± 6.2 g/d at this location.

Figure 14 shows time series plots of daily mercury flux at C11, C08 and Station 17; the upper graph shows the whole range of data obtained during the entire field test while the lower graph is scaled to show more details in fluxes before the major rain event during the post-flow restoration period. The lower graph of Figure 14 shows a drop in flux at both C11 and C08 during flow reduction. This drop in flux carries through the first two days of the post-flow restoration period when the flow augmentation had not been fully restored at the headwaters of UEFPC (see Figure 4). On Days 3 to 5 of the post-flow restoration period when flow augmentation had been restored but before the major rainfall event, the flux at C08 jumped to levels that were comparable to the levels before flow reduction. After Day 5 of the post-flow restoration period when the significant rainfall occurred, large increases in flux were observed at all 3 stations (upper graph of Figure 14).

During the pre-flow reduction period, daily net losses in mercury occurred predominantly between C08 and Station 17 (lower graph of Figure 14 and Figure 15). Under baseline conditions mercury is removed between C08 and Station 17, possibly through biological reactions in the sediment or settlement of particulate-bound mercury. This net loss is also observed in Days 3-5 of the post-flow restoration period before the rainfall and when baseline flow augmentation conditions had been re-established (Figure 15). If the removal of mercury in this reach is due to settlement of particulates during baseflow, the deposited mercury can be mobilized and carried downstream of Station 17 during major storm events, such as that observed during the post-flow restoration period (Figure 15).

During flow reduction, a net gain in mercury between C08 and Station 17 was observed (Figure 15). The source of this net gain is not known at the present, but may be attributed to existing outfalls, emerging subsurface (groundwater or streambed) flow or desorption from the stream bed.

2.3.5 Changes in Subsurface Water Chemistry in Mercury Source Areas

Preliminary results of the evaluation of subsurface and surface water chemistry response to flow management diversion showed results that could have important implications. The shallow streambed piezometer (site SS1) located within the streambed source reach between C11 and Outfall 109 (not shown on Figure 2) contained water with very high dissolved mercury concentrations, generally exceeding 20,000 ng/L. Prior to diversion of the flow management augmentation, much of that dissolved mercury was in the form of elemental mercury, $Hg(0)$. However, by the start of the second week of reduced augmentation, $Hg(0)$ in the SS1 samples dropped to less than 50 ng/L. Dissolved mercury, however, remained very high (8000–36000 ng/L). Redox measurements on SS1 water did not indicate the presence of strong oxidizing conditions, suggesting that oxidation of $Hg(0)$ to $Hg(II)$ was not responsible for this observed result. At the present time we have no explanation for this phenomenon.
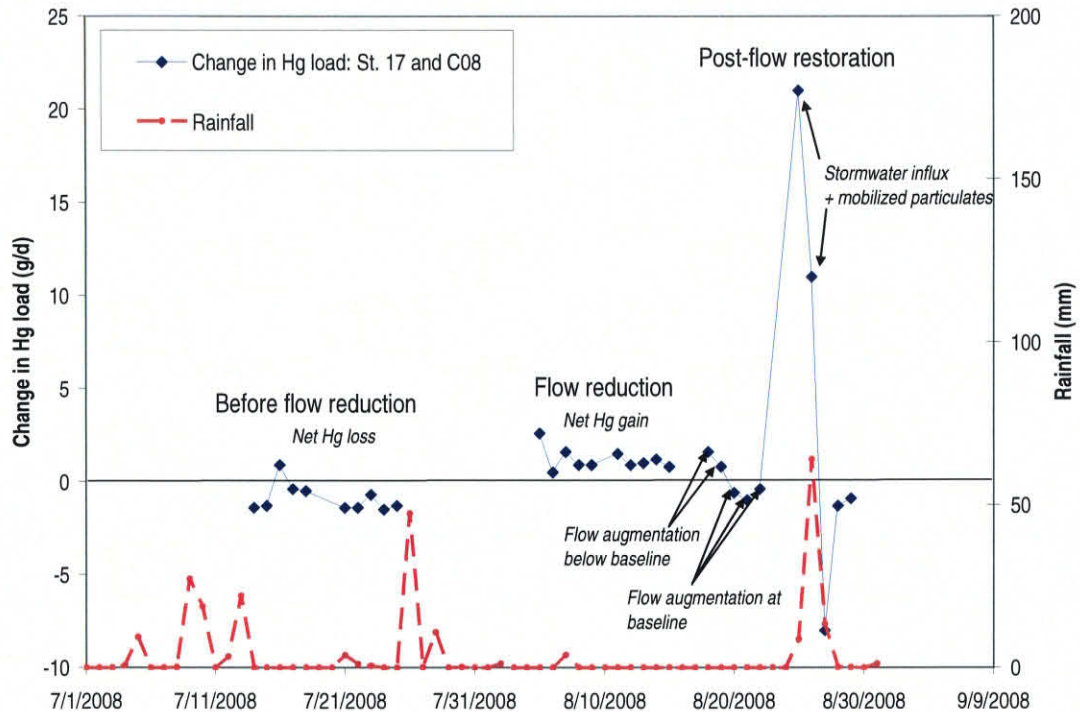
Fig. 15. Change in daily mercury flux (grams per day) vs. time between Station C08 and C17 before, during, and after a 50% reduction in flow augmentation at the headwater of UEFPC. Daily precipitation at the NOAA Oak Ridge station is also shown.

2.4 PRELIMINARY CONCLUSIONS

Diversion of 50% of the flow currently added to UEFPC by the flow management system appeared to reduce mercury inputs from a localized, highly contaminated streambed by 0.6–1.5 g/d, depending on the sampling location. A reduction of 0.6 g/d would represent about a 7-10% decrease in mercury input to UEFPC. Mercury concentrations within UEFPC did not rise proportionally with the loss of dilution, in part because of the reduction in input from the streambed source and in part because of reduced flow from the Y-12 storm drain system (Outfall 200). Although promising, this short-term study cannot verify the sustainability of observed reduction in mercury loading over an extended time period. A longer-term test that includes seasonal variability will be most useful to validate the initial observations of these flow diversion experiments.

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3. INVESTIGATION OF THE USE OF STANNOUS CHLORIDE TO REDUCE MERCURY IN THE Y-12 STORM DRAIN SYSTEM

3.1 BACKGROUND

The chemistry of mercury exiting the Y-12 storm drain at Outfall 200 is unique because residual chlorine (approximately 2 ppm total residual chlorine, TRC) from process water maintains the mercury in a highly reactive dissolved form. This is in stark contrast to mercury within the surface waters of UEFPC a relatively short distance downstream from Outfall 200, where the dissolved reactive inorganic mercury becomes rapidly associated with suspended particulates, dissolved organic matter, and the streambed biofilm. Because mercury within the storm drain system is in a form that can undergo rapid chemical reactions with reductants, complexants, or precipitants, the system provides an exceptional opportunity to chemically reduce mercury and remove it from the water.

Studies conducted in the late 1990s by ORNL in support of the Y-12 Reduction of Mercury in Plant Effluent program (RMPE) demonstrated that the addition of trace concentrations of stannous chloride ($SnCl_2$), a strong reducing tin [$Sn(II)$], was capable of converting inorganic mercury in highly contaminated groundwater (such as that at Outfall 51) to dissolved elemental mercury, $Hg(0)$. RMPE studies also indicated that mercury in the storm drain discharge at Outfall 200 could be converted to $Hg(0)$ by stannous chloride after removal of residual chlorine (Southworth, 1997). In 1997, an experiment was conducted to test whether addition of stannous chloride to UEFPC at the point where it exits the storm drain system could convert a large fraction of mercury to $Hg(0)$. The expectation was that volatile $Hg(0)$ would be lost to the atmosphere through the shallow, turbulent 2.5 km reach of UEFPC between Outfall 200 and Station 17 at the Y-12 NSC boundary. However, the experiment failed to achieve effective production of $Hg(0)$ within the stream. Although the cause of failure was never determined, it is likely that dissolved oxygen and other ephemeral oxidants produced by photochemical reactions oxidized the stannous chloride before it could reduce $Hg(II)$ in the stream flow. Further pursuit of $SnCl_2$ reduction combined with in-situ volatilization as a mercury removal strategy was discontinued.

Although chemical reduction combined with in-situ volatilization did not succeed in sunlight-illuminated surface water, the application of that technology within the enclosed storm drain network holds promise by avoiding complications associated with photochemistry. Within the enclosed system, an enhancement of $Hg(0)$ transfer from water to air may be engineered, with subsequent removal of vapor-phase mercury from air exiting the network. This report summarizes an initial investigation into the feasibility of this technology.

