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Mercury Phase II Study - Mercury Behavior across the High-Level Waste Evaporator System

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EXECUTIVE SUMMARY

The Mercury Program team's effort continues to develop more fundamental information concerning mercury behavior across the liquid waste facilities and unit operations. Previously, the team examined the mercury chemistry across salt processing, including the Actinide Removal Process/Modular Caustic Side Solvent Extraction Unit (ARP/MCU), and the Defense Waste Processing Facility (DWPF) flowsheets. This report documents the data and understanding of mercury across the high level waste 2H and 3H evaporator systems.

Liquid waste samples have been collected from the 2H Evaporator system including the feed (Tank 43), drop (Tank 38) and overheads tanks. The same was performed for the 3H Evaporator system, including the feed (Tank 32), both drop tanks (Tank 30 and 37) and overhead tanks (OHT). The samples were diluted and sent to an off-site laboratory for quantification of seven different mercury species, with an eighth determined by difference. Since evaporator systems are dynamic in nature, mercury speciation analyses presented in this report provide a snapshot of the process at a given point in time with the following assessment:

- The data mostly agrees with the fundamental thermodynamic understanding for the prediction of mercury behavior across the high level waste evaporators. Mercury behavior is more predictable in these unit operations from a thermodynamic principles approach. For example, elemental mercury and dimethylmercury present in the liquid waste in either an immiscible phase or dissolved in solution will readily volatilize upon heating and migrate to the overhead tanks. Once in the vapor phase, condensation to a liquid phase is controlled by vapor pressure. Elemental mercury is known to accumulate and condense as an immiscible phase during evaporator operations. Dimethylmercury has a higher vapor pressure than does elemental mercury and is therefore expected to volatilize more readily. The phase distribution (vapor, liquid, or aqueous) of dimethylmercury during condensation processes has not yet been fully identified, but is still under investigation. Moreover, the mercuric (Hg(II)), mercurous (Hg(I)), and the methylmercury cations remain dissolved in the liquid waste (they are not prone to volatilization) and concentrate as water (solvent) is evaporated. Under normal operations these species will enter the drop tank.
- The 2H Evaporator system feed and product (drop) tanks have high mercury concentrations relative to the 3H Evaporator system and a large fraction of the species present is methylmercury. Whereas, the 3H Evaporator system feed and product (drop) tanks have lower mercury concentrations including lower fractions of organomercury species.
- Cessation of the use of antifoam during tank farm evaporator operations has reduced the concentration of dimethylmercury in the 2H and 3H system.
- Methylmercury produced during DWPF operations and returned to the tank farm in DWPF recycle accumulates in the 2H evaporator system with concentrations approaching 0.2 g Hg/L. Some downstream impacts of this high organomercury concentration are known, such as increased leachable mercury from Saltstone; but, others are not yet well understood.
- Concentrations of dimethylmercury are lower compared to 2003 analyses[5] and perhaps indicate a difference in chemistry for the DWPF antifoam degradation products that reach the 2H evaporator versus that previously found when fresh antifoam was used in the evaporators.

A System Engineering Evaluation (SEE)[25] specifically looked at the technologies that could enhance removal of ionic mercury in the H-area evaporators through the addition of a reducing agent to convert ionic mercury to

elemental mercury. A recommendation was submitted to the Department of Energy – Environmental Management (DOE-EM) to consider this as a candidate for technology development in order to demonstrate a proof of concept, alternate means to remove mercury from the Liquid Waste System (LWS).[1]

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
D	Depth
DMHg	Dimethylmercury
DOE-EM	Department of Energy – Environmental Management
DWPF	Defense Waste Processing Facility
ETP	Effluent Treatment Project
GC	Gas Chromatography
HM	H-Area Modified PUREX
L	Liters
LWS	Liquid Waste System
MCU	Modular Caustic Side Solvent Extraction Unit
MeHg	Methylmercury
MRT	Mercury Removal Tank
ND	Not Detected
NIST	National Institute of Standards and Technology
OHT	Overhead Tank
PUREX	Plutonium Uranium Reduction Extraction
RSD	Relative Standard Deviation
S	Surface
SB	Sludge Batch
SEE	Systems Engineering Evaluation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
WCT	Waste Collection Tank

1.0 Introduction

Over the past several months, a significant effort has been expended to assess and determine the speciation of mercury (Hg(0), Hg(I), Hg(II), organomercury, and soluble versus insoluble mercury) within the liquid waste system.[2] In particular, the discovery of methylmercury (MeHg) in the Tank 50 feed to Saltstone resulted in additional mercury speciation activities throughout the liquid waste facilities and unit operations. This report documents the understanding of mercury behavior across the high-level waste evaporator systems derived from sampling and analysis efforts and is the third of a three part set of reports documenting the baseline mercury flowsheet for the liquid waste facilities.

Evaluating the behavior of mercury within any waste unit operation requires an understanding of the mercury speciation within the waste. The speciation of the mercury strongly effects distribution of mercury in the various phases; i.e. aqueous, gas, or liquid, and the transfer of mercury between these phases. Important chemical properties such as the boiling point, density, vapor pressure, and solubility are all species dependent. A sound understanding of speciation within the waste is critical for evaluating the behavior and distribution within and across the unit operation. Typically, mercury can exist in three various states or conditions including the elemental, ionic, and organic – the latter represented by at least one carbon-mercury covalent bond. In addition, significant quantities of mercury can be bound to a solid phase entrained with the inlet flow or through accumulation from precipitation within the unit operation.

As a unit operation, the 2H and 3H evaporator systems reduce the volume of high level waste to reduce the overall storage volume. The waste feed is transferred from the evaporator feed tank to the evaporator pot and heated (105 to 120 °C for 2H and 145 to 160 °C for 3H) using a process steam bundle. As the waste boils, water vapor passes through a chilled condenser where it condenses into liquid called overheads. The overheads, which are predominantly radiologically decontaminated, flow from the condenser to the Mercury Removal Tank (MRT) where elemental mercury settles to the bottom of the tank and is removed. The remaining overheads are routed to two overhead tanks. At this point, the overheads are either pumped to the Effluent Treatment Project (ETP) or returned to the waste tanks for reprocessing. The concentrate is gravity drained from the evaporator into the drop tank.

