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To: R. E. Edwards

From: C. J. Bannochie
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Results of Hg Speciation Testing on 2Q15 Tank 50 and Tank 21 TCLP Extraction Fluid Samples and Tank 49 Material

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 sixth shipment of samples was designated to include SRNL Toxicity Characteristic Leaching Procedure (TCLP) extraction fluids from the 2Q15 Tank 50 and Tank 21 saltstone waste forms as well as Tank 49 material (HTF-49-15-45) collected on May 7, 2015. The TCLP extraction fluid samples were collected from duplicate extractions of two crushed saltstone fractions, one designated as "large" and one designated as "normal".[iii] Both fractions of 2Q15 Tank 50 and Tank 21 saltstones (eight samples) were collected with the minimum possible free headspace and refrigerated prior to final dilution. The Tank 49 sample was left in its stainless steel dip bottle until it was opened and an aliquot diluted 1:100 with Eurofins deionized water on May 21, 2015. Following initial dilution in the Shielded Cells, the diluted Tank 49 sample was immediately moved to refrigeration and kept in the dark until prepared for shipment to Eurofins.

[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] Reigel, M. M., *Tank 21 and Second Quarter 2015 (2QCY15) Tank 50 TCLP Mercury Analysis Results*, SRNL-L3100-2015-00099, Savannah River National Laboratory, Aiken, SC 29808 (May 2015).

Eurofins supplied deionized water, 250 mL clear and amber glass bottles, and preservative (1.2 mL concentrated HCl). Each of the eight extraction fluids and triplicate Tank 49 samples was prepared for this shipment. Each extraction fluid and Tank 49 sample was analyzed for seven Hg species: total Hg, total soluble Hg, elemental Hg [Hg(0)], ionic 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 and elemental Hg; 3) total Hg and soluble total Hg; and 4) ionic Hg (Hg(I) and Hg(II)).

In total, 52 samples were prepared on May 27, 2015 and shipped by next-day air to Eurofins where they were received on May 29, 2015. Details of the sample preparation activities are recorded in the SRNL E-Notebook system.[iv] SRNL deionized water was employed as the blank for Tank 49 and a blank extraction fluid (never contacted with either saltstone) served as the TCLP extraction fluid blank. The Tank 49 and TCLP extraction fluid samples were diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:2500 by volume (Tank 49) and 1:83 by volume (TCLP Extraction Fluids).

Table 1 provides the average concentrations of Hg species derived from Eurofins reported data corrected for dilutions performed by SRNL. All blanks, not shown in the table, were reported as reporting limits, or 'RL' values. 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. Relative to the measurement uncertainties, the difference in the values determined for total soluble Hg and total Hg are very small, indicating that there is likely little or no particulate Hg in these diluted TCLP extraction fluids or the Tank 49 samples. There is no detectable ethyl Hg in these samples above the reporting limit of the analytical method.

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. The recoveries for the TCLP extraction fluids are all greater than 100%; specifically, 135% and 130%, for the Tank 50 extraction fluids from the large and normal particle distributions, respectively, and 126% and 122%, for the Tank 21 extraction fluids from the large and normal particle distributions, respectively. All these species 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%.

In the TCLP leachates, the methyl Hg is by far the most significant species relative to particulate, elemental, ionic and dimethyl Hg. Within the 20% uncertainty in the methods, it is reasonable to assume that methyl Hg accounts for essentially all the Hg leaching from the saltstone during the TCLP analysis.

[iv] Bannochie, C. J., "Eurofins Sample Preparation for Hg Speciation (Part 6)", Experiment L2320-00016- 47, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (May 2015).

The recovery for Tank 49 material is 91%, if the significant RL for ethyl Hg is included and 74% if it is excluded. It should be noted that the total Hg and analyzed speciation of Tank 49 (salt batch feed tank) in this study is very similar to previous data reported for Tank 21[v] (salt batch preparation tank).

[v] Bannochie, C. J., *Results of Preliminary Hg Speciation Testing on Tank 21 and Solvent Hold Tank (SHT) Material*, SRNL-L3100-2015-00068, Rev. 0, Savannah River National Laboratory, Aiken, SC 29808 (April 2015).

Table 1. Average Concentrations of various Hg species for the 2Q15 Tank 50 Saltstone TCLP Extraction Fluids, Cs-Decontaminated Tank 21 Saltstone TCLP Extraction Fluids, and Tank 49 Waste 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
2Q15 Tank 50 TCLP Large Particles	0.0135 [2.0] (2)	0.0119 [9.9] (2)	0.00162	0.000211 [20] (2)	0.000196 [13] (2)	0.0159 [7.6] (2)	<0.00575	0.000335 [61] (2)	135%
2Q15 Tank 50 TCLP Normal Particles	0.0157 [0.3] (2)	0.0142 [1.5] (2)	0.00148	0.000536 [4.2] (2)	0.000210 [21] (2)	0.0172 [13] (2)	<0.00426	0.000826 [3.6] (2)	130%
Tank 21 TCLP Large Particles	0.0122 [24] (2)	0.0108 [22] (2)	0.00141	0.0000988 [2.1] (2)	0.0000629 [1.4] (2)	0.0137 [30] (2)	<0.00571	0.000124 [47] (2)	126%
Tank 21 TCLP Normal Particles	0.0121 [5.6] (2)	0.0119 [8.1] (2)	0.00020	0.0000925 [12] (2)	0.0000851 [24] (2)	0.0142 [3.9] (2)	<0.00566	0.000129 **	122%
Tank 49	110 [4.1] (3)	109 [0.2] (3)	1	6.35 [110] (3)	15.6 [3.8] (3)	58.1 [6.5] (3)	<18.1	0.471 **	91%

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20% and the difference between these values is very small thus indicating there is little or no particulate Hg.
** Only a single replicate was above the reporting limit.

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