The initial study focused on demonstrating chemical reduction of $Hg(II)$ to $Hg(0)$ within the full flow of UEFPC near the storm drain exit. This probably represents the most challenging point within the system to achieve full reduction of mercury because of high TRC concentrations and the need to mix reagents (dechlorinating agent and reductant) rapidly and efficiently with the entire stream flow. Reduction of $Hg(II)$ within specific mercury-contaminated outfalls, where volumetric flows are much lower and $Hg(II)$ concentrations higher, is likely to be easier to achieve. It, however, is logistically complicated by the need to add reagents simultaneously at multiple sites within the high security zone of the Y-12 complex.

3.2 METHODS

3.2.1 Experimental Sites

Mercury reduction experiments were conducted approximately 64 meters upstream of Outfall 200, where a grating above the junction box at site 200A6 (Figure 2) within the Y-12 NSC was utilized as a portal for introducing reagents to the mercury source water. In the initial two trials conducted on November 17, 2008, sodium thiosulfate and stannous chloride solution were added simultaneously to the pipe exiting 200A6 (Figure 2, Figure 16). Each solution was introduced separately through its own pump and tubing system but the discharge points for both were in close proximity so as to achieve immediate mixing of the two reagents. For the first test, reductant addition was initiated in the morning, after an approximately one-hour period of baseline monitoring, and continued for 1.5 hours with nominal target concentrations of 10 mg/L sodium thiosulfate (0.040 mM) and 20 μg/L Sn(II) (0.168 μM). The reagent feeds were discontinued for a few hours to allow for a return to pre-treatment conditions. A second trial was begun that afternoon with the stannous chloride feed reduced to 50% of that used in the morning trial. The sodium thiosulfate feed was continued at the same rate as in the first trial. Water samples were collected at 10- to 15-minute intervals at Outfall 200 (Figure 2) for analysis of dissolved gaseous elemental mercury, Hg(0) and total mercury, HgT. Samples were collected during the last 30 minutes of each experimental period at downstream locations C03, C05, C08, above Outfall 109, and C11 (Figure 2) to assess the persistence of Hg(0) in the open-stream water. Those samples were analyzed for Hg(0) and HgT.
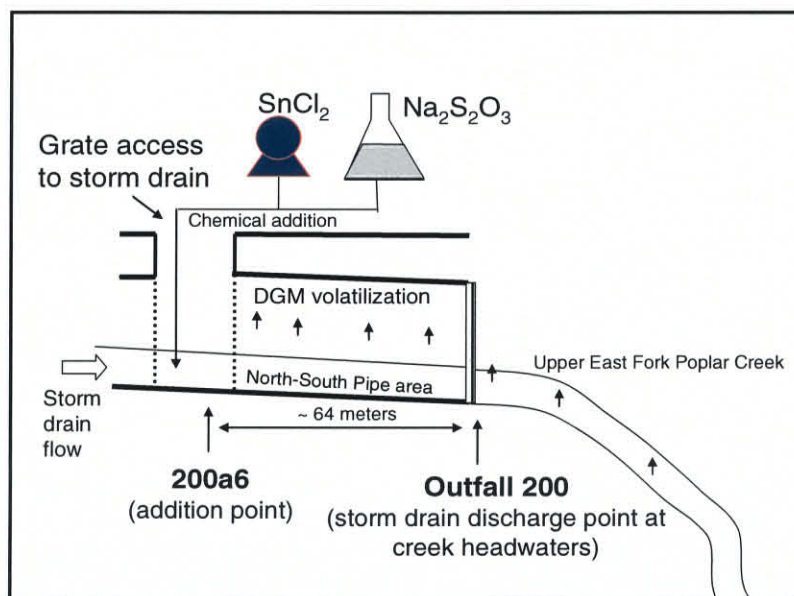
Fig. 16. Schematic of the stannous chloride (SnCl₂) pilot test in the Y-12 storm drain system entering UEFPC.

A third trial was conducted on November 25, 2008, with the objectives of addressing questions raised in the first two tests conducted on November 17 and also of evaluating the reproducibility of results of those tests. The third test differed from the first and second tests in that the sodium thiosulfate feed was initiated and run for one hour before adding the stannous chloride solution. The sodium thiosulfate and stannous chloride feeds were continued for two hours. Baseline monitoring was carried out for one hour after cessation of the two reagent feeds. Downstream sampling of HgT and Hg(0) was carried out during the initial baseline period (before either chemical was added) and near the end of all reductant addition. Two

additional sites located farther downstream were monitored during the third trial, i.e., Station 17 at the Y-12 boundary and the bridge over UEFPC at Lake Reality (Figure 2).

3.2.2 Pre-experiment Estimates of Reagent Addition

Water samples collected from 200A6 on several occasions during October 2008 were used for laboratory work to support pre-experiment estimates of reagent demand during the field tests. These preliminary experiments indicated that total residual chlorine (TRC) ranged up to approximately 2 mg/L (0.028 mM Cl_2). If not removed, this residual chlorine would oxidize the added Sn(II) before it reacted with Hg(II). The TRC was rapidly and effectively removed via sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) addition. Ammonium bisulfite (NH_4HSO_3) was also tested and proved to be a good dechlorinating agent, but it significantly interfered with the reaction between stannous chloride and mercury and was therefore not considered further. Thiosulfate has very low inherent aquatic toxicity. Unlike bisulfite, thiosulfate does not rapidly oxidize and consume aqueous dissolved oxygen. Therefore, no risk to aquatic life was posed by utilizing thiosulfate in excess of that needed to dechlorinate the stream flow effectively. Treating the dechlorinated water with 20 µg/L Sn(II) (0.168 µM), added as $SnCl_2 \cdot 2H_2O$, converted 90% of the Hg(II) into Hg(0). The residual 10% Hg was not converted to Hg(0) at higher Sn(II) concentrations.

3.2.3 Outfall 200 Discharge Estimates

An estimate of the volumetric discharge (L/d) at Outfall 200 was needed to calculate reagent addition for the field experiments. This was estimated using a mixing model and data collected in August 2008 during flow diversion experiments (see sect. 2) which provided the water composition at Outfall 200 and water composition and discharge rates at the Clinch River water input and monitoring station C11. Using this method, Outfall 200 discharge was estimated to be $(4.4 \pm 1.3) \times 10^6$ L/d ($\pm$ 1 std. dev). This method also led to an estimated dilution factor for Outfall 200 water at C11 of 0.21. Subsequent to this estimate, flow data recorded at 200A6 for the month of October 2008 were made available to this study by Bechtel Jacobs Co. LLC (BJC). Mean baseflow discharge from this dataset was $(5 \pm 1) \times 10^6$ L/d, in good agreement with our previous calculations.

3.2.4 Thiosulfate Demand

The reaction of residual chlorine with thiosulfate in natural waters is a complex, multi-step process whose stoichiometry varies with chemical characteristics of the water, primarily pH and hardness. Optimally, one gram of sodium thiosulfate ($Na_2S_2O_3$) reacts with almost 2 grams of chlorine, producing sulfate and chloride as reaction products. Dechlorination of the source water (~2 ppm TRC) required approximately 4 mg/L sodium thiosulfate in a preliminary laboratory test. The recommended application rate of the commercially obtained dechlorinating agent was 1.6 to 2.6 mg/L of sodium thiosulfate. In order to ensure rapid, full dechlorination of the source water, an excess amount of sodium thiosulfate was deemed necessary. Therefore, a target application rate of 10 mg/L sodium thiosulfate was selected. This required that a 10% solution of sodium thiosulfate be added to the estimated flow of 250,000 L/h at the rate of 25 L/h.

Because the Y-12 NSC's Utilities group operates an automated dechlorination system (using ammonium bisulfite) just upstream of the North/South pipe's discharge at Outfall 200 and downstream of our thiosulfate injection point, measurement of total residual chlorine during the test was unnecessary. During our injection periods, the instrument read-out at the automated dechlorination delivery system provides continuous data on the bisulfite demand. The bisulfite demand of the automated system decreased to its minimal level after initiation of the test thiosulfate addition, suggesting that this addition upstream had achieved its goal of dechlorinating the flow.

3.2.5   Stannous Chloride Demand

The stannous chloride reductant was added from a stock solution separate from the thiosulfate solution using its own dedicated pump and tubing. Stannous tin is readily oxidized by atmospheric oxygen with the oxidation rate increasing with increased pH and decreased $Sn(II)$ concentration. To maximize the field life of the $Sn(II)$ stock solution, a 1% (w/v) solution of $SnCl_2 \cdot 2H_2O$ (0.0443 M) was prepared in dilute HCl. Preliminary laboratory experiments using water from 200A6 indicated that 0.168 μM $Sn(II)$ reduced 90% of the 0.005 μM mercury present in the water (Sn:Hg molar ratio of 33.7). Higher concentrations of $Sn(II)$ did not increase the amount of mercury reduced (Figure 17).