From a unit operation’s perspective, the fate of mercury that enters the evaporator system will depend strongly upon speciation and partitioning coefficients between the vapor, aqueous, liquid, and solid (particulate bound) phases. Within the evaporator system the dominant phases are aqueous, elemental, and vapor. As waste enters the evaporator and is heated, the air-water partitioning or Henry’s Law Constant dictates the partitioning of species between the vapor and aqueous phases. Henry’s Law Constant is the ratio between the vapor pressure and aqueous solubility of a specific compound and describes the distribution between these two phases. Elemental mercury and dimethylmercury (DMHg) have a high air-water partitioning coefficient and will readily partition to the vapor phase, especially during heating. Figure 1 demonstrates the effect of temperature on the air-water partitioning coefficient for these species. In the evaporators both the elemental and DMHg species will be liberated from the wastewater during heating and volatilize due to air-water partitioning. Once in the vapor phase these species will accumulate in the overheads.

Elemental mercury is known to accumulate and condense as an immiscible liquid phase from the overheads during evaporator operations. Elemental mercury is routinely recovered from the MRT via condensation as a dense non-aqueous phase liquid. Operational data for the period from January 1, 2015 through September 30, 2015 indicates the collection of approximately 30 liters of elemental mercury from the 2H and 3H Evaporator Systems.[3] In the overheads, condensation to a liquid phase is controlled by vapor pressure. Understanding the vapor pressure difference between these species is important in evaluating the behavior of each species in the evaporator overheads. Figure 2 presents the effect of temperature on the vapor pressure of elemental mercury and DMHg. In this graph the normal boiling point (p = 1 atm) for each species was used to calculate vapor pressure over a range of temperatures using the Clausius-Clapeyron Equation.[4] As illustrated in Figure 2, the vapor pressure of DMHg is much higher than that of elemental mercury (i.e. DMHg is more volatile than elemental mercury). At ambient conditions the vapor pressure of DMHg is over two orders of magnitude greater than that of elemental mercury. At evaporator pot temperatures this increases up to four and a half orders of magnitude. The high vapor pressure of DMHg will limit the amount of this species that can be removed by condensation. The phase distribution (vapor, liquid, or aqueous) of DMHg during condensation processes has not yet been fully identified, but is under investigation.

Of the remaining species, the mercuric, mercurous, and the MeHg cations will remain largely dissolved in the liquid waste and concentrate during heating due to water (solvent) loss during evaporation. Under normal operations these species will enter the drop tank. Previous investigations have postulated that the mercuric ion is chemically reduced to elemental mercury[5] and will volatilize into the overheads and be recovered in the MRT. Mercury also exists as a particulate or non-soluble species, e.g. mercuric oxide. Transport of this species into and out of the evaporator would be by particle entrainment. Inside the evaporator, partial dissolution may occur due to increased operating temperature or particulates may coagulate and precipitate out as larger solids. Table 1 provides a synopsis of the conceptual behavior and likely transformations of the various mercury species across the High-Level Waste Evaporator System.

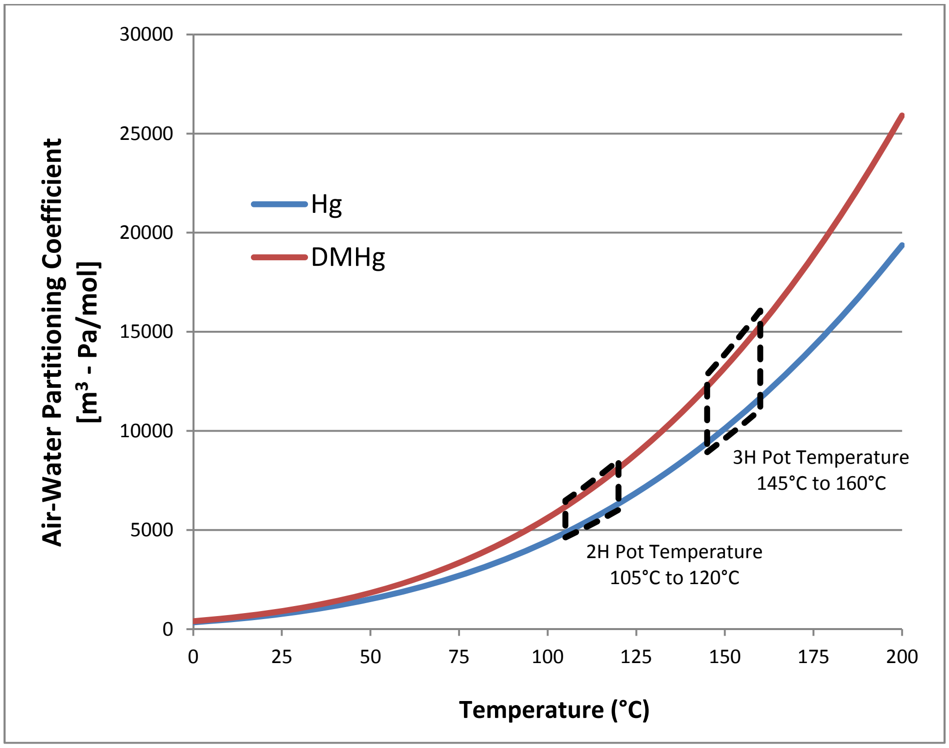

Figure 1. Effect of Temperature on the Air to Water Partitioning Coefficient for Elemental Mercury and DMHg for an Ideal Solution[6]

