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Results of Hg Speciation Testing on the 2Q18 Tank 50 Sample

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 thirty-second shipment of samples contained the 2Q18 Tank 50 WAC.

RESULTS AND DISCUSSION

SRR collected the 2Q18 Tank 50 WAC sample (HTF-50-18-47) on July 12, 2018, and it was placed into the SRNL Shielded Cells and vented on July 13, 2018. The sample for Hg speciation was drawn directly from the 3-L variable depth sample on July 17, 2018 and transferred to refrigerated storage.

One 30-mL portion was placed into a Teflon storage bottle with zero headspace and a separate ~15-mL portion was placed into a glass vial with Teflon-lined cap with zero headspace. Both samples were then removed from the cells and stored in the dark. The Shipment #32 subsamples remained at ~4-6 °C until final dilutions were made on July 31, 2018.

Eurofins supplied deionized water, 250 mL clear and amber glass bottles. SRNL supplied the 1.2 mL concentrated HCl preservative. Triplicate aliquots of the Tank 50 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

[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).

counter anion], and dimethyl Hg [$(CH_3)_2Hg$]. The difference between the total Hg and total soluble Hg measurements gives the particulate Hg concentration after subtracting the Hg(0) contribution, 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 Hg; and 4) ionic (inorganic) Hg and elemental Hg.

Details of the sample preparation activities and dilution calculations are recorded in the SRNL E-Notebook system.[iii] SRNL deionized water was employed as the blank for each tank sample. Prior to shipment, Tank 50 was diluted in a radiochemical hood with deionized water and preservative (preservative for bottle set #1 only) by nominally 1:2500 by volume. All containers were filled close to the maximum allowable volume to minimize headspace within the sealed samples. In total, 16 aqueous samples were prepared on July 31, 2018 and shipped the following day by next-day air to Eurofins where they were received on August 2, 2018. Eurofins reported the aqueous results in units of ng Hg / L sample.

Table 1 provides the average concentrations of Hg species for Tank 50, as derived from Eurofins reported data corrected for dilutions performed by SRNL. All blanks, not shown in the table, were reported at the 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 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). There was no ethyl Hg(II) 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 recovery for the Tank 50 sample is 60-62%. The range of values results from excluding or including the measured reporting limit values in the calculation. This species recovery is low but may be within 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%.

Total Hg measured by SRNL via aqua regia dissolution, followed by Cold Vapor Atomic Absorption (CV-AA) analysis found 66.8 mg/L (0.85 %RSD) in the 2Q18 Tank 50 sample[iv]. This total Hg result is lower than that reported in Table 1 by Eurofins, but within the ±20% uncertainty for these measurements.

[iii] Bannochie, C. J. "Eurofins Sample Preparation for Hg Speciation (Part 32)", Experiment L2320-00194-40, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC (May 2018).
[iv] Crawford, C. L. "2Q CY18 Tank 50 WAC Characterization", Experiment B9108-00026-46, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC (May 2018).

Table 1. Average Concentrations of various Hg species for a 2Q18 Tank 50 sample 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
2Q18 Tank 50	69.8 [2.3] (3)	65.7 [1.2] (3)	2.0*	2.12 [2.4] (3)	9.49 [5.0] (3)	28.5 [5.0] (3)	< 0.86	0.0188 [15] (3)	60-62%

* Uncertainty in the total Hg and total soluble Hg measurements is ± 20%, and the particulate value is the difference of these two measured values after subtracting Hg(0) for the sample.

Figure 1 summarizes the concentrations of several Hg species measured in the quarterly Tank 50 samples from the 4Q14 through the 2Q18. Note, there was no data collected for the 4Q17, so a linear extrapolation was made between the 3Q17 and 1Q18 data for plotting purposes only. Data shown in Figure 1 has been corrected for the Eurofins Data Recall on April 5, 2018[v], which lowered the values for methylmercury for the 1Q17 and 3Q17 Tank 50 data sets. All the total Hg quarterly values fall within ±20% of the 14 quarter average of 87 mg/L. The total Hg trend continues downward since 2Q16.

