STATE OF WASHINGTON
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November 25, 2014

Ron Skinnarland
Waste Management Section
Nuclear Waste Program
Washington Department of Ecology

Re: Second Tier Petition by the U.S. Department of Energy

Dear Mr. Skinnarland:

The Washington State Department of Ecology's Air Quality Program (Ecology) has completed our review of health risks associated with dimethyl mercury (DMM) emissions from proposed operation of up to two platform-mounted core sampling systems in high purge gas flow mode as necessary to obtain samples from waste storage tanks at the Hanford Site in Benton County, Washington.

Ecology's review indicates that exposures resulting from the project's emissions will be miniscule, and that the possibility of any adverse effect as a consequence of this exposure is extremely low. Ecology may permit such trivial emissions under Second Tier toxics review.

The project's emissions will add to existing DMM the environment. The resultin increase in exposure is not likely to appreciably add to health risk in the vicinity of the Hanford site.

Based on the review of the Second Tier petition for the project submitted to Ecology by U.S. Department of Energy and tank operations contract manager Washington River Protection Solutions, LLC, Ecology recommends approval of the proposed project because project-related health risks are permissible under WAC 173-460-090, and the project has satisfied all requirements of a second tier analysis.

The Ecology Nuclear Waste Progrem can incorporate our findings as part of the ambient air impacts analysis and begin the public comment period when appropriate.

If you would like to discuss this project further, please contact or Matt Kadlec at (360) 407-6817 or matthew.kadlec@ecy.wa.gov.

Sincerely,

Jeff Johnston, Ph.D.
Science and Engineering Section Manager
Air Quality Program

jj/te

Enclosure

cc: Dennis Bowser, ORP USDOE
Phil Gent, Ecology
Matt Kadlec, Ecology
Brian Rumburg, Washington River Protection Solutions

DEPARTMENT OF
ECOLOGY
State of Washington

Health Impact Assessment Recommendation Document for

Operation of the High Purge Gas Mode Core Sampler, Hanford Site, Benton County, Washington

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Prepared by

Air Quality Program
Washington State Department of Ecology
Olympia, Washington

November 24, 2014

Reviewed By:

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Clint Bowman, Atmospheric Dispersion Modeler

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Executive Summary

The U.S. Department of Energy and tank operations contract manager Washington River Protection Solutions, LLC (USDOE/WRPS) proposes to operate up to two platform-mounted core sampling systems in high-purge gas flow mode as necessary to obtain samples from the 100/200 series Single Shell Tanks and miscellaneous catch tanks at the Hanford Site in Benton County, Washington. The new core sampler system (NCSS) will use a high-purge gas mode for tank waste characterization as part of the overall plan to treat stored radioactive and chemical wastes from historical plutonium production. USDOE/WRPS determined their operation of the NCSS may result in emissions of substances contained in the wastes. A few of the 177 waste storage tanks have been found to contain dimethyl mercury (DMM). Potential emissions of DMM from the NCSS will exceed the applicable acceptable source impact level (ASIL) promulgated in Washington Administrative Code (WAC) 173-460-150 (May 2009 version). Therefore, on September 8, 2014, in accordance with WAC 173-460-090, USDOE/WRPS petitioned the Washington Department of Ecology (Ecology) for Second Tier review of potential DMM emissions. In their assessment, USDOE/WRPS estimated the health risk to people potentially exposed DMM emissions. The related documents submitted by USDOE/WRPS are a Health Impacts Assessment (HIA).

The Ecology review team concludes the HIA presents appropriate estimates of potential increased health hazards posed by the NCSS toxic air pollutant (TAP) emissions. USDOE/WRPS's HIA for the project includes estimates of DMM doses to hypothetical maximally exposed off-site people that could be attributable to the NCSS. Referring to their estimates, Ecology assessed overall health risks posed by DMM from the NCSS and other sources. The assessment shows that total exposures will be trivial, and that the possibility of any adverse effect as a consequence is extremely low.

There is no evidence that exposure to NCSS DMM emissions, alone or in combination with additional exposure to other DMM sources, will pose health hazards to people in any publicly accessible area near Hanford. Exposures to these new DMM emissions together with exposure to emissions already permitted at Hanford and to existing background concentrations are extremely unlikely to result in neurotoxicity hazards. Treatment of the tank wastes at Hanford is a benefit to the environment to the health of the people now and in future generations.

Based on review of the technical analyses provided by USDOE/WRPS, and provided the NCSS are operated as proposed, their additional health risks are be permissible under Chapter 173-460-090 WAC.

This summary document presents Ecology's review of USDOE/WRPS's and other requirements under WAC 173-460.

Permitting History

Permit issuance history for core sampling systems is documented in the HIA.[1]

The Proposed Project

The U.S. Department of Energy and tank operations contract manager Washington River Protection Solutions, LLC (USDOE/WRPS) has proposed operation of a new core sampler system (NCSS). The new system can operate in different modes depending on the characteristics of the waste sampled. This evaluation is for the NCSS operating in a high purge gas mode for tank waste characterization and future Tank Farm operation activities at the Hanford Site in Benton County, Washington. All emission discussions in this second tier review are referring to operation of the NCSS in high purge gas mode unless explicitly stated otherwise. Operation of the core sampling system in high purge gas mode may result in emissions of substances contained in the tank wastes.[2] USDOE/WRPS seeks State of Washington, Department of Ecology (Ecology) approval to operate up to two platform-mounted core sampling systems in high purge gas flow mode to obtain samples primarily from Hanford's SSTs, 100/200 series waste tanks, and miscellaneous catch tanks on the Hanford Site when necessary.[3]

A few of the 177 waste storage tanks at Hanford have been found to contain dimethyl mercury (DMM), therefore DMM emissions may result from operation of the two proposed core samplers. If any emission of DMM might occur, a regulatory trigger called an Acceptable Source Impact Level (ASIL) is exceeded under Washington Administrative Code (WAC) 173-460-090 (May 2009 version). USDOE/WRPS was therefore petitioned for Second Tier review. A Second Tier review petition requires a health impact assessment (HIA) quantifying the health hazards. This document presents Ecology's review of the HIA for the NCSS proposed by USDOE/WRPS and other requirements under WAC 173-460.

