



# Separation and Speciation of Mercury from Hanford 241-AP- 107 Tank Waste Supernatant

**September 2018**

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Prepared for  
the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory  
Richland, Washington 99352

## Executive Summary

Mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2$ , was introduced into the Hanford flowsheet when it was used to catalyze nitric acid dissolution of certain aluminum alloy fuels and to suppress radioiodine volatilization during nitric acid dissolution of short-cooled uranium metal fuel.<sup>1</sup> Inventory estimates, based primarily on Hanford process-knowledge, suggest a total mercury inventory of 2,100 kg<sup>1</sup> in the Hanford Tank Farms. Aside from the obvious human exposure concerns via tank vapors, mercury species in the tank waste liquid and solid fraction pose risk to the implementation and execution of the River Protection Project mission due to mercury concentration limits imposed under waste acceptance criteria, toxicity characteristic leaching procedure restrictions for secondary waste disposal, and air emission permits. Although there is currently no processing of tank waste at Hanford, waste processing is imminent and representative mercury inventory tracking will be important to anticipate and mitigate stack emissions and secondary liquid waste disposal issues like those experienced at the Savannah River Site.<sup>2</sup>

A methodology to accurately determine total mercury and mercury speciation in Hanford tank waste, while maintaining low mercury detection limits, currently does not exist at Hanford. Moreover, the mercury species in the waste solids are unknown and may be waste type specific. The development of an analytical method to separate mercury from and speciate mercury in tank waste was undertaken by the Pacific Northwest National Laboratory (PNNL) while leveraging an existing non-radiological, ultra-trace mercury detection technique frequently performed at PNNL's Marine Sciences Laboratory (MSL) in Sequim, Washington. The ultimate goal of this work is to develop an analytical method to obtain detailed mercury speciation information and update flowsheet modeling assumptions related to mercury partitioning at Hanford.

This report describes the first phase of a multi-year project to develop technology for the low-level determination of total mercury, elemental mercury, methylmercury, and dimethylmercury in Hanford tank waste. The focus of Phase I was to determine if mercury (Hg) species can be preconcentrated from aqueous Hanford tank waste solution onto a solid substrate while simultaneously eliminating or very significantly reducing the parent radionuclide activity. This was demonstrated by developing protocols for the separation and preconcentration of total mercury and methylmercury onto solid substrates, then measuring the substrates for radiological content at PNNL's Radiochemical Processing Laboratory (RPL) on the Hanford Site.

Total alpha, beta, and gamma activity were determined for the liquid distillate, Carbotrap<sup>®</sup> substrate used to separate methylmercury, soda lime trap to scrub acidic moisture, gold-coated sand substrate used to separate total mercury, and glass wool plugs used to retain the substrates in the collection columns. The mercury separation techniques significantly reduced the radiological background, enabling more efficient and safer handling with subsequent analyses while maintaining maximum mercury detectability. Decontamination factors for <sup>137</sup>Cs, the only detectible gamma-emitting radionuclide, ranged from  $1.79 \times 10^4$  for the liquid distillate, to as high as  $2.34 \times 10^8$  for the Carbotrap<sup>®</sup> used to collect methylmercury. Decontamination factors for total activity showed similar radiological reductions, ranging

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<sup>1</sup> Kupfer MJ, AL Boldt, KM Hodgson, LW Shelton, BC Simpson, RA Watrous, MD LeClair, GL Borsheim, RT Winward, BA Higley, RM Orme, NG Colton, SL Lambert, DE Place, and WW Schulz. 1999. *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tank Wastes*. HNF-SD-WM-TI-740, Rev. 0C, Lockheed Martin Hanford Corporation, Richland, Washington.

<sup>2</sup> Bannochie CJ, TL Fellingner, P Garcia-Strickland, HB Shah, V Jain and WR Wilmarth. 2017. "Mercury in aqueous tank waste at the Savannah River Site: Facts, forms, and impacts." *Separation Science and Technology*, Published online March 28, 2017. <https://doi.org/10.1080/01496395.2017.1310239>.

from  $1.70 \times 10^4$  for the liquid distillate, to  $1.88 \times 10^6$  for the gold-coated sand trap substrate used for total (and elemental) Hg analysis. These results demonstrate  $^{137}\text{Cs}$  to be the primary contributor to radiological dose of the separated samples with very little measured contribution from alpha- and beta-emitting radionuclides.

The mercury content was successfully separated onto stable substrates and the radionuclide activity reduction was significant enough that the preconcentrated samples could be subjected to quantification using far less restrictive handling and radiological controls than would be required for the parent sample (i.e., contamination area fume hood vs. hot cell). This mercury separation method required no sample dilution, which enables maximum mercury detectability, while still allowing mercury speciation.

For the next phase of the work, Hanford tank waste material will be preconcentrated onto solid substrates at RPL and shipped to the MSL in Sequim, Washington, for analysis. Quantification of total, elemental, and methylmercury will be conducted under radiological control at MSL using the ultra-trace analytical capabilities available there.

## Acknowledgments

The authors thank Jacob Reynolds of Washington River Protection Solutions for his technical feedback on and support of this report and funding the experimental work it presents. The authors also thank Karl Pool for his thorough understanding of RPL's analytical capabilities and positive attitude merged with extensive experience in navigating the requirements to conduct this radiological work in RPL. In addition, the authors thank Courtney Bottenus for her detailed and careful reviews of the report and the calculations that underpin its technical basis, Bob Free and Marilyn Wirth for their guidance and dedication to safely mitigating the radiological hazards of these tank waste samples and helping us navigate the protocols for transport offsite, and Gary Cooke of Washington River Protection Solutions, who provided information on analytical capability at the 222-S Laboratory and information on total mercury in Hanford waste tanks. Thank you to Matt Wilburn for his technical editing and Bill Dey for his commitment to ensuring our adherence to quality assurance. Last, but not least, the authors also greatly appreciate Chrissy Charron and Veronica Perez for their consistent and persistent help with capturing project records and for their unwavering mission to consistently apply project standards and efficiently execute work.

## Acronyms and Abbreviations

ASR	Analytical Service Request
ASO	Analytical Support Operations
BBI	best-basis inventory
BNI	Bechtel National Incorporated
CA	contamination area
CRV	Concentrate Receipt Vessel
CVAFS	cold vapor atomic fluorescence spectrometry
DF	decontamination factor
DFLAW	direct feed low-activity waste
DST	double-shell tank
EMF	Effluent Management Facility
EPA	U.S. Environmental Protection Agency
ESP	Environmental Simulation Program
ETF	Effluent Treatment Facility
FMP	Flowsheet Maturation Plan
GEA	gamma energy analysis
HLW	high-level waste
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
LDR	land disposal restrictions
LERF	Liquid Effluent Retention Facility
MDL	method detection limit
MSL	Marine Sciences Laboratory
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
SBS	submerged bed scrubber
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SST	single-shell tank
SWPF	Salt Waste Processing Facility
TCLP	toxicity characteristic leaching procedure
TFCOUP	Tank Farm Contractor Operation and Utilization Plan
TOC	Tank Operations Contractor

TSCR	tank side cesium removal
TWINS	Tank Waste Information Network System
UHP	ultra-high purity
WAC	waste acceptance criteria
WESP	wet electrostatic precipitator
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WVR	waste volume reduction
WWFTP	WRPS Waste Form Testing Program

# Contents

Executive Summary .....	iii
Acknowledgments.....	v
Acronyms and Abbreviations .....	vi
1.0 Introduction .....	1.1
2.0 Quality Assurance.....	2.1
3.0 Hanford Mercury Background.....	3.1
3.1 Waste Acceptance Criterion for Mercury at Hanford .....	3.1
3.2 Hanford Mercury Feed Inventory (Mass, Distribution, and Speciation).....	3.2
3.2.1 Mercury Feed Inventory Mass .....	3.2
3.2.2 Tank Waste Phase Distribution of Mercury .....	3.3
3.2.3 Mercury Speciation .....	3.3
3.3 Hanford Flowsheet Modeling of Mercury Speciation for LAW .....	3.4
4.0 Mercury Analytical Experience at Hanford and Savannah River Site .....	4.1
4.1 Current Hanford Mercury Analytical Capability and Measurements .....	4.1
4.2 Savannah River Site Analytical Experience with Mercury.....	4.2
4.3 PNNL Analytical Experience with Mercury .....	4.3
5.0 Mercury Species Separation Protocol.....	5.1
6.0 Results and Discussion .....	6.1
7.0 Path Forward .....	7.1
8.0 Conclusion .....	8.1
9.0 References .....	9.1

## Figures

Figure 3.1. Simplified DFLAW Flowsheet Modeling of Mercury for SST Retrieval, DST Staging, and Pretreatment .....	3.6
Figure 3.2. Simplified DFLAW Flowsheet Modeling of Mercury for WTP LAW Melter Off-gas Treatment and EMF .....	3.7
Figure 5.1. Photograph of Total Mercury Purging Bubbler System .....	5.2
Figure 5.2. Photograph of Methylmercury Distillation Apparatus .....	5.3
Figure 5.3. Photograph of Bubbler System for Purging Methylmercury onto a Carbotrap® .....	5.3