Using the discharge estimate given above and the average mercury concentration at Outfall 200 (5 nM), the mercury flux was estimated to be 921 μmole/hr, which would require 31.03 mmole $Sn(II)$ per hour. Therefore, the $Sn(II)$ stock solution (44.3 mmol/L) was delivered at a rate of 0.7 L/hr.

Once oxidized via reaction with mercury, the resultant $Sn(IV)$ readily hydrolyzes to form poorly soluble (oxy)hydroxide phases and attaches to available surfaces. Assuming neither one of these reaction pathways occurred to remove Sn from the water, the 0.21 dilution of Outfall 200 water would result in dissolved Sn concentrations of 0.0353 μM (4.2 $\mu g/L$) at C11. Samples for Sn analysis were collected at Outfall 200 and monitoring station C11.

3.2.6   Reagent Delivery in the Field

The stannous chloride solution was prepared fresh each day in the laboratory and transported to the field site. The sodium thiosulfate solutions were prepared in the field immediately prior to use by dissolving the indicated salt in distilled deionized water. A dedicated peristaltic pump was used for each solution; flow rates set in the lab were verified again in the field prior to beginning each experiment. Flexible tygon tubing from each pump was fed through fifteen feet of 0.75-inch PVC well casing which was then inserted through the grate above 200A6 and placed approximately 2 feet into the mouth of the pipe leading out of the vault at 200A6 to Outfall 200 (Figure 16).

Prior to beginning the injection, duplicate samples of water from 200A6 were tested for TRC in case the thiosulfate addition needed to be increased. Because of the benign properties of thiosulfate, it was not deemed necessary to decrease its delivery rate if TRC concentrations were lower than 0.028 mM. For the two experiments conducted on November 17, 2008, TRC was measured to be (0.0178 ± 0.0002) mM and (0.0138 ± 0.0003) mM. On November 25, 2008, TRC was measured to be (0.0169 ± 0.0001) mM. Thus no adjustments to the thiosulfate addition rate were made for these experiments.

3.2.7   Potential Dissolved Elemental Mercury Evasion from Stream Following Stannous Chloride Addition

The potential evasion of dissolved elemental mercury, $Hg(0)$ from water to air was estimated using a two-film gas transfer equation which assumes turbulent mixing in the bulk air and water phases with molecular diffusion across the air-water interface.

$$F = K_g [C_w - HC_w]$$

$F = flux\ (mass\,/\,L^2\,/\,time)$

$C_w = concentration\ in\ water\ (mass\,/\,L^3)$

$K_g = cumulative\ gas\ exchange\ coefficient\ (L\,/\,T)$

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H}{k_l};\quad k_g, k_l = \text{gas transfer coefficients in air and water, respectively (L/T)}$$

and H = Henry's law constant for Hg = 0.323

The gas transfer coefficients have been measured as k_g = 16 cm/h and k_l = 1000 cm/h (Southworth, 1997). Assuming the tin added reacts with 90% of the 5 nM mercury as observed in the preliminary lab tests, the flux of mercury would be 485 nmole Hg/ m^2/ h. This is an ideal estimate of mercury loss. To a first approximation, under baseflow conditions the volume of water under each square meter of water surface in the pipe leading from 200A6 to Outfall 200 contains 763 nmoles of mercury. Recorded flow data and results of our experiments yield an estimated travel time from the injection point to Outfall 200 of about 7 minutes (the distance between the two points was estimated). Theoretically, one would anticipate a loss of approximately 55 to 82 nmoles of total mercury (7-10% of the total) under ideal conditions for this passive mercury evasion mechanism. Several mechanisms may be anticipated *a priori* that would decrease the actual observed mercury loss, including:

- Inefficient water-air exchange of the dissolved gaseous mercury, Hg(0). This could be addressed by engineering more efficient exchange, e.g., forced ventilation, bubble stripping, etc.; and

- Stagnant air within the pipe likely results in k_l to be much less than 1000 cm/h, in which case evasion of Hg(0) would be gas-phase controlled rather than liquid-phase controlled as was assumed in Southworth 1997.

As will be described below, an additional factor was observed during the tests that overwhelmed the ability to document a decrease in total mercury concentration at Outfall 200.

3.2.8   Tin (Sn) Analysis

Samples for tin (Sn) analysis were filtered (0.45 μm) in the field, preserved with HNO_3/HCl, and refrigerated until analysis by inductively coupled plasma-mass spectrometry (ICP-MS). Preliminary analyses of standards indicated that monitoring two stable Sn isotopes, [118]Sn and [120]Sn, was useful as these provided slightly different sensitivities and consequently, detection limits.

3.3   RESULTS

3.3.1   Laboratory Studies

The 1998 RMPE effort to evaluate in-situ reduction of mercury in UEFPC found that the amount of reductant needed to achieve >90% reduction varied over time and may have been associated with ephemeral or volatile substances that interfered with the reaction between tin and mercury (BJC 1998). Typically, 20–100 μg/L Sn(II) was required to achieve 90% reduction. De-aeration of dechlorinated UEFPC water resulted in near stoichiometric reduction of mercury with stannous chloride. Studies conducted in 1994 for the BJC Water Resources Restoration Program (WRRP) used Sn(II) titration to investigate the potential bioavailability of mercury in UEFPC. These experiments found that mercury in

filtered, dechlorinated water at Outfall 200 was readily reduced by traces of Sn(II), but that EFPC water from downstream sites contained materials (probably natural organic matter complexing agents) that interfered with the reduction of mercury (Figure 17).
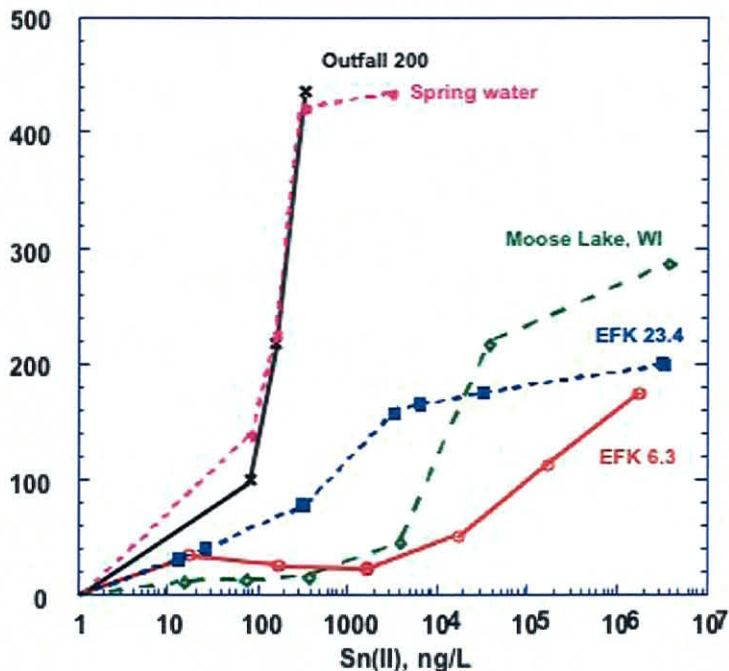
Fig. 17. Titration of filtered water samples spiked with 500 ng/L mercuric nitrate with stannous chloride (SnCl₂). Near 90% of mercury in Outfall 200 water is reduced (~450 ng/L, shown on the graph). Data and figure are from a letter report to Bechtel Jacobs Co. LLC, "Investigating Increased Mercury Bioaccumulation in Fish in Lower East Fork Poplar Creek", G. Southworth, M. Peterson, M. Bogle, and W. Hill, October 2004.

Preliminary results from laboratory studies in summer 2008 using Outfall 200 water indicated that excess ammonium bisulfite interfered with the stannous chloride reaction with mercury. Bisulfite is the dechlorinating agent used at Outfall 200 by the facility operation of Y-12 NSC. Sodium thiosulfate also appeared to interfere with mercury reduction when added to water prior to SnCl₂, but when added simultaneously with Sn(II), 90% of the mercury in water from Outfall 200A6 was reduced to Hg(0) by 20 µg/L Sn(II) (Figure 18). While these results did not approach the highly efficient reduction of mercury by Sn(II) observed in spring water and Outfall 200 water, they did suggest that most of the mercury in UEFPC water could be treated without exceeding 5 µg/L tin at the regulatory monitoring station C11.