Potential Toxic Air Pollutant Emissions

In compliance with WAC 173-460, USDOE/WRPS compared the list of chemicals that have been detected in headspace gases with the list of Toxic Air Pollutants (TAPs) in WAC 173-460-100. They estimated emission rates for the TAPs. To establish a "worst case" tank for calculating emission rates (and for use as a source-term in subsequent air dispersion modeling) USDOE/WRPS queried the Tank Waste Information Network System (TWINS)[4] database to identify the tank with the highest headspace concentration of each TAP among any tank in the

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[1] TOC-ENV-NOC-0008 Section 1.3 CORE SAMPLING PERMITTING HISTORY

[2] TOC-ENV-NOC-0008 Section 4.1 EMISSION

[3] TOC-ENV-NOC-0004, Rev. 1 page *i*

[4] http://readthis.pnl.gov/marketsource/readthis/B2799_not_print_quality.pdf Accessed 9/10/2014

200 Area East and West Tank Farm Facility.[5] They identified the TAPs that might be emitted at rates greater than their *De Minimis* rate and Small Quantity Emission Rate (SQER). They noted "*Core Sampling in high purge gas mode is a short duration activity, the portable exhauster is only turned on when the purge gas is turned on, the estimated total hours of operation for up to two samplers is 300 hours per year.*"[6].

Toxic Air Pollutant Concentrations Assessment

In compliance with WAC 173-460-090, USDOE/WRPS determined only DMM emissions from the NCSS could result in exceedance of any ASIL. In response, they prepared a HIA for their application to emit DMM. To assess atmospheric concentrations of DMM from NCSS emissions, USDOE/WRPS assessed four tank farm areas (A, BX, T and SX). They modeled them separately, then proceeded assessing the most impacted off site receptors. This included modeled gaseous dry deposition of DMM deposition and subsequent transfer into produce for food consumption. USDOE/WRPS also referred to an analysis for an earlier application[7] to estimate potential health hazards to people exposed to the maximum NCSS emissions.[8]

Adverse Health Effects of Dimethyl Mercury

USDOE/WRPS HIAs correctly note that concentrated DMM is an extremely potent neurotoxicant. Effects range from delayed, permanent brain damage, weakness, impaired hearing, difficulty walking, personality changes and tremors to death. Chemists making or using it in their laboratories have been killed by dermal or inhalation exposure to as a few as 400 milligrams.

It is important to know that DMM is an environmental contaminant found in air and in fish and birds in trace amounts along with monomethyl mercury (MMM); and that small exposures to these toxicants can be tolerated without evident neurological harm.

Dimethyl Mercury Toxicological Reference Value

Currently, there is no published exposure limit for DMM for use in screening of its health risk. The DMM ASIL is not based on health risk; rather Ecology chose the ASIL to require any project emitting DMM to go through a Second Tier review. It is also important to know:

1. DMM is not toxic until it is metabolized to a tissue reactive product, which is most likely MMM. When DMM is absorbed internally, some metabolizes to MMM, which is toxic.

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[5] TOC-ENV-NOC-0004

[6] TOC-ENV-NOC-0008

[7] RPP-ENV-48231, *Second Tier Review Petition for the Operation of the 241-SY, 241-AP, and 241-AY/AZ Ventilation Systems.*

[8] TOC-ENV-NOC-0008

2. Neurotoxic effects can occur due to exposure to DMM at any time in life; however, the life-stage most sensitive to DMM toxicity is probably the fetal period.
3. There is a Reference Dose (RfD) for MMM, which based on developmental neurologic abnormalities in human infants. The National Research Council (NRC) recommended a RfD of 0.1-microgram/Kilogram body weight per day (μg/Kg bw-day) to protect pregnant women and developing fetuses.[[9]] In developing the RfD, the NRC applied uncertainty factors of three - each to pharmicokinetic variability and uncertainty, and to pharmicodynamic variability and uncertainty. They rounded the product of these factors to 10 to derive the RfD.[[10]]
4. USDOE/WRPS applied this RfD for estimating the health risk posed by NCSS DMM emissions.
5. Increased cancer risks were not estimated for the NCSS project because emissions rates of TAPs with published carcinogenicity slope factors were less than their ASILs.

Ambient Air Quality Analysis

USDOE/WRPS used AERMOD to estimate concentrations of DMM that could result from the NCSS. NCSS DMM emissions will combine in the atmosphere with ambient airborne DMM from existing natural- and anthropogenic sources.

USDOE/WRPS noted the limited data on observed DMM concentrations in the atmosphere.[[11]] Due to very limited data, there are large uncertainties in what is known about background DMM concentrations.

In their prior HIA,[[12]] USDOE/WRPS reviewed the state of current knowledge on existing levels of DMM as needed for predicting how much exposure there will be from both existing and proposed emissions. As noted in their review, very little research about background atmospheric DMM concentrations has been published; however, a mean of 0.04-ng/m^3 has been observed in Antarctica, [[13]] and a mean of 0.003-ng/m^3 has been observed in Seattle.[[14]]

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[9] Toxicological Effects of Methylmercury. Committee on the Toxicological Effects of Methylmercury, Board on Environmental Studies and Toxicology, National Research Council. 2000. 368 pages.