## Tables

Table 3.1. Best Basis Inventory on August 14, 2018 for Mercury by Waste Phase .....	3.3
Table 4.1. Method Detection Limits (MDLs) for the Determination of Total Mercury and Methylmercury in Water, Sediment, and Tissues at the MSL in Sequim, Washington.....	4.3
Table 4.2. Estimated Method Detection Limits (MDLs) for Total Mercury in Aqueous Tank Waste Samples Based on the Volume of Sample Taken for Analysis.....	4.3
Table 6.1. Gamma Activity of Hg Species Separation Samples Compared to Parent Tank Waste Sample.....	6.1
Table 6.2. Total Activity of Hg Species Separation Samples Compared to Parent AP-107 Sample.....	6.2
Table 7.1. Proposed Radiological Controls Necessary to Conduct Mercury Separation and Quantification Analyses .....	7.1

## 1.0 Introduction

The U.S. Department of Energy's (DOE) Hanford Site in southeast Washington State stores 56 million gallons of chemical and radioactive waste stored in underground tanks. DOE's River Protection Project (RPP) mission is to retrieve the tank waste from single-shell tanks, pretreat the waste, and then immobilize the waste for long-term near-surface geologic disposal. An initial phase of the RPP mission is being described as the direct feed low-activity waste (DFLAW) phase which involves the filtration and cesium decontamination of decanted supernatant liquid before vitrifying the treated low-activity waste (with glass formers) into a glass waste form. The DFLAW flowsheet represents a tracking of mass and concentration of chemicals and radionuclides in the tank waste during retrieval, storage, feed staging, pretreatment, immobilization, and final disposal operations, and includes accounting for all secondary waste streams.

Mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2$ , was introduced into the Hanford flowsheet when it was used to catalyze nitric acid dissolution of certain aluminum alloy fuels and to suppress radioiodine volatilization during nitric acid dissolution of short-cooled uranium metal fuel (Kupfer et al. 1999). Inventory estimates, based primarily on Hanford process-knowledge, suggest a total mercury inventory of 2,100 kg (Kupfer et al. 1999) in the Hanford Tank Farms. Aside from the obvious human exposure concerns via tank vapors, mercury species in the tank waste liquid and solid fraction pose significant risk to the implementation and execution of the (RPP mission due to mercury limits imposed under waste acceptance criteria (WAC), toxicity characteristic leaching procedure (TCLP) restrictions for secondary waste disposal, and air emission permits.

A recent DFLAW feed composition uncertainty evaluation indicated the mercury-to-sodium molarity criterion apparently exceeding the Low-Activity Waste Pretreatment System (LAWPS) WAC for 32 months of the 12-year DFLAW operations phase (Britton 2017). Secondary solid waste disposal considerations and approvals for items such as spherical resorcinol formaldehyde, grouted Effluent Management Facility (EMF) overheads, and the Hanford Tank Waste Treatment and Immobilization Plant (WTP) low-activity waste (LAW) melter are highly dependent on identification of retained mercury species, retention characteristics, and the associated impact on discharge and disposal permits. Although there is currently no processing of tank waste at Hanford, waste processing is imminent and representative mercury inventory tracking is desired to anticipate and mitigate stack emission and secondary liquid waste disposal issues like those experienced at the Savannah River Site (SRS) (Bannochie et al. 2016, 2017).

Metallic mercury is in dynamic equilibrium with mercuric (i.e., valence state of 2) and mercurous (i.e., valence state of 1) ions under the waste storage conditions at Hanford. The mercury species in the waste solids are unknown and may be waste-specific. The liquid phase mercury is believed to be in the mercury (II) ion form ( $\text{Hg}^{2+}$ ). However, mercury detection in supernate has been negligible based on limited aqueous sample data. For example, Tank AY-102 sample data showed about 2% of the total mercury inventory coming from the supernate (Cramer 2001) compared to the sludge.

Closure of this mercury speciation gap can improve the confidence in the WAC-affecting feed mercury inventories during waste processing operations and the conclusions drawn in previous high-level waste (HLW) melter and melter off-gas abatement system testing (Goles et al. 2004) and the WTP mercury pathway and treatment assessment (Cramer 2001).

A methodology to determine mercury speciation and accurately quantify concentrations while maintaining low mercury detection limits currently doesn't exist at PNNL or Hanford. Moreover, the mercury species in the waste solids are unknown and may be waste-specific. Commercial laboratories

such as Brooks Applied Laboratories and Eurofins Frontier Global Sciences, Inc. have successfully completed analyses for seven species of mercury for the SRS, but “[t]he species fraction of total mercury measured has broadly ranged from a low of 32% to a high of 146%” (Bannochie and Wilmarth 2016). This uncertainty in speciation and recovery is primarily driven by large sample dilutions to reduce dose and the separation techniques employed.

The development of an analytical method to separate and speciate mercury from tank waste was undertaken by the Pacific Northwest National Laboratory (PNNL) while leveraging an existing non-radiological, trace mercury detection technique frequently performed at PNNL’s Marine Sciences Laboratory (MSL) in Sequim, Washington. MSL has developed this mercury analytical method for trace detection of non-radiological mercury in air, water, tissues and sediments. The ultimate goal of this work is to develop an analytical method to obtain detailed mercury speciation information and update flowsheet modeling assumptions related to mercury partitioning at Hanford.

This current work partially fulfills Task 1 of the flowsheet maturation plan (FMP), FMP-WASTE-16, “Mercury Speciation and Inventory in Tank Farms During Storage, Waste Treatment, and Secondary Waste Abatement” (Reynolds et al. 2017), and supports PNNL’s continued efforts to provide Washington River Protection Solutions, LLC (WRPS) baseline technical support to the One System RPP Mission Integration team. This work also supports PNNL’s broader mission to help identify and close flowsheet model and operations gaps and realize opportunities to reduce the waste treatment mission cost, schedule, and technical risk associated with the One System RPP Integrated Flowsheet. Gaps and opportunities are documented in the *One System River Protection Project Integrated Flowsheet Maturation Plan* (Reynolds et al. 2017), and solution approaches are proposed and declared in associated FMPs contained in its appendices.

## 2.0 Quality Assurance

This work was conducted with funding from WRPS under PNNL project 71351, contract 36437-239, with the title “Tank Waste Disposition Integrated Flowsheet Support.”

All research and development (R&D) work at PNNL is performed in accordance with PNNL’s Laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level “Applied Research” and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received appropriate technical and QA training prior to performing quality-affecting work.

## 3.0 Hanford Mercury Background

A review of existing mercury knowledge at Hanford and SRS was initially conducted to identify and document flowsheet modeling and operation gaps relating to mercury inventory, speciation, and fate at Hanford. This section first discusses the WAC for mercury in the staged feed and how this drives the need to understand mercury speciation and distribution in the Tank Farms and within the flowsheet. Next, the current Hanford mercury mass inventory estimate, the distribution of that inventory by tank and primary waste phases, and assumptions of mercury speciation are documented to provide background and balance to the subsequent discussion of flowsheet modeling of mercury. Documentation of how current TOPSim and WTP G2 flowsheet models track mercury throughout the DFLAW flowsheet is provided to put into context the operational issues and disposal considerations highlighted by mercury modeling. The summary conclusions drawn from this background evaluation led to the adaptation and development of a new analytical technique, described in Section 5.0, to accurately quantify mercury species in Hanford tank waste.

### 3.1 Waste Acceptance Criterion for Mercury at Hanford

Waste feed acceptance into the Tank Operations Contractor (TOC) pretreatment system (i.e., LAWPS and/or tank side cesium removal [TSCR]) and the subsequent receipt into the WTP LAW Facility is controlled by set limits on chemical, physical, and radionuclide properties of the waste established to ensure safety, regulatory, and design compliance. The waste acceptance criterion for mercury was established to protect the WTP air permit and is conveyed as a ratio not to exceed  $1.4 \times 10^{-5}$  mol Hg/mol Na where the sodium molarity is expected to range from 4 to 6 M (Schappell 2015). This same requirement is imposed on the TOC pretreatment system waste acceptance as a flowback requirement since waste pretreatment only filters solids and removes cesium from the staged feed tank (currently 241-AP-107, hereafter “AP-107”) prior to delivery to the WTP LAW Facility.

In 2017, a WRPS assessment of DFLAW feed constituent uncertainty and its impact on whether staged feed campaigns would meet WAC was completed and reported by Britton (2017). The assessment leveraged a previous PNNL evaluation<sup>1</sup> of the Best-Basis Inventory (BBI) uncertainty ranges for key chemical and radionuclides, including mercury. The assessment utilized TOPSim<sup>2</sup> to predict the DFLAW flowsheet mass and concentration movements within Tank Farms and staged feed campaigns and concluded that under standard BBI inventory assumptions, the maximum mercury-to-sodium molar ratio predicted was  $1.12 \times 10^{-5}$  mol Hg/mol Na, thus, complying with the WAC limit (i.e.,  $< 1.4 \times 10^{-5}$  mol Hg/mol Na). However, full WAC compliance was not predicted when the same TOPSim flowsheet scenario was run, except where increasing select initial analyte masses (including Hg) by +1 relative standard deviation and using a 90% Upper Range value and lowering the initial sodium mass by -1 relative standard deviation and 90% Lower Range value as described by the PNNL BBI uncertainty evaluation<sup>1</sup>. Under this scenario [Case 670 (Run 3) in Britton 2017] the mercury inventory apparently exceed the LAWPS WAC for 32 months of the DFLAW mission phase. It's this uncertainty associated with mercury inventory mass, the waste phase distribution of the mercury inventory, and the liquid and solid phase speciation of mercury within the Hanford flowsheet that creates risk to the DFLAW mission schedule and costs and warranted the work scope completed and proposed here.