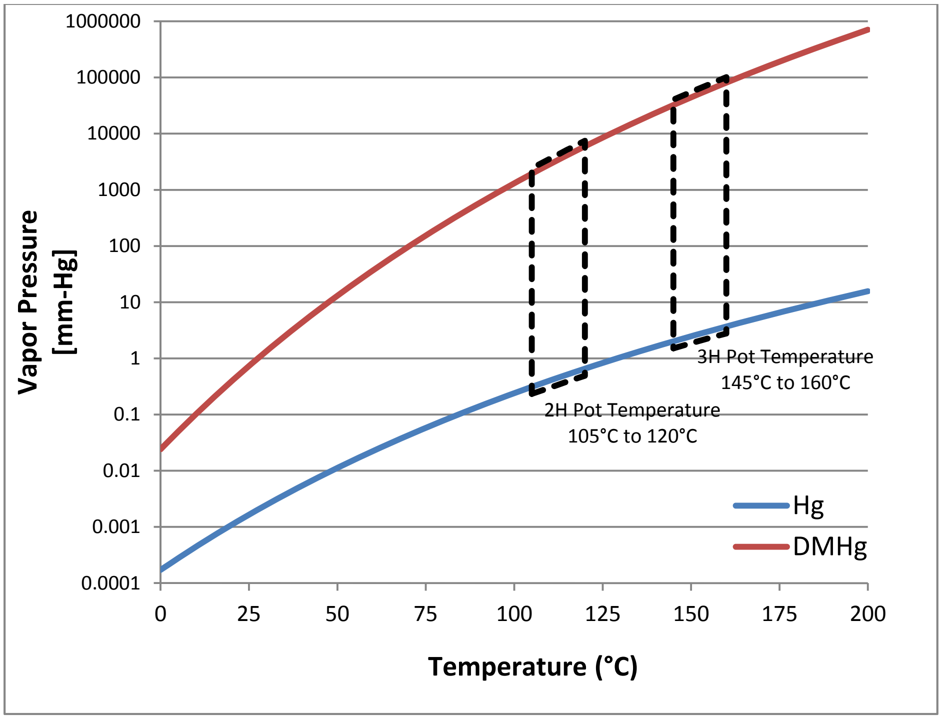

Figure 2. Effect of Temperature on the Vapor Pressure for Elemental Mercury and DMHg. Vapor pressures adjusted using Clausius-Clapeyron equation and gas-phase thermochemistry data from NIST[7, 8, 9, 10]

Table 1. Conceptual behavior and transformations of various Mercury species across the High-Level Waste Evaporator System

Species	Entering	Process Internal to Evaporator	Exiting
Hg(0)	Dissolved aqueous phase or microscopic pure-phase globules. Possible internal production from Hg(I) and Hg(II).	Heating results in transfer to the vapor phase. Cooling of overheads results in pure-phase liquid accumulation.	Liquid from MRT.
Hg(I)	Dissolved in the liquid waste (aqueous).	Possible chemical reduction to Hg(0). Otherwise species will concentrate due to solvent loss. Possible enrichment from dissolution of particulates.	Dissolved species to drop tank.
Hg(II)	Dissolved in the liquid waste (aqueous).	Possible chemical reduction to Hg(I) and/or Hg(0). Otherwise species will concentrate due to solvent loss. Possible enrichment from dissolution of particulates.	Dissolved species to drop tank.
MeHg+	Dissolved in the liquid waste (aqueous).	No identified reactions for this species. Species will concentrate due to solvent loss.	Dissolved species to drop tank.
DMHg	Dissolved in the liquid waste (aqueous).	Heating results in transfer to the vapor phase.	Unknown. Vapor pressure will limit condensation. Possible vapor accumulation or stack release.*
Particulate (various adsorbed species)	Solid phase, particle entrainment in flow.	Coagulation & settling, possible partial dissolution/desorption during heating.	Annual maintenance to clean & remove. Residual deposits on cooling coils.

* Stack height was raised to address release issues some years ago.

1.1 242-16H (2H) Evaporator

The 2H Evaporator directly supports the Defense Waste Processing Facility (DWPF). Condensates collected during the DWPF Chemical Process Cell and Melter operations are returned to the tank farm as DWPF Recycle. DWPF Recycle is the largest influent to the Savannah River tank farms. Historically, Tank 22 has been the DWPF Recycle Receipt Tank; waste from Tank 22 was then transferred to the Evaporator Feed and Vent Tank, Tank 43. Tank 38 is the Evaporator Concentrate Receipt Tank. Periodically, Tank 38 has undergone partial de-inventories as concentrated material is used to supplement salt batch compositions. Since June 3, 2015, Tank 22 is transferred to Tank 38 and then Tank 38 is transferred to Tank 43. Note that this change was made after the samples analyzed in this report were collected. Operational data for the period from January 1, 2015 through

September 30, 2015 records the collection of 3.235 L of elemental mercury from the 2H Evaporator System.[3] Figure 3 shows the layout of the 2H system. Each pass through the evaporator system produces approximately a 30% concentration factor.[11]

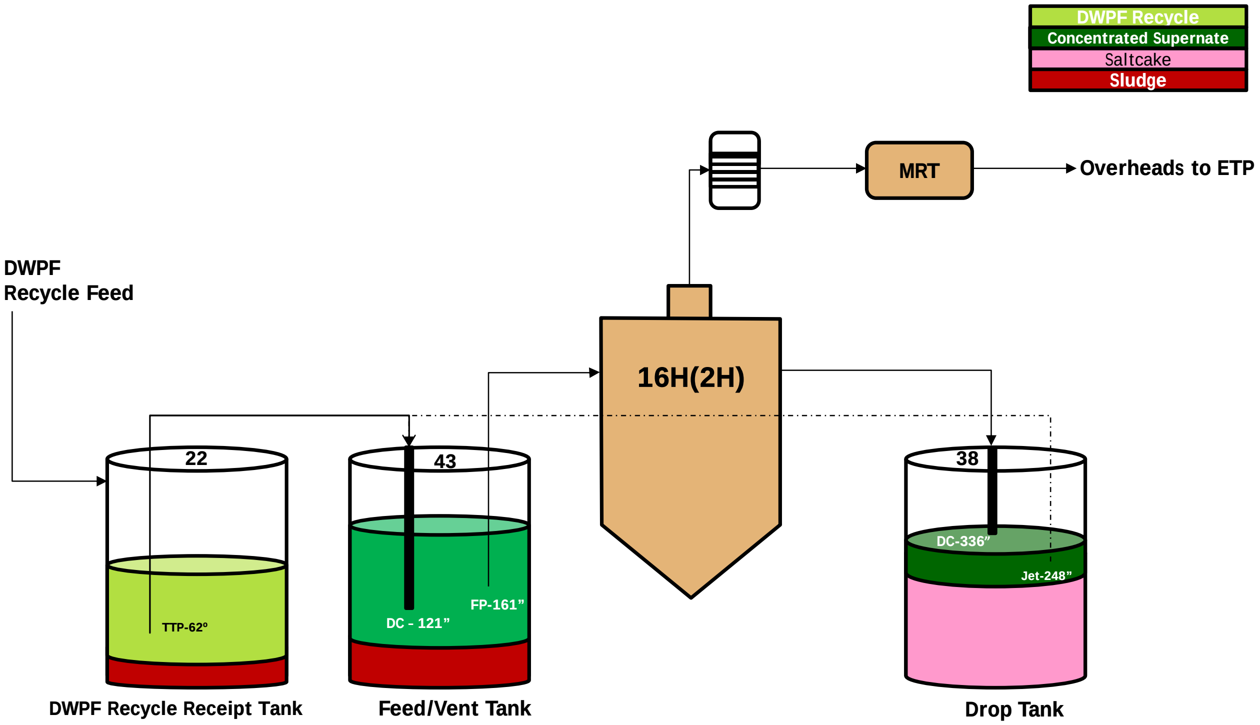

Figure 3. Typical Layout for the 2H Evaporator[12]