The discharge of Outfall 200 into the UEFPC headwaters is a sensitive area because a dense population of fish inhabits the stream immediately downstream of the outfall. Water approximately 30 meters upstream is acutely toxic to fish because of high concentrations of TRC. Before the initiation of flow augmentation at Outfall 200 in 1996, fish kills were a relatively common occurrence in UEFPC. An automated system to dechlorinate the source water a short distance upstream from Outfall 200 adds a slight excess of ammonium bisulfite. During this experiment, risks to the fish population were minimized by selecting a low toxicity dechlorinating agent that could be added a short distance upstream at 200A6. Sodium (or ammonium bisulfite) is more toxic to aquatic life than sodium thiosulfate and it also reacts with dissolved oxygen in water. If utilized in excess to ensure full dechlorination at Outfall 200, there is a risk of depleting dissolved oxygen and causing a fish kill. Therefore, sodium thiosulfate was chosen as a safer

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agent to use where no chlorine-dechlorinator feedback system could be employed to minimize the amount of agent added.
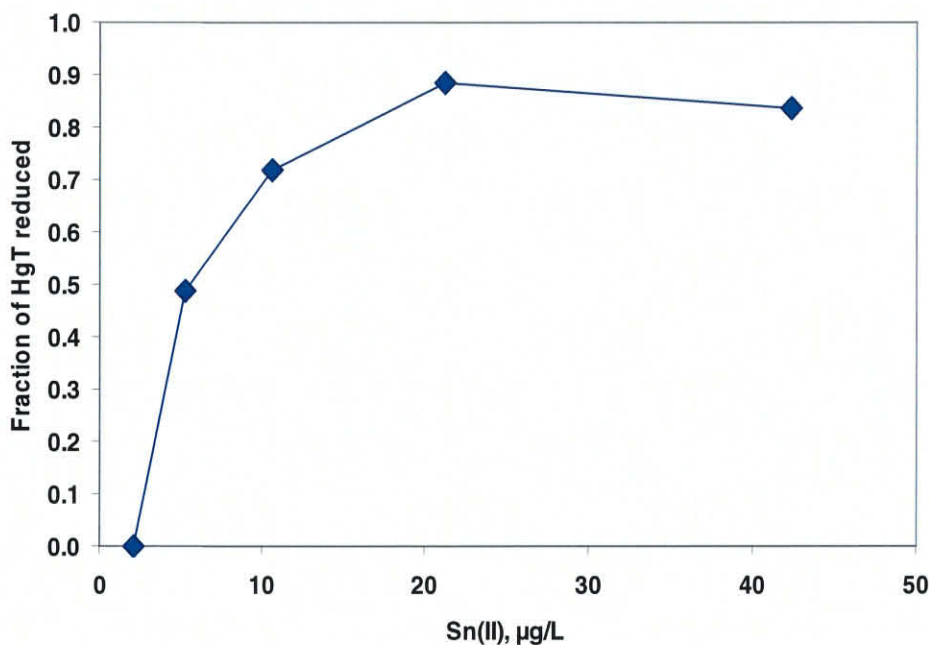
Fig. 18. Titration of Outfall 200A6 water from UEFPC with stannous chloride (SnCl₂) added simultaneously with sodium thiosulfate. Final concentration in water was 20 mg/L sodium thiosulfate in all samples. Mercury in the original solution was ~ 1400 ng/L.

3.3.2   Field Test of Mercury Reduction

The first test of chemical reduction of mercury within the storm drain system of UEFPC, for which the target concentration of Sn(II) was 20μg/L at Outfall 200, was successful at reducing 30% of the baseflow mercury concentration in the outfall to Hg(0) (Figure 19). Shortly after dechlorination and reduction were initiated, aqueous Hg(0) increased from <10 to 340 ng/L and remained relatively unchanged throughout the period of stannous chloride addition, averaging (±SE) 310 ± 9 ng/L. Upon cessation of the thiosulfate and stannous chloride input, Hg(0) concentration rapidly decreased to the very low levels observed before the commencement of the experiment.

The second experiment, carried out in the afternoon of 11/17/2008, maintained thiosulfate at the same level used earlier, but lowered the SnCl₂ to 50% of that used in the first experiment. The concentration of Hg(0) attained at this lower Sn(II) addition rate was 198 ± 7 ng/L, about 65% of the concentration attained at the higher reductant concentration. The non-linear response to changing the concentration of SnCl₂ was similar to that observed in preliminary laboratory tests (Figure 17). As in the first test, Hg(0) rapidly increased following the start of SnCl₂ addition, and similarly decreased rapidly after stopping SnCl₂ addition.
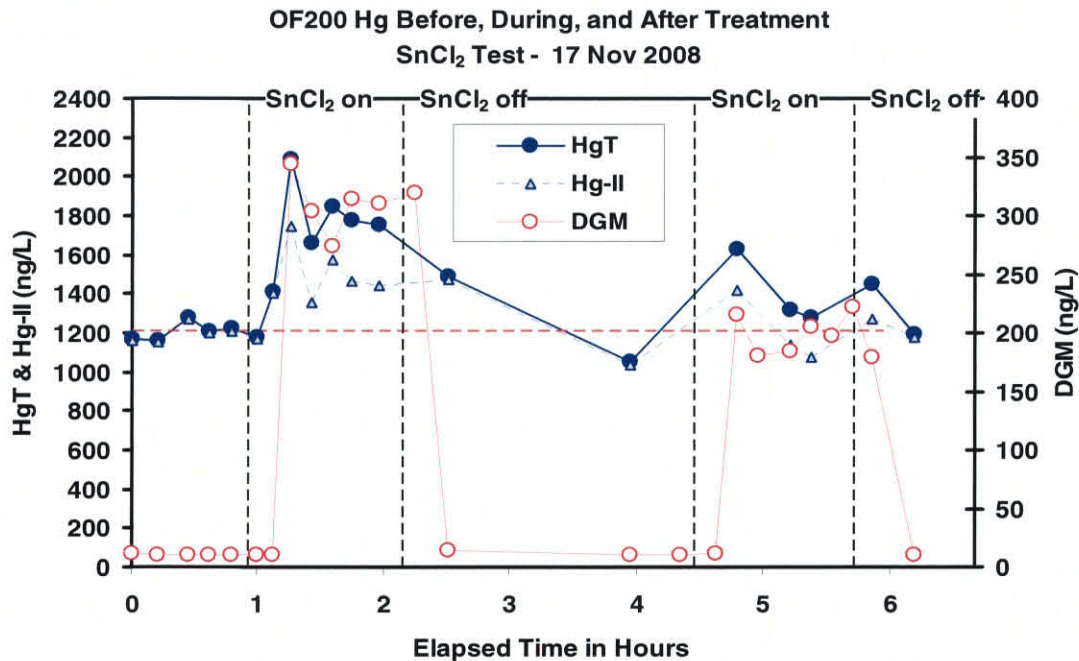
Fig. 19. Concentrations of total mercury (HgT), dissolved gaseous mercury [representing Hg(0)] and Hg(II) (shown as Hg-II, estimated as HgT-DGM) in UEFPC at Outfall 200 before and after injection of SnCl₂ with sodium thiosulfate. Target Sn(II) concentration at Outfall 200 after mixing was 20 ng/L in the first experiment (before hour 4) and 10 ng/L in the second trial (after hour 4).

Total aqueous tin concentration was measured at Outfall 200 and the regulatory monitoring point 200 meters downstream at C11 to demonstrate that tin did not exceed 5 µg/L at location C11. Tin at C11 did not exceed the detection limit of the ICP/MS analysis. A maximum concentration of 8µg/L was observed at Outfall 200. A water sample for toxicity testing was also taken at C11 one hour after initiation of the high dose SnCl₂. That test found no toxicity (100% survival of *Ceriodaphnia sp.* test organisms in treated and control water), as was expected. Airborne mercury concentrations measured at the Outfall 200 pipe-face and within the Station 200A6 location where sodium thiosulfate and stannous chloride were added remained low during the test, with maximum concentrations of about 1200 ng·m⁻³ observed at each location. Air flow through the system was low during the test, never reaching velocities high enough to measure on the hand held anemometer. If airborne mercury within the storm drain system were assumed to be at the maximum observed value (1200 ng·m⁻³) for the duration of the two trials (7 h) and the velocity of air moving through the N/S pipe was 0.05 m/s (lowest measurement the anemometer could make), the mass flux of mercury to the atmosphere was calculated to be 0.012 g over the 7-h period, a small fraction of the daily waterborne export of 5 to 6 g/d at Outfall 200.

In each of the first two tests, the concentration of total mercury (HgT) at the Outfall 200 monitoring point increased very soon after addition of the reagents, and appeared to decline gradually over the course of the experiments. Measurement of air flow and airborne mercury concentration at the Outfall 200 discharge point was required by TDEC. This requirement necessitated wading into the stream to measure wind speed at the pipe face. Although an effort was made to avoid re-suspending sediments in the course of taking those measurements, it was possible that some of the excess mercury observed in the tests was a result of this disturbance. However, a similar increase in total mercury concentration was not observed when measuring air flow at the pipe face during the baseline monitoring period (before 10:30 am, hour 1, in Figure 19). If sediment re-suspension was not the cause of the excess mercury observed at Outfall 200

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during the experiment, it was probable a result of mobilization of sorbed mercury from the lining of the pipe by thiosulfate.

