

Ultralow Level Mercury Treatment Using Chemical Reduction and Air Stripping

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Ultralow Level Mercury Treatment Using Chemical Reduction and Air Stripping

Abstract

Field, laboratory and engineering data collected during the project confirmed the efficacy of chemical reduction and air stripping/sparging as an ultralow level mercury treatment concept for waters containing Hg(II). The process consists of dosing the water with low levels of stannous chloride to convert the mercury to Hg⁰. This form of mercury can easily be removed from the water by air stripping or sparging. Samples of Savannah River Site (SRS) groundwater containing approximately 130 ng/L of total mercury (as Hg(II)) were used for the field study. In undosed samples, sparging removed 0% of the initial mercury. Removal in the treated samples varied by dose. Low doses (<0.0001 mg/L as stannous chloride dihydrate) showed little removal. Reagent doses above 0.01 mg/L showed relatively complete removal (>94%) – the residual total mercury in all of these samples was reduced to levels below 10 ng/L. Reagent doses between 0.0001 mg/L and 0.01 mg/L responded in a regular manner. Mercury removal in this critical range was achieved with doses between 1 and 25 the theoretical minimum stoichiometric amount (for the redox reaction between Hg(II) and Sn(II)). In the laboratory, a kinetic study indicated that addition of Sn(II) results in extremely rapid reduction of Hg(II) to Hg(0). For all of the Sn(II) addition experiments, the mercury removal rate from solution appeared to be controlled by the purging process rather than the mercury conversion rate. In general, the data indicate that the reduction of mercury is highly favored and that stannous chloride reagent efficiently targets the Hg(II) contaminant in the presence of competing reactions. Based on the results, we estimated that the costs of implementing and operating an ultralow level mercury treatment process based on chemical reduction and stripping/sparging are competitive with traditional treatment technologies. For a hypothetical 200 gpm system, capital costs ranged from \$50,000 to \$250,000 and operating costs ranged from \$0.11 to \$0.31 per m³ of water treated (approximately \$0.50 to \$1.50 per 1000 gallons). This project was supported by the Savannah River Technology Center (SRTC) Strategic Research and Development Program.

Ultralow Level Mercury Treatment Using Chemical Reduction and Air Stripping

Objectives

The overall objective of this work is to develop a reasonable and cost-effective approach to meet the emerging mercury standards, especially for high volume outfalls with concentrations below the drinking water standard (DWS). The specific objectives of the various tasks are to determine the efficacy and practicality of treating aqueous mercury to ng/L levels using a combination of chemical reduction (to Hg^0) followed by stripping/sparging.

Background:

Over the past ten years the Environmental Protection Agency (EPA) has developed a policy aimed at elimination of mercury emissions. This policy has been articulated in the PBT (Persistent, Bioaccumulative and Toxic) Pollutants Program, the White House Clean Water Action Plan, the Mercury Report to Congress, the executive order for federal agency assessments of risks to children, and the U.S.-Canada Bilateral Toxics Agreement. In each case, mercury was identified as the most significant contaminant and specific actions to reduce and/or eliminate mercury were required. Proposed ecological protection mercury standards are well below drinking water standards and are so low that new analytical methods have been developed and were approved in 1999 (EPA method 1631). Carol Browner of the EPA recently announced a plan to eliminate dilution from mixing calculations in permitting some National Pollutant Discharge Elimination System (NPDES) outfalls, primarily to meet mercury commitments made in the US-Canada Bilateral Toxics Agreement. A policy of regulating mercury to ultralow levels may affect many outfalls at SRS and will impact industry, municipalities and other government agencies. New water treatment approaches are needed. To be viable, these approaches must treat large volumes of water containing trace levels of mercury in the presence of other ions at a unit cost that is below conventional metals removal methods.

In South Carolina, the Department of Health and Environmental Control (SCDHEC) has indicated that future discharge permits will be based on ambient water quality criteria (AWQC). The current AWQC is 12 ng/L -- a level that is near background concentration, approximately one tenth of traditional detection limits, and approximately one hundredth of DWS. Draft surface water protection standards (e.g., those currently proposed by EPA for Total Daily Maximum Load (TMDL) in the Savannah River) are even lower -- 1 to 3 ng/L. A challenge for large facilities such as the Savannah River Site (SRS) is developing reasonable and cost-effective approaches to meet the emerging standards, especially for high volume outfalls with concentrations below the DWS (currently 2000 ng/L). The mercury issue has been identified as a substantive issue in setting limits for the A-01 Outfall at SRS.

SRS has formed a task team to identify traditional commercial treatment options for metals. Unfortunately, traditional treatments typically cost approximately \$1 to \$2 per m³ of water (\$5 to \$10 per 1000 gallons). This is equivalent to a cost of more than \$1,000,000/year for a 2 m³/min (400 gpm) outfall. We are examining an alternative treatment method. This approach is a modification of analytical methods for mercury in which stannous chloride is used to rapidly convert inorganic mercury into volatile-dissolved metallic mercury. The inorganic mercury is removed from the water using air stripping or air sparging. Such a system consists of a reagent infusion pump (or system), a mixing zone, and an air-water contactor (e.g., stripper). If successful, the system would be widely applicable because it would cost much less than traditional water treatment methods. Analytical methods typically employ a large stoichiometric excess of stannous ion but the literature hints that lesser quantities are sufficient. Development of this treatment system requires answering a few key scientific questions (stoichiometry, robustness, etc.) and developing a prototype to show that reliable long-term operation can be achieved. These research questions and objectives are listed and discussed below.

Summary Description of Research

The basis for this project is the chemistry embodied in various analytical methods for mercury. In these methods, inorganic mercury is reduced to Hg⁰ using stannous (tin) chloride. Hg⁰ is volatile and can be removed from the water by simple air-water contact. In the lab, a small sparge is used to strip the mercury into an analyzer. For treatment, air stripping, spraying, or sparging are examples of inexpensive methods applicable to large water volumes. The reaction of tin and inorganic mercury is rapid and thermodynamically favored. Nonetheless, tin-based analytical methods rely on using significant excess reagent to assure that the reaction is complete. Research by Southworth (1996) suggested that tin levels that are only 4 to 5 times stoichiometry may convert the available inorganic mercury to Hg⁰. This stoichiometry, under one particular set of water chemistry conditions, suggests that the mercury-tin reaction is relatively specific. These ratios also indicate that treatment is possible using tin concentrations that are well within safe-protective levels for both ecological and human health. Further, the research documented that the strippability of the resulting Hg⁰ is predictable and that required air-water ratios are favorable (e.g., ratios less than 20 provide good removal). The proposed work will attempt to confirm the concept and support practical application.

The research was conducted in two stages: (1) Scoping Studies and (2) Proof of Principle. This report documents the successful completion and results for both stages.

The Studies were performed using “real-world” water collected from groundwater wells. We selected this water, with a nominal concentration near 150 ng/L, to represent a potential SRS treatment need. In Stage 1 we treated the water with a range of stannous chloride concentrations. We sparged each sample using ultraclean equipment and an excess air-water ratio of approximately 30 to 1. The resulting samples were sealed and sent for total mercury analysis in the laboratory using cold vapor atomic fluorescence

spectrometry. We collected a large 5 L sample for a kinetic study to further examine the reaction and mixing times needed. The kinetic study and further tests of treatment effectiveness (at lower tin doses) were completed during Stage 2 of the project. Also in Stage 2, design criteria and equipment options were evaluated to support future full-scale implementation. The overall objective of the Stage 2 was to support long-term design simplicity and robustness (reagent stability, equipment longevity and performance, and the like). All work was performed in accordance with the original test plan (Vangelas, 2000) and is documented in a project specific laboratory notebook (Looney, 2000). Based on the results of the Scoping Studies, we will assemble a prototype treatment system during Stage 2.

Technical Approach

Mercury Chemistry

The chemistry of mercury in the environment is complicated by multiple redox states, a tendency to form complex ions, and potential biological transformations. Mercury can exist naturally as the elemental form (zero valent), a univalent form [Hg(I)], and a divalent form [Hg(II)]. The univalent form occurs predominantly in solid phases such as calomel (Hg₂Cl₂), but typically dissociates into the elemental and divalent forms when in solution. Hg(II) has a strong tendency to form complex ions with hydroxyls, chloride, and other common anions. The relative stability of these complexes varies with parameters such as pH and thus, understanding the chemistry of the solution is important to remediation design. Under moderately reducing conditions Hg(II) can be converted to elemental mercury. In this redox state mercury can co-exist as liquid metal, vapor, and aqueous solute. Under more reducing conditions where sufficient organic matter is present, microbiological transformations of mercury to methylated forms can occur. These species are the most toxic forms of mercury and are mobile in the environment. However, most groundwater at the Savannah River Site contains very little, if any, methylated mercury (Denham et al, 1999).

Figure 1 shows the relationship between the Sn(II)/Sn(IV) couple and the speciation of mercury in aqueous solution. In highly oxidized natural waters (above a pE of approximately 8), mercury occurs as Hg(II), typically as a chloride or hydroxide complex. That the equal activity line of the Sn(II)/Sn(IV) couple is located within the field of dominance of elemental mercury indicates that Sn(II) will reduce Hg(II) to elemental mercury. This occurs by the following reaction:



Thus, when sufficient stannous chloride is added to water containing dissolved Hg(II) virtually all Hg(II) is reduced to elemental mercury. Importantly, mercury occurs primarily as Hg(II), and its complexes, in most natural waters, even water where Hg⁰ is thermodynamically predicted (e.g., pE < 8). In these systems, the reaction with tin facilitates the transformation of the Hg(II) to the expected zero valence oxidation state.

In all cases, the stannous ion must be added in sufficient quantity that a 1:1 Hg:Sn stoichiometry is available in the presence of competing redox reactions.