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<sup>1</sup> Peterson RA. 2016. *Best Basis Inventory (BBI) Data Quality and Uncertainty for Direct Feed Low-Activity Waste (DFLAW) Summary*. Attachment to LTR-EMSP-0105, Pacific Northwest National Laboratory, Richland, Washington. This PNNL evaluation was not publically released.

<sup>2</sup> TOPSim was developed within the Gensym G2® platform and is a software application “used to host and simulate models of the Hanford tank farms and processing plant operations” (Bernards et al. 2018). G2 is a registered trademark of Gensym Corporation, Austin, Texas.

## 3.2 Hanford Mercury Feed Inventory (Mass, Distribution, and Speciation)

Hanford engineers desire to understand mercury movements, the chemical consequences, and the fate of mercury in the Hanford flowsheet. Necessary inputs to evaluate the impact of mercury include the magnitude of the mercury feed inventory, how the inventory is distributed throughout the tank farms, how the tank-by-tank mercury inventory is distributed by waste phases (i.e., sludge, saltcake, and supernatant), the expected mercury species during waste processing, and finally, the degree of uncertainty in this information.

Mercury is one of the standard 25 non-radioactive chemical components tracked on a tank-by-tank basis in the BBI at Hanford (Kupfer et al. 1999). Access to the BBI is made through the Tank Waste Information Network System (TWINS) (<https://twins.labworks.org/twinsdata/Forms/About.aspx>). This inventory is documented by mass in the sludge, saltcake, and supernatant waste phases and has varying data source “quality” designations for the analyte concentrations, which include Sample-Based (S), Process Knowledge (E), Template Sample (TS), and Template Engineering (TE). Sample-based values have the least uncertainty, followed by process knowledge, and then template-based values being the most uncertain.

### 3.2.1 Mercury Feed Inventory Mass

In 2001, an estimated 2,100 kg total mercury mass was the best available Hanford tank waste mercury inventory based on a process-history assessment of historical fuel processing operations using mercuric nitrate [ $\text{Hg}(\text{NO}_3)_2$ ] to catalyze nitric acid dissolution of certain aluminum alloy fuels and to suppress radioiodine volatilization during nitric acid dissolution of short-cooled uranium metal fuel (Meacham 2015; Cramer 2001). According to the August 1, 2001 BBI inquiry made by Cramer (2001), the mercury inventory was distributed throughout 77 of the 177 Hanford single-shell tanks (SSTs) and double-shell tanks (DSTs) with only 15 of the 77 tanks having had some form of sample analysis [i.e., Sample-Based (S)] to inform the mercury inventory, and with these samples primarily being taken from DSTs. For comparison, the BBI for mercury was obtained from TWINS on August 14, 2018, and is summarized, by waste phase, in [Table 3.1](#) ~~Table 3-1~~. Now, 171 tanks indicate some mercury mass inventory, more than double the tanks (i.e., 77 vs. 171). Of these 171 tanks, 47 tanks now have some form of sample-based analysis for mercury, at least triple the number of tanks reported by Cramer (2001). It appears that a considerable improvement in mercury accounting has occurred in the last 17 years. However, it’s noted by Cramer (2001) that some of these sample-based results are the reported detection limits (i.e., not actual measured mercury concentrations) and only 11 tanks have mercury inventory values for all three waste phases. The primary conclusion drawn is that the tank-by-tank basis for mercury inventory has improved, but still remains uncertain for a majority fraction of Hanford tanks.

**Table 3.1.** Best Basis Inventory on August 14, 2018 for Mercury by Waste Phase

	Waste Phase	Mercury Mass (kg) <sup>(a),(b)</sup>	Mercury Percent by Waste Phase	Number of Tanks with Reported Mercury Inventory	Number of Tanks With Sample-Based Mercury Inventory
All Tanks	Saltcake	140	7.9%	105 out of 177	7
	Sludge	1,630	91.8%	134 out of 177	36
	Supernatant	5.95	0.3%	45 out of 177	12
	All Phases	1,780	100%	171 <sup>(c)</sup>	47 <sup>(d)</sup>

(a) BBI Inventory pulled on August 14, 2018.

(b) BBI data is presented with 3 significant figures, however, the BBI inventory is built on a tank-by-tank basis and trace constituents like mercury have large uncertainties.

(c) Total number of tanks with at least one waste phase inventory value.

(d) Total number of tanks with a sample of at least one waste phase analyzed for mercury.

### 3.2.2 Tank Waste Phase Distribution of Mercury

The distribution of mercury by tank waste phase is an important consideration in the mission phases of the flowsheet. In the context of the DFLAW mission, the tank waste staging strategy is leveraging the success of a double-decant process to provide predominantly supernatant liquid to pretreatment systems. In contrast, for the full waste treatment mission, mercury inventory associated with the sludge solids will dominate process considerations and secondary waste impacts. Preliminary insight into the mercury inventory waste phase distribution is provided by [Table 3.1](#). According to August 14, 2018 BBI estimates, 91.8 % of the mercury is associated with the sludge solids phase, 0.3% estimated in the supernatant phase, and the remainder in the saltcake. These results are in general agreement with Cramer (2001), which reported negligible mercury detection in supernate based on limited aqueous sample data and also Tank AY-102 sample data showing about 2 percent of the total mercury inventory coming from the supernate. Gimpel (2007) cites a Tank Farm Contractor Operation and Utilization Plan (TFCOUP) 6 estimated mercury inventory of 1,752 kg, with 657 kg proportioned to the liquid phase and 1,059 kg in the solid phase, directly contradicting the evidence presented in Cramer (2001) and the current BBI-estimated distribution in [Table 3.1](#). However, upon further investigation, estimates of mercury in TFCOUP 6 were discovered to assume that a large fraction of the mercury bound by the solids is transferred to the liquid during caustic leaching. Nonetheless, there is technical consensus with the assumption that a majority of the mercury at Hanford is associated with the waste solids; however, it appears there is only modest certainty in the actual phase distribution of mercury. Also note the excellent agreement in mercury mass between TFCOUP 6 and 2018 BBI estimates (1,752 kg vs. 1,780 kg, respectively) while a clear disparity is observed for the 2,100 kg estimate reported by Cramer (2001).

### 3.2.3 Mercury Speciation

Mercury speciation at Hanford has largely been derived from thermodynamic arguments using the Environmental Simulation Program (ESP), a chemical thermodynamic simulator. The ESP-predicted mercury species in the liquid and solid waste inventory, at equilibrium, have been evaluated on a tank-by-tank basis for assessing potential chemical consequences in the documented safety analysis. Mercury hydroxide (Hg[OH]<sub>2</sub>) and mercury chloride (HgCl<sub>2</sub>) are the prevalent liquid species predicted while mercury oxide (HgO) is the only form predicted by ESP in the waste solids (Anderson 2016; Meacham 2015).

For the liquid, metallic mercury is believed to be in dynamic equilibrium with mercuric (i.e., valence state of 2) and mercurous (i.e., valence state of 1) ions under the waste storage conditions at Hanford. The predominant liquid phase mercury in the waste tanks is believed to be in the mercury (II) ion form (Hg<sup>2+</sup>)

and is tracked by flowsheet modeling in this form. Liquid phase mercury species in the tank farms are primarily believed to be elemental, methylmercury, and dimethylmercury—listed in order of decreasing stability and increasing volatility. However, considerable uncertainty exists as no mercury speciation is currently measured and only a total mercury measurement is conducted at Hanford as described and discussed in Section 4.1.

The mercury species in the waste solids are largely unknown, likely waste type specific, and currently assumed to exist predominantly as HgO (based on high waste pH) for flowsheet assessment and modeling purposes.

### 3.3 Hanford Flowsheet Modeling of Mercury Speciation for LAW

The primary flowsheet modeling objective of tracking mercury inventory is for evaluation of secondary waste disposition primarily through adsorption on activated carbon absorbers in the off-gas and vessel ventilation cleanup systems in both the WTP LAW and HLW facilities (Fleming 2016). Key mercury tracking points also include the liquid recycle stream (EMF bottoms liquor) to WTP LAW and the 242-A evaporator and EMF evaporator overhead liquids transferring to Liquid Effluent Retention Facility (LERF) followed by treatment in the Effluent Treatment Facility (ETF) and final land disposal restriction (LDR) disposition.

It's important to note that the TOPSim (maintained by the TOC) and WTP G2 [maintained by Bechtel National Incorporated (BNI)] mission-level flowsheet models track different processes based on their contract responsibility for the DFLAW and full mission. The TOC models the entire flowsheet. So, for the DFLAW mission, the TOC uses the TOPSim model to track tank waste mass and concentration from SST retrievals, to DST staging, through pretreatment, to immobilization, and subsequent dispositions of solid and liquid secondary wastes. In contrast, during the DFLAW mission, the WTP G2 model receives TOC-derived feed vector inputs (treated LAW batches) to predict immobilization in the WTP LAW Facility and subsequent evaporation of the melter off-gas condensate in the EMF. The WTP G2 modeling responsibility exists in these two facilities only for the DFLAW mission and the discussion of flowsheet modeling of mercury below will reflect this reality.