[10] EPA 2001 IRIS, http://www.epa.gov/iris/subst/0073.htm Accessed 9/24/2014

[11] TOC-ENV-NOC-0008 Section 5.3

[12] RPP-ENV-48231, Rev. 0, part 5.3 BACKGROUND CONCENTRATIONS, pp. 27-28

[13] De Mora, S.J. Patterson, J.E. Bibby, D.M. Baseline atmospheric mercury studies at Ross Island, Antarctica. *Antarctic science* 5(3): 323-326, 1993.

[14] Prestbo EM, Bloom NS, Pontgratz R, Heumann KG. 1996. A global view of the sources and sinks for atmospheric organic mercury. *Presented at the* Fourth International Conference on Mercury as an Environment Pollutant, Hamburg, Germany.

DMM is also biogenically formed and released from marine sediments, [[15]] and municipal landfills have been identified as sources of atmospheric DMM.[[16]]

Dimethyl Mercury Environmental Fate

USDOE/WRPS performed a search of scientific literature on the atmospheric terrestrial and aquatic fate of DMM.[[17]] They found information about atmospheric transformation rates abut not on the fate of DMM deposited in terrestrial and aquatic environmental compartments.

Land Uses and Sensitive Populations

USDOE/WRPS cited earlier analyses[[18]] of the population around Hanford site that might be exposed to NCSS emissions. They evaluated population demographic characteristics and land-use zoning in the area around the Hanford site.[[19],[20]]

Exposure Scenarios

Examining the AERMOD output, USDOE/WRPS identified locations of two types beyond the controlled access area of the Hanford Site where DMM concentration maxima could occur. One was the maximally impacted extra-boundary receptor (MIBR), the other was the maximally impacted residential receptor (MIRR) – the dwelling that could experience highest average concentrations among any existing dwelling. USDOE/WRPS did not identify the maximally impacted commercial receptor (MICR). Instead they stated the "*nearest resident is impacted more than the highest commercial receptor so the resident scenario is assumed to be more conservative*."[[21]]

For the MIBR assessment, USDOE/WRPS assumed a mother-child pathway among human receptors who would live at that location for 30 years. Their estimate utilized the maximum 24-hr average concentration and deposition values to assess the 30-year exposure.

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[15] Lehnherr I, St. Louis VL, Hintelmann H, Kirk JL. 2011. Methylation of inorganic mercury in polar marine waters. *Nature Geoscience* 4:298–302

[16] Frontier Geosciences. Determination of Total and Dimethyl Mercury in Raw Landfill Gas with Site Screening for Elemental Mercury at Eight Washington State Landfills for the Washington State Department of Ecology. August 2005. Publication number 05-07-039.

[17] TOC-ENV-NOC-0008 Section 5.4

[18] PNNL-14428, *Hanford Area 2000 Population*, 2004

[19] RPP-ENV-48231, Rev. 0, Part 6.0 SENSITIVE POPULATION ANALYSIS pp. 29- 34

[20] RPP-ENV-48231 also shows the shows the land use and zoning for the surrounding counties Benton, Franklin, and Grant

[21] RPP-ENV-48231, Rev. 0, Part 4.3 AIR DISPERSION MODELING. p. 21

For the MIRR assessment, USDOE/WRPS assumed the receptor would live at the same location (an existing house west of the 241-SX Tank Farm) for 70 years. Their estimate utilized the maximum 24-hr average concentration and deposition values to assess the 70-year exposure.

USDOE/WRPS also calculated the amount of NCSS-attributable atmospheric DMM that would enter plants and soil in the vicinity of Hanford.

Health Risks

USDOE/WRPS evaluated the potential for adverse health effects from exposure to DMM by comparing estimated doses at each receptor location to the RfD of a similar toxicant. They calculated maximum daily doses via inhalation of ambient air and ingestion of produce at the MIBR (as described) and at the existing MIRR. They then compared the doses to the RfD for MMM. This comparison is known as a hazard quotient (HQ) and is given by the equation below:

$$Hazard\ Quotient = \frac{\text{Average dose of toxicant (µg/Kg body wt. day)}}{\text{Reference Dose (µg/Kg body wt. day)}}$$

They interpreted the HQ results in the standard way: When the dose of a given toxicant exceeds its reference toxicological value, adverse health effects are possible. The magnitude of the potential for effects can be inferred from the magnitude by which a dose exceeds the reference value. Interpret of risks are uncertain when HQs are in the magnitude of one. As a HQ increases above one, the probability of adverse effects increases by an uncertain amount. A HQ of less than one indicates that the exposure to a toxicant is not likely to result in adverse health effects. As a HQ decreases from one, the probability of adverse effects decreases by an uncertain amount.

Results of the USDOE/WRPS Assessment

Project Emissions

Of the 91 TAPs USDOE/WRPS identified as potential NCSS emissions, four exceeded their *De Minimis* and three exceeded their SQER under WAC 173-460-100. Only DMM exceeded its ASIL.

Project-Attributable Concentrations and Deposition

In their Second Tier Review Petition for the Operation of the 241-SY, 241-AP and 241-AY/AZ Ventilation Systems, USDOE/WRPS estimated the maximum offsite 24-hr average DMM

concentration to be 7.7E-08-μg/m^3.[22] In contrast, in their present analysis of the maximal DMM emissions from NCSS operation at the 241-SX Farm, USDOE/WRPS estimated the maximum offsite concentration attributable to be 5.3E-09-μg/m^3[23], which is less than 7% as much as is permitted for the operation of the 241-SY, 241-AP and 241-AY/AZ ventilation systems. They also reported the maximum 24-hr concentration at a residential receptor (the MIRR) would be 1.3E-10 μg/m^3. They stated this residence would be impacted more than the MICR.

