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Potential Dimethylmercury Concentration in Water and Organic Condensate

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Abstract: This document bounds potential dimethylmercury concentration in water or organic condensate that might form in ventilation systems or cooler tank regions. Dimethylmercury concentrations were extremely low and would be below drinking water standards in the water condensate.

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POTENTIAL DIMETHYLMERCURY CONCENTRATION IN WATER AND ORGANIC CONDENSATES

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

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POTENTIAL DIMETHYLMERCURY CONCENTRATION IN WATER AND ORGANIC CONDENSATES

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CONTENTS

TABLES

1.0 OBJECTIVE

Mercury and dimethylmercury have been detected in the headspaces of several waste tanks at the Hanford Site. This report examines the concentrations of dimethylmercury that might exist in organic liquid or water condensed in the cooler regions of risers, transfer pipes and ventilation systems. Dimethylmercury headspace data are currently available for four C Farm tanks (241-C-103, 241-C-104, 241-C-107, and 241-C-109); therefore, calculations and conclusions in this report are limited to C Farm until results from other tank farms are evaluated.

2.0 BACKGROUND

Dimethylmercury, which has a gram molecular weight (MW) of 230, is a liquid under ordinary conditions with a boiling point of about 95 °C at atmospheric pressure (760 torr). The vapor pressure of pure liquid dimethylmercury is 59 torr at 25 °C. It is only slightly soluble in water and many sources simply indicate that its solubility in water is negligible. TR-2003-00238, *Studies of Mercury in High Level Waste Systems*, shows that the concentration of dimethylmercury in water can be as high as 14 mg/L at ambient temperature. In contrast, dimethylmercury is quite soluble in many organic solvents. For comparison, metallic mercury has a boiling point of about 356 °C, its solubility in water is about 0.06 mg/L at 20 °C and 0.25 mg/L at 50 °C, and has negligible solubility in organic solvents.

Dimethylmercury, like mercury, is ubiquitous in the environment and there is vast literature on its rather facile formation from inorganic mercury compounds and naturally-occurring organic compounds. When it is carefully sought, it is usually found. For example, "Occurrence of Dimethylmercury in Organic Solvents" (Liang et al. 2004) indicates that dimethylmercury has been detected (0.075 mg/L) in "pure" methanol.

At the Hanford Site, mercury is found as hydrated mercuric oxide and mercuric hydroxide in the solid waste layers. These solids are in equilibrium with the related soluble forms in the associated aqueous liquid as illustrated for mercuric hydroxide:

$$\begin{gathered}\mathrm{Hg(OH)_2(s)} \leftrightarrows \mathrm{Hg(OH)_2(aq)}\\ \mathrm{Hg(OH)_2(aq)} \leftrightarrows \mathrm{Hg(OH)^+(aq)} + \mathrm{OH^-(aq)}\\ \mathrm{Hg(OH)^+(aq)} \leftrightarrows \mathrm{Hg^{2+}(aq)} + \mathrm{OH^-(aq)}\end{gathered}$$

Aqueous mercuric ion is in equilibrium with metallic mercury and mercurous ion and, if the solubility of mercury is exceeded, mercury will separate as a second liquid phase as shown in the next equations:

$$\begin{gathered}\mathrm{Hg^{2+}(aq)} + \mathrm{Hg(aq)} \leftrightarrows \mathrm{{}^+HgHg^+(aq)}\\ \mathrm{Hg(aq)} \leftrightarrows \mathrm{Hg(l)}\end{gathered}$$

Dimethylmercury is formed in waste by the reactions of inorganic mercury compounds such as mercuric hydroxide with organic constituents including compounds as simple as acetate ion (TR-2003-00238).

Dimethylmercury will be retained in the waste in the same manner as the other volatile and semivolatile organic compounds and will be distributed between the organic and aqueous phases. Inasmuch as its solubility in the organic phase is much higher than in the aqueous phase, the substance will preferentially accumulate in organic phases:

$$\mathrm{Hg(CH_3)_2(aq)} \leftrightarrows \mathrm{Hg(CH_3)_2(org)}$$

Dimethyl mercury will evolve into the headspace by one of the several mechanisms identified in PNNL-14831, *Overview of Hanford Site High-Level Waste Tank Gas and Vapor Dynamics*, such as by passage from one of the condensed liquid phases into bubbles of retained gas which eventually migrate to the headspace.