A simplified DFLAW flowsheet illustrating mercury mass movements, phase changes, and stream splits is provided in [Figure 3.1](#) ~~Figure 3.1~~ to facilitate the summary that follows. The detailed flowsheet modeling discussion that follows focuses on the TOPSim modeling by TOC and any differences in BNI's WTP G2 modeling are highlighted if the TOC and BNI modeling approaches are not equivalent.

Mercury mass, denoted as Hg<sup>2+</sup> in TOPSim model documentation, enters the flowsheet model with no implied speciation (i.e., all Hg<sup>2+</sup>) and on a tank-by-tank basis from BBI tracked in the liquid or solid phase (Rasmussen 2017). However, the mercury form is most accurately denoted as Hg (II) (e.g., HgCl<sub>2</sub> or HgO) and is not likely to exist in the flowsheet as a free ion with a +2 oxidation state. During SST and DST solids retrievals, wash-leach factors (as specified in Pierson 2012) are applied converting a fixed portion of the solid phase Hg into the liquid phase. All 177 waste tanks have associated wash-leach factors (as specified by Pierson 2012) for Hg that vary from 0 (representing the case of no solid to liquid phase transfer of Hg) to 1 ( a case where complete transfer of all solid phase mercury to the liquid phase occurs). For example, a phase transfer of 57% or greater (i.e., 0.57 wash factor) for Hg, from the sludge or saltcake phase to the liquid phase, occurs in 11 DSTs and 24 SSTs per the TOPSim model assumptions during solids retrievals. These retrieval assumptions significantly affect the Hg inventory phase distribution within model space, may or may not be representative of reality, and have their underlying basis documented by Hendrickson et al. (1998).

The liquid phase mercury mass is then either stored in DSTs, fed forward into pretreatment facilities through a staged feed tank (currently AP-107), or evaporated in the 242-A evaporator. During evaporation, as specified by model equipment split factors<sup>3</sup> captured in Eslin (2015), a portion of the mercury is lost to the evaporator overheads, emitted out the stack or condensed, and transferred to LERF/ETF and disposed of per LDR regulations. The iodine model splits at the evaporator are dynamic while the condenser splits are static.

In the next stage, pretreatment by the TSCR system or a LAWPS-like solids filtration and cesium removal facility is assumed to create no change in mercury inventory or phase distribution within the flowsheet model. At this point in the flowsheet, Treated LAW feed has been generated by the TOC and is ready to deliver in feed batches to BNI’s WTP LAW Facility. During receipt, preparation, and staging of the melter feed in the WTP LAW Facility, again, no mercury inventory or phase distribution changes are modeled within the flowsheet.

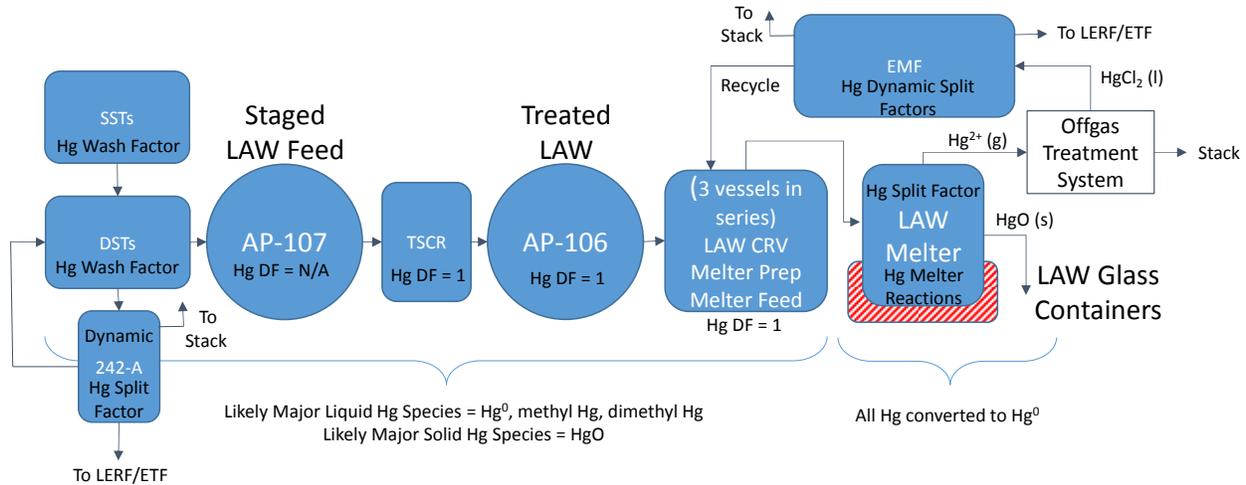
When the waste enters the WTP LAW melter, the TOPSim model first applies a split factor (as specified by Eslin 2015) to partition a portion of the mercury to the off-gas and the remainder to the glass. Currently, the baseline split factor for mercury is set to “0” to signify the assumption that all mercury entering the WTP LAW melter goes to the glass melt. This setting can be adjusted to consider varying splits or could be set to “1” to assume all mercury evolves to the off-gas. After this initial split factor is applied, the TOPSim model then applies a fixed set of potential mercury reactions [see Eqs. (3.1)(3.1) and (3.2)(3.2)] as part of a larger set of “LAW Glass Melt Reactions.” These fixed reactions are given “extent of reaction” values, which control partitioning and mercury conversion to the gas phase as  $Hg^{2+}$  and/or to the solid phase as  $HgO$ .



The current “extent of reaction” value is “1” for the liquid/solid-to-gas reaction [Eq. (3.1)(3.1)] while the liquid/solid-to-solids reaction [Eq. (3.2)(3.2)] “extent of reaction” value is set to “0” for the LAW melter (Fleming 2016). Therefore, per the most recent TOPSim model design document (Fleming 2016), no mercury oxide ( $HgO$ ) is formed to leave with the LAW glass canisters and all entering mercury inventory reacts to form gas phase mercury in the melter plenum. The WTP G2 model only considers Eq. (3.1)(3.1) (“extent of reaction” equals 1) in its model documentation and assumes the same behavior as the TOPSim model (Deng 2018).

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<sup>3</sup> Split factors can vary between 0 and 1 and represent a simple ratio of a specified destination stream (“TO”) divided by an inlet stream carrying the material into the operation (“FROM”); split factor = TO/FROM. These split factors are applied to all chemical and radionuclides tracked by the model in the liquid, solid, and gas phases.

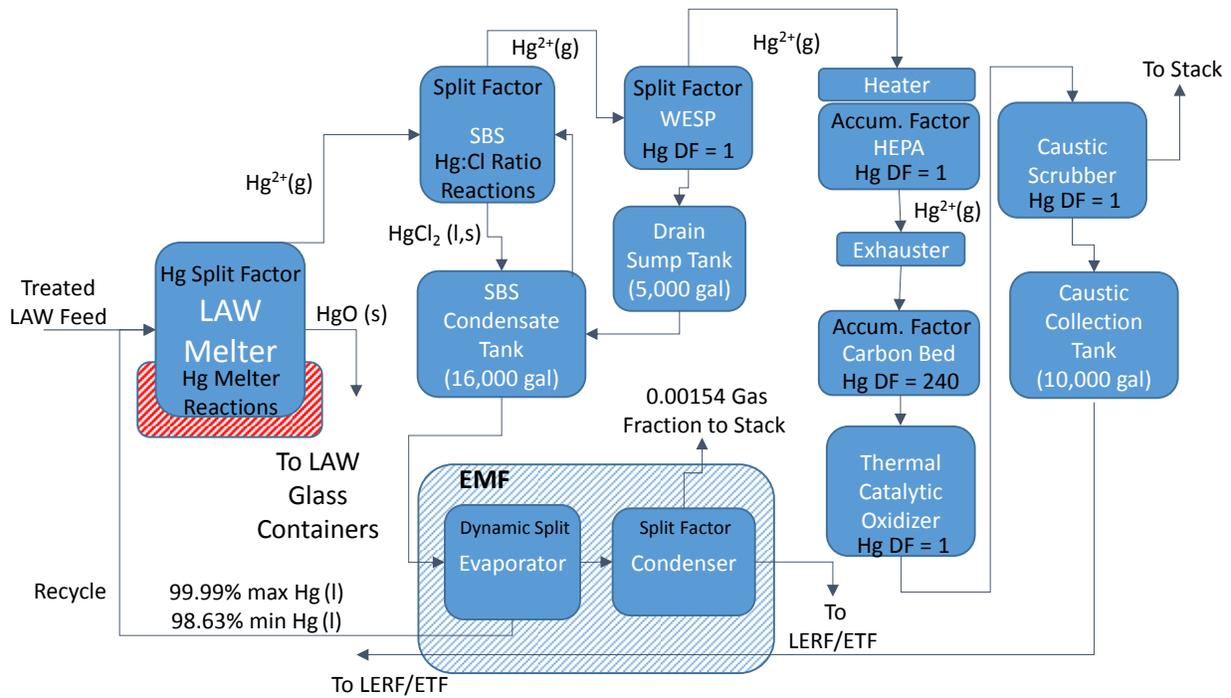


**Figure 3.1.** Simplified DFLAW Flowsheet Modeling of Mercury for SST Retrieval, DST Staging, and Pretreatment

The gas phase mercury portion passes through the LAW melter plenum and enters the LAW melter off-gas treatment system. A simplified flow diagram of the WTP LAW melter off-gas treatment system and EMF is depicted in [Figure 3.2](#) to aid the discussion. Similar to the LAW melter modeling, both models (TOPSim and WTP G2) treat the mercury entering the LAW off-gas process with split factors [per Eslin (2015) and Table D-13 of Deng (2018), respectively] and then fixed reactions occur based on “extent of reaction” values provided in Fleming (2016) and Deng (2018). The gas phase mercury from the LAW melter plenum enters the submerged bed scrubber (SBS) and a split factor of “0” is applied first, which signifies no mercury partitioning to the wet electrostatic precipitator (WESP). Mercury reactions are applied next in the SBS according to Hg:Cl ratio limits, with a fixed distribution of ionic Hg and HgCl<sub>2</sub> based on the following rules described in both Fleming (2016) and Deng (2018):