USDOE/WRPS reported that the maximum 24-hr deposition attributable to NCSS emissions at the MIBR would be 7.1E-13 g DMM/m^2, and the maximum 24-hr deposition "at the nearest residence" would be 3.4E-14 g/m^2.[24]

Background Concentrations

Table 1. Background DMM concentrations

Measurement	Concentration	
	ng/m^3	**μg/m^3**
Antarctica Mean (24 or 48 hr TWA) [25]	0.04	0.00004
Antarctica Maximum	0.63	0.00063
Antarctica Minimum	0	0
Seattle, Washington Maximum [26]	0.007	0.000007
Seattle, Washington mean	0.003	0.000003
Seattle, Washington Minimum	0	0

[22] RPP-ENV-48231, *Second Tier Review Petition for the Operation of the 241-SY, 241-AP, and 241-AY/AZ Ventilation Systems* lists this maximum inconsistently in several places: 7.8E-08 μg/m^3 on p. 19, 7.7E-08 μg/m^3 on p. 20, and 8.5E-08 μg/m^3 on p. 31.

[23] Page 13, Figure 4 of TOC-ENV-NOC-0008

[24] TOC-ENV-NOC-0008

[25] De Mora *et al.*, 1993

[26] Prestbo *et al.*, 1996

Environmental Fate

USDOE/WRPS cited estimates of atmospheric lifetime of DMM in the range of 1 to 100 hours. Gas phase DMM may photodegrade or oxidize to MMM. DMM reacts with atmospheric hydroxyl, chloride and nitrate ions and with ozone.[27] The products can be taken into cloud droplets.[28,29]

Exposure Scenarios and Doses

Based on AERMOD output, the MIBR and MIRR locations are to the west and south of the site. USDOE/WRPS cited an earlier analyses of land uses in the area surrounding Hanford.[30] The maximally impacted areas are zoned for public road right-of-way and agricultural use.[31]

USDOE/WRPS estimated MIBR total dose attributable to NCSS emissions would be 6.9E-07-μg/Kg bw-day, based on a total inhalation dose of 2.2E-08-μg/Kg bw-day and an ingestion dose of 6.7E-07-μg/Kg bw-day. Similarly, they estimated the NCSS-attributable dose at the MIRR would be 6.9E-08- μg/Kg bw-day (one ten as much as the MICR).

Health Risks in each Scenario

The HIA states that the NCSS-attributable HQ at the MIBR is 2.6E-07, and that the NCSS-attributable HQ at MICR is 2.4E-08. These HQs are many orders of magnitude less than one. This indicates DMM emissions from each proposed NCSS will not pose any threat to the public.

Adequacy of the USDOE/WRPS NCSS Assessment

Ecology reviewed the HIA to determine if the methods and assumptions used were appropriate for assessing and quantifying the health risks to the surrounding community. There were some notable omissions:

Emissions: The Notice of Construction for the Operation of the Core Sampling System in High Purge Gas Mode[32] and the accompanying HIA found that USDOE/WRPS did not clearly

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[27] Literature cited in TOC-ENV-NOC-0008 Table 6

[28] Brosset C, Lord E. 1995. Methylmercury in ambient air: Method of determination and some measurement results. *Water Air Soil Poll.* 82:739–50

[29] Lee YH, Wangberg I, Munthe J. 2003. Sampling and analysis of gas-phase methylmercury in ambient air. *Sci. Total Environ.* 304:107–13

[30] RPP-ENV-48231, *Second Tier Review Petition for the Operation of the 241-SY, 241-AP, and 241-AY/AZ Ventilation Systems.*

[31] RPP-ENV-48231 (shows land use and zoning for the surrounding counties Benton, Franklin, and Grant Cos.)

disclose whether or not simultaneous emissions from both samplers had been estimated. However, Phil Gent and the Washington Department of Health have received assurance from USDOE/WRPS only one sampler is being built. Nonetheless, even if two samplers were built and operated at the same time, causing DMM emissions as much as twice as much as with one sampler, the emissions would still be trivial. In light of there being only one sampler, with operation time limited to 300 hours per year in total, the emissions are as modeled. Mr. Gent will note in the Approval Order that only one sampler can be used.

Modeling: Ecology reviewed the AERMOD modeling input and output files but did not find that all significant figures had been included in the modeled ambient air concentrations output report. This initial lack of AREMOD data in significant figures rendered the application incomplete and delayed Ecology's risk evaluation. Ecology received the missing data from USDOE/WRPS on November 20, 2014. The next day, Clint Bowman checked the data and confirmed the peak air concentration/location and the peak deposition/location were the same as those listed in the HIA.

DMM environmental transport and fate: Although DMM is slightly soluble in water and its atmospheric reaction products are soluble, the HIA did not examine wet deposition. As part of his Second Tier review, Clint Bowman stated wet deposition would be trivial. Therefore Ecology concludes wet deposition and the consequences of wet deposition would not affect exposure estimates significantly. Omission of exposure via dermal exposure to- and by ingestion of water, or by uptake via ingestion of soil, plants or animals exposed through wet deposition are deemed insignificant. DMM exposure via soil ingestion was not included in the HIA; however uptake by that route will also be trivial. Due to DMM's greater volatility than that of elemental mercury (~8300 Pa @ 25°C vs. ~241 Pa @ 25°C), elimination of DMM from soil is likely to occur more quickly than the rate used for calculation of soil concentrations, therefore DMM plant uptake and rates of uptake resulting from ingestion of pants, which are trivial when calculated using the exaggerated soil concentrations, will in fact be even less.