The follow-up third test was carried out one week after the first two tests. It was designed to test the hypothesis that thiosulfate was mobilizing mercury from within the storm drain, presumably by reacting with mercury sorbed to the wetted portion of the pipe. In that experiment, the thiosulfate feed was started and run for an hour with no $SnCl_2$ addition. The Sn(II) feed was then initiated and continued for two hours at a rate intended to attain a concentration of 20 µg/L Sn.

The follow-up study was successful at identifying the source of excess total mercury in UEFPC stream flow upon reagent injection. When the thiosulfate feed was started, total mercury in water exiting the storm drain system at Outfall 200 rapidly increased from 1060 ng/L to 1810 ng/L (Figure 20). The peak concentration was observed in the initial sample. Thereafter total mercury concentration decreased gradually, as it did in the previous experiment, and returned to near the baseline concentration by the end of the three-hour period of thiosulfate addition (Figure 20). There was no evidence of mercury mobilization associated with the initiation or continuation of the $SnCl_2$ feed. The effectiveness of the 20 µg/L Sn(II) addition was very similar in this experiment to that observed on 11/17/2008. Approximately 30% of the baseline total mercury concentration was converted to Hg(0), reaching a concentration of 360 ± 4 ng/L. Again, a rapid increase to a stable concentration was followed by a rapid decrease to baseline concentrations (<10 ng/L) after the addition of dechlorinator and reductant stopped.
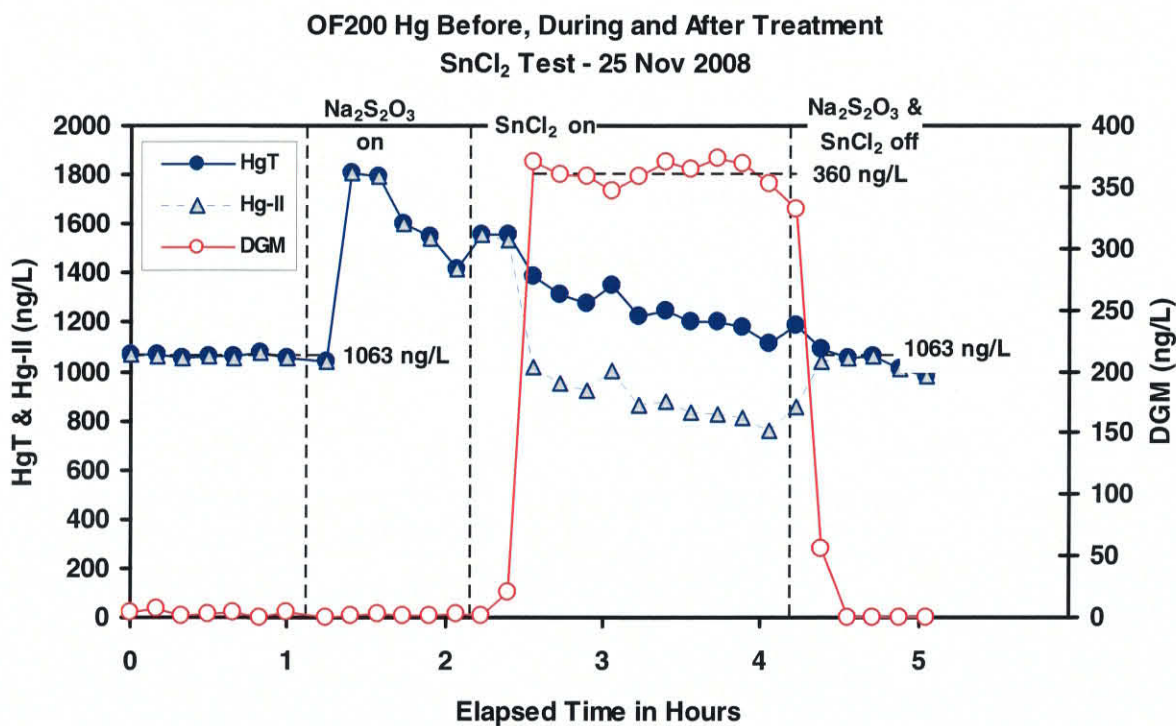
Fig. 20. Concentrations of total mercury (HgT), dissolved gaseous mercury [representing Hg(0)] and Hg(II) (shown as Hg-II, estimated as HgT-DGM) in UEFPC at Outfall 200 following addition of 10 mg/L sodium thiosulfate and followed one hour later by continued thiosulfate and 20 ng/L Sn(II).

Total mercury in Outfall 200 water increased in response to thiosulfate addition and decreased monotonically over the course of the injection period, falling slightly below the pre-injection baseline by the time monitoring stopped. Total mercury flux over that period was estimated by integrating the area

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under the concentration versus time curve using Romberg integration. Time was converted to volume of water discharged using the measured flow recorded at the instrument station at 200A6. Mercury flux during the thiosulfate injection was estimated to be (1.08 ± 0.01) grams (± 95% confidence interval) over the duration of the test which represents (0.19 ± 0.09) grams or (21 ± 12) % more than would have been measured in the absence of thiosulfate. On a daily basis at Outfall 200, this amount of mercury represents an excess of (3.3 ± 1.5) % above the baseline.

Thiosulfate is known to form a moderately strong complex with Hg(II). When in excess (above the stoichiometric chlorine demand in water) thiosulfate may form a stable aqueous complex thus shifting the aqueous-surface equilibrium toward releasing surface bound mercury. Equilibrium geochemical modeling is used below to validate the field observation.

3.3.3 Geochemical Modeling Results

Thiosulfate forms strong aqueous complexes with Hg(II) and may therefore decrease Hg(II) sorption or increase the rate and extent of Hg(II) release from surfaces. This scenario was tested using a numerical model to simulate equilibrium aqueous mercury speciation and sorption reactions. A comprehensive mercury thermodynamic database, compiled under the ORNL SFA project, was used. Mercury sorption isotherms onto ferrihydrite (as a representative solid phase) were simulated using the surface complexation modeling approach as described in Dzombak and Morel (1990) at the ionic strength of Outfall 200 water in the absence and presence of the estimated excess added thiosulfate (Figure 21). In the absence of thiosulfate, mercury exhibits strong sorption onto ferrihydrite with a derived $K_d = 10^6$ which is very similar to that observed for samples from UEFPC. The presence of 20 μM thiosulfate eliminates all mercury sorption due to the formation of stable aqueous complexes (Figure 21). Therefore, the simulation results are consistent with the hypothesis that excess thiosulfate desorbed mercury from the pipe surfaces resulting in transient increased total mercury concentrations at Outfall 200 as observed in the field tests.

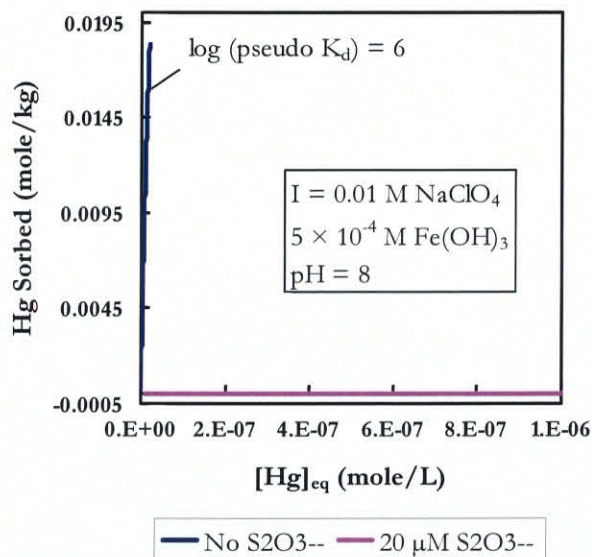**Fig. 21. Isotherms for simulated mercury sorption onto ferrihydrite in the absence and presence of 20 μM thiosulfate.** In the absence of thiosulfate mercury exhibits strong sorption onto ferrihydrite with a derived $K_d = 10^6$, very similar to that observed for samples from EFPC. The presence of 20 μM thiosulfate eliminates all Hg sorption due to the formation of stable aqueous complexes.

