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To: R. E. Edwards

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Results of Hg Speciation Testing on DWPF SMECT-8, OGCT-1, and OGCT-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 sixteenth shipment of samples was designated to include a Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Condensate Tank (SMECT) sample from Sludge Receipt and Adjustment Tank (SRAT) Batch 738 processing and two Off-Gas Condensate Tank (OGCT) samples, one following Batch 736 and one following Batch 738. The DWPF sample designations for the three samples analyzed are provided in Table 1. The Batch 738 'End of SME Cycle' SMECT sample was taken at the conclusion of Slurry Mix Evaporator (SME) operations for this batch and represents the fourth SMECT sample examined from Batch 738. Batch 738 experienced a sludge slurry carryover event, which introduced sludge solids to the SMECT that were particularly evident in the SMECT-5 sample[iii], but less evident in the 'End of SME Cycle' SMECT-8 sample.

[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-8	Batch 738 End of SME Cycle	13	200020896
OGCT-1	Batch 736 End of Batch	12	200020884
OGCT-2	Batch 738 End of Batch	14	200021045

RESULTS AND DISCUSSION

SRNL received the SMECT-8 sample on November 17, 2015 and transferred it to B-103 refrigerated storage where it was subsampled on November 23, 2015 in a radiological hood. The OGCT-1 sample arrived on December 8, 2015 and the OGCT-2 sample arrived on December 9. Both the OGCT samples were diluted 1:10 in the SRNL Shielded Cells and subsampled on December 10, 2015. The subsamples were sent to Analytical Development for radionuclide analyses needed for Hazardous Material Transportation calculations, with the balance of the sample (SMECT-8) or subsamples (OGCT-1 / -2) placed in or returned to refrigerated storage, where they remained at 4°C until final dilutions were made on January 13, 2016.

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 SMECT sample was diluted and OGCT subsamples were further 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 January 13, 2016 and shipped the following day by next-day air to Eurofins where 36 samples were received on January 15, 2016. The remaining acid preserved samples (bottle set #1) were delivered on January 18, 2016 after FedEx reported a delay due to weather conditions. Since the delayed samples were acid preserved, Eurofins did not see a concern with proceeding with the analysis. Eurofins reported the aqueous sample results in units of ng Hg / L sample on January 29, 2016.

Separate dilutions, similar to those above at nominally 1:2500 by mass, of all three samples were prepared for Purge & Trap (P&T) activities conducted at SRNL. Portions of these dilutions, 130 mL, were purged with N_2 gas and the purge gas passed through an activated carbon trap for dimethylmercury collection. To avoid previous

saturation issues, only 13 mL of these dilutions were purged with N_2 gas and the purge gas passed through a combination soda lime and two gold traps in series for collection of Hg(0). The carbon and gold traps for this work were supplied by Eurofins. Details of the sample preparation and Purge & Trap (P&T) activities[iv,v,vi] are recorded in the SRNL E-Notebook system. This work is still scoping in nature and designed to determine whether we can reduce the variability, especially for Hg(0), seen in replicate measurements made by Eurofins on the solution samples they have received. This memo will be revised if useful information is reported by Eurofins for these traps.

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 SMECT-8 blank analyzed for total Hg, but the measured value was six orders of magnitude lower than the samples analyzed along with it. 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 for dimethylmercury leads 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-8 material in this sample set – the second highest determined to date, which accounted for approximately 42% of the total Hg. The total Hg value for the SMECT-8 material was the highest concentration measured to date at 2.67 g/L

Ethyl Hg was not measured above the reporting limit in any of the samples, but the three replicates for the SMECT-8 sample gave values above the detection limit that were in excellent agreement with each other. These have been shown in Table 2 with the appropriate qualifying footnote. Dimethyl Hg, on the other hand, was not measured above the reporting limit or the detection limit in any of the samples.

Methylmercury appears to be produced and collected in the SMECT as a result of SRAT & SME 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), to 139 mg/L at the completion

[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).
[vi] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 16)", Experiment L2320-00194-13, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (December 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).

of the SRAT cycle, and finally ending at 80 mg/L at the end of the SME cycle.[viii, ix] 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,[ix] Batch 736 had no caustic boiling, but the final methyl Hg concentration in the SMECT 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.