Exposure to existing ambient DMM: USDOE/WRPS did not estimate increased risk from exposure to both project and background DMM in the current HIA in accordance with 173-460-090(5).

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[32] Criteria & Toxics Air Emissions Notice of Construction for the Operation of the Core Sampling System in High Purge Gas Mode. TOC-ENV-NOC-0004, Rev. 1

The Maximally Impacted Commercial Receptor: USDOE/WRPS identified appropriate receptors to capture the highest exposures for residential and fenceline receptors, but they did not disclose the location of the MICR. They asserted that "*The nearest resident is impacted more than the highest commercial receptor so the resident scenario is assumed to be more conservative*."[[33]] This assertion may be accepted if another USDOE/WRPS assertion is true - specifically that "modeling has been performed to assess [onsite] worker exposure (See *RPP-RPT-47978, Atmospheric Modeling of the Stack Heights for the AP and SY Exhausters, 2010*). Workers at locations enclosed within the controlled access boundary of the Hanford site (such as those at US Ecology and LIGO) have been deemed exempt from inclusion in risk assessment under Second Tier Review authority: A decision made during a meeting about the process for Second Tier Review of 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System.[[34]]

Exposure durations: 30 and 70 year intervals are much longer than the window of fetal vulnerability to developmental neurotoxicity. Ecology's recalculation using physiologically possible parameters did not result in doses notably different than those described in the HIA. Exposure for three months (the duration of the first trimester of fetal life) is appropriate; however, the maximum 24-hr inhalation and deposition rates were assumed to last for 30 and 70 years so shorter intervals of high exposure weren't diluted into longer term averages. Thus, exposures would not be underestimates. Also, USDOE/WRPS state that operation of the NCSSs will not continue for more than 40-years.[[35]]

Potential for harm from new exposures together with permitted and background exposures

USDOE/WRPS did not estimate exposure to background DMM in the current HIA, but in accordance with 173-460-090(5), Ecology considered background concentrations of DMM as part of this Second Tier review. Before it came to light that only one NCSS will be permitted, Ecology added two simultaneous NCSSs impacts, together with previously permitted emissions impacts from the 241-SY, 241-AP and 241-AY/AZ ventilation systems, and together with Antarctica background — all as concurrent exposures. These calculations are shown in Table 2.

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[33] TOC-ENV-NOC-0008 p. 12

[34] Upgrades (See email: From: Miera, Felix R Jr; Sent: Monday, July 19, 2010 1:57 PM; To: Ogulei, David (ECY); Hendrickson, Douglas (ECY); Cc: Fletcher, Thomas W; Bowser, Dennis W; Rumburg, Brian P; Wheeler, Isabelle; Donnelly, Jack W; Subject: DRAFT LETTER & PROCESS OUTLINE).

[35] TOC-ENV-NOC-0008 p.20

Table 2. Receptor DMM exposure estimates

		MIBR	MIRR [36]
NCSS-attributable maximum inhalation exposure (µg/Kg body weight- day)	a	1.40E-09	3.40E-11
times 2[37]	2a	2.80E-09	6.80E-11
NCSS-attributable maximum ingestion exposure (µg/Kg bw-day)	b	2.50E-08	2.40E-09
times 2	2b	5.00E-08	4.80E-09
maximum total NCSS-attributable exposure (µg/Kg bw-day)	2a+2b	5.3E-08	4.9E-09
Ingestion / Inhalation exposures ratio	b/a	17.9	70.6
Background source inhalation exposure based on average Antarctica DMM conc. (µg/Kg bw-day) [38]	c	1.08E-05	1.08E-05
Background source ingestion (µg/Kg bw-day) given project ingestion / inhalation ratios applied to average Antarctica DMM conc.	cb ÷ a	1.93E-04	7.62E-04
Background source exposure (µg/Kg bw-day) ingestion + inhalation assuming average Antarctica atmospheric DMM conc.	c+(cb ÷ a)	2.04E-04	7.73E-04
Inhalation attributable to Operation of the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System (µg/Kg bw-day)	d	2.20E-08[39]	NR[40]

[36] *"a person living at the site of the highest residential exposure to the west of the 241-SX Tank Farm for 70 years. The peak 24-hour concentration and deposition values were used to assess the 70-year exposure."*

[37] Double the impacts from one NCSS since two might operate simultaneously at times.

[38] Antarctica had the highest average reported atmospheric DMM in available literature. To estimate high end but conceivable risk, Ecology used the average DMM concentration in Antarctica to obtain hazard quotients. The average Seattle DMM concentration is reportedly more than 13-times lower that average in Antarctica. More than 99% of the exposure would be due to background DMM.

[39] RPP-ENV-48231, Rev. 0. Part 7 ESTIMATION OF EXPOSURE

[40] Not reported

		MIBR	MIRR [36]
Ingestion attributable to operation of the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System (µg/Kg bw-day)[41]	f	6.70E-07[42]	NR[43]
Total exposure attributable to operation of the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System (µg/Kg bw-day)	d+f	6.92E-07	6.90E-08[44]
Total ingestion (µg/Kg bw-day)	2b+(cb ÷ a)+f	0.00019	0.00076
Total inhalation (µg/Kg bw-day)	2a+c+d	1.08E-05	1.08E-05
Total exposure (µg/Kg bw-day)	2a+2b+c+(cb ÷ a)+d+f	2.04E-04	7.73E-04
RfD (µg MMM/Kg bw-day)[45]	RfD	0.1	
Project Hazard Quotient [46]	(2a+2b) ÷ RfD	5.3E-07	4.9E-08
Total exposure Hazard Quotient (NCSS project + 241-SY, 241-AP, and 241-AY/AZ Tank Ventilation + background) ÷ MMM RfD	Total exposure ÷ RfD	2.04E-03	7.73E-03

Uncertainty Characterization

'Uncertainty' may be defined as imperfect knowledge concerning present and future conditions of a system. In risk assessments undertaken in support of regulatory decisions, many uncertainties are encountered. Recognition of these uncertainties allows the risk manager to assess the overall strength of information on which decisions must be based.