3.3.4   In-stream Volatilization of Hg(0)

The high concentrations of Hg(0) in UEFPC water exiting the storm drain system at Outfall 200 provided an opportunity to observe the expected downstream decrease in Hg(0) concentration and loading. The concentration of Hg(0) decreased 4 to 5 fold upon dilution with Clinch River water input, and then decreased at an apparent first order rate with downstream distance in the creek (Figure 22).
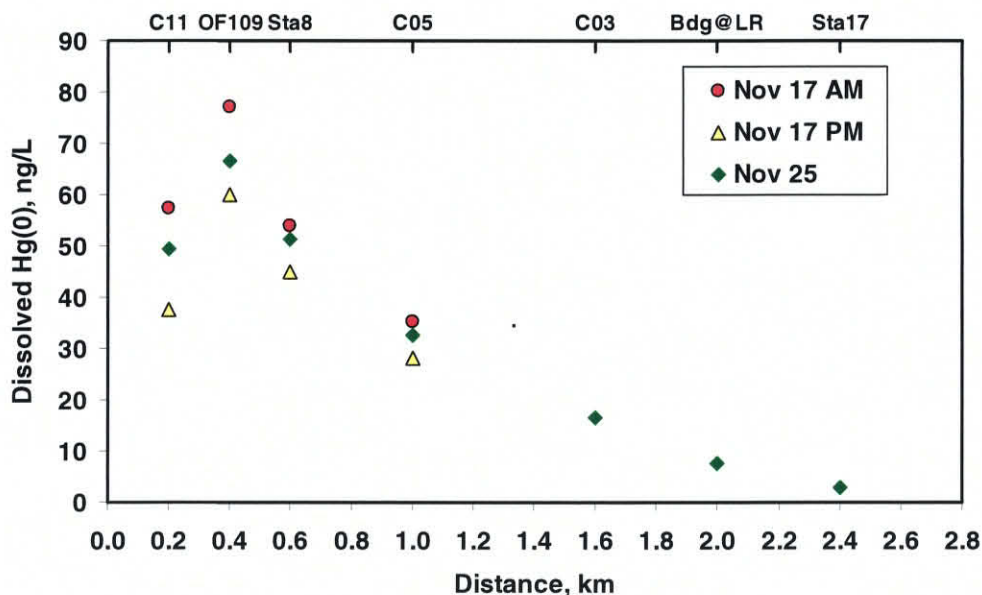

Fig. 22. Downstream decrease in concentration of dissolved gaseous mercury (DGM or Hg(0)) in UEFPC following 1 – 2 hours of reduction of Hg(II) to Hg(0) in UEFPC at Outfall 200. Sampling locations include C11, Outfall 109, Station 8, C05, C03, Bridge at Lake Reality and Station 17 (shown in abbreviation).

In all three trials, Hg(0) concentration inexplicably increased between C11 and the next sampling location downstream near Outfall 109. This is the reach where subsurface deposits of metallic mercury produce high concentrations of dissolved mercury [much of which is Hg(0)] in the streambed sediments. The stream gains additional mercury loading as it transits this reach; however, Hg(0) concentrations in the baseline period (before thiosulfate and SnCl$_2$ addition) were barely detectable. The generation of additional Hg(0) between C11 and Outfall 109 must therefore represent an effect of the experimental treatment, but the causal mechanism is unknown. The first order rate constant for the decrease in Hg(0) concentration with distance downstream from Outfall 109 were remarkably similar in all three trials, ranging from 1.17 to 1.27 km^{-1}.

The change in downstream loading of Hg(0) was computed using the dissolved mercury concentration multiplied by measured flow at 200A6, C11, and Station 17 and interpolated flow estimates at other locations (measured flows at C08 were not used because they appeared to be erroneously low - much lower than that measured at C11 upstream). Results of that analysis are shown in Figure 23. If all of the downstream decrease in Hg(0) is a result of the evasion of volatile mercury from the water to the atmosphere, virtually all the mercury reduced at Outfall 200 would be removed from the creek by the time it reached Station 17 at the boundary of the Y-12 NSC. Studies carried out in 1998 (BJC 1998) under RMPE in UEFPC downstream of the Outfall 51 source of Hg(0) found that Hg(0) decreased even more rapidly downstream than was observed in the 2008 experiments discussed here, and the rate of decrease was substantially higher in daylight than at night. The rate constant of decrease observed in the dark in that study nevertheless exceeded the daylight observations in the 2008 study (1.6 km^{-1} versus ~1.2 km^{-1},

respectively). Follow-up studies by RMPE in UV transparent bottles demonstrated that Hg(0) was readily oxidized in the presence of sunlight in oxygenated water (BJC 1998). The RMPE studies were carried out in summer when solar intensity would have been higher and warmer air and water temperatures would have promoted Hg(0) volatilization.
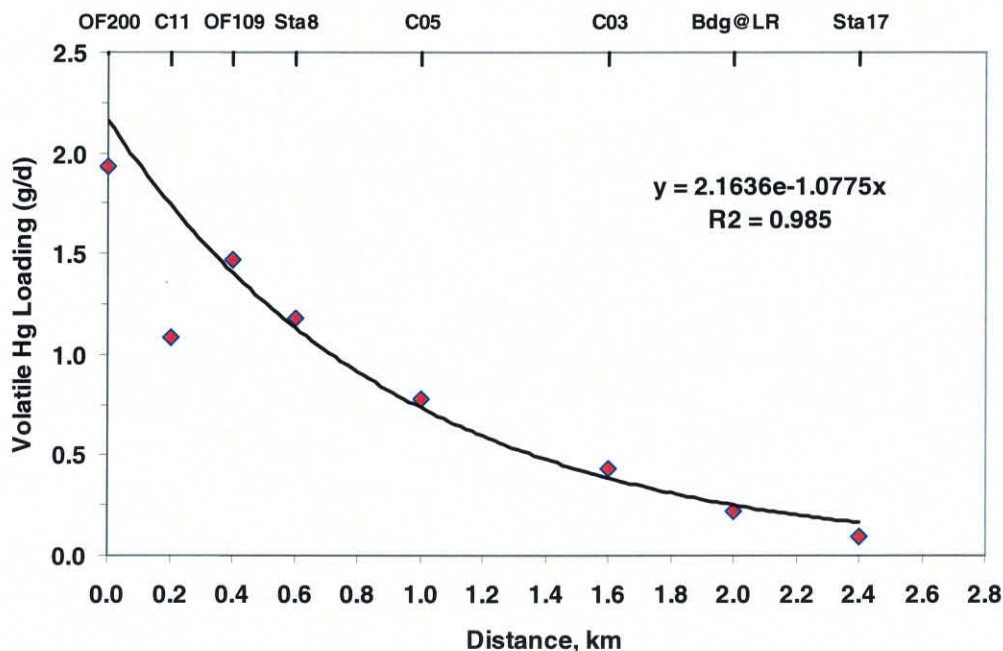

Fig. 23. Downstream decrease in volatile mercury, Hg(0) loading in UEFPC near the end of the Nov. 25, 2008 Hg(II) reduction experiment. Sampling locations include C11, Outfall 109, Station 8, C05, C03, Bridge at Lake Reality and Station 17 (shown in abbreviation).

The theoretical rate of volatilization of Hg(0) from UEFPC calculated in Southworth, 1997 (Y/TS-1663) was 0.56 km^{-1}, compared to the observed rate constant in the 1998 study of 1.2 km^{-1}. It remains likely, however, that both volatilization and photo-oxidation play major roles in determining the downstream loss of Hg(0) from UEFPC water following chemical reduction of mercury at the Outfall 200 source.

The downstream pattern of nominal Hg(II) concentrations was determined by subtracting the measured Hg(0) concentration from the measured total Hg (HgT) concentration in each sample (Figure 24). Although there is a downstream decrease in Hg(II) in two of the three trials, the rates of loss are much less than those observed for Hg(0). It is not surprising to see a downstream decrease in Hg(II) concentration in this reach of stream. A snapshot survey of UEFPC carried out by ORNL and Y-12 NSC staff in December 2007 under low baseflow conditions found that a substantial fraction of the mercury load (and TSS as well) originating near Outfall 200 was retained within the streambed before reaching Station 17.