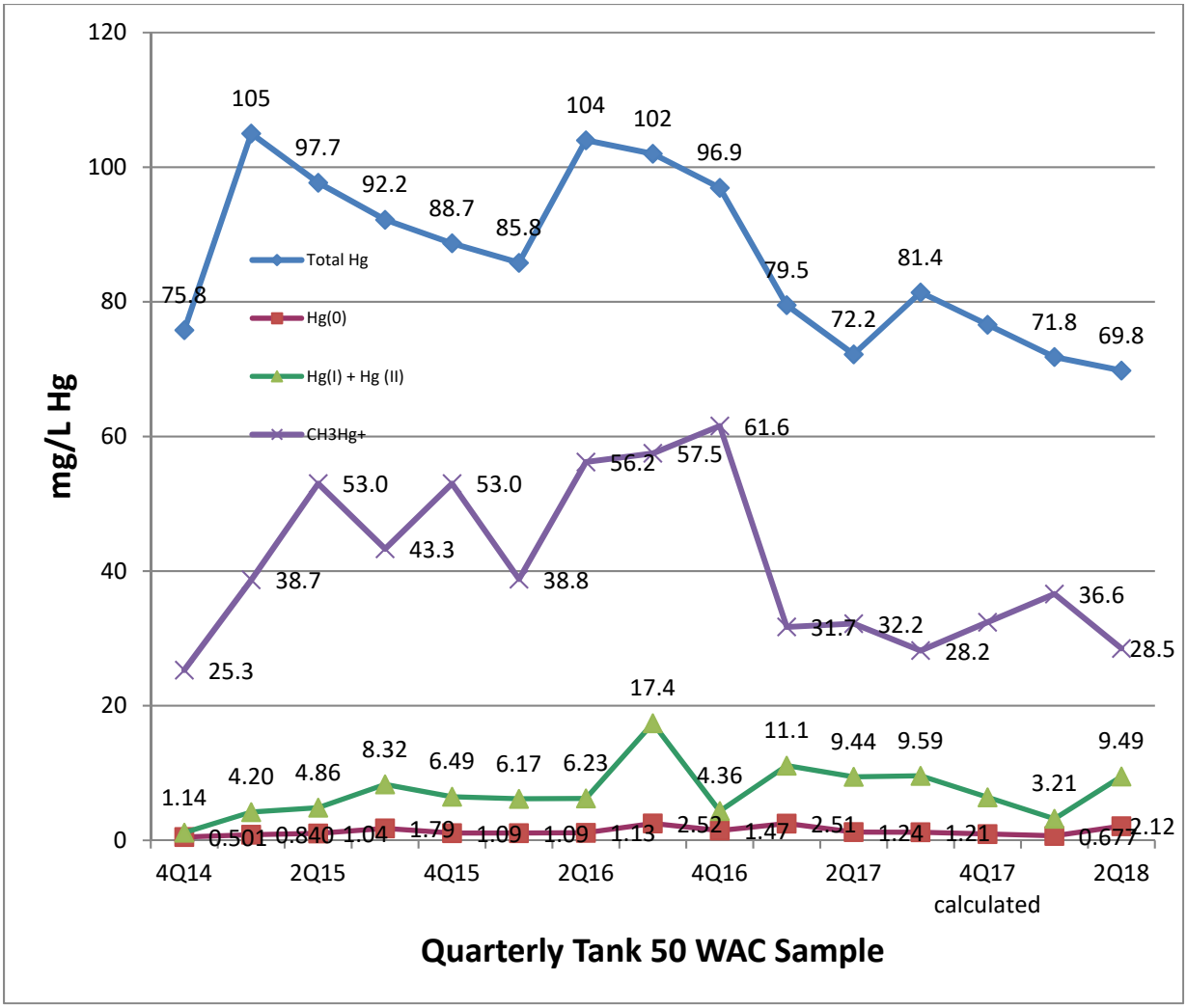

Figure 1 Mercury concentrations (mg/L) in Tank 50 Quarterly WAC samples taken from 4Q14 through 2Q18. Data for 4Q17 is calculated for plotting purposes only and is shown unlabeled.

[v] Bannochie, C. J. "Eurofins Data Recall Adjustments", Experiment L2320-00194-39, SRNL E-Notebook (Production), Savannah River National Laboratory, Aiken, SC (April 2018).

If we compare the data in Figure 1 and the ratios of several species to the concentrations of total Hg (Figure 2), one can observe several points. The ratio of Hg(0) to total Hg varies across a factor of about five. Second, the ratio of ionic Hg to total Hg, which rose slightly from the 4Q14 through 3Q15, then trended down slightly over the next three quarters, before spiking up in the 3Q16 sample and dropping back in the 4Q16 sample, has risen to its highest level in the past year. Third, if one plots a trend line (shown as the linear line in Figure 2) for the ratio of methyl Hg to total Hg (HgT) based on the data from the past 14 quarterly samplings, the ratio of methyl Hg to total Hg over time is nearly flat following the revised 1Q17 and 3Q17 Eurofins methyl Hg data, despite the nearly two-fold difference between the minimum and maximum values.