As in any risk assessment, the NCSS assessment involved incomplete scientific information: emission rate estimates, air dispersion and fate modeling, and resulting environmental

[41] Adding the maximum impacts of operation of the 241-SY, 241-AP, and 241-AY/AZ Tank vents.

[42] RPP-ENV-48231, Rev. 0. Part 7 ESTIMATION OF EXPOSURE

[43] Not reported

[44] RPP-ENV-48231, Rev. 0. Part 7 ESTIMATION OF EXPOSURE

[45] *Toxicological Effects of Methylmercury*. Committee on the Toxicological Effects of Methylmercury, Board on Environmental Studies and Toxicology, National Research Council. 2000. 368 pages.

[46] Hazard Quotient = Dose DMM (ug/Kg body wt. day) ÷ RfD

concentrations, exposures and dose estimates, also assumptions about dose-response relationships and resulting estimates of the possibilities of different types of health impacts. USDOE/WRPS evaluated uncertainties in the assessment.[47] Overall risk uncertainties are summarized in Table 3. The uncertainties in specific aspects of the assessment are noted following the table.

Table 3. Summary of how uncertainties may affect the estimates of health risk
Table 3. Summary of how uncertainties may affect the estimate of health risk

Source of Uncertainty	Potential Effect
Emissions estimates	Likely to overestimate average exposures and consequently their risks because worst tanks used as the source terms in dispersion modeling.
Concentration modeling	Possibly overestimate or underestimate risk.
Deposition modeling	Dry deposition estimate may overestimate or underestimate risk. Lack of wet deposition approximation may lead to slight risk underestimate.
Background concentrations	Possibly overestimate or underestimate risk.
Plant uptake	Possibly overestimate or underestimate risk.
DMM Fate	Possibly overestimate or underestimate risk.
Toxicity of low dose DMM	Likely to overestimate risk.
Exposure Scenarios and Receptors assumptions	Likely to overestimate risk.

Emissions Uncertainty and variability

Emissions rate and frequency uncertainties include measurement uncertainty and process variability. The emissions factors used to estimate emission rates from the proposed NCSS are estimates based on concentrations measured tank head spaces. It was assumed that the tank farms had DMM at the highest concentration found in any of the tanks, but only ten of the 177 tanks have been found to have DMM. Also, the assumption that NCSS operation will be continuous for 40 years is an exaggeration. USDOE/WRPS state that core sampling in high

[47] Part 9 (p.27) of *Second Tier Review Petition for the Operation of the Core Sampler in High Purge Gas Mode. TOC-ENV-NOC-0008. Washington River Protection Solutions LLC, for United States Department of Energy, Office of River Protection, Richland, Washington.* Received August 14, 2014

purge gas mode is a short duration activity. They state the portable exhauster will be turned on only when the purge gas is turned on, the estimated total hours of operation for up to two samplers is 300 hours per year. Given that operation of only one sampler will be permitted, precluding the simultaneous operation of two won't occur, the above operation scenario is more conservative than necessary. These continuous operation and emissions assumptions result in overestimation of consequent exposures.

TAP Concentration Modeling Uncertainties

TAP concentration modeling uncertainty results from measurement variability and uncertainty in future meteorology and the applicability of past meteorological conditions in the current analysis. Additionally, TAP concentration uncertainty arises from uncertainty in the precision and accuracy of the air pollutant dispersion model used: EPA's AERMOD and its associated pre- and post-processors. Even if the DMM emission rate source term is accurate, the results of concentration modeling are just as likely to be underestimates as to overestimates. These uncertainties in air concentrations propagate and add to overall uncertainty in modeled deposition estimates.

Existing nearby TAP Source Uncertainties

The uncertainties in the current health risk assessment are the same those encountered in the assessment of DMM emitted by the nearby permitted operation of the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System.

Background TAP Concentration Estimates Uncertainties

Due to very limited data, there are large uncertainties in background DMM concentrations. The uncertainty results in large differences in DMM concentrations in different parts of the world such as in Seattle relative to Antarctica. An atmospheric DMM monitoring study in Antarctica found 0.63-ng/m3 on the most extreme occasion. In contrast, in a monitoring study in Seattle, 0.007-ng/m3 was the maximum concentration: Far less than the Antarctica. It is not clear if the Seattle and/or Antarctica reports are accurate. The background DMM concentration in the present assessment may be an underestimate or overestimate the actual concentration. Although there are no available atmospheric DMM monitoring data for the Hanford area, it is likely background concentrations there are more similar to those in Seattle than in Antarctica.

Deposition Uncertainty

The HIA did not examine wet deposition. Not accounting for wet deposition might have led to a slightly lower estimate of risk than justified. However, Ecology concludes this omission did not affect exposure estimates significantly.

Plant Uptake and Consumption Uncertainty

Further uncertainly arises due to the plant uptake factor USDOE/WRPS used, which they based on a soil concentration derived from the octanol water partition coefficient (Kow) and soil organic carbon partition coefficient (Koc) for inorganic mercury not for DMM.[[48]] This likely underestimated the root uptake factor for leafy vegetables. This would lead to a slightly lower estimate of risk than justified.