The increase in mercury loading associated with the streambed source between C11 and Outfall 109 is also apparent, although data from the first test on 11/17/2008 appear anomalously high and may have been influenced by suspended solids. The mean (± SE) increase in total mercury loading to the creek observed for the three trials was 4.7 ± 2.0 g/d, a value heavily influenced by the anomalous measurement in the November 17 AM trial. The average with that value excluded was 2.7 ± 1.6, similar to observations in part 1 of this report.
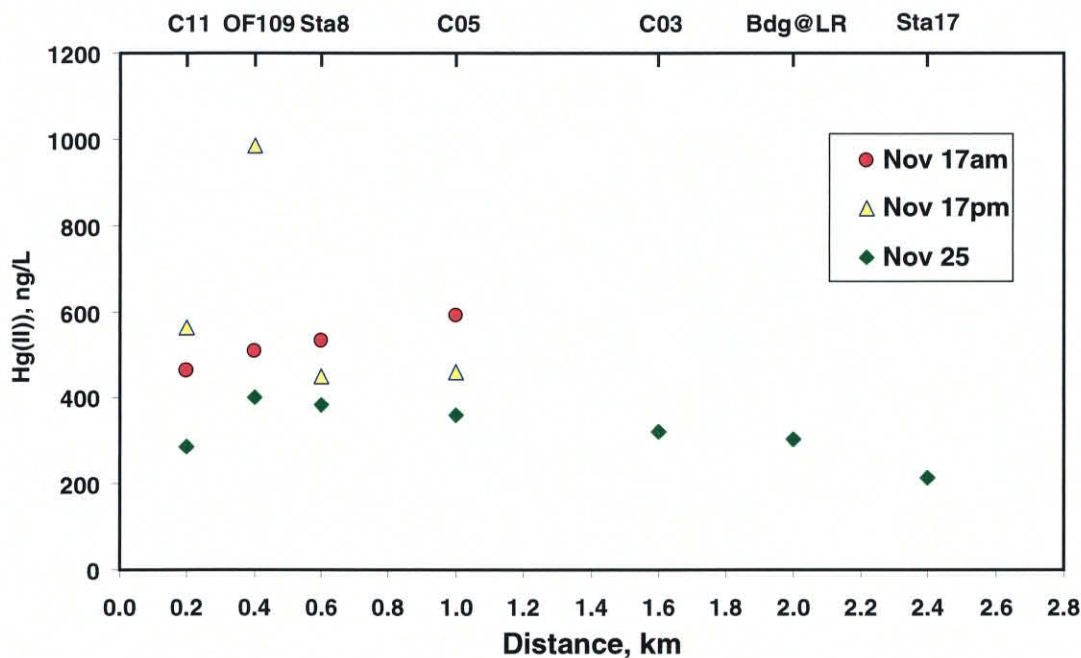
Fig. 24. Downstream pattern of nominal Hg(II) concentration, calculated as HgT– Hg(0), in UEFPC in each of the three mercury reduction trials. Sampling locations include C11, Outfall 109, Station 8, C05, C03, Bridge at Lake Reality and Station 17 (shown in abbreviation).

3.4   PRELIMINARY CONCLUSIONS

The preliminary laboratory experiments clearly demonstrated that it was possible to reduce a large fraction (~90%) of the dissolved Hg(II) to volatile Hg(0) in the Outfall 200 discharge by adding a low concentration of Sn(II). The amount of Sn(II) required exceeded that needed to effectively reduce mercury added to other waters, indicating that an opportunity exists to optimize the efficiency of Hg(II) reduction through appropriate pre-treatment (dechlorination, scavenging of interfering substances) and perhaps protection of the dilute stannous chloride with a non-toxic anti-oxidant.

The field demonstration of in-situ reduction of Hg(II) to Hg(0) in UEFPC source water by adding low concentrations of Sn(II) to the storm drain system was successful in converting a substantial fraction of the mercury load to Hg(0). The degree of reduction was not as high as observed in laboratory studies, which may due to an inadequate mixing of the reagents by natural turbulence in the field. Although a complete mixing can fully dechlorinate the source water within the short distance between the reagent addition point and Outfall 200, it may not have been thorough enough to prevent traces of residual chlorine from reacting with the Sn(II). Additionally an ephemeral constituent in mercury source water can interfere with the reaction between Sn(II) and Hg(II) in the field. Between water collection in the field and experiment in the laboratory, short-lived substances could have disappeared thus does not influence laboratory reduction experiments. The experience of the RMPE project in the late 1990s suggests that unknown short-lived substances that interfere with the tin-mercury reaction can be eliminated by de-aeration (BJC 1998).

Even at a Hg(II) reduction efficiency of ~30%, in-situ reduction coupled with air stripping has the potential to remove a large quantity of mercury from the UEFPC flow. With a 95% efficiency of air stripping, ~2 grams per day of mercury could be removed from Outfall 200 water. The most recent remedial measure to

reduce Hg export from the Y-12 NSC via UEFPC was the Big Spring Treatment System completed in 2005. That multi-million dollar facility was designed to remove mercury from the Outfall 51 spring, a source that contributed 2–3 g/d of mercury to UEFPC. Optimization of combined in-situ reduction and air stripping has the potential to greatly improve reduction in mercury loading to UEFPC originating at Y-12 NSC.

4. PROJECT SUMMARY

A summary of the relevance of the 2008 pilot test results to remediation goals and decision making in Oak Ridge is summarized in Section 4.1. A brief summary of proposed next steps for 2009, focused on testing and engineering evaluations, is provided in Section 4.2.

4.1 RELEVANCE OF 2008 RESULTS TO THE OAK RIDGE MERCURY PROBLEM

The success of the 2008 field studies has significant implications to the ultimate goal of reducing mercury bioaccumulation in fish in EFPC to safe levels. Despite effective actions that have been taken over the past two decades to reduce mercury export from Y-12 NSC and reduce concentrations in UEFPC by greater than 90%, mercury levels in fish have not declined. The remaining mercury inputs to the creek are those that are least amenable to source reduction actions, thus further reductions in waterborne mercury concentrations using conventional approaches are likely to be difficult and expensive. The potential response (reducing mercury in fish) of conventional remediation approaches remains uncertain.

Each of the two unconventional approaches investigated in this study have potential for reducing mercury loading in EFPC that arises from the remaining intractable sources. Figure 25 depicts the change in mercury loading to EFPC if the flow management water input were reduced by 50% and the dissolved gaseous mercury generated by stannous chloride treatment at test location 200A6 were removed by air stripping at Outfall 200. These results assume the improvement observed in the first set of experimental trials, i.e., 35% reduction in baseflow mercury loading to UEFPC, from approximately 8 g/d to 5 g/d.

Reduced flow management options therefore offer reduction of 0.6 to 1.5 grams of mercury. This is a significant percentage of the current total flux. The low costs associated with reduced flow augmentation should result in overall cost saving to Y-12 NSC. The 50% reduction of flow augmentation evaluated in 2008 can be obtained without diversion and still maintain a flow of 5 million gallons per day at Station 17. A NPDES Permit change to allow for that reduction was requested by the Y-12 NSC and approved by TDEC in December 2008. The reduction in flow to UEFPC will be implemented in 2009, after careful consideration of the best timing. A greater flow reduction could reduce the mercury loading even further in the creek. The flow regime for the 2008 test appeared to be capable of eliminating about 50% of the streambed loading into UEFPC. Eliminating flow augmentation completely to the upper section, e.g. by diverting some of the flow to Outfall 2 further downstream, has the potential to remove much or all of the remaining flux. Further evaluation of the ecological and toxicological consequences of very low and no augmentation in UEFPC requires investigation. The 2008 flow management study was a very short-term test. Longer term testing is therefore necessary to evaluate reduction outcomes under varying seasonal flow conditions.

Chemical reduction using stannous chloride and air stripping at Outfall 200 can remove larger quantities of mercury that contribute EFPC contamination. If the chemical reduction efficiency can exceed 90%, in line with laboratory studies, and an efficient in-situ air stripping system engineered, then removal of >80% of the mercury exiting Outfall 200 could be achieved. Thus, the combined effects of flow management diversion (with no flow added) and stannous chloride addition (assuming 80% efficient reduction and air stripping at source) would eliminate ~6 g/d of mercury from the UEFPC. The residual loading (~2 g/d) would correspond to a typical waterborne mercury concentration of ~100 ng/L at the Station 17 regulatory monitoring point. A decrease in mercury loading of this magnitude would meet the target (threefold reduction) expected to be set by TDEC in the mercury TMDL for EFPC.
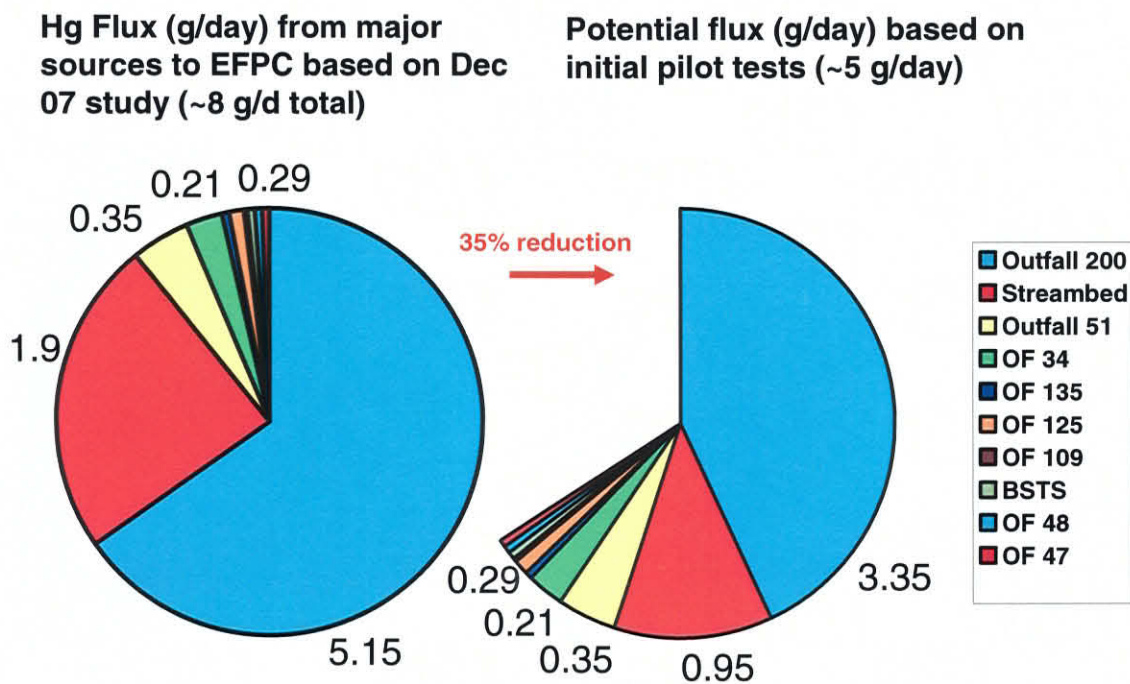
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Fig. 25. Potential reduction in mercury loading to UEFPC based on results of initial trials of flow management reduction and stannous chloride treatment with hypothetical air stripping.