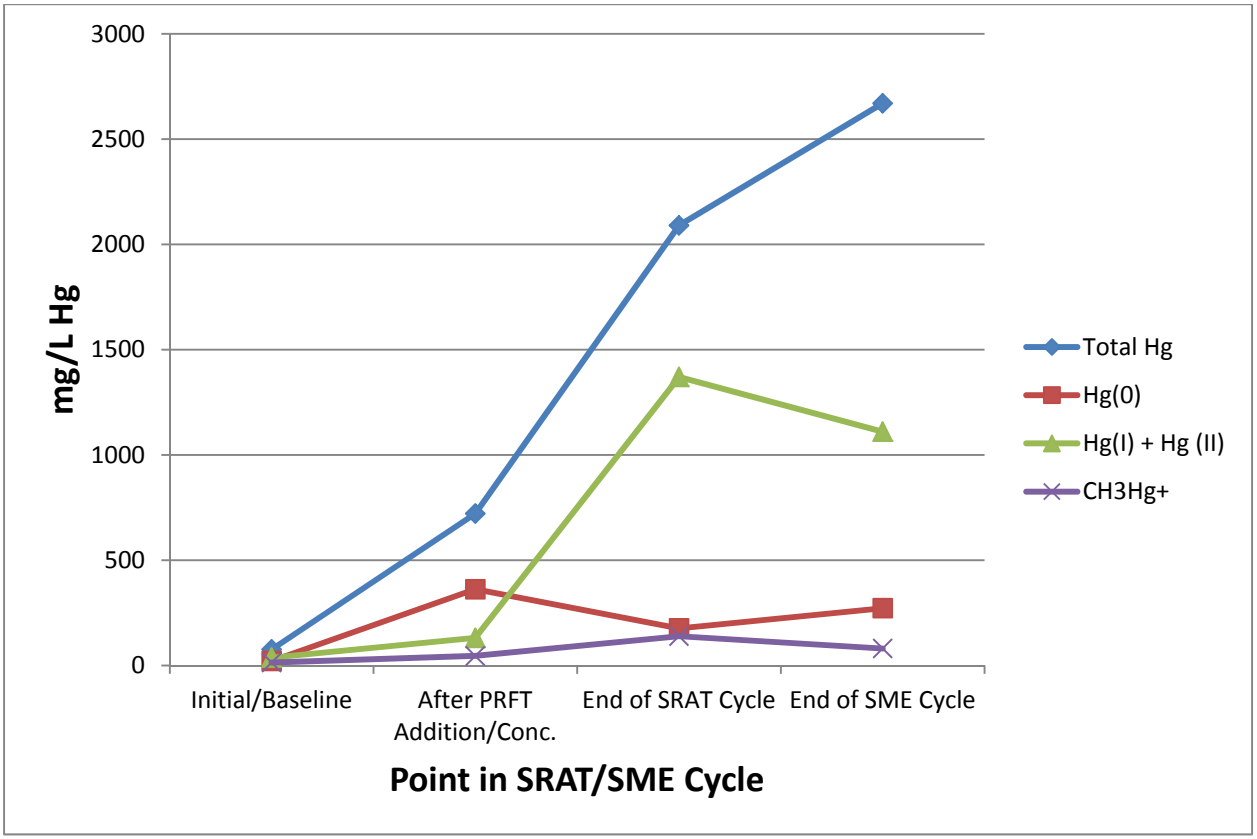

Figure 1. Mercury concentrations (mg/L) in SMECT samples taken during various portions of the SRAT/SME Batch 738 cycle. SMECT-4, initial/baseline; SMECT-5, after PRFT addition/concentration; [iii] SMECT-6, end of SRAT cycle; and SMECT-8, end of SME cycle.

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, methyl Hg, and/or ethyl Hg species. The recoveries for the

[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).
[ix] Bannochie, C. J., *Results of Hg Speciation Testing on DWPF SMECT-4, SMECT-6, and RCT-2 Samples*, SRNL-L3100-2016-00016, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (February 2016).

SMECT-8, OGCT-1, and OGCT-2 analyses are 81%, 95 – 100+%, and 90 – 100+%, respectively. 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%.

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-8	2670 [5.6] (3)	1700 [1.5] (3)	698*‡	272 [12] (3)	1110 [7.4] (3)	80.3 [3.5] (3)	1.37 [6.7] (3) ≠	<0.00049	81%
OGCT-1	130 [1.7] (3)	120 [1.6] (3)	7.18*‡	2.82 [6.6] (3)	113 [1.6] (3)	<0.55	< 17	< 0.050	95 –100+%
OGCT-2	138 [1.9] (3)	134 [2.0] (3)	2.10*‡	1.90 [12] (3)	119 [0.88] (3)	0.642 [NA] (1)	< 18	<0.050	90 – 100+%

* 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.

≠ All three replicates were in reasonable agreement above the detection limit for the method (<1.2 mg/L), but were below the reporting limit for the method (<8.6 mg/L).

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