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To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on DWPF SMECT-4, SMECT-6, and RCT-2 Samples

Approved by:

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INTRODUCTION

The Savannah River National Laboratory (SRNL) was tasked with preparing and shipping samples for Hg speciation by Eurofins Frontier Global Sciences, Inc. in Seattle, WA on behalf of the Savannah River Remediation (SRR) Mercury Task Team.[i,ii] The fifteenth shipment of samples was designated to include Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Condensate Tank (SMECT) samples from Sludge Receipt and Adjustment Tank (SRAT) Batch 738 and a Recycle Condensate Tank (RCT) sample from SRAT Batch 736. The DWPF sample designations for the three samples analyzed are provided in Table 1. The Batch 738 'Baseline' SMECT sample was taken prior to Precipitate Reactor Feed Tank (PRFT) addition and concentration and therefore, precedes the SMECT-5 sample reported previously.[iii] The Batch 738 'End of SRAT Cycle' SMECT sample was taken at the conclusion of SRAT operations for this batch (PRFT addition/concentration, acid additions, initial concentration, MCU addition, and steam stripping). Batch 738 experienced a sludge slurry carryover event, which introduced sludge solids to the SMECT that were particularly evident in the SMECT-5 sample, but less evident in the 'End of SRAT Cycle' SMECT-6 sample. The Batch 736 'After SME' RCT sample was taken after completion of SMECT transfers at the end of the SME cycle.

[i] Sudduth, C. B., *Mercury Speciation*, X-TTR-G-00002, Savannah River Remediation, Aiken, SC 29808 (May 2015).
[ii] Crawford, C. L., Bannochie, C. J., *Task Technical and Quality Assurance Plan for Mercury Speciation Analyses in Savannah River Site Liquid Waste Systems*, SRNL-RP-2015-00320, Savannah River National Laboratory, Aiken, SC 29808 (May 2015).
[iii] Bannochie, C. J., *Results of Hg Speciation Testing on DWPF SMECT-1, SMECT-3, and SMECT-5 Samples*, SRNL-L3100-2015-00218, Rev. 1, Savannah River National Laboratory, Aiken, SC 29808 (February 2016).

Table 1 Sample Designations for DWPF Samples Analyzed by Eurofins

SRNL Sample ID	DWPF Description	DWPF Sample ID	DWPF LIMS No.
SMECT-4	Batch 738 Baseline	10	200020840
SMECT-6	Batch 738 End of SRAT Cycle	23	20020860
RCT-2	Batch 736 After SME	9	200020827

RESULTS AND DISCUSSION

SRNL received the samples on November 17 and transferred them to B-103 refrigerated storage where they were subsampled on November 23. The DWPF samples were subsampled in a radiological hood and the subsamples sent to Analytical Development for radionuclide analyses needed for Hazardous Material Transportation calculations, with the balance of the sample returned to refrigerated storage, where they remained at 4°C until final dilutions were made on December 8.

Eurofins supplied deionized water and 250 mL clear and amber glass bottles. SRNL supplied the 1.2 mL concentrated HCl preservative. Triplicate samples of each material were prepared for this shipment. Each replicate was analyzed for seven Hg species: total Hg, total soluble (dissolved) Hg, elemental Hg [Hg(0)], ionic (inorganic) Hg [Hg(I) and Hg(II)], methyl Hg [CH_3Hg-X, where X is a counter anion], ethyl Hg [CH_3CH_2-Hg-X, where X is a counter anion], and dimethyl Hg [$(CH_3)_2Hg$]. The difference between the total Hg and total soluble Hg measurements gives the particulate Hg concentration, i.e. Hg adsorbed to the surface of particulate matter in the sample but without resolution of the specific adsorbed species. The analytes were determined from samples in four separate bottles: 1) methyl Hg and ethyl Hg; 2) dimethyl Hg; 3) total Hg and soluble total (dissolved) Hg; and 4) ionic Hg (Hg(I) & Hg(II)) and elemental Hg.

Prior to shipment, the samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:2500 by mass. SRNL deionized water was employed as the blank. All containers were filled close to the maximum allowable volume to minimize headspace within the sealed samples. In total, 48 aqueous samples were prepared on December 8, 2015 and shipped the following day by next-day air to Eurofins where 48 samples were received on December 10, 2015. Eurofins reported the aqueous sample results in units of ng Hg / L sample on December 31, 2015.

Due to the high elemental Hg results obtained on previous SMECT samples from Shipments #13 and #14 the SRNL prepared traps were not shipped to Eurofins for these samples since dimethyl Hg was expected to be once again below detection and the elemental Hg to have exceeded the trap capacity. Future SRNL Hg(0) trapping will be done with a 1:10 diluted sample. Details of the sample preparation and Purge & Trap (P&T) activities[iv,v,vi] are

[iv] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 11 & 12), Experiment L2320-00194-04, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (June 2015).
[v] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 13, 14, 15, 16)", Experiment L2320-00194-09, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (September 2015).

recorded in the SRNL E-Notebook system.

