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7 March 2016 SRNL-L3100-2016-00021 Rev. 0

To: R. E. Edwards

From: C. J. Bannochie

Results of Hg Speciation Testing on Tank 39 and 1Q16 Tank 50 Samples

Approved by:

C. L Crawford, Technical Reviewer per E7, 2.60 Date

W. R. Wilmarth, SRNL Mercury Task Lead Date

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 seventeenth shipment of samples was designated to include two Tank 39 samples and the 1Q16 Tank 50 Quarterly WAC sample. The surface Tank 39 sample was pulled at 262.1" from the tank bottom, and the depth Tank 39 sample was pulled at 95" from the tank bottom. The 1Q16 Tank 50 WAC sample was drawn from the 1-L variable depth sample received by SRNL.

RESULTS AND DISCUSSION

SRNL received the Tank 39 samples (HTF-39-15-132 and -133) on November 19, 2015, and they were placed in the SRNL Shielded Cells on November 30, 2015. On December 4, 2015, the two 85 mL doorstop samples were subsampled and diluted 1:100. The diluted samples were placed in Teflon® bottles with zero headspace, then removed from the cells, with one set sent to Analytical Development for radionuclide analyses needed for Hazardous Material Transportation calculation, and the balance of the diluted subsamples placed in refrigerated storage. The 1Q16 Tank 50 WAC (HTF-50-16-163) was received by SRNL on January 14, 2016 and a subsample with zero headspace placed in a Teflon® bottle on January 15, 2016 and transferred to refrigerated storage. All the Shipment #17 samples remained at ~4-6°C until final dilutions were made on January 27, 2016.

[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).

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 1Q16 Tank 50 sample was diluted and Tank 39 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 27, 2016 and shipped the following day by next-day air to Eurofins where 36 samples were received on January 29, 2016. The remaining acid preserved samples (bottle set #1) were delivered on February 1, 2016 after FedEx reported a delay due to weather. 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 February 11, 2016. SRNL requested re-examination of the values reported for ionic Hg and Hg(0) in the 1Q16 Tank 50 samples after comparing the data with previous quarterly Hg data from this tank. Eurofins discovered some data inconsistencies and proceeded to repeat these two analyses on this sample set a second and third time, with final results reported on March 2, 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[iii,,iv] 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 1 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 Tank 39 depth sample blank analyzed for total Hg and dissolved Hg, but the measured values were four orders of magnitude lower than the samples analyzed along with

[iii] 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).
[iv] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 17)", Experiment L2320-00194-02, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (February 2016).

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. Elemental Hg 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.[v] Dimethyl Hg was measured in only the quarterly Tank 50 sample and ethyl Hg was not measured above the reporting limit in any of the samples.

The last column of Table 1 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 two Tank 39 samples are relatively low, 47 – 51% excluding detection limit values, compared to many recent DWPF samples analyzed,[vi, vii, viii, ix] but are similar to earlier Tank 30 and 32 surface samples.[x] No explanation for the low recoveries on these two samples can be offered at this time. The 1Q16 Tank 50 sample species recovery was better, and similar to earlier quarterly samples from this tank.

[v] 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).
[vi] 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).
[vii] 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).
[viii] 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).
[ix] Bannochie, C. J., *Results of Hg Speciation Testing on DWPF SMECT-8, OGCT-1, and OGCT-2 Samples*, SRNL-L3100-2016-00018, Rev. 0, Savannah River National Laboratory, Aiken SC 29808 (February 2016).
[x] Bannochie, C. J., *Results of Hg Speciation Testing on Tank 30, 32, and 37 Surface Samples*, SRNL-L3100-2015-00202, Rev. 0, Savannah River National Laboratory, Aiken SC 29808 (November 2015).

Table 1. Average Concentrations of various Hg species for Tank 39 and 1Q16 Tank 50 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
Tank 39 Surface	36.2 [3.0] (3)	30.2 [1.9] (3)	5.49*‡	0.507 [4.8] (3)	10.0 [9.4] (3)	2.35 [26] (3)	<15	<0.042	51 – 92%
Tank 39 Depth	32.3 [5.0] (3)	29.3 [1.7] (3)	1.88*‡	1.12 [1.8] (3)	9.33 [10] (3)	2.84 [32] (3)	< 14	< 0.041	47 – 90%
1Q16 Tank 50	69.2 [1.5] (3)	59.0 [1.9] (3)	9.32*‡	0.882 [12] (3)	4.97 [17] (3)	31.3 [4.4] (3)	< 7.0	0.172 [14] (3)	67 – 78 %

* 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.

Figure 1 summarizes the concentrations of several Hg species measured in quarterly Tank 50 samples from the 1Q14 through the 1Q16.[vii, xi, xii, xiii] Total Hg is lower than the historic highs measured in early 2015. If one compares the ratios of several species to the concentration of total Hg, one can observe several points from Figure 2. First the ratio of Hg(0) has been relatively constant. Second, the ratio of ionic Hg rose from the 4Q14 through 3Q15, but has been relatively constant the past two quarters. Third, and possibly most interestingly, the ratio of methyl Hg to total Hg is relatively stable at 0.5 ± 0.1; though if one plots a trend line (shown as the linear line in Figure 2) based on the data for the past six quarters, it reveals a slight increase in the ratio of methyl Hg to total Hg over time, though there is a large degree of uncertainty in the six available data points. It will be interesting to see if this trend continues as future quarterly samples are measured.