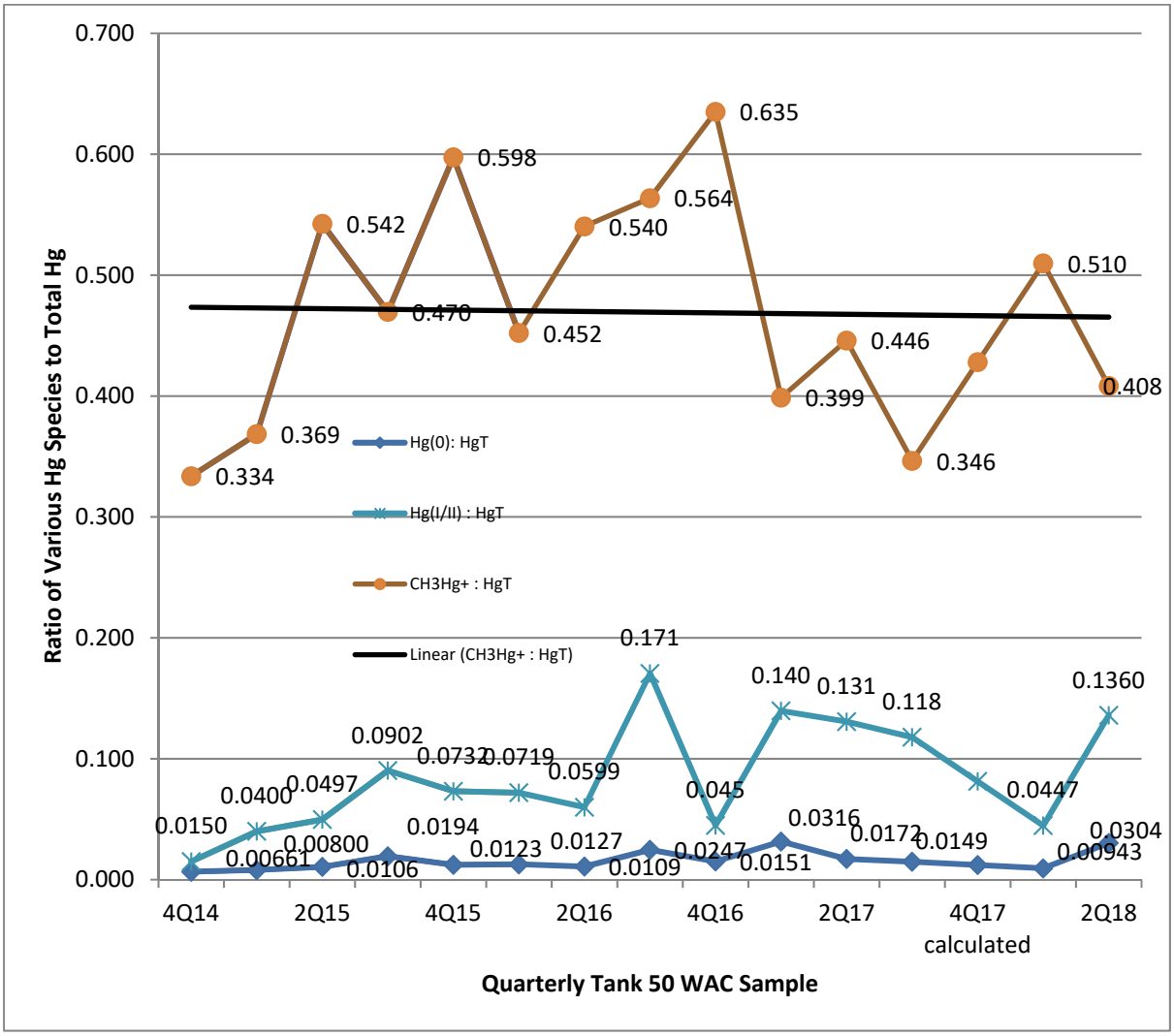

Figure 2 Ratio of several Hg species to the concentration of total Hg (HgT) in Tank 50 Quarterly WAC samples taken from 4Q14 through 2Q18. Data for 4Q17 is calculated for plotting purposes only and is shown unlabeled.

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