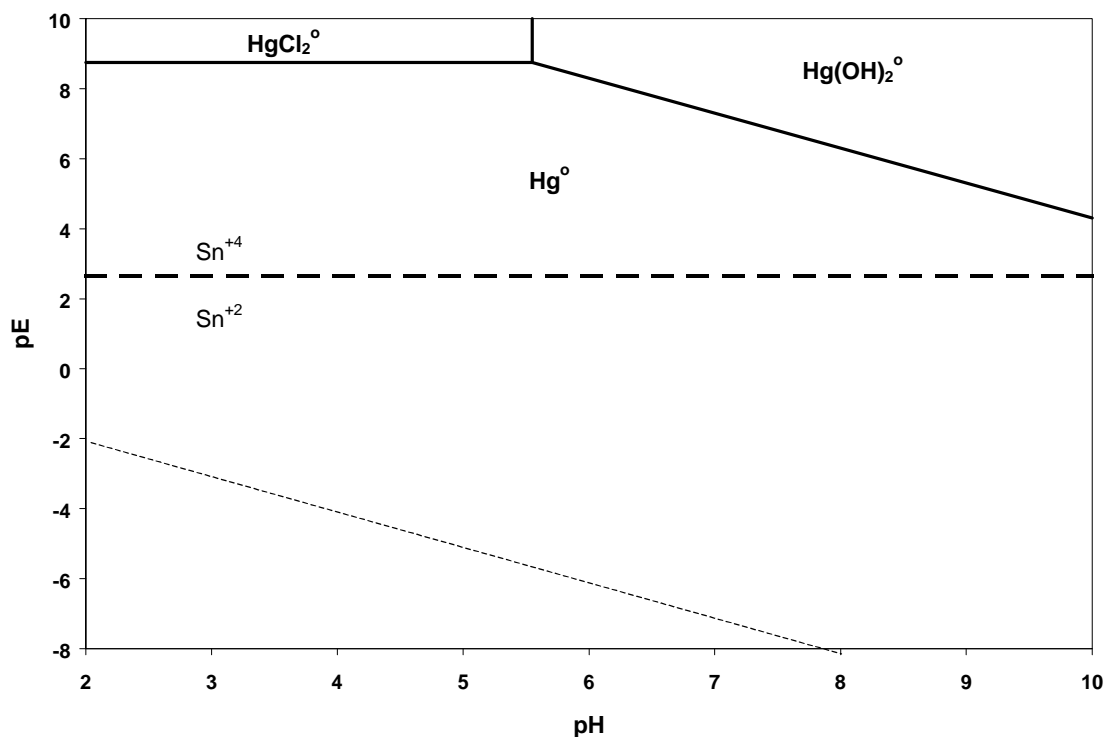


Figure 1: Relation between the Sn(II)/Sn(IV) redox couple and mercury speciation. $[Cl^-] = 2 \text{ mg/L}$. The coarse dashed line shows the boundary between Sn(II) and Sn(IV) fields of dominance. The fine dashed line represents the lower stability limit of water.

The remediation technology being tested exploits the redox chemistry of mercury and the relatively high vapor pressure of elemental mercury. Stannous chloride (SnCl_2) is used to reduce dissolved divalent mercury to elemental mercury. The dissolved elemental mercury is then stripped from solution by air sparging. Stannous chloride will also reduce other dissolved constituents such as oxygen, nitrate, and contaminants such as trichloroethylene (TCE). Table 1 shows the Standard Potential of the Sn(IV)/Sn(II) half-cell reaction relative to the mercury couple and to other potential interfering constituents. Oxygen and nitrate are typically present in groundwater at concentrations that are much greater than concentrations of mercury. Likewise, in groundwater contaminated with TCE, mercury concentrations may be small compared to TCE concentrations. The high concentrations of these constituents relative to mercury may require use of a higher concentration of stannous chloride than needed for stoichiometric reduction of mercury.

Table 1: Half-cell reactions for tin, mercury, and potential interferences. Standard Potentials are in volts vs. the Standard Hydrogen Electrode (SHE).

Half-cell Reaction	Standard Potential vs. SHE (volts)
$\text{Sn}^{+4} + 2\text{e}^- = \text{Sn}^{+2}$	0.16
$\text{C}_2\text{HCl}_3 \text{ (TCE)} + \text{H}^+ + 2\text{e}^- = \text{C}_2\text{H}_2\text{Cl}_2 \text{ (1,1-DCE)} + \text{Cl}^-$	0.54
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$	0.83
$\text{Hg}^{+2} + 2\text{e}^- = \text{Hg}$	0.85
$\text{O}_{2(a)} + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	1.27

Selection of Water for Stage 1 and Stage 2 Dose-Response Tests

We used “real-world” samples for the stage 1 tests. In selecting the source of contaminated water, we reviewed outfalls and wells at SRS. The primary criteria for the selection were:

- 1) concentrations of mercury should be well characterized and stable,
- 2) concentrations of mercury should be elevated above background but less than DWS,
- 3) water from the selected source should be accessible for sampling and study,
- 4) mercury in the water should be primarily in the form of Hg(II), and
- 5) if possible, the water should discharge to a surface water outfall and represent a possible future treatment target.

Based on these criteria, we selected the influent and effluent of the A-Area stripper for the work. The source of the water is groundwater remediation wells located in the northern sector of A/M Area near SRTC. The feed and effluent of the air stripper have been well characterized and provide a very stable source of water that contains between approximately 120 and 150 ng/L total mercury -- concentrations that are ideal for the scoping study. Previous speciation studies on these waters indicated that almost all of the mercury is Hg(II). Interestingly, since an air stripper is already in place, the measured concentrations indicate that mercury is not being removed by this unit operation without the benefit of reagent addition. The use of both feed and effluent water provides an interesting comparison of stannous chloride effectiveness in the presence of varying competing reactions (the feed contains significant levels of chlorinated organic solvents and the feed and effluent both contain dissolved oxygen). Finally, a run was performed on A-Area Stripper feed water that was pre-sparged with nitrogen to remove both dissolved oxygen and volatile organic compounds to evaluate the optimum theoretical performance of the treatment method. The effluent from the A-Area Stripper discharges to the A-01 Outfall and represents a significant fraction of the outfall flow volume. Thus, the stripper represents a potential treatment target if ultralow level outfall standards are promulgated.

Equipment

Figures 2a and 2b are drawings of the equipment setup used for the dose-response study. The ultra-low levels of mercury in the samples required using materials that do not contain mercury and will not absorb mercury from their surroundings. Furthermore, to be compatible with EPA cleaning protocol, equipment materials should be stable in hot (70° C) hydrochloric acid. The majority of the equipment was composed of glass, teflon, polypropylene or polyvinylidene difluoride (PVDF) which meet these various requirements. In general, the project used nonmetallic components when possible.

We performed all sample preparation and manipulation inside a field glovebox. We used the glovebox to minimize the possibility of contaminating the samples from outside sources and to protect the reagents from the air.