$$Hg(CH_3)_2(aq) \leftrightarrows Hg(CH_3)_2(vapor)$$
$$Hg(CH_3)_2(org) \leftrightarrows Hg(CH_3)_2(vapor)$$

3.0 ANALYSIS METHOD

When volatile or semivolatile organic compounds evolve from the liquid and solid layers of the waste, they mix rapidly with the other gaseous constituents in the headspace and eventually are released from the tank (PNNL-14831). However, condensation may occur on the cooler surfaces within the waste tank or ventilation system. If water will condense on a cold surface, then the less volatile organic compounds such as the paraffinic hydrocarbons will also condense. Water condensates contain substances such as ammonia and water-soluble organic compounds including methanol, ethanol, formaldehyde, acetaldehyde, acetone, and 2-butanone. Organic condensates also contain these compounds, but are predominantly composed of volatile and semivolatile hydrocarbons and other carbon and oxygen containing compounds with six or more carbon atoms.

Two different physical situations are examined in this report, (1) the concentration of dimethylmercury in a organic/water droplet at equilibrium with the headspace concentration, and (2) the maximum concentration of dimethylmercury in an organic/water droplet hypothetically condensed instantaneously from the vapor phase (i.e., non-equilibrium).

3.1 EQUILIBRIUM

Dimethylmercury in the headspace vapor would achieve equilibrium with dimethylmercury in droplets or films of water or with dimethylmercury in droplets or films of organic compounds that have condensed in the cool regions of risers and ventilation lines. These steady state conditions justify the application of conventional thermodynamic models for the calculation of the equilibrium concentration of dimethylmercury in the condensed liquids when the concentration of dimethylmercury in the vapor is known.

The vapor pressure of an organic compound, such as dimethylmercury, above a dilute organic solution that is in thermodynamic equilibrium with the surrounding vapor is determined by Raoult's law

$$p = xp^0 \tag{3-1}$$

where p is the partial pressure of dimethylmercury in the vapor, x is the mole fraction of the compound in the liquid, and p^0 is the vapor pressure of liquid dimethylmercury at the selected temperature.

When the concentration of dimethylmercury in the gas phase is known, its partial pressure can be evaluated from the ideal gas law

$$p = \frac{nRT}{V} \tag{3-2}$$

where p is the partial pressure in atmospheres, n is the number of moles, R is the gas constant, T is the temperature in Kelvin, and V is the volume in liters. For convenience, it is assumed that the temperature in the region where the liquid has condensed is 298 K (25 °C).

3.2 NON-EQUILIBRIUM

A maximum concentration can be calculated if it is assumed that the water and the organic compounds from the headspace vapor simply condense on the cool surface and that dimethylmercury in the vapor is dissolved either in the condensed organic liquid or in the condensed water. In this circumstance, the dimethylmercury concentration in the condensate is equivalent to

$$\text{Dimethylmercury concentration} = \frac{\text{mg of dimethylmercury in headspace vapor}}{\text{mg of organic or water condensed from headspace vapor}} \tag{3-3}$$

4.0 ASSUMPTIONS

Some parameters and effects do not lend themselves to easy quantification; therefore, conservative assumptions were necessary to estimate potential dimethylmercury concentration in a hypothetical organic or water droplet.

Non-equilibrium is conservatively assumed to produce a bounding dimethylmercury maximum concentration. Dimethylmercury is hypothetically entirely condensed from the vapor phase; however, such a state would be unlikely in a droplet or thin film of organic/water.

The organic carbon in the tank headspaces is a complex mixture of lighter compounds that have relatively high vapor pressures (e.g., propane) and semivolatiles (e.g., tridecane, tributyl phosphate) that have low vapor pressures. Therefore, only 50% (by mass) of the organic compounds is assumed to condense.

The molecular weight of the organic compounds in a droplet is assumed to be equivalent to heptane, about 100 g/mole. The average molecular weight is assumed to be 100 g/mole on the basis of the wide distribution of abundant compounds in the liquid ranging from small molecules such as methanol (MW = 32) to much larger paraffinic hydrocarbons such as tridecane (MW = 184).

Tanks with dimethylmercury concentrations less than the detection limit were assigned a concentration equal to the detection limit.

No Henry's law coefficient for dimethylmecury was readily available in the open literature. Equilbrium concentrations were calculated using the dimethylmercury distribution coefficient between air and water reported in TR-2003-00238, which was 0.31.