The approaches explored in this study have the potential for rapid, inexpensive deployment on an interim basis, prior to CERCLA actions in the future. Flow management alteration is expected to be implemented early in 2009 and should result in significant savings for the Y-12 NSC from the diminished need to purchase Clinch River water. If a compatible mixture of dechlorinating agent and stannous chloride can be developed and fed into the dechlorinating system currently employed at Outfall 200, in-stream volatilization of Hg(0) could be used to remove mercury from UEFPC. Although less efficient than air stripping, such a system would have very low start-up and operational costs. Engineering and developmental work will continue to optimize the system. Longer-term testing of the two approaches, as is proposed in the following section, could provide the information necessary to inform the Y-12 facility and regulators as to the merit of specific operational strategies (e.g., short-term approaches vs. full-scale technology implementation).

Any actions that can reduce the mean baseflow concentration of mercury in UEFPC have the potential to reduce mercury bioaccumulation. Mercury levels in fish are expected to respond to changes in aqueous mercury at some threshold. One of the largest uncertainties associated with remedial actions at the Y-12 site is the concentration to which aqueous mercury must be reduced in order to attain safe levels of mercury in fish. Actions taken as a result of this project thus have the benefit of bridging knowledge gap on the site-specific relationship between mercury in water and mercury in fish. That knowledge is critical to mercury-related decision making, affecting compliance operations, CERCLA remediation, and D&D activities at Y-12 NSC.

4.2 PROPOSED FUTURE TESTING

A detailed sampling and analysis plan for follow-on research in 2009 is being developed. Two activities will be carried out: 1) longer-time evaluation of the changes in stream mercury in response to the planned flow reduction, and 2) optimization of the mercury removal by stannous chloride reduction and enhanced volatilization.

We will to follow up the flow management testing with a longer-term evaluation of the magnitude and persistence of the removed mercury. Initial results of the 2008 experiment indicate that diversion of 50% flow volume may reduce baseflow mercury export from the Y-12 facility by up to 10%. Longer pre- and post-flow reduction monitoring is necessary to reduce uncertainty associated with the 2008 observations which showed significant mercury variation within treatment periods. In order to observe the influence of seasonal variation in local water table levels on mercury flux from the contaminated streambed, experiments need to cover at least two seasons with a relatively low and high rainfall, respectively. A sampling and analysis plan will need to consider the timing of the flow change which will be dependent, in part, on operational considerations and the potential impacts to stream biological communities. Baseline sampling of mercury prior to the 50% reduction of flow augmentation began in January 2009.

Further field and laboratory testing of stannous chloride reduction of Hg(II) to Hg(0) coupled with enhanced volatilization of Hg(0) is planned for 2009. Optimization of this technology will require improvements in the chemistry of the dechlorination and reduction reactions, determination of the best means and locations to add chemicals, and design a cost effective, efficient air stripping system to remove Hg(0) from water. Such efforts will necessarily entail simultaneous laboratory and field investigations along with concurrent engineering development. Laboratory work will investigate alternative dechlorinating agents and mixtures of dechlorinating agents, as well as investigate pre-treatment by air sparging to remove possible interfering constituents. It is also possible that introducing highly reactive stannous chloride in combination with an anti-oxidant such as ascorbic acid will allow it more time to react with mercury rather than other oxidants in the water. Field efforts will refine the reagent addition system at 200A6 to achieve more rapid mixing with the stream flow. More effective Hg(II) reduction may also be attained by staging reagent additions and using new reagent combinations based on laboratory studies.

It time permits, evaluation of other locations for reagent addition may be performed. Most mercury enters the drainage system via four smaller tributary lines a few kilometers upstream from Outfall 200. Mercury concentrations in these drains are higher than in the main trunk line at 200A6 and flows are much lower. Thus, dechlorination can be achieved with less dechlorinating agent and much higher Sn(II) concentrations than used in the test at 200A6. Full dechlorination of the main trunk line into which these tributaries drain would still be required, but conversion of Hg(II) to Hg(0) would occur upstream of that line. Effective reduction of Hg(II) within these tributary drains will be necessary in order to utilize the main trunk line leading to Outfall 200 as an in-situ air stripping system. Simultaneous dechlorination and reduction at those locations may have substantial short-term potential to achieve a high degree (>90%) of mercury reduction at Outfall 200.

As noted above, an in-situ air stripping system could be designed utilizing the length of trunk line downstream from mercury sources as a reaction vessel. The large junction box at 200A6 may be another option as an air stripping system, with a grid of diffusers on the bottom supplying a high flow of air to sparge Hg(0) from the water. Lastly, the pool at the Outfall 200 may provide sufficient size (and room for modification) to construct an in-situ air stripping system capable of efficiently removing Hg(0) from the 1–1.5 million gallon per day flow leaving the N/S pipe. Photochemical reactions may be a problem there. Obviously, engineering evaluations of various purging and stripping alternatives need to be carried out before these systems can be applied effectively in the field.

Finally, in-stream volatilization, while not a preferred long-term option, has the potential to act as an interim technology for removing a large fraction of the mercury loading from UEFPC. Studies in concert with the field tests of mercury reduction will be conduced to evaluate the fate of Hg(0) downstream from Outfall 200. Data collected on the fate of Hg(0) under daylight and night conditions will provide quantitative information on the feasibility of in-stream volatilization when a high degree of mercury reduction is achieved at Outfall 200.

Discussions with Y-12 NSC staff are ongoing with regard to the timing and method of flow reduction; a mercury sampling and analysis plan is being developed. Future field studies using chemical reagents (including stannous chloride) will be dependent on approvals from the Y-12 NSC and state and federal regulatory agencies. A stakeholder meeting to discuss the findings of this report is planned in spring 2009.

REFERENCES

BJC (Bechtel Jacobs Co. LLC). 1999. Mercury Abatement Report for the U.S. Department of Energy Oak Ridge Y-12 Plant for Fiscal Year 1999, Oak Ridge, Tennessee. BJC/OR-422. Prepared by Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN.

BJC (Bechtel Jacobs Co. LLC). 1998. Mercury Abatement Report for the U.S. Department of Energy Oak Ridge Y-12 Plant for Fiscal Year 1998. BJC/OR-183. Prepared by Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Dzombak, D.A. and F.M.M. Morel. 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. John Wiley & Sons.

Looney B, C.Eddy-Dilek, R.Turner, G.Southworth, M. Peterson, and A.Palumbo, 2008. Recommendations to Address Technical Uncertainties in the Mitigation and Remediation of Mercury Contamination at the Y-12 Plant, Oak Ridge, Tennessee. WSRC-STI-2008-00212.

NOAA/ATDD (National Oceanic and Atmospheric Administration/Atmospheric Turbulence and Diffusion Division). 2008. Oak Ridge Climatological Data.
http://www.atdd.noaa.gov/Oak_Ridge_Climate_Additions/oakridgemetcurrent.htm

Southworth, G. 1997. Proposed Experiment for $SnCl_2$ Treatment of Outfall 200 for the Purpose of Mercury Removal from East Fork Poplar Creek, Y-12 Plant, Oak Ridge, Tennessee. Y/TS-1663. Martin Marietta Energy Systems Y-12 Plant, Oak Ridge, TN, 7 pp.

USDOE (U.S. Dept. of Energy). 2001. Treatability Study Report for the Upper East Fork Poplar Creek Bank Stabilization at the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee. DOE/OR/01-1890&D3. Prepared by ORNL/ESD and Tetra Tech, Inc., U.S. Dept. of Energy Office of Environmental Management, Oak Ridge, TN.