1.2 242-25H (3H) Evaporator

The 3H Evaporator concentrates high level liquid waste from H-Canyon and F- and H-Tank Farms including Sludge Batch decants. The Evaporator Feed Tank is Tank 32. There are two Evaporator Concentrate Receipt Tanks, Tanks 30 and 37. Presently, Tank 30 is the Concentrate Receipt Tank because Tank 37 has a high level of salt and is currently undergoing salt dissolution. Periodically, Tank 37 is partially de-inventoried via salt dissolution campaigns. The dissolved salt solution from the current campaign will be transferred to either Tank 35 or 23 and later used as a component of the next salt batch recipe. Operational data for the period from January 1, 2015 through September 30, 2015 records the collection of 26.8 L of elemental mercury from the 3H Evaporator System.[3] The 3H Evaporator pot is approximately ten fold larger than the 2H Evaporator pot and is shown in Figure 4, where Tank 29 is the Alternate Evaporator Vent Tank.

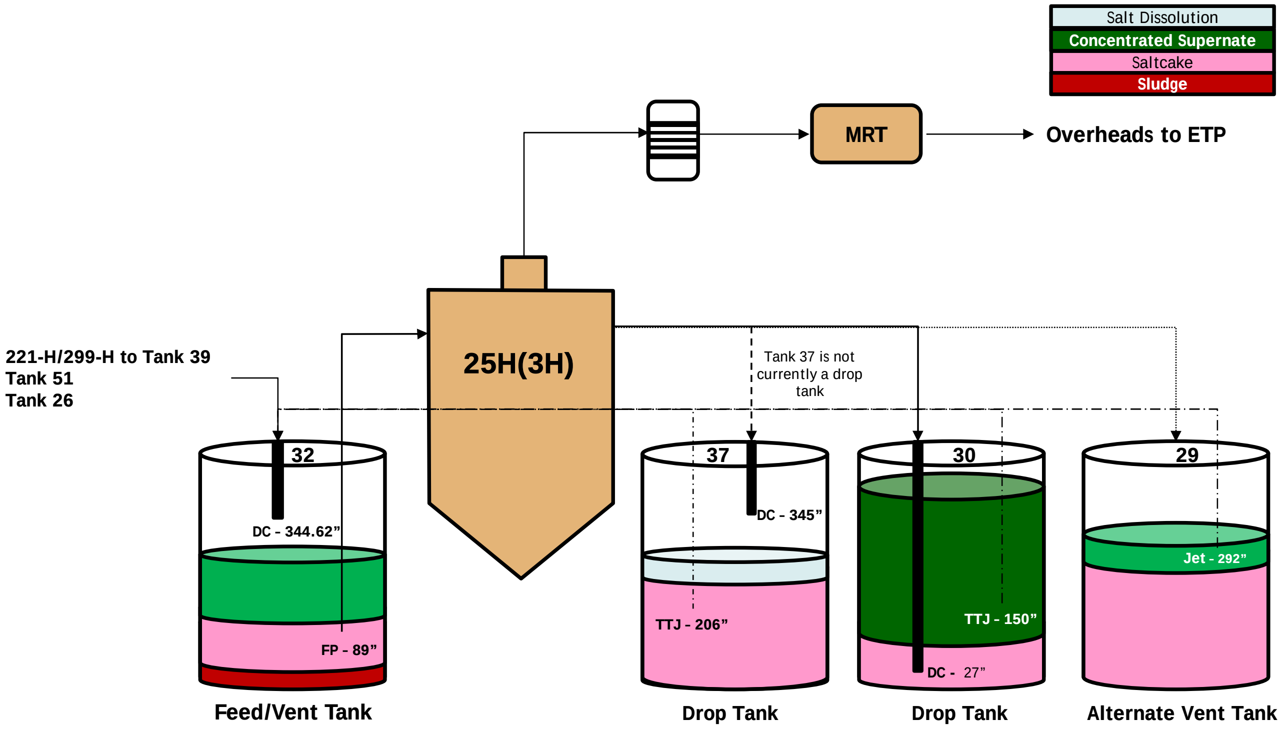

Figure 4. Typical Layout for the 3H Evaporator[12]

1.3 Mercury Collection in the Evaporator Systems

The amount of mercury collected in the 2H and 3H evaporator systems is highly variable month-to-month depending upon evaporator operations, material transfers, etc. Figure 5 provides the 2015 history of Hg collection when both evaporator systems were operational throughout the year. The large increase in mercury extracted by the 3H evaporator is attributable to Tank 22 slurry (about 25,000 kg insoluble solids) transferred to Tank 51 during the formation of Sludge Batch 9 (SB9). As previously noted, Tank 22 contains DWPF recycle, and DWPF recycle contains a large amount of mercury.[13] When Tank 22 feeds the 2H evaporator system, supernate is generally transferred, but when Tank 22 was transferred to Tank 51, an effort was made to slurry the tank and transfer as much of the sludge solids as possible. As washing progressed on Sludge Batch 9, decants from Tank 51 were transferred to Tank 32 in Oct '14 (222K gallons) and Dec'14 (215K gallons) – thus it is believed a large amount of mercury began entering the 3H evaporator system.[14] The 3H evaporator was run for a short period from Dec. 12 – 16, 2014, but more regular operations began on January 6, 2015 and nearly 6 L of Hg(0) was collected in two days. Additional decants of Tank 51 SB9 supernate were transferred to the 3H evaporator system tanks as shown in Table 2. The Tank 51 supernate (HTF-51-14-77) from July 2014 was shown to contain 480 mg/L soluble Hg.[15] Each successive decant during SB9 washing would have delivered less mercury to the 3H system.