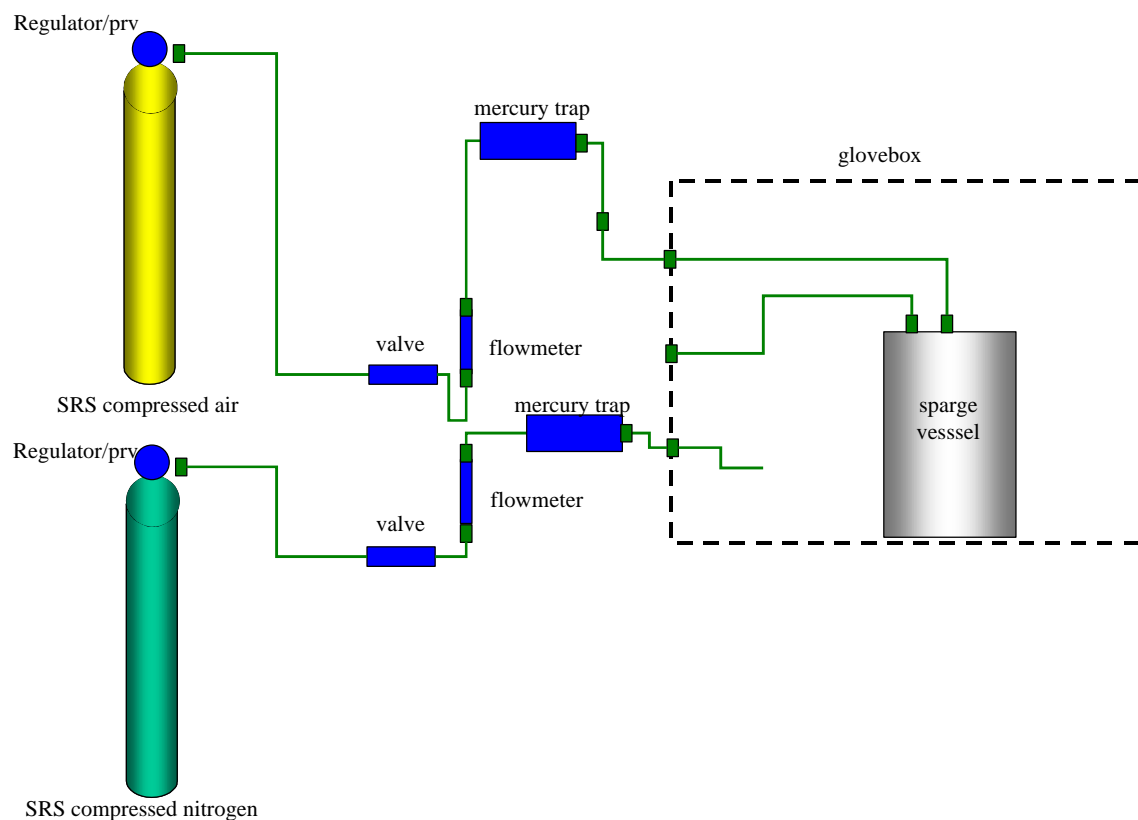


Figure 2a. Overall schematic of system

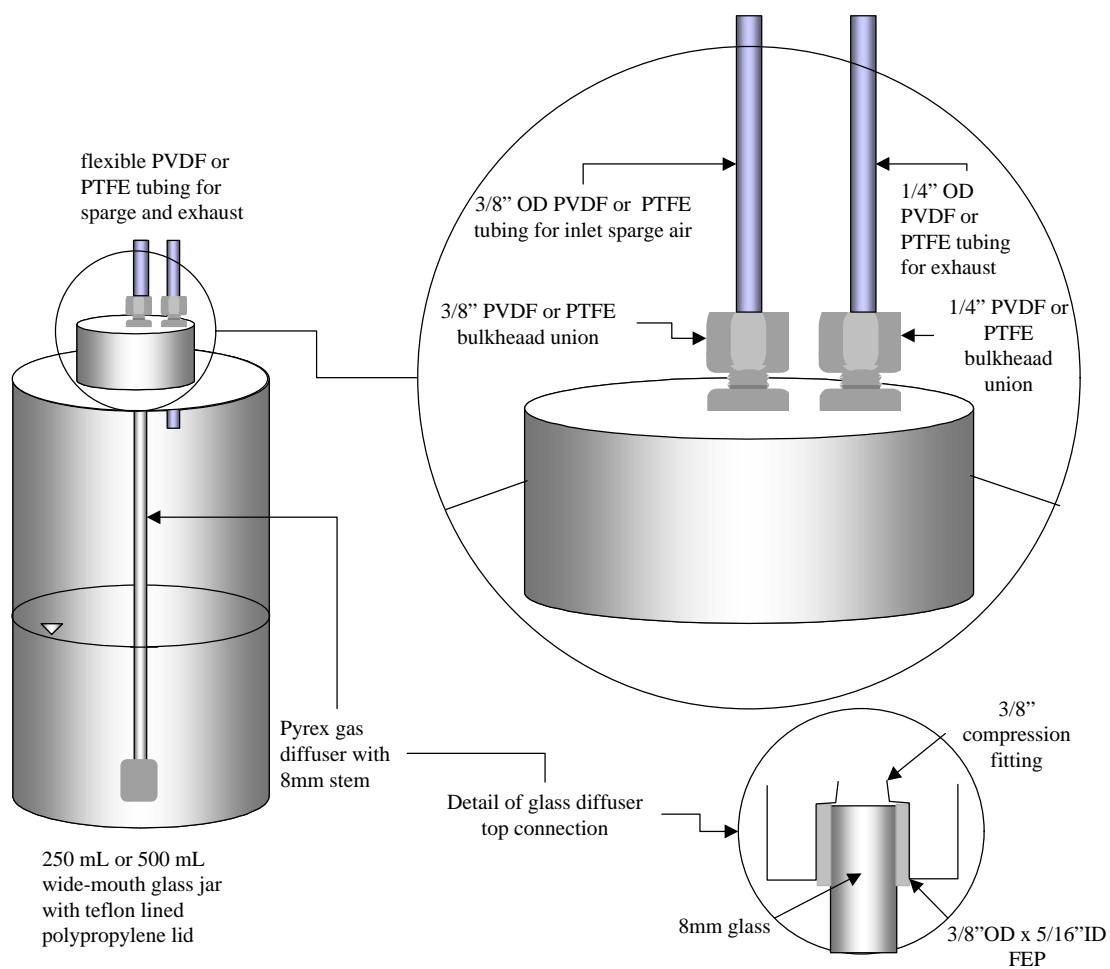


Figure 2b. Detail of bottle/reactor design

General Protocol – Dose Response Studies

The Stage 1 experiments evaluated the response of mercury concentration in a treated sample to the stannous chloride dosage. Prior to Stage 1, a blank run was performed on every cleaned sparge vessel as a QA step. This blank run was followed by an experimental run that tested stannous chloride dosages from 0 to approximately 800 mg/L (doses expressed in terms of stannous chloride dihydrate). The doses, along with the effectiveness results, are tabulated in Appendix A. During Stage 1 we tested doses of 0 mg/L, 0.003 mg/L, 0.15 mg/L, 1.54 mg/L, 76.6 mg/L, and 766 mg/L. Because of the relatively high treatment efficiency observed for doses greater than 0.003 mg/L we examined lower doses in Stage 2: 0.000000616 mg/L, 0.00000616 mg/L, and 0.000308 mg/L (with replication of 0 mg/L and 0.003 mg/L). The protocol allowed study of doses at basic science and practical engineering levels and extended up to the actual high dosages used in the 1631 analytical method. All Stage 1 work was performed in the field in a glove box set up near the A-Area Stripper. Stage 2 work was performed in the glovebox set up in a nearby support laboratory (704D). Figures 3 through 5 are photographs of the field operations.

General Protocol – Kinetic Study

A separate study was performed during Stage 2 to confirm that the reaction was sufficiently rapid and complete to be practical. This study was performed in the laboratories of Frontier Geosciences in Seattle WA to allow rapid subsampling following dosing and to avoid any possible artifacts associated with dosing and shipping. The study was designed to collect the gas phase reaction product (Hg(0)) as it was generated and sparged from the system. A range of concentrations, doses and temperatures were examined (Table 2).

Table 2. Various conditions tested in Stage 2 Kinetic Study

Run No.	Sample Matrix	Total Mercury (ng/L)	Temperature (degrees C.)	Stannous chloride dose (mg/L as dihydrate) (note a)	pH
1 (note b)	DI water	100	22.8	760	0.9
2	DI water	100	0	0	5
3 (note c)	groundwater	138	22.8	0.019	ambient
4	groundwater	138	22.8	0	
5	groundwater	138	22.8	0.0076	
6	groundwater	138	22.8	0.0019	

Notes:

a = original dosing data from Frontier Geosciences were reported in terms of ug/L as [Sn(II)]; these were converted for consistency with the remainder of this report

b = these are the same conditions as EPA Method 1631. DI water = deionized water.

c = ambient pH approximately 5

The following is a summary excerpt of the full kinetic study report that is provided in Appendix B. Figure 6 shows collection of a 5L sample in a precleaned teflon container for the kinetic study. The 5 L sample of “groundwater” (effluent water from the A Area stripper) was received on August 8, 2000 and stored at 0 C. and in darkness for 4 days prior to the actual experiment. Purging experiments were conducted in acid cleaned 500 mL borosilicate gas washing bottles. Each bottle had a total volume of 575 mL and was charged with 500 mL of aqueous sample for each experiment. After dosing with stannous chloride, each sample was purged with ultrapurified nitrogen at a flow rate of 220 mL/min. Hg(0) evaded from the sample was collected on freshly blanked gold coated quartz sand traps (the same traps used in performing EPA analytical method 1631). Based on the gas flow rate and water volume, the purge rate with regard to the aqueous sample was 0.38 volumes/min. The samples were each purged for a total of 60 minutes. All of the stripped Hg(0) was collected on sequential gold/sand traps. In general, the traps were collected in 5-minute increments (or composited to 5 minute increments for reporting as discussed in Appendix B). Each 5-minute increment represents an air-water ratio of 1.9. In addition to the experimental runs, two blank runs were performed. For the blank runs, all of the Hg(0) collected during a 60 minute purging of mercury free reagent water was collected. These runs indicated a very small procedural blank of 0.0006 ng/minute – this value was subtracted from the raw results prior to final tabulation and further calculation. To provide an overall mass balance and assure experimental quality, samples of the bulk solution before and after the purging period were collected for each run. The mass balances (recovery of evaded mercury plus residual mercury in the reaction vessel) for all of the runs ranged from 85% to 109%. Additionally, the initial groundwater sample was analyzed specifically for Hg(II) (in addition to total mercury) to help interpret the sparging data. To simplify the analysis and calculations presented below, mercury removals are expressed in terms of actual mercury recovered in each run.

Analytical

EPA method 1631 (total mercury method described below) was used for analysis of samples for this work. A recognized and experienced ultralow level mercury analysis laboratory (Frontier Geosciences, Seattle WA) was chosen to support this research. Nicholas Bloom of Frontier Geosciences was a principal contributor to the development of EPA Method 1631. He and his staff provided sample containers, bottle cleaning, quality assurance and other support under a subcontract to SRTC.

Aqueous samples were oxidized in their original bottles by the addition of 1.0% (v/v) of 0.2 N BrCl in 12 N HCl. A 50 to 125 mL aliquot of the acidified sample was then placed into a clean teflon bottle and the excess BrCl oxidant was pre-reduced by the addition of NH_2OH . The pre-reduced solution was then poured into the purge vessel and SnCl_2 was added to reduce the free Hg(II) to elemental Hg(0). The elemental mercury was purged from the solution and collected on a gold-coated sand trap. After collection, the mercury on the gold trap was collected and “refocused” onto a second “analytical” trap by rapid desorption into a gas stream of pure argon. Finally, the mercury was desorbed from the analytical trap into the cold vapor atomic fluorescence spectrometer (CVAS) cell where it

was detected and quantified. For these analyses, QA steps included: determining the detection limit and standard curve, analyzing a certified reference material, and analyzing at least three method blanks for every 20 samples. All of the analytical results are tabulated in Appendix A and Appendix B.