$$\begin{aligned} \text{Hg:Cl} \leq 0.1, \text{ Hg} &= 83.3\% \text{ HgCl}_2, \\ \text{Hg:Cl} = 0.1 \text{ to } 0.5, \text{ Hg} &= 55.9\% \text{ HgCl}_2, \text{ or} \\ \text{Hg:Cl} \geq 0.5, \text{ Hg} &= 28.6\% \text{ HgCl}_2. \end{aligned}$$

These reactions signify the conversion of gas phase mercury to the HgCl<sub>2</sub> condensed phase in the SBS, and the remainder gas fraction continues downstream to the WESP. The gas phase mercury entering the WESP is assumed to pass through completely (a split factor of 1 for TOPSim) and with no reactions. The HEPA filter is the next treatment unit and the gas phase mercury is similarly modeled to have no accumulation or reaction in the HEPA unit prior to entering the LAW carbon bed adsorber. At the carbon adsorber, 99.583% [decontamination factor (DF) ~ 240] of the mercury gas is captured per the applied split in Eslin (2015), leaving the remainder gas phase mercury to exit unreacted through to the thermal catalytic oxidizer unit, the caustic scrubber, and finally out the LAW off-gas stack. The WTP G2 model handles mercury equivalently per the WTP model design document reported by Deng (2018).



**Figure 3.2.** Simplified DFLAW Flowsheet Modeling of Mercury for WTP LAW Melter Off-gas Treatment and EMF

The condensed phase mercury fraction, assumed to be  $\text{HgCl}_2$ , is modeled to enter the SBS condensate tank after a portion of the total mercury is partitioned via split factors and Hg:Cl reaction rules are applied as described above. Flowsheet modeling continues to track this mercury partitioned to the condensed phase due to its potential to impact LERF/ETF and the recycle stream to the WTP LAW receipt tank.

After leaving the SBS condensate tank, the waste is transferred to the EMF for volume reduction of the secondary liquid (off-gas condensate) waste. Any liquid or solid phase mercury entering the evaporator is volatilized initially to the vapor stream according to the split factor ( $SF_i$ ) equation derived and reported in Stamper (2012):

$$SF_i = \frac{1}{\left[1 + \frac{Kp_i}{18600} \left(\frac{1 - WVR}{WVR}\right)\right]} \quad (3.3)$$

where  $WVR$  (waste volume reduction) is the fractional waste volume reduction and the conversion factor ( $Kp_i$ ) for mercury is  $1.77 \times 10^6$  as dictated by Eslin (2015). Assuming a maximum fractional  $WVR$  of 0.57, as defined by Bernards et al. (2018), the maximum predicted mercury split factor equals 0.014. In reality, the mercury (and component) split factor can vary per Eq. (3.3) as  $WVR$  values change depending on evaporator operating conditions; however, the split factor will decrease with decreasing  $WVR$  and the vast majority of the mercury remains in the evaporator bottoms as modeled. The vapor stream off the evaporator (i.e., overheads) is modeled to pass through the demister/condenser unit where the mercury partitioning is controlled by a liquid and solid phase split factor of 0.00154, which represents a small fraction released to the EMF stack and a majority remaining in the condensate for disposition to LERF/ETF.

As the flowsheet model discussion highlights, the fate of mercury is highly dependent on liquid, solid, and gas phase mercury speciation as dictated by the chemical and thermal conditions of the various waste processing unit operations. These assumed flowsheet model stream partitions and associated mercury species remain largely unverified by analyses of samples from representative processes using actual Hanford tank waste.

An opportunity to leverage current tank waste unit operations testing in PNNL's Radioactive Test Platform exists and can close these flowsheet gaps with mercury speciation and quantification measurements of representative flowsheet streams using the first feed campaign for DFLAW (e.g., AP-107). However, an analytical technique to speciate mercury currently doesn't exist at PNNL or Hanford.

## 4.0 Mercury Analytical Experience at Hanford and Savannah River Site

Upon initial completion of the mercury background evaluation, the authors concluded that extensive work on mercury speciation and flowsheet tracking has been completed at SRS and this can be readily leveraged to support a Hanford evaluation. However, a primary gap identified at Hanford was the unavailability of an analytical method to accurately and reproducibly quantify mercury species throughout multiple key flowsheet interfaces (e.g., staged feed, evaporator overheads, post-melter off-gas). In addition, the Hanford waste processing design differs from SRS, and Hg partitioning is not equivalent at the two sites; although the Hg behavior should be similar, Hg measurements are necessary. Historically, total mercury measurements have been made and speciation usually inferred from thermodynamic considerations. Only recently have speciation measurements been made at SRS (Boggess et al. 2018). A review of analytical capabilities at SRS, PNNL, and the Hanford 222-S Laboratory was completed in the context of fulfilling the need to inform the mercury feed inventory, distribution, and speciation in Hanford tank waste liquids. The discussions below summarize the current Hg analytical measurements at Hanford and those being developed at SRS.

### 4.1 Current Hanford Mercury Analytical Capability and Measurements

The 222-S Laboratory at Hanford has the capability to conduct measurements of total mercury in aqueous and solids matrices. The laboratory also has the capability to measure mercury and methylmercury in tank vapors by collection onto solid substrates prior to analysis. No capability currently exists in the 222-S Laboratory for measurement of mercury speciation in aqueous or solid matrices.

Total mercury measurements in the 222-S Laboratory are conducted using a cold vapor atomic absorption spectrophotometric technique following bulk sample oxidation. Liquid and solid samples are subjected to a nitric acid, sulfuric acid, and potassium permanganate digestion process. Elemental mercury vapor is generated from the digestate by reduction and swept into the gas cell situated in the light path of a PerkinElmer atomic absorption spectrometer. A flow injection mercury system (FIMS 400) is used to reduce mercury in the aqueous sample to elemental mercury, separate the gas phase mercury from the aqueous sample, and sweep the elemental mercury into the gas cell of the spectrophotometer where its absorbance is read at 253.7 nm. This procedure is based on SW-846, Methods 7470A, *Mercury in Liquid Waste (Manual Cold-Vapor Technique)*, and 7471B, *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)* (U.S. Environmental Protection Agency [EPA] 1994; 2007).

Using this system, the method detection limit of the total mercury analytical capability in the 222-S Laboratory using the PerkinElmer FIMS system is approximately 20 µg/L, or 20 ppb. Based on 590 analyses conducted to date, mercury levels in the DST supernates are all less than 20 ppm. If three tanks are excluded (AY-101, ca. 15 ppm; AN-106, ca. 9 ppm; and AN-107, ca. 5 ppm), all DST tank supernates are below 3 ppm<sup>1</sup>.

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<sup>1</sup> The details regarding 222-S mercury detection capability were obtained through a personal email communication between Gary Cooke (WRPS) and Gary Gill (PNNL) on August 15, 2018, 4:35 PM.

## 4.2 Savannah River Site Analytical Experience with Mercury

Approximately 60 metric tons of mercury exist in the 43 underground storage tanks at the SRS (Suggs and Edwards 2015; Jain et al. 2017). The mercury at SRS was used as a catalyst for dissolving the aluminum cladding of reactor fuel. Similar to Hanford, mercury represents a significant risk to worker and environment health and carries negative impacts to waste processing and secondary waste disposition. Mercury is removed from the liquid waste system via similar routes as Hanford, including the tank farm evaporators condensate, the Defense Waste Processing Facility melter off-gas treatment, secondary liquid effluents discharged to the Effluent Treatment Plant, and through an immobilized low-level, grout waste form in the Salt Waste Processing Facility (SWPF). However, unique to SRS, an engineered mercury removal capability was designed into the flowsheet. The mercury water wash tank is the designed collection location.