Table 2. Sludge Batch 9 Washing Decant Transfers to 3H Evaporator Tanks[14]

Tank Transfers	Date	Gallons	Designation
51 → 32	Oct ‘14	222,000	SB9 Decant G
51 → 32	Dec ‘14	215,000	SB9 Decant H
51 → 32	Feb ‘15	148,000	SB9 Decant I
51 → 30	Mar ‘15	124,000	SB9 Decant J
51 → 30	Jun ‘15	29,000	SB9 Decant K1
51 → 37	Aug ‘15	172,000	SB9 Decant L
51 → 30	Sep ‘15	134,000	SB9 Decant M

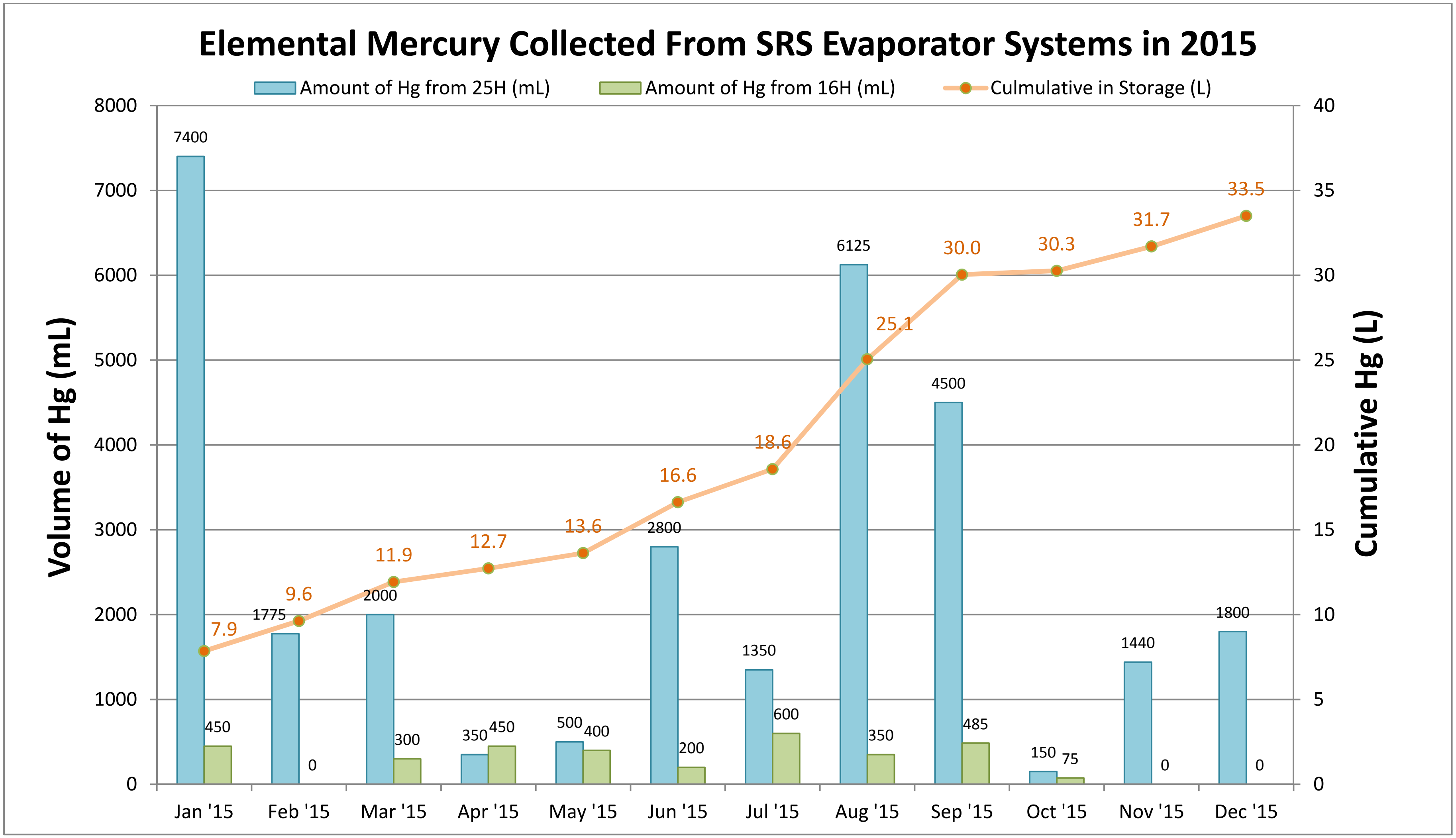

Figure 5. Elemental Mercury Collected from the 2H (16H) and 3H (25H) Evaporator Systems in 2015[3]

2.0 Experimental Procedure

Samples drawn from the various salt processing facilities and waste tanks were predominately collected from the waste tank in small stainless steel bottles. It is recognized that there could be large uncertainties with such small samples from such a large volume. Every attempt was made by operations personnel to obtain a zero headspace sample. The bottles were capped, packaged for transfer to SRNL, and received into ether a shielded cell or radiological fume hood depending on the activity of the sample and its associated radiation dose rate. For samples received into the SRNL Shielded Cells, an intermediate dilution of generally 1:100 was made into a Teflon bottle and immediately removed from the cells for refrigerated storage prior to final dilution and shipment. Final aliquot dilutions were prepared, packaged, and shipped to an offsite laboratory within 24-36 hours and maintained as close to 4 °C as possible. The descriptions below are details of the offsite laboratory methods, as previously documented in Reference 16.

2.1 Dissolved Versus Total Hg

The samples were filtered through 0.45 µm disposable filtration devices for dissolved mercury. When using filtration, an unquantifiable fraction of the dissolved volatile species could be lost, leading to an understatement in the dissolved total Hg concentration. Direct analysis of the solids collected on the filter membrane could also be used to quantify particulate mercury.

2.2 Quantification of Dimethylmercury

Dimethylmercury is first extracted from a sample aliquot (0.025 to 2.00 mL, depending upon expected concentration) by dilution into 50 mL of reagent water, and direct purged for 17 minutes at a flow rate of 200 mL/min from solution into Carbotrap columns. After collection on the Carbotrap, the columns were dried by sparging with nitrogen for seven minutes. For analysis, the loaded Carbotrap column is placed in-line with a packed column isothermal Gas Chromatograph (GC) (1-m column, 4 mm ID, packed with 15% OV-3 on Chromasorb-WAW-DMSC; held at a constant 80 °C), and thermally desorbed into an argon stream which carries the Hg species into the GC column.[17] In the column, the following species can be easily separated: elemental, Hg(0); dimethylmercury, $(CH_3)_2Hg$; methylethylmercury, $CH_3HgC_2H_5$; and diethylmercury, $(C_2H_5)_2Hg$. Under the conditions of these experiments, however, the only quantifiable peak is $(CH_3)_2Hg$, which passes through the column with a retention time of approximately 2.5 minutes, after a meaningless “marker” peak of elemental Hg at about 1 minute.[18] The gas stream from the GC column passes through a pyrolytic column held at approximately 800 °C, which breaks down all Hg species to elemental Hg, that are then quantified by cold vapor atomic fluorescence spectrometry (CVAFS), as detailed elsewhere.[17] The mass (ng) of Hg contained in each aliquot analyzed is quantified by comparison of the measured peak heights to the slope of a calibration curve analyzed from aliquots of a $(CH_3)_2Hg$ stock solution analyzed in the same manner. The initial stock solution was custom prepared in isopropanol and certified for concentration by oxidization and analysis for total mercury after confirming the absence of other known species. A working solution of 1.0 ng/mL in methanol was prepared as a calibration standard. Recertification of the concentration is performed annually by oxidation and analysis for total mercury.