Fate Uncertainty

The persistence of DMM in the environment is proportional to potential exposure time. Reactions of DMM with Cl^-, OH^-, and NO_3^- are the most dominant in the atmosphere. Given the concentrations of these radicals, the atmospheric lifetime of DMM is likely to range from roughly 1 to 100 hours.[[49]] The broad interval indicates substantial uncertainty. In addition, a soil half-life of DMM estimate was not found in available scientific literature. Therefore, USDOE/WRPS used the soil half-life of value for inorganic mercury. This most likely overestimated the soil elimination constant, yielding unrealistically prolonged DMM persistence.

Exposure Uncertainty

Exposure uncertainty results partly from uncertainty in atmospheric DMM concentrations arising not only from the new source(s) but also from existing nearby sources and the regional background level. Exposure uncertainty also results from potential inaccuracies of the assumptions about how much time people will spend in various locations, and about variation in DMM intakes. The intake uncertainties result from uncertainties in deposition estimates, plant uptake rates and subsequent consumption by humans. The rate of plant uptake of DMM is likely to be greater than the rate of inorganic mercury uptake but USDOE/WRPS used the later rate since the former is unknown. There is also substantial uncertainly in the final fate of DMM in the environment. Due to the greater volatility DMM than that of inorganic mercury, soil elimination of DMM is likely to occur more quickly than USDOE/WRPS calculated when using the inorganic mercury rate. Together, these uncertainties likely overestimate the levels of exposure what will occur.

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[48] DMM Log Kow 2.59. But Hg ° Kow 4.15 (Nilsson A, Hakanson, L. *Hydrobiologia* 1992, 235/236, 675-83) Hg ° Log Kow 0.62. And although no one may have published a Koc for DMM, Kocs for lipophilic chemicals are correlated with their Kows. The correlation is Koc = 0.35 Kow (subject to variation by a factor of 2.5 in either direction) [Seth R, Mackay D, Muncke J. 1999. Estimating the Organic Carbon Partition Coefficient and Its Variability for Hydrophobic Chemicals. *EST* 33(14):2390–4]. Thus the Koc for DMM can be estimated as 1.45 (0.58 to 3.63) or Log Koc 0.16 (-0.24 to 0.56).

[49] Sommar J, Hallquist M, Ljungstrom E, Lindqvist O. 1997. On the Gas Phase Reactions between Volatile Biogenic Mercury Species and the Nitrate Radical. *J Atmos Chem* 27: 233-47

Receptor Uncertainties

It is impossible to know the lengths of time that people will actually be exposed to DMM emissions. USDOE/WRPS assumed the maximum exposure could be a continuous for a hypothetical resident at the location along Highway 240 where the maximum DMM concentration is most likely to occur. USDOE/WRPS assumed this resident would occupy the location for 30 years. USDOE/WRPS also assumed the hypothetical Highway 240 location resident would routinely consume homegrown produce. The most life-stage is likely to occur during the prenatal period. Less than 1 percent of the overall human population is in that life stage. Together, these conditions for receptor exposure are extremely unlikely. The resulting calculation of risk based on these conditional scenarios therefore overestimates health risk.

Uncertainty in DMM Toxicity

The potential neurotoxic effects of elevated exposure to DMM are fairly certain; however, uncertainty arises from potential inaccuracies in the MMM RfD used in the NCSS risk characterization. Derivation of the RfD for MMM involved application of uncertainty factors to data from epidemiological studies. Further, the paucity of low-dose effects data for DMM prevents developing a RfD for it in the ordinary way. Available evidence suggests DMM is slightly less toxic than MMM but the data needed to confirm or refute this are sparse. USDOE/WRPS's characterization of potential neurotoxicity risk involved comparisons of possible exposures to the RfD for MMM under the assumption that its potency is equal to that of DMM. It is likely that use of the MMM RfD in this assessment led to a slightly higher estimate of DMM health risk than justified.

Conclusions and Recommendation

Second Tier Review Processing and Approval Criteria

In order for Ecology to review a Second Tier petition, each of the following regulatory requirements under Chapter 173-460-090(2) must be satisfied:

(a) The permitting authority submits to Ecology a Preliminary Order of Approval that addresses all applicable New Source Review issues with the exception of the outcome of the Second Tier Review, State Environmental Policy Act review, Public Notification, and Prevention of Significant Deterioration Review; and

(b) The emission controls contained in the Preliminary Order of Approval represent at least tBACT; and

(c) The applicant has developed a Health Impact Assessment Protocol that has been approved by Ecology;

(d) The ambient impact of the emissions increase of each TAP that exceeds Acceptable Source Impact Levels has been quantified using refined air dispersion modeling techniques as approved in the Health Impact Assessment Protocol; and

(e) The petition contains a Health Impact Assessment conducted in accordance with the approved Health Impact Assessment Protocol.

Each of these requirements has been met as follows.

Second Tier Review Processing Requirements Approval

The project review team has reviewed the HIA:

(a) Acting as the "permitting authority" for this project, the Second Tier Review Engineer at Ecology's Richland Field Office (Ecology-RFO) submitted a preliminary Notice of Construction Order of Approval for the project to Ecology HQ on 10/22/2014. Ecology-RFO determined that other conditions for processing the Notice of Construction Order of Approval have been met. Delays in preparing the draft were a result of conversations with USDOE/WRPS about conditions of the permit. USDOE/WRPS requested changes in tracking hours of operation of the sampler (they wanted a straight forward 300 hours per year in high purge mode regardless of exhauster system in use). These changes necessitated completely rewriting the order twice.