In 2014, the SRS observed high levels of mercury in a TCLP as part of normal monitoring of the low-level cementitious waste form produced at SWPF (Jain et al. 2015; Bannochie et al. 2017). The TCLP value was higher than the LDR treatment standard for mercury of 0.025 mg/L. Moreover, the dominant form of mercury that was released was methylmercury, the highly toxic mercury form due to its ability to bioconcentrate in biological tissues and magnify up the food chain (Weiner et al. 2002). This unexpected discovery prompted investigations into the speciation of mercury in the liquid waste stream (Jain et al. 2015). It was subsequently discovered that there were elevated levels of methylmercury in the decontaminated salt feed to the low-level waste operations. This resulted in further mercury speciation determinations throughout the liquid waste facilities and unit operations.

In February 2015, the U.S. Department of Energy requested that Savannah River Remediation “... *take an integrated, system-wide approach to evaluating the movement, monitoring, and collection of mercury through the entire Liquid Waste System/Facilities and utilize external expertise as needed*” (Jain et al. 2017).

After finding unexpectedly high mercury and methylmercury levels in tank and waste streams, scientists at Savannah River National Laboratory (SRNL) were tasked with conducting mercury speciation measurements on tank wastes and at various points in the waste treatment process. The analytical results of these mercury characterization studies are documented in a series of SRNL sample analysis reports by Bannochie (2015a,b,c,d,e,f,g,h,i; 2016a,b,c), and Bannochie and Crawford (2015a,b), and summarized in a peer-reviewed publication by Bannochie et al. (2017).

Since SRNL did not have mercury speciation capability, they worked with Eurofins Frontier Global Sciences, Inc. (Bothell, Washington) to conduct measurements of seven Hg species: total Hg, total soluble Hg, elemental Hg, ionic mercury [both Hg (I) and Hg (II)], methylmercury, ethylmercury, and dimethyl mercury. In order to ship radioactive tank waste samples to Eurofins for analysis, the parent waste had to be significantly diluted, up to as high as 300,000-fold. This dilution was necessary to reduce the background radioactivity to levels that the receiving laboratory could accept under their radiochemical license. However, this high level of dilution significantly affects the ability to detect mercury species of concern in the tank waste and achieve quantitative agreement between a total mercury measurement and the sum of the species fractions.

Most recently, SRNL has established new in-house total and mercury speciation technology for the determination of sub-picogram level determinations of total mercury, methylmercury, and ethylmercury in caustic tank waste (Bogges et al. 2018). The method development is based on the EPA methods for the determination of total and methylmercury (U.S. EPA 1998, 2002). The technique employs the mercury analytical instrumentation for total mercury and methylmercury developed by Brooks Rand Instruments (Seattle, Washington). Because of the sensitivity of the instruments, signals were detectable

even though the highly radioactive raw tank waste sample was significantly diluted (in a series of dilution steps), with the final dilution factor between 1,000,000- and 4,000,000-fold, to reduce radiation exposure and radiological controls. This method imparts considerable uncertainty with large dilutions and does not have the ability to isolate and quantify elemental mercury, dimethylmercury, or inorganic mercury forms.

### 4.3 PNNL Analytical Experience with Mercury

The Radiochemical Processing Laboratory (RPL) at PNNL maintained the capability to measure total mercury in aqueous samples until approximately 2008, at which time the capability was discontinued due to lack of need. The instrumentation that was employed was a CETAC Model 6000A mercury analyzer. The CETAC instrument was a cold-vapor atomic absorption spectrophotometer with an instrument detection capability of 5 ng Hg/L.

PNNL’s MSL in Sequim, Washington, maintains a dedicated research laboratory for the ultra-trace level determination of mercury and methylmercury in air, water, biological tissues, and sediments (see <https://marine.pnnl.gov/mercuryanalyticallab.asp>). Mercury measurements are based on modified versions of the EPA procedures for the determination of mercury and methylmercury using atomic fluorescence spectrometry (U.S. EPA 1998, 2002). Scientists at MSL have been conducting environmental mercury measurements and biogeochemical mercury investigations in air, water, biological tissues, and sediments for more than 35 years took part in the development of the EPA standard methods noted previously. The current detection capability of these methods is highly sensitive, which reduces radiological control and exposure for sample analysis because small (~1µl) tank waste samples are sufficient for analysis, while still achieving excellent detection capability (Table 4.1Table 4.1). To illustrate this, Table 4.2Table 4.2 provides an estimate of the detection capability for total mercury and methylmercury by the methods used at MSL for various tank waste sample volumes. This estimate is based primarily on the absolute detection capability of the atomic fluorescence detector of ~6 pg Hg.

**Table 4.1.** Method Detection Limits (MDLs) for the Determination of Total Mercury and Methylmercury in Water, Sediment, and Tissues at the MSL in Sequim, Washington

Matrix	Total Hg	Methylmercury
Water	0.10 ng/L	0.025 ng/L
Sediment	0.36 ng/g	0.010 ng/g
Tissue	0.37 ng/g	1.5 ng/g

**Table 4.2.** Estimated Method Detection Limits (MDLs) for Total Mercury in Aqueous Tank Waste Samples Based on the Volume of Sample Taken for Analysis

Sample Volume (mL)	MDL (mg/mL or ppb)
10	0.0006
1	0.006
0.1	0.06
0.01	0.6
0.001	6

Denoted in Table 4.1Table 4.1, PNNL’s MSL MDLs for total mercury and methylmercury in water, 0.10 ng/L and 0.025 ng/L, respectively, compare well with the expected EPA method total mercury and

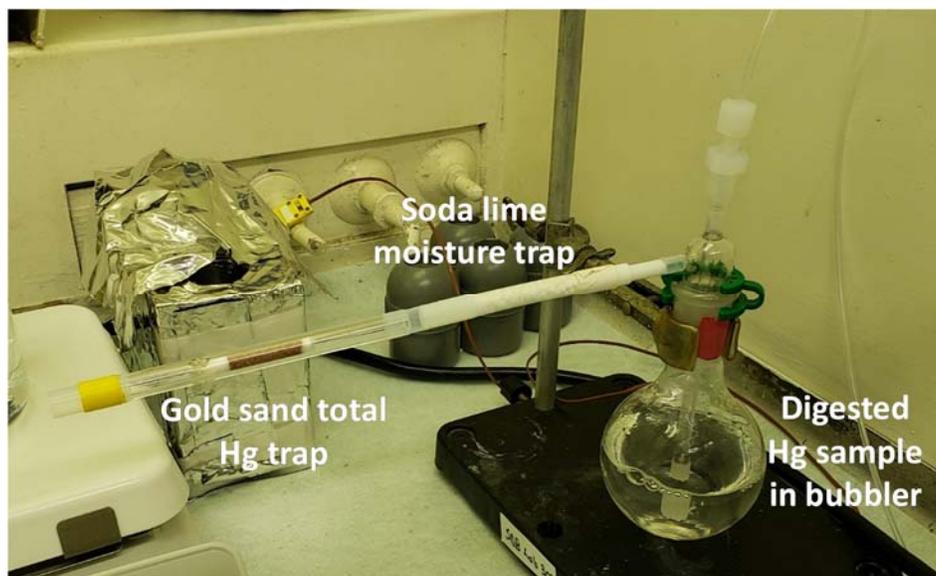
methylmercury MDLs of 0.2 ng/L and 0.02 ng/L, respectively, “when no background elements or interferences are present” (EPA 2002; EPA 1998). Furthermore, this method detection capability is adequate to meet the required detection limit (RDL) for total mercury of 1.4ug/ml (1400 ppb) as defined in the DFLAW feed qualification data quality objectives.

## 5.0 Mercury Species Separation Protocol

The protocol developed for the separation of mercury was adapted from several methods that are currently used at PNNL's MSL in Sequim, Washington, for determinations of mercury and methylmercury in atmospheric, aqueous, tissue, and sediment matrices. Mercury in solid matrices is released into aqueous solution by digestion (total Hg) or extraction (methylmercury). Mercury species in aqueous solution are then separated and isolated onto solid substrates (i.e., traps) in the gas phase through direct purging of the sample (elemental mercury and dimethylmercury), followed by reduction to elemental mercury with stannous chloride (total Hg) or a derivatization to ethyl analogs (methylmercury). The substrates can then be heated to release the Hg species into an inert gas stream for quantification using cold vapor atomic fluorescence spectrometry (CVAFS) following pyrolysis of the organo-mercury species to elemental Hg. For adapting these separation protocols to Hg quantification in tank waste samples, the Hg species must be separated from solid particulates as well as radionuclides in the waste sample.

The objective of this Phase I work was to determine whether Hg species could be trapped onto a solid substrate while simultaneously eliminating or significantly reducing undesirable radionuclides that require radiological safety controls. This objective was achieved by demonstrating an adapted non-radiological technique for the separation and preconcentration of total mercury and methylmercury onto solid substrates and then measuring the substrates for radiological content. This same approach is also appropriate for elemental mercury and dimethylmercury, as the only difference for isolation of these mercury forms is that chemicals are not added to the process to reduce or ethylate mercury, respectively.