2.3 Quantification of Methyl- and Ethylmercury

Methylmercury (CH_3Hg^+) and ethylmercury ($C_2H_5Hg^+$) were analyzed similarly to the $(CH_3)_2Hg$ described above, except that the aliquot of the sample was diluted with a pH 4.9 acetate buffer, and the sample first ethylated for 17 minutes with sodium tetraethyl borate for MeHg[17,18] or propylated with sodium tetrapropylborate for ethylmercury. This reagent converts CH_3Hg^+, which is non-volatile, into methylethylmercury ($CH_3HgC_2H_5$), which is volatile. This species is then analyzed by purge and trap using a Carbotrap, and isothermal GC-CVAFS. The initial calibration standard employed for MeHg was a 100 µg/mL stock solution prepared by Absolute Standards (Hamden, CT), which was used to prepare a 1 ng/mL working standard. The accuracy of this standard was verified by daily comparison to a secondary standard prepared by Sigma Aldrich (St Louis, MO). The initial calibration standard employed for ethyl mercury was a 4.4 µg/mL stock solution prepared by Applied Isotope Technologies (Sunnyvale, CA). The accuracy of this standard was verified by daily comparison to a secondary standard prepared by Sigma Aldrich (St Louis, MO) and certified for concentration by oxidization and analysis for total mercury after confirming the absence of other known species.

2.4 Quantification of Total, Inorganic and Elemental Mercury

Prior to analysis for total Hg, bromine monochloride (0.2M BrCl in 12M HCl) was added to the samples in their collection containers, at level of 1 mL per 100 mL of sample for total mercury analysis. The samples were then allowed to digest overnight at room temperature. Aliquots of each digest (0.01 to 100 mL, depending upon concentration) were reduced to elemental Hg in reagent water by the addition of $SnCl_2$, and then the elemental Hg purged onto gold traps as a pre-concentration step.[19] The Hg contained on the gold traps was desorbed and reabsorbed on Carbotraps then analyzed by thermal desorption at 450 °C into a CVAFS, using the dual amalgamation technique. Peak heights were accessed by chart recorder, and the mass (ng) present in the sample calculated by comparison to a standard curve spanning the range of 0-2.00 ng Hg. The calibration standard employed is 10,000 µg/mL Hg diluted to a working laboratory concentration (10 ng/mL). The accuracy of this standard is verified daily by the analysis of the National Institute of Standards and Technology (NIST) NIST-1641d (mercury in river water matrix) reference material, which is diluted 200x with 1% BrCl solution prior to use. Inorganic mercury is determined using the same procedure after purging the sample to remove elemental mercury without the addition of BrCl that will give results of both ionic and elemental mercury. Elemental mercury is determined as well using the same procedure except without the addition of BrCl and $SnCl_2$.

2.5 Calculation of Particulate Mercury

Particulate Hg is determined from the difference between the total and dissolved mercury analysis values after reducing this difference by the elemental Hg measurement. Elemental Hg is lost during the vacuum filtration that precedes the dissolved mercury determination.

3.0 Results and Discussion

3.1 242-16H (2H) Evaporator

The recycle water coming to the tank farm from the DWPF contains 100-300 mg/L of total mercury and a significant fraction of the total is MeHg and nearly half of the mercury is in the form of elemental and inorganic mercury.[13] Tank 22 (DWPF Recycle) is given in Table 3, but it should be noted that this data was collected before the high level of elemental mercury in these samples was appreciated. This high elemental mercury can artificially inflate the ionic mercury concentration. The revised protocol for these analyses now purges the sample of elemental mercury prior to the determination of ionic mercury. During 2H evaporator system operations, feed from Tank 22 was transferred into Tank 43 through a down comer that discharges at a height of 121" from the floor of the tank, where it mixes with other waste contained in the tank. As previously stated, since June 3, 2015 Tank 22 is transferred to Tank 38, which in turn is then transferred to Tank 43. Waste is then transferred to the evaporator pot without mixing using the feed pump at an elevation of 161". Following evaporation, waste is gravity drained to the concentrate tank (Tank 38) through a down comer that introduces the discharges at 336". Periodically, waste is recycled without mixing back to the feed tank through a transfer jet that is located at an elevation of 248" in the concentrate tank and discharges through the down comer in Tank 43. In this dynamic system, a mercury speciation analysis provides a snapshot of the process at a given point in time, but makes it difficult to establish a flowsheet.

Samples were obtained from the feed (Tank 43) and the concentrate tank (Tank 38) and delivered to SRNL on May 11, 2015.[20, 21] The data collected in this sampling effort agrees with the results presented to the Mercury Program Team.[2] Concentrations of total mercury in Tank 43 on the surface are similar to those taken at depth but are within the twenty percent measurement uncertainty and reflect a mercury concentration on the order of 260 mg/L Hg. The measured MeHg concentration was 135 mg/L Hg. Over time, the ratio between MeHg and total mercury has increased in relation to that in the DWPF recycle Tank 22 (52% and 26%, respectively). This increase may reflect changes within the recycle stream over time as DWPF transitioned from processing high fractions of Plutonium Uranium Reduction Extraction (PUREX) sludge to high fractions of H-Area Modified PUREX (HM) sludge.

For the drop tank (Tank 38), the effect of evaporation is observed as total mercury concentrations increase by nearly 50% with total mercury concentrations rising to approximately 485 mg/L Hg on average across the surface and variable depth samples. Methylmercury concentration increased to 180 mg/L Hg as expected due to the low volatility of the salt. The ratio of MeHg to total mercury in Tank 38 remains lower than in Tank 43 at 37%, indicating formation of MeHg in the evaporator does not appear to be occurring – though the impact of return transfers from Tank 38 back to Tank 43 cannot be accounted for in this assessment. What is not known is the degree to which MeHg is insoluble in the system. There is little elemental mercury in either the feed or drop tanks, as would be expected. It would be difficult to transfer any elemental mercury from Tank 22 due to the height of the transfer jet and the conditions in the feed and drop tanks. A decrease in DMHg is observed going from the feed to the drop tank at the lower elevation, as expected from the Henry's Law correlation, but the opposite is observed for the surface samples.

