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To: R. E. Edwards

From: C. J. Bannochie

Results of Preliminary Hg Speciation Testing on Tank 22 and Waste Concentrate Hold Tank (WCHT) Material

Approved by:

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

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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. The third shipment of samples was designated to include Tank 22 material (HTF-22-15-34) collected on March 23, 2015, and Waste Concentrate Hold Tank (WCHT) material (ETP LIMS #30170) collected on March 16, 2015. Samples were collected with the minimum possible free headspace.

Eurofins supplied deionized water, 250 mL PETG bottles, 250 mL amber glass bottles, and preservative (1.2 mL concentrated HCl). Tank 22 and WCHT samples were prepared in triplicate plus a blank with the exception of the preserved dilution for methyl and ethyl speciation, which was prepared in duplicate for Tank 22. Each Tank 22 and WCHT 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] by calculation, 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 three separate bottles: 1) methyl Hg and ethyl Hg; 2) dimethyl Hg, elemental Hg, and ionic Hg; and 3) total Hg and soluble total Hg. Initially it was communicated that Eurofins would determine Hg(0) and ionic Hg from bottle #3, but they were reported from bottle #2, hence this change is not reflected on the Chain of Custody (COC) forms for this shipment since the samples were shipped prior to our receipt of this information from

Eurofins. Due to the large number of analyses being conducted, Eurofins has suggested increasing from three to four sample bottles.

In total, 23 samples were prepared on March 31, 2015 and shipped by next-day air to Eurofins where they were received on April 2, 2015. Details of the sample preparation activities are recorded in the SRNL E-Notebook system.[i] SRNL deionized water was employed as the blank for the Tank 22 and WCHT samples. The Tank 22 original sample was intially diluted with deionized water in the SRNL Shielded Cells by nominally 1:100 to reduce the radiation dose. This diluted Tank 22 sample was then further diluted in the radiochemical hood with deionized water and preservative by nominally 1:3500 (polybottles) or 1:2800 (glass bottles). Thus the Tank 22 samples sent for analyses were diluted nominally in the range of 1:280,000 or 1:350,000. The Hg species reported for the WCHT samples were all collected from supernate samples diluted by nominally 30X into deionized water. The WCHT material was not filtered, but allowed to settle, and the sample for dilution taken from the top.

Table 1 provides both the original Eurofins reported data corrected for dilutions performed by SRNL, as well as the remeasured Hg(0) values. All blanks, not shown in the table, were reported as Non Detect (ND) with one exception. A small signal was reported on the blank for the calculated ethyl Hg determination corresponding to about 0.461 mg/L; however, no ethyl Hg was reported for any of the samples. There is a ± 20% uncertainty in the measurement of total Hg and total soluble Hg, which are used to determine the particulate Hg value, i.e. the value for Hg species adsorbed to particulate matter in the samples. In light of this measurement uncertainty, 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 highly diluted Tank 22 and and minimally diluted WCHT samples.

The repeat measurements of Hg(0) in these two samples provides no further insight. First, all the values are lower, indicating that this species is likely being lost from solution. Second, there is still a great deal of variability in the Hg(0) measurements, particularly for the WCHT sample.

The last column of Table 1 provides the percent of total Hg that the six measured species (elemental, ionic, methyl, ethyl, dimethyl, and particulate) represent. The recovery for Tank 22 is very good and stands at 80% if the original Hg(0) is not included. The original measurements of Hg(0) for the Tank 22 material varied from ‘undetectable’ to 159 mg/L, so there appears to have been subsampling or species loss issues at play because it is not possible for there to have been more Hg(0) than either total Hg or total soluble Hg. In the reanalysis, two samples gave ‘undectable’ measurements, and a third gave 20 mg/L. If this value is included in the fraction of species total, it increases to 97%.

Two of the original three replicates for the Hg(0) measurement in the WCHT samples were in good agreement, but a third was low by an order of magnitude. Since this species was the largest contributor to the calculated Hg species recovery for the WCHT material, the recovery percentage is sensitive to what values are included in the average. Eurofins reanalyzed these samples to see if they could reduce the variability in this measurement, but while the new measurements were lower, they were equally variable. Eurofins suspects that Hg(0) is off-gassing

[i] Bannochie, C. J., “Eurofins Sample Preparation for Hg Speciation (Part 3)”, Experiment L2320-00016- 43, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC 29808 (March 2015).

from these samples and has proposed modified sampling techniques to SRNL. The WCHT sample did not contain a lot of Hg of any species; total Hg exclusive of settled solids was 0.0816 mg/L. This value agrees within the ±20% uncertainty of the method (range 0.0653 – 0.0979 mg/L) with that determined by SRNL, 0.0627 mg/L (range 0.0502 – 0.0752 mg/L). The WCHT sample did appear to contain species of Hg that are not yet accounted for by the speciation conducted. Unfortunately, additional species beyond those reported here would require analytical development work on the part of Eurofins, Inc. since the commercial interest in other organo-Hg species is limited. To address the Hg(0) issue, Eurofins has proposed a purge and trap method where in the diluted samples is sparged with Ar or N_2, and the off-gas passed through a gold filter media to collect the elemental Hg. SRNL is exploring the implimentation of this method for future shipments.

Table 1. Concentrations of various Hg species for Tank 22 and WCHT 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 22	119 [2.9] (3)	111 [2.5] (3)	8	77.0 [103] (3)**	56.5 [6.5] (3)	31.2 [7.4] (3)	ND	ND	80% **
Tank 22 Reanalysis	---	---	---	20.0 [NA] (1)	---	---	---	---	97% ‡
WCHT	0.0816 [0.06] (3)	0.0798 [0.80] (3)	0.0018	0.0198 [77] (3)***	0.00494 [3.4] (3)	ND	ND	ND	32% ***
WCHT Reanalysis	---	---	---	0.00280 [148] (3)‡‡	---	---	---	---	12% ‡‡
WCHT SRNL	0.0627 [3.9] (3)	---	---	---	---	---	---	---	---

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20%, hence the difference between these values is very small thus indicating there is little or no particulate Hg.

** Excludes Hg(0) for Tank 22, where the three replicates were highly variable: Non Detect, 72.5, and 159, respectively, this could be a result of sampling errors.

*** For the WCHT sample, two of the three replicate Hg(0) values were in reasonable agreement, 0.0310 and 0.0261 mg/L, but one was an order of magnitude lower, 0.00245 mg/L. Since this species is the largest contributing component to the fraction calculation, factoring in the lower value drops the species fraction from 43% to 32%.

‡ Includes the reanalyzed Hg(0) value for the one sample above the detection limit.

‡‡ For the reanalyzed WCHT sample for Hg(0) the following were measured: 0.0310 mg/L became Non Detect, 0.0261 mg/L became 0.00757 mg/L, and 0.00245 mg/L became 0.000829 mg/L. Due to the uncertainty in this species, its contribution swings the species fraction calculation from 32 - 43% originally, to 9 - 17% now, depending upon which values are included.

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