Figure 3: Experimental apparatus set up in the field near the A-Area Stripper. Photographs show (A) general set up and (B) arrangement of glovebox and support equipment

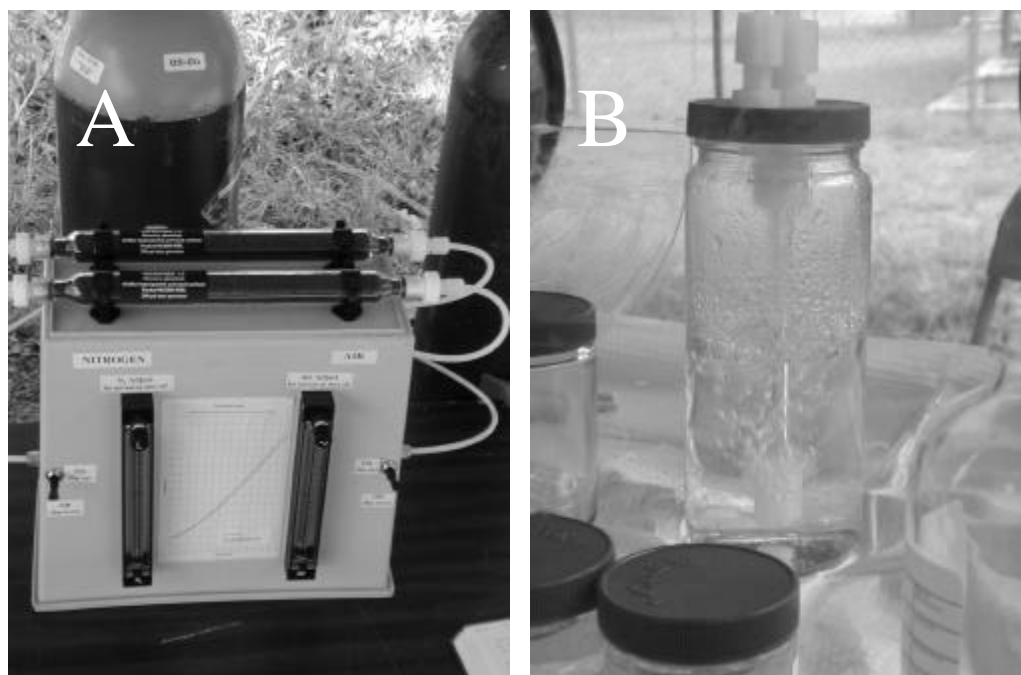


Figure 4: Photograph of (A) gas delivery system and (B) operating sparge vessel



Figure 5: Miscellaneous photographs of SRTC researchers performing study



Figure 6: SRTC researcher Miles Denham collects large volume sample for a kinetic study of mercury-tin reaction rates.

Results

The mercury treatment was extremely efficient as documented by the dose-response studies. The dose response results for both project stages are shown in Figure 7. In the undosed samples, the treatment removed 0% (\pm approximately 15%). Removal in the treated samples varied by dose. Low doses (<0.0001 mg/L stannous chloride dihydrate) showed little removal. Stannous chloride dihydrate reagent doses above 0.01 mg/L showed relatively complete removal ($>94\%$) – the residual total mercury in all of these samples was reduced to levels below 10 ng/L.

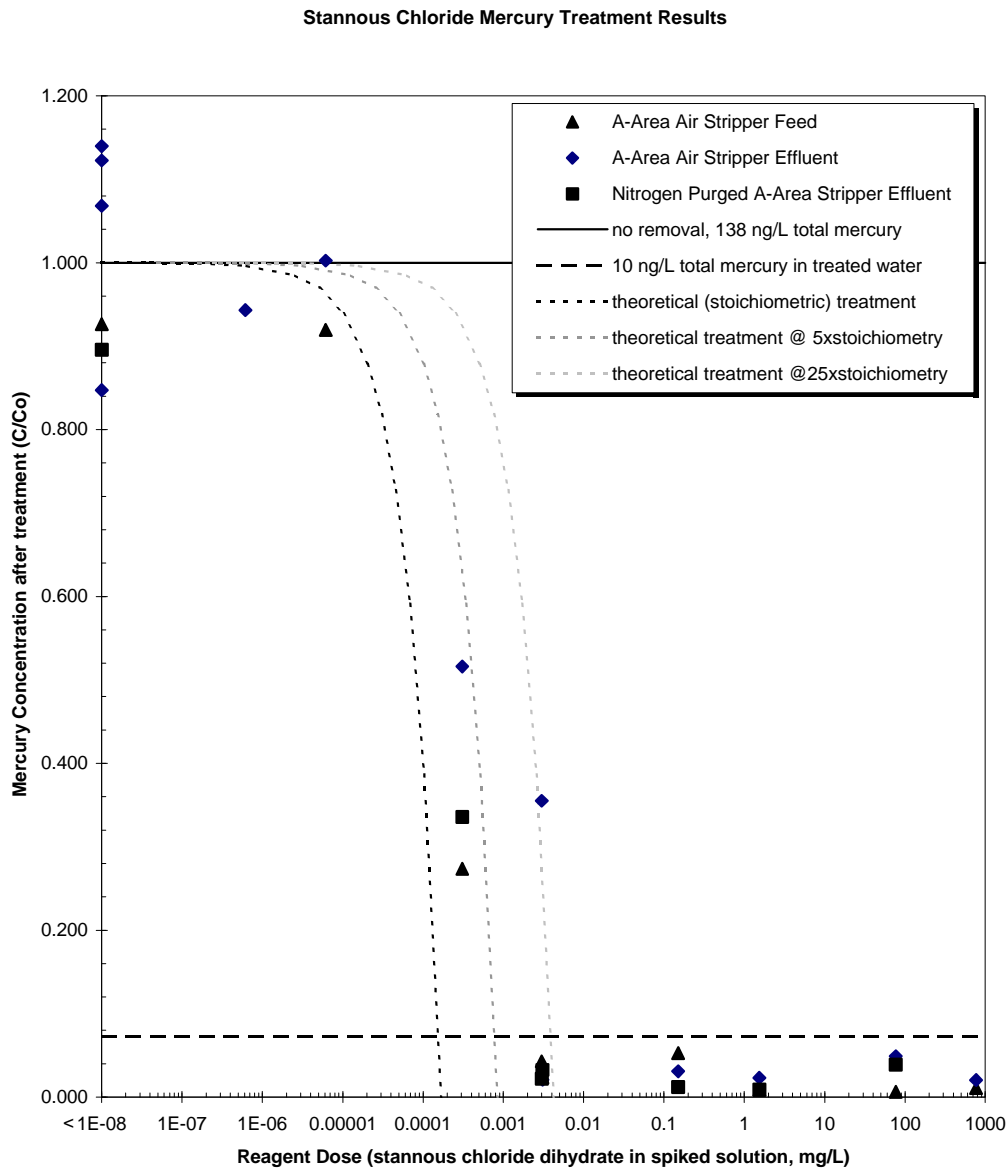


Figure 7: Mercury Treatment – Various Runs Performed at the A-Area Stripper at SRS

Reagent doses between 0.0001 mg/L and 0.01 mg/L responded in a regular manner generally consistent with the stoichiometry of the redox reaction between Hg(II) and Sn(II). The curved lines on Figure 7 are calculations indicating expected performance based on 1x, 5x and 25x the theoretical stoichiometry. With only one exception, the data in this critical reagent dose range fell between 1x to 5x the theoretical optimum performance. This suggests that the desired reaction is favored and that the process is viable for the tested environmental conditions. Competing reactions (e.g., with the organic contaminants in the stripper feed water and/or dissolved oxygen in the stripper feed water and the stripper effluent) are not adversely scavenging the reagent, despite the presence of competing molecules in solution at levels that are several orders of magnitude higher than the target Hg(II). Notably, the dose-response in one sample fell between 5x and 25x the theoretical stoichiometry. Because of the upstream treatment in an air stripper, this “effluent” sample was relatively high in dissolved oxygen (approximately 10 mg/L dissolved oxygen versus the stripper feedwater at about 3 mg/L). This single data point may indicate a detectable influence of high (saturated) dissolved oxygen on treatment efficiency. A replicate of this sample, however, showed effective mercury removal to <10 ng/L. Based on the results, a target dose range of 5x to 25x stoichiometry would be a reasonable design basis for treatment of waters similar to those tested.

The kinetic study indicated that addition of Sn(II) results in extremely rapid reduction of Hg(II) to Hg(0). For all of the Sn(II) addition experiments, the mercury evasion rate appears to be controlled by the purging process rather than the reaction rate. In the three experiments conducted at 22.8° C., the mean removal rate ranged from about 27 to 29% of the Hg present per volume of purge gas (i.e., for each 500 mL of purge gas representing a 1:1 air:water ratio). For the single experiment at 0° C., the mean removal rate fell to about 19% of the Hg present per volume of purge gas. In both deionized water and in groundwater, virtually no mercury was evaded without the addition of Sn(II). These conclusions are clearly documented in Figure 8. This figure plots the laboratory data along with lines showing theoretical performance. The theoretical lines have not been fitted to the data and are based solely on purge efficiency calculated from literature values of solubility and vapor pressure of elemental mercury (Table 3).

For these relatively simple conditions, the literature values of vapor pressure and solubility can be combined into a “dimensionless” Henry’s Law constant (H’):

$$H' = \frac{(\text{vapor pressure in units of mg Hg per L of air})}{(\text{solubility in units of mg Hg per L of water})} \quad (2)$$

Based on mass balance and integration over time, the purge efficiency can then be approximated as a function of H' and the ratio of air volume purged to water volume in vessel (η'):

$$Hg_{(\eta)}/Hg_{(0)} = e^{-(H' \eta')} \quad (3)$$

Normalized removal rates calculated using this equation correspond well with the those reported from the raw data (29% of the Hg present per volume of purge gas at 22.8 °C. and 16% of the Hg present per volume of purge gas at 0 °C). The theoretical lines in Figure 8, based solely on expected sparge rate, provide a reasonable match the measured data. This suggests that sparging controlled the mercury removal rate in the experiments and that the reaction kinetics ($Hg(II) \Rightarrow Hg(0)$) are relatively fast.

Table 3. Literature values of solubility and vapor pressure used to calculate Henry's Law and theoretical sparge performance

Temperature (° C)	vapor pressure (mg Hg / L air)	solubility (mg Hg / L water)	H' ("dimensionless" Henry's Law Constant)
0	0.0027	0.015	0.18
22.8	0.018	0.053	0.34

Chemistry data interpolated from Sanamesa, 1975. See also Clever, 1987.