For the isolation of total mercury, a 1-mL AP-107 supernatant subsample was digested in a 50-mL bromine monochloride (BrCl) solution (0.025%, w/v) for 24 hours to release mercury from organic complexes and solid phases. After digestion, 0.25 mL of hydroxylamine hydrochloride (NH<sub>2</sub>OH•HCl) (30% w/v) was added to neutralize any unreacted BrCl. A 250-mL sparging system was charged with a volume of acidic stannous chloride (SnCl<sub>2</sub>) solution (0.13%, w/v) sufficient to cover the glass frit in the bubbler. A soda lime filled column, constructed with soda lime substrate between glass wool plugs, was attached at the outlet of the bubbler, which prevented acidic moisture from reaching the gold-coated sand trap. The blank system was purged with ultra-high purity (UHP) nitrogen (N<sub>2</sub>) for approximately 20 minutes to remove any residual Hg prior to adding the sample. After blank purging, the gold-coated sand trap, constructed with substrate between quartz wool plugs, was attached downstream of the soda lime trap, and the digested sample was introduced to the bubbler. A photograph of the assembled bubbler system is shown in [Figure 5.1](#)~~Figure 5-1~~. The system was then purged at ~350 mL/min for 25 minutes. Both the soda lime and gold-coated sand traps were recovered for analyses of radiological content.

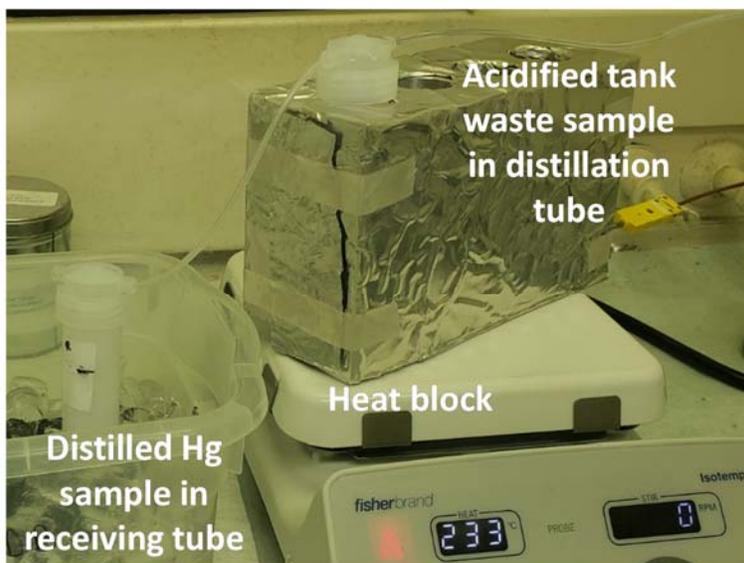


**Figure 5.1.** Photograph of Total Mercury Purging Bubbler System

The isolation of methylmercury was conducted as a two-step process: (1) a distillation to prepare a less complex matrix, and (2) a preconcentration step that traps a volatilized mercury form on a graphitized carbon black substrate commercially referred to as a Carbotrap<sup>®1</sup> adsorbent. The distillation step was conducted on two separate 1 mL AP-107 supernatant subsamples: one distillation to evaluate the radiological content of the distillate, and one distillation for evaluating radiological content during sample purging and trapping on the Carbotrap<sup>®</sup> substrate.

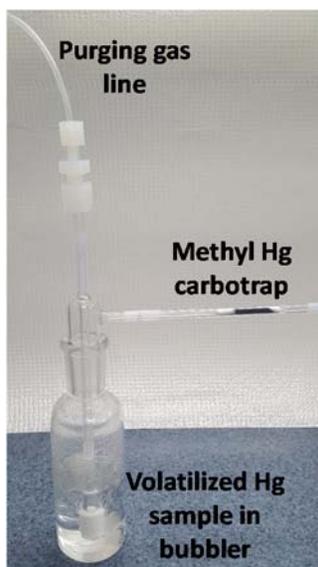
For the distillation step, a 1-mL AP-107 supernatant subsample was diluted to 50 mL in a 0.5 % hydrochloric acid (HCl) solution within a poly(tetrafluoroethylene) distillation tube. The distillation vessel was placed in an aluminum block fixture on a hot plate and attached to a receiving vessel, which was filled with ~5 mL of water (H<sub>2</sub>O) and submerged in an ice bath. A photograph of the distillation system is shown in [Figure 5.2](#). The distillation vessel was heated at ~135 °C for approximately 3 to 4 hours, until ~45 mL of distillate was collected in the receiving tube. The distillate was evaluated for radiological content by PNNL's Analytical Support Operations (ASO) organization.

<sup>1</sup> Carbotrap is a registered trademark of Sigma-Aldrich Co. LLC.



**Figure 5.2.** Photograph of Methylmercury Distillation Apparatus

A separate distillate sample (~45 mL) was transferred into a bubbler filled with 50 mL of dilute sodium acetate buffer solution (0.14% w/v). The distillate solution was spiked with an ethylating agent, sodium tetraethylborate ( $C_8H_{20}BNa$ ) (0.125 mL, 1% w/v), and allowed to react for approximately 17 minutes. The ethylating reagent converts methylmercury into methylethylmercury, which is volatile and can be stripped from solutions by purging with an inert gas. The Carbotrap<sup>®</sup> column, constructed with adsorbent between glass wool plugs, was then attached to the outlet of the bubbler and the system was purged with UHP  $N_2$  for approximately 17 minutes, trapping the methylmercury on the substrate. The Carbotrap<sup>®</sup> substrate and glass wool plugs were recovered for analyses of radiological content. The bubbler system is shown in [Figure 5.3](#).



**Figure 5.3.** Photograph of Bubbler System for Purging Methylmercury onto a Carbotrap<sup>®</sup>

## 6.0 Results and Discussion

The objective of this Phase I work was to determine whether Hg species could be trapped on a solid substrate while simultaneously eliminating or significantly reducing undesirable radionuclides that require radiological safety controls. Therefore, the total gamma/beta/alpha activity was determined for the liquid distillate and Carbotrap<sup>®</sup> substrate (used to separate methylmercury) and the soda lime and gold-coated sand substrates (used to separate total mercury). Measurements were conducted by PNNL's ASO organization in RPL according to the Analytical Service Requests (ASR) 0543 (gamma) and 0552 (total activity). The activity for each sample was measured and compared to the parent AP-107 feed analysis completed and reported by Rovira et al. (2018) as part of PNNL's Radioactive Test Platform<sup>1</sup> work.

Gamma energy analysis (GEA) was completed for each sample and results are reported in [Table 6.1](#) ~~Table 6.1~~, with <sup>137</sup>Cs being the only detectable radionuclide. A DF [see Eq. (6.1)] ~~(6.1)~~ is included to highlight the magnitude of activity reduction in each sample compared to the parent feed. The DF is represented mathematically by

$$DF = \frac{A_p}{A_s} \quad (6.1)$$

and defined as the ratio of activity of the parent sample ( $A_p$ ) to the activity of the separation sample ( $A_s$ ). The sample exhibiting the highest activity was the liquid distillate ( $2.44 \times 10^2$  Bq/g) from the methylmercury separation protocol ([Table 6.1](#) ~~Table 6.1~~), which was expected since the sample had not yet been purged onto a Carbotrap<sup>®</sup> substrate (as illustrated in [Figure 5.3](#) ~~Figure 5.3~~). This initial distillation step resulted in a DF on the order of  $10^4$ . A second distillate was prepared and then purged onto a column filled with Carbotrap<sup>®</sup>. The gamma activity measured on the Carbotrap<sup>®</sup> substrate decreased substantially resulting in a DF on the order of  $10^8$ , thereby reducing the activity to levels easily managed outside a hot cell and within a typical contamination area (CA) fume hood.

The purpose of the soda lime trap was to capture any acidic moisture before it could reach and damage the gold-coated sand trap. As expected, the measured <sup>137</sup>Cs activity was slightly higher on the soda lime trap than on the gold-coated trap, since it was placed upstream of the gold trap ([Figure 5.1](#) ~~Figure 5.1~~). The soda lime and gold-coated sand traps exhibited DFs on the order of  $10^7$  and  $10^8$  relative to the parent feed sample, respectively. Dose reduction at these levels demonstrates acceptability for reduced radiological controls and enables release of mercury separation samples to other low-level radiological permitted facilities (e.g., MSL or commercial laboratories).

**Table 6.1.** Gamma Activity of Hg Species Separation Samples Compared to Parent Tank Waste Sample

Sample Description	Hg Separation Method	Cs-137 (gamma), Bq/g $\pm 1\sigma$	Decontamination Factor
Liquid distillate	Methyl Hg	$2.44 \times 10^2 \pm 2\%$	$1.79 \times 10^4$
Carbotrap <sup>®</sup>	Methyl Hg	$1.86 \times 10^{-2} \pm 13\%$	$2.34 \times 10^8$
Soda lime trap	Total Hg	$3.87 \times 10^{-1} \pm 2\%$	$1.13 \times 10^7$
Gold-coated sand trap	Total Hg	$4.30 \times 10^{-2} \pm 2\%$	$1.01 \times 10^8$
AP-107 parent sample	None	$4.35 \times 10^6 \pm 2\%$ <sup>(a)</sup>	$1.00 \times 10^0$

<sup>1</sup> PNNL's Radioactive Test Platform is a capability developed to provide representative bench-scale unit operations for the DFLAW mission phase using actual tank waste. The real waste platform capability can be used for troubleshooting, waste feed qualification, data collection, checking new or alternative unit operations, and closing flowsheet gaps.