(b) Ecology-RFO was responsible for establishing Best Available Control Technology (BACT) and tBACT (Best Available Control Technology for Toxics for the NCSS. The Preliminary Order of Approval issued by Ecology-RFO indicates these controls (a HEPA filter and a 20

foot stack [[50]]) constitute tBACT for NCSS TAP emissions, and that the emissions estimates presented in the HIA represent reasonable estimates of the project's emissions.

(c) Given their previously demonstrated abilities in modeling and writing a HIA[[51]], Ecology HQ waived the requirement for USDOE/WRPS to submit a HIA protocol for NCSS.[[52]]

(d) Using refined air dispersion modeling techniques USDOE/WRPS has quantified the ambient impact of the emissions increase of the only TAP that exceeds its ASIL.[[53]]

(e) A Second Tier Review petition containing a HIA[[54]] was received by Ecology on Sept 8, 2014. The HIA, in combination with information in the USDOE/WRPS HIA of the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System Upgrades, which was conducted in accordance with an approved HIA protocol[[55]], contained sufficient information to assess the health risks posed by new TAP emissions.

Second Tier Review Approval Criteria

As specified in WAC 173-460-090(7), Ecology may recommend approval of a project that is likely to cause an exceedance of ASILs for one or more toxic air pollutants (TAPs) only if:

(a) Ecology determines that the emission controls for the new and modified emission units represent tBACT.

(b) The applicant demonstrates that the increase in emissions of TAPs is not likely to result in an increased cancer risk of more than one in one hundred thousand.

(c) Ecology determines that the non-cancer hazard is acceptable.

Each of these criteria has been met as follows.

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[50] HEPA treatment of emitted mass alone may not reduce onsite concentrations near the exhausters to tolerable levels because DMM is a volatile liquid at ambient temperatures. It may readily evaporate from the filter; however, emission through a 20-foot stack may result in sufficient dilution that onsite bystanders will not be harmed.

[51] Draft HIA Protocol for the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System Upgrades (circa December 14, 2009).

[52] Email from Clint Bowman; Sent Tuesday, August 12, 2014 to Matt Kadlec; Cc: Jeff Johnston; Re: Upcoming project at Hanford.

[53] Ecology's air dispersion modeler found the refined modeling conducted by USDOE/WRPS, and submitted by them in complete form November 19, 2014, to be acceptable. Clint Bowman verbally confirmed this to Matt Kadlec on November 20, 2014.

[54] The HIA received by Ecology on August 14, 2014: *Second Tier Review Petition for the Operation of the Core Sampler in High Purge Gas Mode. TOC-ENV-NOC-0008. Washington River Protection Solutions LLC, for United States Department of Energy, Office of River Protection, Richland, Washington.*

[55] Draft HIA Protocol for the 241-SY, 241-AP, and 241-AY/AZ Tank Farm Ventilation System Upgrades (circa December 14, 2009).

Second Tier Review Approval

(a) Ecology's Second Tier review engineer reviewed the USDOE/WRPS NOC submittal and found that the controls proposed satisfy t-BACT.

(b) The applicant demonstrated DMM is the only TAP that will be emitted that will produce an offsite concentration greater than its ASIL. Because DMM is not suspected to be carcinogenic, exposure to even the maximum concentration offsite concentration will not increase cancer risk.

(c) Ecology has determined that the non-cancer hazard is acceptable. There is no conceivable risk of neurotoxicity attributable to the NCSS.

Treatment of the tank wastes at Hanford is a benefit to the environment to the health of the people in the surrounding communities now and in future generations. The project review team concludes the HIA presents an appropriate estimate of potential increased health hazards posed by NCSS TAP emissions. There is no evidence the DMM emissions – alone or in combination with other DMM sources - could pose health hazards. Exposures to these new DMM emissions together with exposure to emissions already permitted at Hanford and to existing background concentrations are extremely unlikely to result in neurotoxicity hazards. The highest conceivable hazard quotient at a publicly accessible location, a trivial 0.0045, might occur at a point along Highway 240 a person who remained in that same location a full day, which is unlikely. Because the increase in neurotoxicity hazard attributable to the USDOE/WRPS does not exceed an acceptable level of non-cancer hazard allowed by a Second Tier review, and because there are no appreciable cancer hazards likely to result, the project can be approved under WAC 173-460-090.

At this time, the expected start of the Public Comment Period is in late November, 2014.

List of Acronyms and Abbreviations

AERMOD	Air dispersion model
ASIL	Acceptable Source Impact Level
BACT	Best Available Control Technology
C	Celsius
Conc.	Concentration
DMM	Dimethyl mercury
Ecology	Washington State Department of Ecology
Ecology-RFO	Washington State Department of Ecology–Richland Field Office
EPA	United States Environmental Protection Agency
g/m^2	Grams per Square Meter
HIA	Health Impact Assessment
HQ	Hazard Quotient

hr	Hour
Max.	Maximum
MIBR	Maximally Impacted Boundary Receptor
MICR	Maximally Impacted Commercial Receptor
MIRR	Maximally Impacted Residential Receptor
$\mu g/m^3$	Micrograms per Cubic Meter
µg/Kg bw-day	Micrograms per kilogram of body weight per day
MMM	Monomethyl Mercury
ng/m^3	Nanograms per Cubic Meter
NOC	Notice of Construction
NRC	National Research Council
RfD	Reference Dose
SQER	Small Quantity Emission Rate
TAP	Toxic Air Pollutant
TAPs	Toxic Air Pollutants
tBACT	Best Available Control Technology for Toxics
TWA	Time-weighted Average
TWINS	Tank Waste Information Network System
USDOE	United States Department of Energy
USDOE/WRPS	USDOE and Washington River Protection Solutions, Llc
WAC	Washington Administrative Code
WRPS	Washington River Protection Solutions, Llc.