Kinetic Experiment

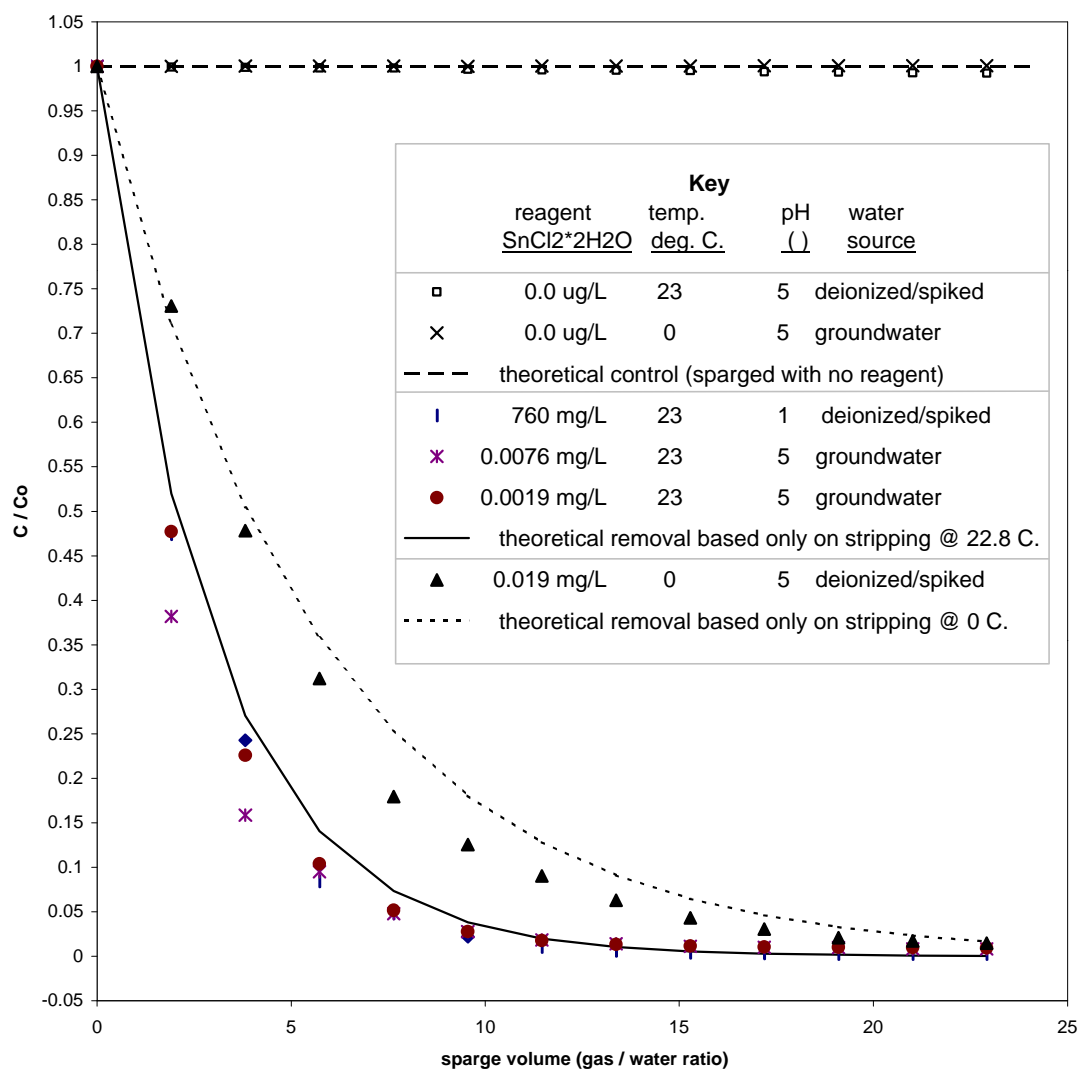


Figure 8: Results of Kinetic Study

Engineering Considerations

Two key engineering considerations were preliminarily evaluated during Stage 2 of the project. These were: 1) equipment materials selection and compatibility, and 2) alternative stannous chloride delivery options.

All of the materials in a full scale system (including storage vessels, and downstream fittings, seals, tubing, valves, flow meters, check valves, and the like) need to be compatible with the stannous chloride reagent. Table 4 presents a list of potentially acceptable and unacceptable construction materials. Several commonly available materials were identified as “excellent” in standard 48 hour compatibility tests – 316 stainless steel, bronze, teflon (PTFE®), various elastomers, and many other materials. These represent first choices in future designs. Confirmation that selected materials will perform over an extended period of time is recommended to support long-term operation.

Two basic options are available for delivery of the stannous chloride solution to a process. The simplest is a pressure infusion system that uses an inert gas to force the solution into the process water. In this system, the operator modulates the flow using a high precision needle valve (or other flow controller). The reagent solution is maintained under a blanket of inert gas. The advantages of this system are its simplicity and elegance. The disadvantages of this system are the requirement to place the entire volume of stored reagent under moderate pressures (circa 50 to 100 psig) and potential operational problems associated with the needle valve / flow controller. These issues would require appropriate engineering-design responses. For example, assuring proper certification and pressure protection for the reagent tank, as well as documenting that the flow controller would operate reliably and robustly under field conditions (especially in the case where small amounts of particulates - oxidized stannous chloride precipitate - may be passing through the system).

The second stannous chloride delivery approach, uses a high-precision positive-displacement infusion pump to deliver the reagent into the process water. In this system, the operator adjusts the delivery using the pump controls and confirms the flow using a monitoring system. The advantages of this system relative to pressure infusion include: reduction of pressure needed in reagent storage reservoir, more robust to the presence of small quantities of stannous chloride precipitate, and process control compatible and easily integrated with most common systems. Disadvantages include: higher initial cost, and the need to properly maintain the pump. It is important to note that in the pump system, the reagent would still need to be blanketed with inert gas (but the pressure could be set to levels far below those that would require code certification (e.g., 2 psig versus 15 psig)). The disadvantages could be minimized / mitigated by careful selection of a high quality pump that is designed for continuous-duty high-precision low-flow infusion in an industrial setting. Many such pumps are available.

Initial prototypes of both a pressure infusion and a pump system were assembled during Stage 2. The prototypes, sized for a 200 gpm water treatment plant, were constructed of

materials rated as excellent – notably 316 stainless steel for the storage container, tubing and pump head, glass for the flow meter tube, and PTFE or viton for seals. Preliminary evaluation of the systems suggests that successful full-scale implementation is probable. Additional long-term testing of reagent stability and operational robustness is recommended.

Table 4. Compatibility data for materials in contact with high concentration stannous chloride solutions

Materials with EXCELLENT Compatibility (footnotes)	Materials with GOOD Compatibility (footnotes)	Materials with FAIR Compatibility (footnotes)	Materials with POOR Compatibility (footnotes)	Some materials with no tabulated data on compatibility
316 ss (2)	Hastelloy-C®	304 ss (2)	Aluminum	ABS plastic
Bronze (1)	LDPE (2)	EPDM	Carpenter 20	Acetal - Delrin®
Buna N - Nitrile	Silicone	Hytrell®		Brass
Ceramic – Al ₂ O ₃		Nylon (1)		Carbon – graphite
CPVC (2)				Cast iron
Epoxy				Ceramic magnet
Glass				Copper
Hypalon® (1)				FEP - teflon®
Kel-F®				PFA -- teflon®
Natural rubber				polycarbonate
Neoprene (1)				
NORYL® (2)				
Polypropylene				
PPS - Ryton® (1)				
PTFE - teflon®				
PVC (1)				
PVDF - Kynar®				
Titanium				
Tygon®				
Viton®				

Compatibility Terminology Definitions:

Excellent = No observable effects during standard (48 hr) testing procedures under listed conditions

Good = Minor effects observed (such as discoloration or slight corrosion)

Fair = Moderate effect observed (such as softening, loss of strength, or swelling), not recommended for continuous use.

Poor – Severe effects, not recommended for any use

Footnotes:

(1) = Meets listed performance up to 72° F. (22° C.)

(2) = Meets listed performance up to 120° F. (48° C.)

Data from public sources such as Cole Parmer, New Age Industries, Good Year, etc.

Scoping Analysis

The data indicate that chemical reduction combined with sparging/stripping is a viable mercury treatment for waters containing Hg(II). A scoping calculation for a scenario similar to the A-Area Stripper illustrates the nature of a potential implementation. Specific assumptions for the scenario are the following:

- dose rate of 0.01 mg/L stannous chloride dihydrate (approximately 3x the lowest tested dose in this study) will provide effective-continuous-robust mercury removal, and
- water flow of 0.8 m³/min (approx. 200 gpm) to be treated containing 150 ng/L total mercury as Hg(II)

For this case, realistic design, capital and installation costs for a good quality dosing system are < \$50,000. Approximately 5 Kg of reagent are needed to treat an entire year of flow. In such a quantity, reagent grade stannous chloride dihydrate costs approximately \$150/Kg for a yearly reagent cost of less than \$1000. Dosing would need to be performed from a high concentration reagent reservoir using a high precision pump or pressure infusion system. The reservoir requires a nitrogen (or inert gas) headspace for reagent stability. All construction materials up to the infusion point need to be compatible with high concentration stannous chloride solutions. Logistics appear reasonable for either dosing option. Reagent can be mixed at 60,000 mg/L in batches of 20 L and infused at a rate of approximately 0.15 mL/min. Each batch would last three months (i.e., operators would need to prepare reagent only 4 times per year). Reagent preparation, combined with maintaining logs, periodic adjustments and repairs, should represent less than 0.2 FTE (approximately \$40,000/year). If costs for reagents were approximately \$800 (as described above) and replacement parts and other supplies was \$5000, annual operational costs would be \$46,000. This represents an operating cost of about \$0.11/m³ (< \$0.5 per 1000 gallons). These costs assume that an air stripper is in place (such as the case of treating the feed water to the A-Area Stripper). Air stripping/sparging costs on the order of \$250,000 (capital), with operations typically costing \$0.2/m³ (< \$1 per 1000 gallons). Thus, a complete 200 gpm system would have approximate costs of \$300,000 and an operating cost of <\$0.3/m³ (< \$1.50 per 1000 gallons). This cost, conservatively calculated, is significantly less than traditional metals treatment technology costs – especially for target treatment concentrations below 10 ng/L.