Table 2 provides the average concentrations of Hg species in the aqueous samples derived from Eurofins reported data corrected for dilutions performed by SRNL. All but one blank, not shown in the table, were reported at the reporting limits, or 'RL' values. The exception was the RCT-2 blank analyzed for total Hg and dissolved Hg, but these measured values were four orders of magnitude lower than the samples analyzed along with them. The RL values given by Eurofins are typically 1X to 7X higher than the associated detection limits, or 'DL' values. The RL values typically are associated with the 'quantification' limit for a given analyte and analytical method. There is a ± 20% uncertainty that Eurofins reports in the measurement of total Hg and total soluble Hg, which are used to determine the particulate Hg value for aqueous samples. There was high elemental Hg in the SMECT samples, a species which may be removed when the aqueous samples are filtered for total soluble Hg; hence, the reported particulate values have been corrected by subtracting out the contribution from Hg(0). The elemental Hg values reported were determined from the ionic Hg bottles (Set #4) because it was clear that analyzing the Hg(0) after sampling the Set #2 bottles for dimethylmercury led to a significant loss of Hg(0) to the headspace created in the sample bottle.

Eurofins purged the Hg(0) from the ionic Hg bottles prior to determining ionic Hg, as they had implemented for Shipment #12 following our discussion about the data sets that contain high elemental Hg as noted in a previous memo.[vii] There was still a significant ionic Hg concentration for the SMECT-6 material in this sample set – the highest determined to date, which accounted for approximately 65% of the total Hg. As previously noted,[viii] this may indicate that elemental Hg from the Mercury Water Wash Tank (MWWT) decantor is flowing back into the SMECT during concentration mode, re-oxidizing, and raising both the total Hg level as well as the ionic Hg fraction. One of the three replicates for the RCT-2 sample gave an ionic Hg value that was 5-15X larger than the other two replicates, this replicate also showed twice the Hg(0) concentration. If Hg(0) were not completely removed from this sample, it would bias the ionic Hg analysis high.

Ethyl Hg was not measured above the reporting limit in any of the samples, likely due to the greater methyl Hg content as discussed previously.[iii] Dimethyl Hg above the reporting limit of the analytical method was only found in the SMECT-4 sample and in only one of the three replicates.

Methylmercury appears to be produced and collected in the SMECT as a result of SRAT operations. As shown in Figure 1, the concentration of methyl Hg rises from a baseline value of 37 mg/L at the start of the SRAT cycle, to 45 mg/L following PRFT addition and concentration (i.e. caustic boiling), and ending at 139 mg/L at the completion of the SRAT cycle.[iii] So it appears either some methyl Hg is produced during caustic boiling or methyl Hg already present in the system is transferred to the SMECT as a result of boiling, but more methyl Hg is produced during subsequent portions of the cycle which include acid and MCU additions and steam stripping. As previously discussed,[viii] Batch 736 had no caustic boiling, but the final methyl Hg concentration in the SMECT

[vi] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 15)", Experiment L2320-00194-12, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (November 2015).
[vii] Bannochie, C. J., *Results of Hg Speciation Testing on Tanks 30, 32, and 37 Depth Samples*, SRNL-L3100-2015-00206, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (November 2015).
[viii] Bannochie, C. J., *Results of Hg Speciation Testing on 4Q15 Tank 50, DWPF SMECT-2 and RCT-1 Samples*, SRNL-L3100-2015-00219, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (February 2016).

was the same as for Batch 738. It remains clear from Table 2 and Figure 1 that the SMECT contains a variety of Hg species (particulate, Hg(0), ionic Hg, and methyl Hg) at appreciable concentrations that vary over time.