Table 3 also contains the results of mercury speciation from the 2H Evaporator's OHT-1 and OHT-2. These results show small mercury concentrations between 3.8 and 4.8 mg/L Hg as total mercury and between 2.4 and 5.6 mg/L Hg as MeHg. Almost no DMHg is measured in these samples as would be expected based on volatility. Table 4 contains data previously published[5] for samples taken in the early 2000s for DMHg. Note that for consistency, the concentration values reported in Table 4 have been converted to mg Hg/L basis from the mg Hg-species/L basis that is given in the original reference document. The same unit conversion applies to the concentration values reported in Table 7. The mercury behavior is not similar. MeHg is now a measurable species. The behavior of DMHg is different now too. For the current data set, the concentrations are 0.9 µg/L to 5.4 µg/L; whereas, the concentration in the 2000s was three orders of magnitude higher ranging from 0.013 mg/L to 1.9 mg/L. One potential explanation for this discrepancy is there is a different chemistry and utilization for the antifoam agent used in DWPF compared to the antifoam previously used in the evaporator system. From this data, one can claim that the DWPF antifoam is only singly methylating the mercury giving rise to higher MeHg concentrations in the overhead tanks, i.e. the system is methyl limited, compared to the higher DMHg concentrations measured in the past. Alternatively, any DMHg formed in DWPF would likely be vented based upon the agitated vessels in use.

Table 3. Mercury Species Concentrations (mg Hg/L) across the 2H Evaporator System [%RSD] (No. of Replicates)

Tank	Sampling Date	Total Hg	Dissolved Hg	Particulate Hg‡	Elemental Hg	Ionic Hg	Methyl Hg	Dimethyl Hg	Ethyl Hg
22	3/23/2015	119 [2.9] (3)	111 [2.5] (3)	0	116 [53] (2)‡‡	56.5 [6.5] (3)*	31.2 [7.4] (2)	ND	ND
43S	5/11/2015	286 [2.7] (3)	208 [0.75] (3)	77	1.44 [18] (3)	44.0 [5.6] (3)	135 [12] (3)	0.00468 [0.32] (2)	<8.7
43D	5/11/2015	234 [1.8] (3)	186 [1.3] (3)	45	3.46 [20] (3)	30.5 [2.1] (3)	134 [8.1] (3)	0.613 [24] (3)	<8.5
38S	5/11/2015	496 [2.6] (3)	325 [2.5] (3)	168	3.58 [46] (3)	29.8 [7.1] (3)	200 [6.2] (3)	0.148 [52] (3)	<35
38D	5/11/2015	476 [14] (3)	316 [1.3] (3)	156	4.07 [90] (3)	31.6 [4.7] (3)	160 [6.8] (3)	0.0525 [48] (3)	<34
2H OHT1	5/11/2015	3.78 [6.5] (3)	3.65 [7.5] (3)	0.071	0.0587 [9.8] (3)	0.505 [1.2] (3)	2.45 [3.6] (3)	0.000899 [42] (3)	<0.12
2H OHT2	5/11/2015	4.80 [6.8] (3)	4.64 [1.6] (3)	0.094	0.0636 [20] (3)	0.224 [61] (3)†	5.58 [10] (3)	0.00536 [8.0] (3)	<0.57

S = Surface; D = Depth, OHT = Overheads Tank, ND = Not Detected and Reporting Limit not provided for this sample.

* Value is inflated by the high elemental Hg content, which at the time of this analysis was not being purged prior to determination of ionic Hg.

† One replicate was 4-5x smaller than the other two, if it is excluded, the average = 0.302 [11].

‡ The Hg(0) measured for these samples inflates the particulate Hg values. The particulate value shown here was corrected by subtracting the value of the Hg(0) from the difference between the total and dissolved Hg values.

‡‡ Only the two values above the detection limit were included in the average. One of the three values was a “non detect” as noted in the footnote on Table 1 in SRNL-L3100-2015-00079, Rev. 1.

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Table 4. Results (mg Hg/L) of Previous Sampling of the 2H Evaporator Overheads [%RSD] (No. of Replicates)

Location	Date	Total Hg	DMHg
Alternate Overheads Sample Point 1	2/5/2003	1.01	0.991
Alternate Overheads Sample Point 2	2/5/2003	1.28	1.90
Primary Overheads Sample Station	2/20/2003	2.32 [0.90] (3)	0.0128 [3.5] (3)
Primary Overheads Sample Station	3/4/2003	2.93	0.832
Alternate Overheads Sample Point 1	3/4/2003	3.13	1.07
Alternate Overheads Sample Point 2	3/4/2003	3.37	1.30

MeHg = methylmercury; DMHg = dimethylmercury; ND = Not Detectable

(Please note: The total mercury may or may not contain a contribution from elemental mercury.)

There is extremely limited vapor phase data that can be compared between 2003[5] and 2011-12.[22] While in 2003 a concerted effort was made to look for mercury hot spots, most recent sampling has focused on human exposure areas. Table 5 provides the available results for the limited common data collection points in the 2H Evaporator and the Effluent Treatment Project (ETP) Waste Collection Tank (WCT). There appears to be a reduction of DMHg in the 2H Evaporator dike area and around the ETP WCT, but it is difficult to extrapolate these findings to any general conclusions about the evaporator system.

Table 5. Vapor Phase Concentrations of DMHg (mg/m^3) at Various Locations in 2003 and 2011-12

Location	2003		2011-12	
2H Evaporator Mercury Removal Station	2/5/2003	0.0046	4/26/2011	0.0057
2H Evaporator Dike Area	3/4/2003	>0.089	4/27/2011	<0.000036
Effluent Treatment Project Waste Collection Tank	3/13/2003	0.00034	2/28/2012	<0.000036

3.2 242-25H (3H) Evaporator

The 3H Evaporator is a comparable technology to the 2H Evaporator but as previously mentioned is much larger and runs at higher steam flows and operating temperature. Following the discovery in the early 2000s that there was measurable DMHg present in the evaporator systems, both systems ceased the use of antifoam agents. The data for the 2H system indicates that antifoam breakdown products and the methylated byproducts of mercury are still entering the system from DWPF. This is not the case for the 3H system. The speciation data for the 3H system is shown in Table 6.