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APPENDIX A – DOSE RESPONSE STUDY DATA

SUMMARY DOSE VS. MERCURY DATA FOR FIELD EXPERIMENT

Stage 1 Dose Response Results:

Sample No.	sparge	Dose Protocol	Dose of stannous chloride dihydrate (mg/L)	Final Hg (ng/L)	C/C0
SRDHG 01	--	0	0	146.9	1.417
SRDHG 02	--	0	0	116.5	1.124
SRDHG 03	--	1 ml A	766	2.83	0.027
SRDHG 04	--	0.1 ml A	76.6	6.72	0.065
SRDHG 05	--	1 ml B	1.54	3.18	0.031
SRDHG 06	--	0.1 ml B	0.15	4.26	0.041
SRDHG 07	--	1 ml C	0.003	48.83	0.471
SRDHG 10	--	0	0	127.4	1.229
SRDHG 13	--	1 ml A	766	1.47	0.014
SRDHG 14	--	0.1 ml A	76.6	0.89	0.009
SRDHG 15	--	1 ml B	1.54	1.16	0.011
SRDHG 16	--	0.1 ml B	0.15	7.24	0.070
SRDHG 17	--	1 ml C	0.003	5.92	0.057
SRDHG 8	N2	1 ml C	0.003	3.03	0.029
SRDHG 9	N2	0.1 ml B	0.15	1.67	0.016
SRDHG 11	N2	1 ml B	1.54	1.24	0.012
SRDHG 12	N2	0.1 ml A	76.6	5.35	0.052
average Co				103.6517	

effluent

feed

N2 - effluent

Stage 2 Dose Response Results:

Sample No.	sparge	Dose Protocol	Dose of stannous chloride dihydrate (mg/L)	Final Hg (ng/L)	C/C0
SRDHG-18		0	0	156.7	1.140
SRDHG-19		0	0	154.4	1.123
SRDHG-20		0	0	2.88	0.021
SRDHG-21		0.1 ml D	6.16E-07	129.7	0.943
SRDHG-22		1 ml D	6.16E-06	137.8	1.002
SRDHG-23		0.1 ml C	0.000308	70.94	0.516
SRDHG-24		1 ml C	0.00308	2.88	0.021
SRDHG-25		0.1 ml D	0.0	123.2	0.896
SRDHG-26		1 ml D	6.16E-06	73.88	0.537
SRDHG-27		0.1 ml C	0.000308	46.13	0.335
SRDHG-28		1 ml C	0.00308	4.47	0.033
SRDHG-29		0	0	95.43	0.694
SRDHG-30		0.1 ml D	6.16E-07	4.80	0.035
SRDHG-31		1 ml D	6.16E-06	126.4	0.919
SRDHG-32		0.1 ml C	0.000308	37.64	0.274
SRDHG-33		1 ml C	0.00308	3.25	0.024

effluent

N2 - effluent

feed

RAW DATA FROM STAGE 1 FIELD EXPERIMENT

Total Mercury in Water Samples (Westinghouse Savannah River Site)					
<i>analyzed by</i>					
Frontier Geosciences Inc. 414 Pontius North, Suite B Seattle WA 98109					
phone: 206-622-6960 fax: 206-622-6870 e-mail: nicolasb@frontier.wa.com					
sample ID	bottle number	collection date	analysis date	[Hg], ng/L	comment
SRDHG-01	glass	6/21/00	6/23/00	146.90	
SRDHG-02	glass	6/21/00	6/23/00	116.5	
SRDHG-03	glass	6/21/00	6/23/00	2.83	
SRDHG-04	glass	6/21/00	6/23/00	6.72	
SRDHG-05	glass	6/21/00	6/23/00	3.18	
SRDHG-06	glass	6/21/00	6/23/00	4.26	QA Sample
SRDHG-07	glass	6/21/00	6/23/00	48.83	
SRDHG-08	glass	6/21/00	6/23/00	3.03	
SRDHG-09	glass	6/21/00	6/23/00	1.67	
SRDHG-10	glass	6/21/00	6/23/00	127.40	
SRDHG-11	glass	6/21/00	6/23/00	1.24	
SRDHG-12	glass	6/21/00	6/23/00	5.35	
SRDHG-13	glass	6/21/00	6/23/00	1.47	
SRDHG-14	glass	6/21/00	6/23/00	0.89	
SRDHG-15	glass	6/21/00	6/23/00	1.16	
SRDHG-16	glass	6/21/00	6/23/00	7.24	
SRDHG-17	glass	6/21/00	6/23/00	5.92	
blank-1			6/23/00	0.12	
blank-2			6/23/00	0.1	
blank-3			6/23/00	0.13	
mean				0.12	
SD				0.02	estimated MDL = 0.04 ng/L
repeatability					
SRDHG-06 rep 1	glass	6/21/00	6/23/00	4.45	
SRDHG-06 rep 2	glass	6/21/00	6/23/00	4.07	
mean				4.26	8.5% RPD
standard addition					
SRDHG-06 + 20.20 ng/L MS	glass	6/21/00	6/23/00	23.29	94.2% recovery
SRDHG-06 + 20.20 ng/L MSD	glass	6/21/00	6/23/00	23.38	94.7% recovery
mean				23.34	0.3% RPD
certified standard					
NIST-1641-d			6/23/00	7,663	96.4% recovery
certified value				7,950	

BLANKS PERFORMED ON EVERY CLEANED PURGE VESSEL

Total Mercury in Purge Vessel Blanks (Westinghouse Savannah River Site)					
analyzed by					
Frontier Geosciences Inc. 414 Pontius North, Suite B Seattle WA 98109					
phone: 206-622-6960 fax: 206-622-6870 e-mail: nicolasb@frontier.wa.com					
sample ID	bottle number	collection date	analysis date	[Hg], ng/L	comment
field purge vessel blank test #1	glass	n/a	3/9/00	0.30	
field purge vessel blank test #2	glass	n/a	3/9/00	0.35	
field purge vessel blank test #3	glass	n/a	3/9/00	0.27	
field purge vessel blank test #4	glass	n/a	3/9/00	0.26	
field purge vessel blank test #5	glass	n/a	3/9/00	0.29	
field purge vessel blank test #6	glass	n/a	3/9/00	0.17	
field purge vessel blank test #7	glass	n/a	3/9/00	0.47	
field purge vessel blank test #8	glass	n/a	3/9/00	0.27	
field purge vessel blank test #9	glass	n/a	3/9/00	0.35	
field purge vessel blank test #10	glass	n/a	3/9/00	0.73	
field purge vessel blank test #11	glass	n/a	3/9/00	0.19	
field purge vessel blank test #12	glass	n/a	3/9/00	0.40	
field purge vessel blank test #13	glass	n/a	3/9/00	0.28	mean: 0.33 ng/L
field purge vessel blank test #14	glass	n/a	3/9/00	0.36	SD: 0.14 ng/L
field purge vessel blank test #15	glass	n/a	3/9/00	0.16	N: 16
field purge vessel blank test #16	glass	n/a	3/9/00	0.43	
blank-1			3/9/00	0.08	
blank-2			3/9/00	0.05	
blank-3			3/9/00	0.1	
mean				0.08	
SD				0.03	estimated MDL = 0.08 ng/L
NIST-1641-d rep 1			3/9/00	7,801	98.1% recovery
NIST-1641-d rep 2			3/9/00	7,728	97.2% recovery
certified value				7,950	0.9% RSD

RAW DATA FROM STAGE 2 FIELD EXPERIMENT

Total Mercury in Water Samples (Westinghouse Savannah River Site)					
<i>analyzed by</i>					
Frontier Geosciences Inc. 414 Pontius North, Suite B Seattle WA 98109					
phone: 206-622-6960 fax: 206-622-6870 e-mail: nicolasb@frontier.wa.com					
sample ID	bottle number	collection date	analysis date	[Hg], ng/L	comment
SRDHG-18	FGSB-547	7-Aug-00	9-Aug-00	156.7	
SRDHG-19	FGSB-384	7-Aug-00	9-Aug-00	154.4	
SRDHG-20	glass	7-Aug-00	9-Aug-00	2.88	
SRDHG-21	glass	7-Aug-00	9-Aug-00	129.7	
SRDHG-22	glass	7-Aug-00	9-Aug-00	137.8	
SRDHG-23	glass	7-Aug-00	9-Aug-00	70.94	
SRDHG-24	glass	7-Aug-00	9-Aug-00	2.88	
SRDHG-25	glass	7-Aug-00	9-Aug-00	123.2	
SRDHG-26	glass	7-Aug-00	9-Aug-00	73.88	
SRDHG-27	glass	7-Aug-00	9-Aug-00	46.13	
SRDHG-28	FGSB-202	7-Aug-00	9-Aug-00	4.47	
SRDHG-29	SK10-27	7-Aug-00	9-Aug-00	95.43	
SRDHG-30	CMC-319	7-Aug-00	9-Aug-00	4.80	QC Sample
SRDHG-31	FGSB-002	7-Aug-00	9-Aug-00	126.4	
SRDHG-32	TSL-8	7-Aug-00	9-Aug-00	37.64	
SRDHG-33	FGSB-929	7-Aug-00	9-Aug-00	3.25	
blank-1			9-Aug-00	0.05	
blank-2			9-Aug-00	0.07	
blank-3			9-Aug-00	0.07	
mean				0.06	
SD				0.01	estimated MDL = 0.03 ng/L
blank spike @ 5.00 ng/L rep 1			9-Aug-00	4.77	95.4 % recovery
blank spike @ 5.00 ng/L rep 2			9-Aug-00	5.19	103.8% recovery
mean				4.98	8.4% RPD
SRDHG-30 rep 1	CMC-319	7-Aug-00	9-Aug-00	5.16	
SRDHG-30 rep 2	CMC-319	7-Aug-00	9-Aug-00	4.44	
mean				4.80	15.0% RPD
SRDHG-30 + 20.20 ng/L MS	CMC-319	7-Aug-00	9-Aug-00	23.60	93.1% recovery
SRDHG-30 + 20.20 ng/L MSD	CMC-319	7-Aug-00	9-Aug-00	24.58	97.9% recovery
mean				24.09	4.1% RPD
NIST-1641-d (200:1 dilution)			9-Aug-00	7,327	92.2% recovery
certified value				7,950	at 200:1 dilution