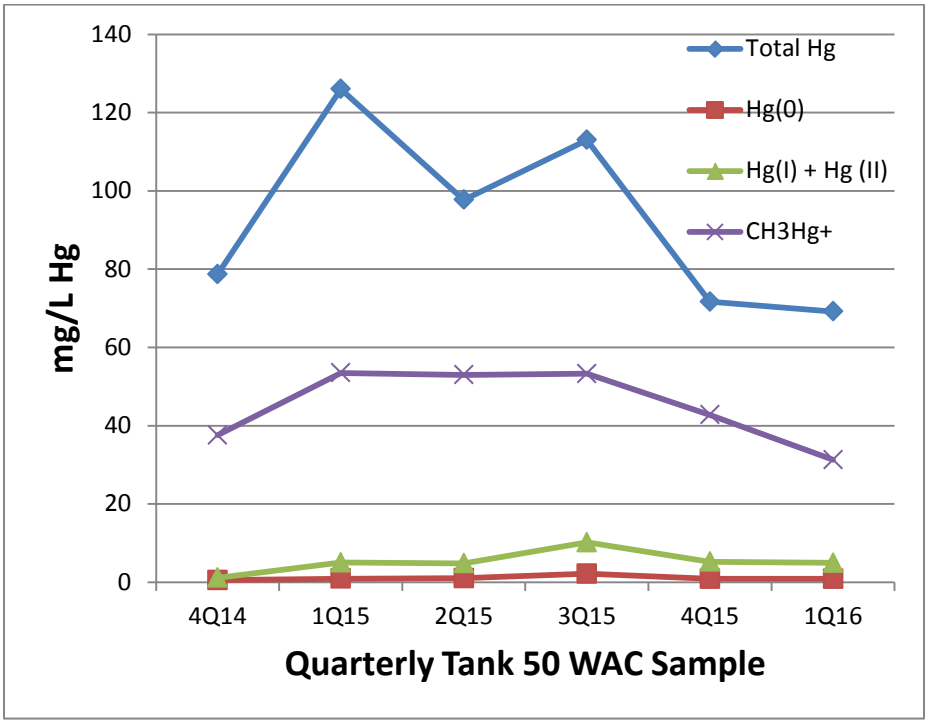

Figure 1. Mercury concentrations (mg/L) in Tank 50 Quarterly WAC samples taken from 4Q14 through 1Q16

[xi] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on 4Q14 Tank 50, 1Q15 Tank 50, and SRNL 14 Day TCLP Leachate*, SRNL-L3100-2015-00054, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (April 2015).
[xii] Bannochie, C. J., *Results of Hg Speciation Testing on 2Q15 Tank 50 WAC and Cs-Decontaminated Tank 21 Waste Samples*, SRNL-L3100-2015-00084, Rev. 1, Savannah River National Laboratory, Aiken, SC 29808 (September 2015).
[xiii] Bannochie, C. J., *Results of Hg Speciation Testing on 3Q15 Tank 50, Salt Solution Feed Tank (SSFT), and Solvent Hold Tank (SHT) Materials*, SRNL-L3100-2015-00144, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (August 2015).

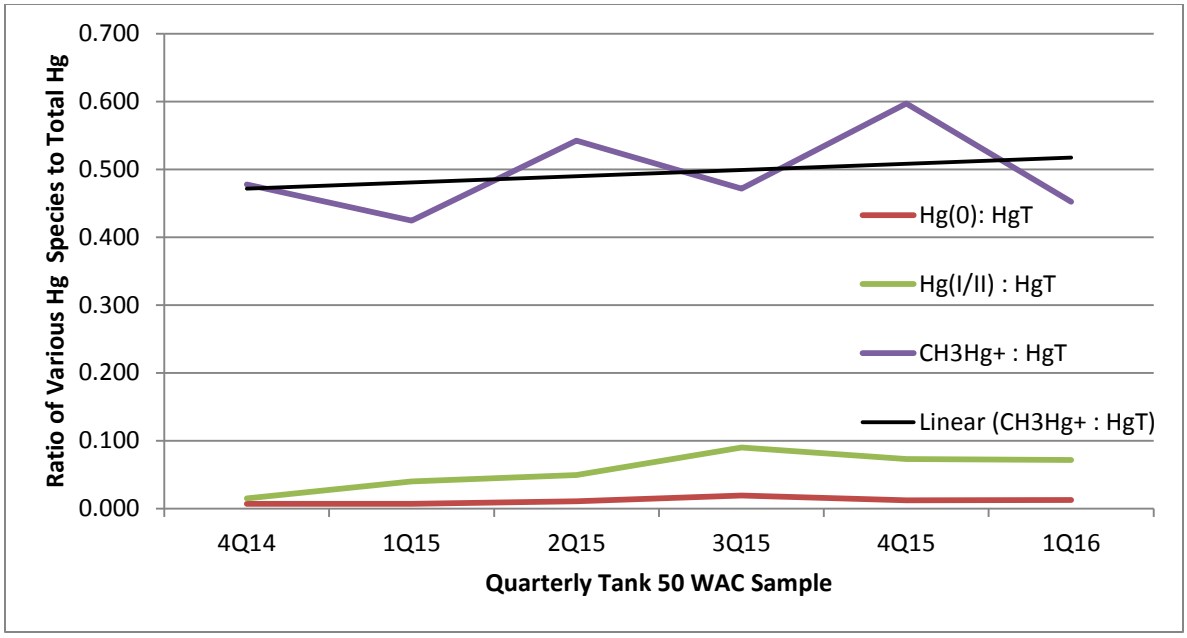

Figure 2. Ratio of several Hg species to the concentration of total Hg in Tank 50 Quarterly WAC samples taken from 4Q14 through 1Q16

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