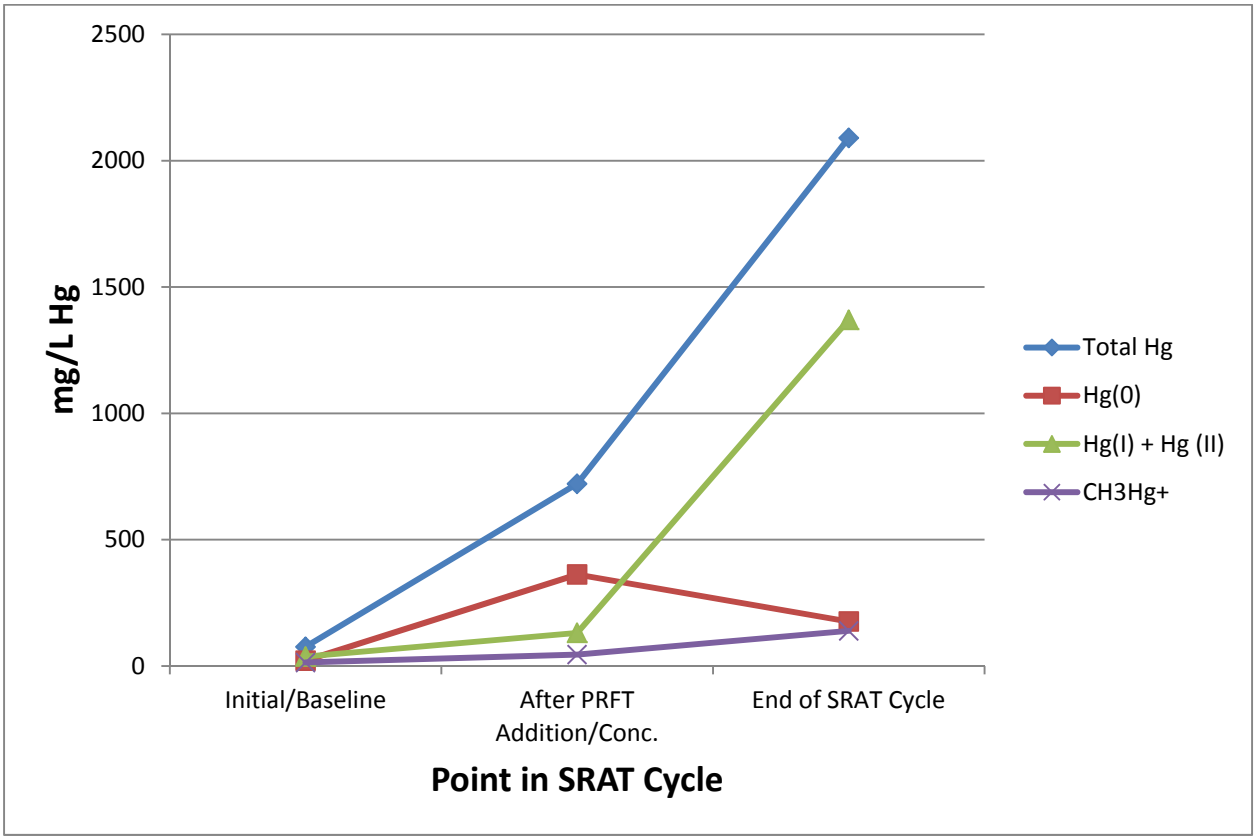

Figure 1. Mercury concentrations (mg/L) in SMECT samples taken during various portions of the SRAT Batch 738 cycle. SMECT-4, initial/baseline; SMECT-5, after PRFT addition/concentration; [iii] and SMECT-6, end of SRAT cycle.

The last column of Table 2 provides the percent of total Hg that the six measured species (particulate, elemental, ionic, methyl, ethyl, and dimethyl) represent. A range is provided for each sample to account for the uncertainty of the detection limit values reported for dimethyl Hg and/or ethyl Hg species. The recoveries for the SMECT-4, SMECT-6, and RCT-2 analyses are 95 – 97%, 88 – 89%, and 49 – 50%, respectively. With the exception of the low recovery for the RCT-2 sample, these recoveries are in the range of where the method uncertainties and the impact of combining results analyzed from four separately prepared dilutions could account for the difference between the sum and 100%. The low RCT-2 recover stands in contrast with the recovery for the RCT-1 sample reported previously (73 – 76%),[viii] and cannot be explained at this time.

Table 2. Average Concentrations of various Hg species for DWPF SRAT Batch 736 and 738 Samples expressed as mg Hg/L (ppm) [%RSD] (No. of Replicates)

Sample	Total Hg	Total Soluble Hg	Particulate Hg	Elemental Hg [Hg(0)]	Ionic Hg [Hg(I) & Hg(II)]	Methyl Hg	Ethyl Hg	Dimethyl Hg	Species Fraction of Total Hg
SMECT-4	75.7 [6.7] (3)	60.2 [21] (3)	~0*‡	21.2 [4.2] (3)	37.2 [4.7] (3)	13.4 [1.4] (3)	<1.7	0.000530 [NA] (1)	95 – 97%
SMECT-6	2090 [0.95] (3)	1750 [1.0] (3)	164*‡	176 [18] (3)	1370 [10] (3)	139 [4.7] (3)	< 17	< 0.00049	88 – 89%
RCT-2	98.0 [12] (3)	93.7 [1.6] (3)	3.0*‡	1.32 [32] (3)	5.29 [67] (2)	25.7 [10] (3)	< 1.7	<0.00048	36 – 38%

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20%, the particulate value is the difference of these two measured values for the aqueous samples.

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

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