APPENDIX B – KINETIC STUDY DATA

Kinetics of Hg Volatilization from WSRC Well Water using Sn(II) as a reductant

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Seattle, WA 98109

August 16, 2000

I. Objectives

The objective of this project was to determine the rate of purging for Hg^0 from aqueous solutions, after reduction with low stoichiometric ratios of Sn(II). This work is in relation to the development of a method of treating Hg contaminated ground water by SnCl_2 reduction and air stripping. Analysis was performed with standard (Level-2) QA/QC documentation, using EPA Method 1631 for total Hg and EPA draft method 1630 for methyl mercury.

II. Sample Receipt

1 five litre sample was received on August 8, 2000. The sample was received in good condition (although the cooler was at ambient temperature upon arrival) and was preserved by keeping cool (0°C) and dark, until the volatilization experiment could be conducted, 4 days later. The sample received is listed below:

date rec.	bottle #	location	analysis	comments
8/8/00	FGS-001	5-litre	kinetic expt.	cooler @ 8.8°C

III. Experimental Methods

Experimental Setup. Purging experiments were conducted from acid-cleaned 500 mL borosilicate glass gas-washing bottles. These bottles had a volume of 575 mL, and were charged with 500 mL of aqueous sample for each experiment. The samples were purged with ultra-purified N_2 , at a flowrate of 220 ± 20 mL/min, and Hg^0 evolved collected onto freshly blanked gold coated quartz sand traps.

(the same traps as are used in EPA Method 1631). Taking into account the flowrate and the total volume of the purge vessels, the purge rate can also be expressed as 0.382 volumes/min. A total of six experiments were conducted, with the conditions as described in the table below.

experiment	sample matrix	[Hg] μg/L	T °C	Sn(II) μg/L	pH
#1*	DIW	0.100	22.8	400,000	0.9
#2	DIW	0.100	0.0	0.0	5.0
#3	well H ₂ O	0.138	22.8	10.0	ambient
#4	well H ₂ O	0.138	22.8	0.0	ambient
#5	well H ₂ O	0.138	22.8	4.0	ambient
#6	well H ₂ O	0.138	22.8	1.0	ambient

*same conditions as EPA M-1631

The samples were each purged for 60 minutes, with all of the evaded Hg⁰ being trapped by the use of sequential gold/sand traps. Because most of the Hg⁰ purges out over the first 5 minutes, an attempt was made to collect more traps over shorter intervals (15 seconds to 60 seconds per trap), and then longer intervals (5-10 minutes per trap) as the Hg⁰ levels in solution dropped. At the beginnings of the experiments with SnCl₂, from 4-10 traps were collected to provide the sum of Hg for the first interval, but for most 5 minute intervals, a single trap was needed. In the end, to present all data in a simplified and similar manner, data were combined into five-minute intervals. In a few cases, where 10 minute collections were used (very low concentrations at the end of the purge time), the measured value was split into 5 minute parts, with 67% of the measured Hg on the first 5 minutes and 33% in the second five minutes. This factor was determined empirically from the data collected earlier by 5 minute intervals. In some cases, even with the very short purge times, the amount of Hg collected was slightly off scale. Since such samples can not be re-run, the peak height for these off-scale evens was estimated by the analyst by how long the pen was off scale (a surprisingly accurate technique when an highly experienced analyst is employed). These results are noted in the raw data sheets, and account for little variability overall, since any given data point is only a small part of the evasion curve.

In addition to the experimental measurements, two blanks were determined by integrating all of the Hg⁰ collected in 60 minutes by purging Hg-free reagent water. These results were averaged and divided by 60, to yield a very small blank of 0.0006 ng/min for the purging procedure, which was subtracted from

the results prior to reporting and further calculations. The water samples were quantified for total Hg before and after the purging period, to allow quantification of a mass balance for each experiment. The initial water was also measured for Hg speciation (dissolved Hg, Hg(II), and by implication from the no SnCl₂ purging experiment, Hg⁰). These results showed that virtually all of the mercury in the WSRC samples is as Hg(II). The form of the Hg(NO₃)₂ spiked DIW samples was assumed to be at the spiked concentration, and all as Hg(II), but no measurements were made to confirm this.

Total Hg Analysis. After the samples were oxidized for at least 4 hours in their original bottles by the addition of 1.0% (v/v) of 0.2 N BrCl in 12 N HCl (Bloom and Crecelius, 1983), they were analyzed according to EPA method 1631, as follows. A 50-125 mL aliquot of the acidified sample is placed into a clean Teflon bottle, and the BrCl oxidant was pre-reduced by the addition of NH₂OH. The pre-reduced solution is then poured into the purge vessel, and SnCl₂ added to reduce the free Hg(II) to Hg⁰. The Hg⁰ is then purged from solution, and collected onto a gold coated sand trap (Bloom and Crecelius, 1983). After collection, the Hg on the gold trap is re-focused on a second "analytical" trap, by thermal desorption into a gas stream of pure argon. Finally, the Hg was thermally desorbed from the analytical trap into the CVAFS cell, where it was detected and quantified. For this analyses, full QC including an MD and MS/MSD for every 20 samples, certified reference material, and at least three method blanks per 20 samples were analyzed.

III. Conclusion

The results have been summarized into 5 minute intervals in the data tables. It is very clear that even the smallest amounts of Sn(II) will result in extremely fast reduction of Hg(II) to Hg⁰, meaning that for all of the SnCl₂ addition experiments, the Hg evasion rate is simply a function of the purging rate. In the three experiments conducted at 22.8°C, the mean Hg⁰ purge rate was $28.0 \pm 1.0\%$ of the Hg present per volume of purge gas. For the single experiment at 0°C, the rate fell to 19.1% per volume. In both deionized water and the ambient sample, virtually no Hg⁰ was evaded (0.026% per volume in DI water, <0.002% per volume in the actual sample) without the addition of SnCl₂. Even at the lowest concentration of Sn(II) tried (1 µg/L = 12:1 molar ratio of Sn to Hg), the reduction kinetics appeared to be much faster than the purging kinetics. This is supported by WSRC field results showing the reduction reaction to be quantitative even at a 1:1 mole ratio.

IV. Analytical Issues

All analytical data generally showed good QA and coherence, and the data appears to be of high quality. One point that should be made clear is that in several instances, the Hg evaded from the purge vessel was so high as to result in an off-scale reading, and in a couple of other instances, a data point went missing due to a broken analytical trap, or missed sampling interval during the experiment. To allow a full accounting of the Hg purging, these compromised points (about 5-10% of the total number of collected data points, which averaged about 20 per experiment) were estimated, either from how long the chart pen appeared to be off scale (for slightly off scale points), or by calculation from the evasion rates from the surrounding data points (for missing data). This estimation procedure was necessary for completeness, since none of the points could be re-run (once you analyze a trap, the Hg is gone, there is no more "sample" to go back to). By doing so, complete purging curves were possible for each experiment. I do not feel that this procedure materially compromises the results, because each particular data point only contributes slightly to the whole curve, and so an error in its estimation is not significant, over all. As can be seen from the tables, over the six experiments conducted, mass balances averaged $97.1 \pm 8.8\%$ recovery of the expected Hg, which is pretty good, since over 20 measurements went into each mass balance.

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analysis using EPA Method 1631(modified)

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EXPERIMENT #1:
100 ng/L Hg(II) in DI Water (500 mL); Sn(II) = 400 ppm @ pH 1 (M-1631 Conditions)
T = 22.8oC; purge rate = 0.382 volumes/min (220 mL/min N2)
12-Aug-00

time interval	cumulative time	cumulative purge vol's	cumulative ng Hg	purged ng Hg	ng/min	ng per purge vol	%/min	% per purge vol	comment
0-5 min	5	1.91	27.02	27.02	5.40	14.15	10.5	27.6	estimated by difference
5-10 min	10	3.82	38.92	11.90	2.38	6.23	9.8	25.7	approx due to slightly off scale
10-15 min	15	5.73	47.07	8.15	1.63	4.27	13.2	34.6	approx due to timing error
15-20 min	20	7.64	48.90	1.83	0.366	0.958	8.8	22.9	approx due to timing error
20-25 min	25	9.55	50.25	1.35	0.270	0.707	11.5	30.1	
25-30 min	30	11.46	50.84	0.588	0.1176	0.308	11.8	30.8	
30-35 min	35	13.37	51.08	0.240	0.0480	0.126	11.7	30.5	
35-40 min	40	15.28	51.18	0.100	0.0200	0.0524	11.6	30.4	
40-50 min	45	17.19	51.23	0.0500	0.0100	0.0262	13.9	36.4	10 min runs, divided 67%:33%
50-60 min	50	19.10	51.25	0.0220	0.0044	0.0115	20.0	52.4	10 min runs, divided 67%:33%
50-55 min	55	21.01	51.25	0.0014	0.00028	0.0007	13.3	34.9	10 min runs, divided 67%:33%
55-60 min	60	22.92	51.25	0.0007	0.00014	0.0004	20.0	52.4	10 min runs, divided 67%:33%
average							11.11	29.08	
stdev							1.37	3.58	