The actual samples of interest for the purpose of Hg species quantification using CVAFS are the Carbotrap<sup>®</sup> and gold-coated sand substrate materials. These traps will eventually be heated and purged with an inert gas to desorb, volatilize, and deliver the mercury to the fluorescence detector. However, the soda lime trap is also important and necessary element in the separation process, not for retention of Hg, but for tracking radionuclide migration during this initial separation demonstration. Understanding how and where the radionuclides migrate during the mercury separation provides a basis for future separations and sample release.

All three columns were disassembled and the substrates, glass wool, and quartz wool plugs for each trap were measured for total activity (i.e., alpha/beta/gamma); results are reported in [Table 6.2](#)~~Table 6-2~~. The activity of the liquid distillate was measured for comparison. The column substrates and wool plugs were recovered and acid-leached, separately. The leach solutions were then counted for total activity using liquid scintillation counting, with errors reported at  $1\sigma$ . As with the GEA results reported in [Table 6.1](#)~~Table 6-1~~, the liquid distillate sample exhibited the highest total activity at  $7.36 \times 10^{-3} \mu\text{Ci/g}$  ([Table 6.2](#)~~Table 6-2~~). However, this still represents a substantial reduction in radiological dose, as illustrated by the resulting  $1.70 \times 10^4$  DF when compared to the parent sample feed.

The Carbotrap<sup>®</sup> filled column used during the methylmercury separation protocol was analyzed as two subsamples: the glass wool plugs and the substrate. The total activity levels for both the glass wool and Carbotrap<sup>®</sup> substrate samples were below detection limits, which demonstrates trace radiological content. Both the soda lime and gold-coated sand traps showed similar trends, where the measured activities on the substrates were below detection limits and exhibited DFs on the order of  $10^6$ . While the glass wool plugs were above the detection limit, the DFs for each subsample were on the order of  $10^5$  when compared to the parent sample feed. Since the Carbotrap<sup>®</sup> and gold-coated sand columns both yielded activities below the detection limits, and therefore well within the normal radiological control limits for work in a CA fume hood, no further radiological interrogation was warranted. Based on these results, radiological controls such as a benchtop CA or CA fume hood are recommended for the quantification of Hg species using CVAFS and discussed in the Path Forward (Section 7.0).

**Table 6.2.** Total Activity of Hg Species Separation Samples Compared to Parent AP-107 Sample

Sample Description	Hg Separation	Subsample	Total $\alpha/\beta/\gamma$ , $\mu\text{Ci/g} \pm 1\sigma$	Decontamination Factor
Liquid distillate	Methyl Hg	None	$7.36 \times 10^{-3} \pm 4\%$ <sup>(a)</sup>	$1.70 \times 10^4$
Carbotrap <sup>®</sup> trap	Methyl Hg	Glass wool	$<3.00 \times 10^{-4}$ <sup>(a,b)</sup>	$4.16 \times 10^5$
		Substrate	$<1.40 \times 10^{-4}$ <sup>(a,b)</sup>	$8.92 \times 10^5$
Soda lime trap	Total Hg	Glass wool	$1.32 \times 10^{-3} \pm 13\%$ <sup>(a)</sup>	$9.46 \times 10^4$
		Substrate	$<6.90 \times 10^{-5}$ <sup>(a,b)</sup>	$1.81 \times 10^6$
Gold-coated sand trap	Total Hg	Quartz wool	$4.61 \times 10^{-4} \pm 33\%$ <sup>(a)</sup>	$2.71 \times 10^5$
		Substrate	$<6.65 \times 10^{-5}$ <sup>(a,b)</sup>	$1.88 \times 10^6$
AP-107 parent sample	None	None	$1.25 \times 10^2 \pm 4\%$	$1.00 \times 10^0$

(a) Average of duplicate samples.  
(b) Error not calculated for samples below detection limit

## 7.0 Path Forward

The work completed in Phase I has demonstrated that the preconcentration steps used to isolate mercury and methylmercury from the Hanford tank waste substantially reduce the radiological content of the sample ([Table 6.1](#)~~Table 6.1~~ and [Table 6.2](#)~~Table 6.2~~). This preliminary processing thereby allows the subsequent mercury quantification step by CVAFS to be conducted under less demanding radiological controls while maintaining maximum mercury detection ability. [Table 7.1](#)~~Table 7.1~~ outlines the radiological controls that will be required at PNNL to conduct the detection step in a radiologically controlled area.

**Table 7.1.** Proposed Radiological Controls Necessary to Conduct Mercury Separation and Quantification Analyses

Sample Type	Radiological Controls
Distillate for methylmercury analysis.	Conduct measurement in CA fume hood with the instrument posted as a high contamination area.
Carbotrap <sup>®</sup> column for methylmercury analysis.	Conduct measurement in benchtop CA with instrument posted as an CA.
Gold-coated sand column for elemental and total mercury analysis.	Conduct measurement in CA fume hood.

The next phase of this project (Phase II) will be measurement of total mercury, elemental mercury, and methylmercury in a Hanford tank waste sample. Separation and concentration of the mercury species from the native tank waste will be conducted in the RPL facilities in Richland, Washington, and the samples isolated onto the Carbotrap<sup>®</sup> and gold-coated sand columns will be sent to MSL in Sequim, Washington, for quantification by CVAFS. Sample quantification will initially be conducted in the radiologically controlled area at the MSL using the ultra-trace techniques used for environmental mercury measurements, with radiological controls as indicated in [Table 7.1](#)~~Table 7.1~~.

Prior to initiating full-scale measurement of mercury in tank waste, some QA tests to demonstrate the accuracy and robustness of the overall approach and the ability to reliably quantify mercury speciation in the tank waste are necessary. These tests will include the following:

1. Evaluation of the stability of methylmercury and dimethylmercury on the Carbotrap<sup>®</sup> substrate is necessary to validate the proposed separation method. In a normal methylmercury analysis, the sample is preconcentrated onto a substrate in a column and analyzed within a few hours of collection. For this work, there will be several days to a week between preconcentration and analysis, since the samples will be shipped from RPL to MSL for analysis.
2. Measurement of mercury species at three different sample volumes to ensure that the collection substrates are not saturated. Since minimal knowledge exists of the levels of total mercury and no knowledge of mercury species concentrations to expect in the tank waste, it is proposed to initially measure three different volumes of tank waste (1, 0.1, and 0.01 mL), spanning two orders of magnitude, to identify a suitable range for the analytical methods. Ideally, analyses use the smallest volume of tank waste that provides a reliable detection, thereby reducing the radiological controls needed.

3. Determine the recovery of methylmercury during the distillation step to close the mass balance. The recovery of methylmercury during the distillation step of the analysis is not 100% efficient, typically ranging from 85 to 95% recovery. The recovery factor is highly dependent on the performance of the distillation system, but it is also quite reproducible once set conditions are established. As part of the analytical effort, recovery tests for the distillation system in RPL will be conducted using (non-radioactive) spikes of methylmercury.

Additional scope includes initial development of protocols for the isolation and detection of dimethylmercury. Dimethylmercury measurements present a special risk, as dimethylmercury is volatile and lipophilic, which makes it highly toxic. Particular concern arises in the measurement due to the necessity to maintain dimethylmercury standards for instrument calibration. Because dimethylmercury is volatile, it can be isolated and preconcentrated from the tank waste by simple gas phase stripping onto a substrate, as with methylmercury, but without the distillation step or the ethylation step used to determine methylmercury. One option being considered is to work with Brooks Analytical Laboratories (Bothell, Washington), an analytical laboratory with particular expertise in mercury speciation measurements, to conduct the detection of the dimethylmercury, following its isolation and concentration onto a substrate material in PNNL's RPL. This pathway avoids bringing dimethylmercury into laboratories at PNNL or MSL and allows an existing capability to be leveraged at a commercial facility such as Brooks Analytical Laboratories.

## 8.0 Conclusion

The direct measurement of total mercury and mercury speciation analysis in Hanford tank waste samples poses a significant safety and radiological handling issue due to the high radioactivity levels present in the parent sample. Previous analytical approaches to dealing with the high radioactivity background used large dilution factors (often 100,000-fold or greater) to reduce radiological background to levels that would permit safe handling and sample analysis. The Phase I work has demonstrated that applying ultra-trace environmental mercury analytical techniques to the analysis of mercury in a Hanford tank waste sample, a significant reduction in radiological dose can be achieved ( $DF > 10^4$ ). This preliminary processing thereby allows the subsequent mercury quantification step by CVAFS to be conducted under less stringent radiological controls (e.g., benchtop and/or fume hood CA) and without any sample dilution while maintaining excellent mercury detection ability.

The ultimate goal of this work is to develop an analytical method to obtain detailed mercury speciation information to verify or update flowsheet modeling assumptions related to mercury speciation and partitioning at Hanford. In the next phase of the work, total mercury, elemental mercury, and methylmercury concentrations will be quantified in a Hanford tank waste sample, with no sample dilution, using the developed protocols. In Fiscal Year 2019, an opportunity to leverage current tank waste unit operations testing in PNNL's Radioactive Test Platform exists where this mercury speciation and quantification methodology will be applied to representative flowsheet streams (i.e., post filtration, post ion exchange, and post melter submerged bed scrubber) using a liquid sample from the first feed campaign for DFLAW (stored in Tank 241-AP-107).

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