The overall concentration of mercury in the 3H Evaporator system is currently lower than the 2H system except for the variable depth sample taken from Tank 32. The data from the surface samples show a general trend for total mercury: the feed tank (Tank 32) was 48 mg/L Hg, the drop tank (Tank 30) increased to ~76 mg/L Hg, and the spare drop tank (Tank 37) measured ~23 mg/L. There is little MeHg in the system, on the order of 2 – 8 mg/L Hg. The variable depth sample taken from Tank 32 shows a higher elemental and total mercury concentration than the surface sample, and is at a level comparable to the 2H evaporator system. One possible explanation for this observation is that mercury is being leached from the sludge layer that exists in this tank. By comparison, the Tank 30 variable depth data is in reasonably good agreement with that of the surface sample – Tank 30 does not contain a sludge layer.

Table 6. Mercury Species Concentrations (mg Hg/L) across the 3H Evaporator System [%RSD] (No. of Replicates)

Tank	Sampling Date	Total Hg	Dissolved Hg	Particulate Hg‡	Elemental Hg	Ionic Hg	Methyl Hg	Dimethyl Hg	Ethyl Hg
32S	6/30/2015	48.2 [2.0] (3)	42.6 [6.7] (3)	5.4	<0.13	3.38 [31] (3)	7.59 [4.4] (3)	<0.025	<18
32D	6/29/2015	182 [3.6] (3)	118 [2.0] (3)	8.9	55.4 [14] (3)	87.2 [5.7] (3)	3.84 [3.0] (3)	<0.025	<18
30S	6/29/2015	75.5 [4.4] (3)	66.0 [4.0] (3)	8.4	1.03 [2.4] (3)	22.2 [20] (3)	7.28 [5.2] (3)	<0.026	<18
30D	6/29/2015	71.4 [3.4] (3)	49.1 [3.7] (3)	20.9	1.41 [25] (3)	15.2 [14] (3)	6.19 [4.7] (3)	<0.025	<18
37S	7/21/2015	22.8 [8.9] (3)	11.7 [3.8] (3)	11.0	<0.13	4.41 [20] (3)	2.46 [1.8] (3)	<0.026	<18
37D	7/21/2015	26.0 [3.6] (3)	16.1 [8.6] (3)	9.5	0.431 [8.8] (3)	8.81 [14] (3)	1.64 [6.1] (3)	<0.025	<17
3H OHT1	8/11/2015	1.15 [5.8] (3)	1.06 [4.8] (3)	0.074	0.0202 [12] (3)	0.0319 [5.9] (3)	1.42 [5.3] (3)	7.20E-05 [3.4] (3)	<0.017
3H OHT2	8/11/2015	1.21 [2.4] (3)	1.17 [3.5] (3)	0.026	0.0194 [5.7] (3)	0.0844 [1.8] (3)	1.26 [7.6] (3)	9.40E-04 [6.2] (3)	<0.017

S = Surface; D = Depth, OHT = Overheads Tank.

‡ The Hg(0) measured for these samples inflates the particulate Hg values. The particulate value is corrected by subtracting the value of the Hg(0) from the difference between the total and dissolved Hg values.

There is considerable difference between the concentrations of DMHg seen in the current 3H evaporator overheads and that found previously and shown in Table 7.[5] Previous concentrations of DMHg were 2 – 4 orders of magnitude higher when antifoam was being introduced into the 3H evaporator compared to the current values. The change in the level of MeHg measured is less significant, showing an inconsistent but minor reduction over earlier measurements. Similarly, total Hg is now lower by a factor of 3 – 8. Curiously, all the mercury that makes it into the overhead tanks is MeHg, which is unexpected since it is not a simple entrainment issue, this would result in a constant ratio of total to MeHg, and its low vapor pressure precludes evaporation. If we look at cesium levels as a measure of entrainment, the overheads are five orders of magnitude below those of the feed; however, the MeHg level does not show this degree of reduction in the overheads. Whatever mercury specie(s) that is (are) carried into the overheads appears to be converted to MeHg through a vapor phase or condensate phase reaction. In light of the significant compositional, temperature, and potential redox changes associated with moving from liquid in the evaporator pot to vapor and ultimately being condensed and retained as overhead liquids, there are means for such a transformation to occur in the system.

Table 7. Results (mg Hg/L) of Previous Sampling of the 3H Evaporator Overheads [%RSD] (Replicates)

Location	Date	Total Hg	MeHg	DMHg
Alternate Overheads Sample Point 1	11/6/2002	9.12	5.98	3.03 [16] (3)
Alternate Overheads Sample Point 2	11/6/2002	7.10	6.77	2.42 [9.2] (2)
Primary Overheads Sample Station	11/6/2002	7.16	1.86	2.57 [2.6] (2)
Primary Overheads Sample Station	2/20/2003	3.70	ND	1.70
Alternate Overheads Sample Point 1	2/20/2003	4.52	ND	0.0817

MeHg = methylmercury; DMHg = dimethylmercury; ND = Not Detectable
(Please note: The total mercury may or may not contain a contribution from elemental mercury.)

4.0 Conclusions

The ability to be able to predict the behavior of mercury across the high level waste evaporator systems requires knowledge about the particular mercury species contained in each thermodynamic state. The partitioning between the liquid, solid, and vapor phases is directly correlated to the speciation. The major contribution of this work is to provide an initial analytical speciation for various aspects of the evaporator system. With this information, the following conclusions are drawn from the data:

- The data mostly agrees with the fundamental thermodynamic understanding for the prediction of mercury behavior across the high level waste evaporators.
- Relative to the 3H Evaporator, the 2H Evaporator has high mercury concentrations and a large fraction of the species present is MeHg. The 3H Evaporator has lower mercury concentrations including lower fractions of organomercury species.
- Cessation of the use of antifoam in the tank farm evaporators has reduced the concentrations of DMHg in the 2H and 3H system.
- Methylmercury is probably produced during DWPF operations and returned to the tank farm in DWPF recycle and accumulates in the 2H evaporator system with concentrations approaching 0.2 g/L. Some downstream impacts of this high organomercury concentration are known, such as increased leachable mercury from Saltstone;[23, 24] but, others are not yet well understood.
- Concentrations of DMHg are lower than expected compared to 2003 analyses[5] and perhaps indicate a difference in chemistry for the DWPF antifoam versus that previously found when antifoam was used in the evaporators.

5.0 Recommendations for Future Work

A System Engineering Evaluation (SEE)[25] specifically looked at the technologies that could enhance removal of ionic mercury in the H-area evaporators through the addition of a reducing agent to convert ionic mercury to elemental mercury. A recommendation was submitted to the Department of Energy – Environmental Management (DOE-EM) to consider this as a candidate for technology development in order to demonstrate a proof of concept, alternate means to remove mercury from the LWS.[1]

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