EXPERIMENT #2:
100 ng/L Hg(II) in DI Water (500 mL); Sn(II) = 0.00 ppb @ pH 5 (blank)
T = 22.80C; purge rate = 0.382 volumes/min (220 mL/min N2)
12-Aug-00

time interval	cumulative time	cumulative purge vol's	cumulative ng Hg	purged ng Hg	ng/min	ng per purge vol	%/min	% per purge vol	comment
0-5 min	5	1.91	0.021	0.021	0.0042	0.011	0.008	0.021	
5-10 min	10	3.82	0.041	0.020	0.0040	0.010	0.008	0.020	approx due to lost one trap
10-15 min	15	5.73	0.068	0.027	0.0054	0.014	0.011	0.028	approx due to lost one trap
15-20 min	20	7.64	0.081	0.013	0.0026	0.007	0.005	0.013	
20-25 min	25	9.55	0.127	0.046	0.0092	0.024	0.018	0.047	
25-30 min	30	11.46	0.153	0.026	0.0052	0.014	0.010	0.027	
30-35 min	35	13.37	0.180	0.027	0.0054	0.014	0.011	0.028	
35-40 min	40	15.28	0.203	0.023	0.0046	0.012	0.009	0.024	10 min runs, divided 67%/33%
40-50 min	45	17.19	0.249	0.046	0.0092	0.024	0.018	0.047	10 min runs, divided 67%/33%
50-60 min	50	19.10	0.272	0.023	0.0046	0.012	0.009	0.024	10 min runs, divided 67%/33%
50-55 min	55	21.01	0.305	0.033	0.0066	0.017	0.013	0.034	10 min runs, divided 67%/33%
55-60 min	60	22.92	0.321	0.016	0.0032	0.008	0.006	0.016	10 min runs, divided 67%/33%
average							0.010	0.026	
stdev							0.004	0.010	

Summary Results for Hg(o) Purging Kinetic Experiments

analysis using EPA Method 1631(modified)

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EXPERIMENT #3:

12-Aug-00

WSRC Well Water 138.4 +/- 8.9 ng/L, n=4 (500 mL); Sn(II) = 10.0 ppb @ ambient pH

T = 0oC; purge rate = 0.382 volumes/min (220 mL/min N2)

time interval	cumulative time	cumulative purge vol's	cumulative ng Hg	purged ng Hg	ng/min	ng per purge vol	%/min	% per purge vol	comment
0-5 min	5	1.91	20.36	20.36	4.0720	10.660	5.468	14.314	
5-10 min	10	3.82	39.44	19.08	3.8160	9.990	7.052	18.462	approx due to slightly off scale
10-15 min	15	5.73	52.00	12.56	2.5120	6.576	7.171	18.772	
15-20 min	20	7.64	62.04	10.04	2.0080	5.257	8.936	23.394	
20-25 min	25	9.55	66.10	4.06	0.8116	2.125	6.529	17.093	
25-30 min	30	11.46	68.78	2.68	0.5360	1.403	6.402	16.760	
30-35 min	35	13.37	70.83	2.06	0.4112	1.076	7.224	18.911	
35-40 min	40	15.28	72.33	1.50	0.2996	0.784	8.240	21.570	lost, calculated from adjacent rates
40-45 min	45	17.19	73.27	0.940	0.1880	0.492	8.793	23.019	
45-50 min	50	19.10	74.02	0.748	0.1496	0.392	12.467	32.690	
50-55 min	55	21.01	74.30	0.276	0.0552	0.145	12.267	32.112	
55-60 min	60	22.92	74.47	0.178	0.0356	0.093	20.460	53.560	
average							7.31	19.14	
stdev							1.15	3.02	

EXPERIMENT #4:

12-Aug-00

WSRC Well Water 138.4 +/- 8.9 ng/L, n=4 (500 mL); Sn(II) = 0.00 ppb @ ambient pH

T = 22.8oC; purge rate = 0.382 volumes/min (220 mL/min N2)

time interval	cumulative time	cumulative purge vol's	cumulative ng Hg	purged ng Hg	ng/min	ng per purge vol	%/min	% per purge vol	comment
0-5 min	5	1.91	-0.009	-0.009	-0.0018	-0.005	-0.002	-0.006	
5-10 min	10	3.82	-0.012	-0.003	-0.0006	-0.002	-0.001	-0.002	
10-15 min	15	5.73	-0.019	-0.007	-0.0014	-0.004	-0.002	-0.005	
15-20 min	20	7.64	-0.015	0.004	0.0008	0.002	0.001	0.003	
20-25 min	25	9.55	-0.010	0.005	0.0010	0.003	0.001	0.004	
25-30 min	30	11.46	-0.015	-0.005	-0.0010	-0.003	-0.001	-0.004	
30-35 min	35	13.37	-0.023	-0.008	-0.0016	-0.004	-0.002	-0.006	
35-40 min	40	15.28	-0.030	-0.007	-0.0014	-0.004	-0.002	-0.005	
40-45 min	45	17.19	-0.032	-0.002	-0.0004	-0.001	-0.001	-0.001	10 min runs, divided 67%/33%
45-50 min	50	19.10	-0.034	-0.002	-0.0004	-0.001	-0.001	-0.001	10 min runs, divided 67%/33%
50-55 min	55	21.01	-0.035	-0.001	-0.0002	-0.001	0.000	-0.001	10 min runs, divided 67%/33%
55-60 min	60	22.92	-0.036	-0.001	-0.0002	-0.001	0.000	-0.001	10 min runs, divided 67%/33%
average							-0.001	-0.002	
stdev							0.001	0.004	

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EXPERIMENT #5: 13-Aug-00											
WSRC Well Water 138.4 +/- 8.9 ng/L, n=4 (500 mL); Sn(II) = 4.0 ppb @ ambient pH T = 22.8oC; purge rate = 0.382 volumes/min (220 mL/min N2)											
time interval	cumulative time	cumulative purge vol's	cumulative ng Hg	purged ng Hg	ng/min	ng per purge vol	%/min	% per purge vol	comment		
0-5 min	5	1.91	43.44	43.44	8.6880	22.743	12.47	32.64	approximate due to off scale values		
5-10 min	10	3.82	59.13	15.69	3.1374	8.213	11.96	31.30			
10-15 min	15	5.73	63.61	4.48	0.8956	2.345	8.49	22.22			
15-20 min	20	7.64	66.91	3.30	0.6600	1.728	10.86	28.44			
20-25 min	25	9.55	68.31	1.40	0.2808	0.735	10.12	26.49			
25-30 min	30	11.46	68.99	0.676	0.1352	0.354	9.86	25.82			
30-35 min	35	13.37	69.29	0.303	0.0606	0.159	8.72	22.83			
35-40 min	40	15.28	69.48	0.193	0.0386	0.101	9.85	25.78			
40-45 min	45	17.19	69.56	0.083	0.0166	0.043	8.34	21.84			
45-50 min	50	19.10	69.59	0.029	0.0058	0.015	5.00	13.09			
50-55 min	55	21.01	69.67	0.079	0.0158	0.041	18.16	47.54			
55-60 min	60	22.92	69.68	0.011	0.0022	0.006	27.50	71.99			
average							10.35	27.10			
stdev							1.51	3.96			
EXPERIMENT #6: 13-Aug-00											
WSRC Well Water 138.4 +/- 8.9 ng/L, n=4 (500 mL); Sn(II) = 1.0 ppb @ ambient pH T = 22.8oC; purge rate = 0.382 volumes/min (220 mL/min N2)											
time interval	cumulative time	cumulative purge vol's	cumulative ng Hg	purged ng Hg	ng/min	ng per purge vol	%/min	% per purge vol	comment		
0-5 min	5	1.91	33.29	33.29	6.6580	17.429	10.56	27.63	one missing interval estimated		
5-10 min	10	3.82	49.28	15.99	3.1980	8.372	10.74	28.11			
10-15 min	15	5.73	57.02	7.74	1.5486	4.054	11.23	29.40			
15-20 min	20	7.64	60.38	3.36	0.6710	1.757	11.10	29.05			
20-25 min	25	9.55	61.88	1.50	0.3008	0.787	11.17	29.25			
25-30 min	30	11.46	62.54	0.658	0.1316	0.345	11.08	29.00			
30-35 min	35	13.37	62.81	0.266	0.0532	0.139	10.04	26.28			
35-40 min	40	15.28	62.93	0.126	0.0252	0.066	9.55	24.99			
40-45 min	45	17.19	62.99	0.062	0.0124	0.032	8.99	23.52			
45-50 min	50	19.10	63.03	0.031	0.0062	0.016	8.16	21.36			
50-55 min	55	21.01	63.04	0.017	0.0034	0.009	7.56	19.78			
55-60 min	60	22.92	63.07	0.027	0.0054	0.014	19.29	50.49			
average							10.68	27.96			
stdev							0.61	1.59			

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EXPERIMENTAL MASS BALANCES (500 mL sample volumes)									
experiment	expected	total mass of Hg per experiment (ng)	purged	residue	sum	% of expected			
#1	50.2	51.25	0.13	42.36	51.38	102.4			
#2	50.2	0.33	74.47	1.12	42.69	85.0			
#3	59.2	-0.04	64.13	54.09	75.59	109.2			
#4	59.2	69.68	0.58	70.26	64.09	92.6			
#5	59.2	63.07	0.58	53.65	70.26	101.5			
#6	59.2				53.65	92.0			
mean						97.1			
SD						8.8			
INITIAL SPECIATION OF WSRC WELL WATER									
sample	total	Aqueous Total Hg, ng/L	dissolved	ionic					
rep 1	137.2	131.70	127.89	131.69					
rep 2	131.2								
rep 3	151.2								
rep 4	134.1								
mean	138.4	129.8		131.7					
SD	8.9								
percent	100.0	93.7		95.2					