5.0 INPUT DATA

Table 1 summarizes the measured dimethylmercury concentrations. Samples were analyzed at Frontier Geosciences Inc. and the results electronically transmitted to CH2M Hill. Table 2 shows the headspace average summation of organic vapor concentrations from the Tank Characterization Database accessed through the Tank Waste Information Network (TWINS 2004). The partial pressure of dimethylmercury at 25 °C is 59 torr.

Table 1. Total Mercury and Dimethylmercury Headspace Sampling Results.

Tank	Sample Date	Total Mercury (mg/m^3)	Dimethylmercury (mg/m^3)
241-C-103	09/20/2004	4.8E-02	4.0E-05
241-C-103	09/20/2004	5.0E-02	4.2E-05
241-C-104	09/21/2004	1.0E-01	1.1E-04
241-C-104	09/21/2004	1.2E-01	1.1E-04
241-C-107	09/22/2004	3.4E-02	<2.4E-06
241-C-107	09/22/2004	2.6E-02	<1.9E-06
241-C-107	09/22/2004	3.0E-02	<1.9E-06
241-C-109	09/07/2004	2.6E-02	<1.7E-06
241-C-109	09/07/2004	2.1E-02	<1.9E-06

Table 2. Average Summation of Organic Vapor Headspace Concentrations.

Tank	Organic Carbon (mg/m^3)
241-C-103	2139
241-C-104	25
241-C-107	5.6
241-C-109	0.9

6.0 RESULTS

6.1 EQUILIBRIUM

6.1.1 Organic Condensate

The results for tank 241-C-104 are used to illustrate the calculation. The partial pressure in the headspace gas is obtained from the ideal gas law:

$$p = \left(\frac{1.1 \text{ x } 10^{-4} \text{ mg/m}^3}{230{,}000 \text{ mg/mol}} \right) \left(8.314 \text{ m}^3 \cdot \text{Pa/mol} \cdot \text{K}\right) \left(298 \text{ K}\right) \left(\frac{760 \text{ torr}}{101325 \text{ Pa}} \right)$$

$$p = 8.9 \text{ x } 10^{-9} \text{ torr}$$

Raoult's Law is used to evaluate the mole fraction in the condensed organic liquid:

$$x = \frac{p}{p^0} = \frac{8.9 \text{ x } 10^{-9} \text{ torr}}{59 \text{ torr}} = 1.51 \text{ x } 10^{-10}$$

The condensed organic liquid is a mixture of compounds with many different molecular weights. The average molecular weight was assumed to be as 100 g/mole. The mole fraction of dimethylmercury is then equal to the moles of dimethylmercury in 1 g of the liquid, and the concentration can be determined by multiplication by the molecular weight.

$$\text{Dimethylmercury in 1 g of organic} = \left(1.51 \text{ x } 10^{-10}\right) \left(\frac{2.30 \text{ x } 10^{8} \ \mu\text{g/mole}}{100 \text{ g/mole}} \right) = 3.5 \text{ x } 10^{-4} \mu\text{g/g}$$

Results for the four tanks for which data are now available are shown in Table 3.

Table 3. Concentration of Dimethylmercury in an Organic Liquid.

Tank	Dimethylmercury Headspace Concentration (mg/m^3)	Dimethylmercury partial pressure[a] (torr)	Dimethyl Mercury Concentration in liquid[b] (µg/g)
241 C-103	4.0E-05	3.2E-09	1.3E-04
241 C-103	4.2E-05	3.4E-09	1.3E-04
241 C-104	1.1E-04	8.9E-09	3.5E-04
241 C-104	1.1E-04	8.9E-09	3.5E-04
241 C-107	<2.4E-06	1.9E-10	<7.6E-06
241 C-107	<1.9E-06	1.5E-10	<6.0E-06
241 C-107	<1.9E-06	1.5E-10	<6.0E-06
241 C-109	<1.7E-06	1.4E-10	<5.4E-06
241 C-109	<1.9E-06	1.5E-10	<6.0E-06

Notes: [a] Calculated from ideal gas law as discussed in the text.
[b] Calculated by using Raoult's Law with a molecular weight of 100 for the liquid as discussed in the text.

This approach indicates that the concentration of dimethylmercury in an organic droplet in equilibrium with the dimethylmercury in the headspaces of these four tanks ranges from less than 0.0000054 to about 0.00035 µg/g of the organic liquid. Using the highest concentration calculated for 241-C-104, and assuming a drop of organic has a volume of 0.05 mL and a density of 0.7g/mL, then the mass of dimethylmercury in this hypothetical droplet would be 0.0000012 mg.

6.1.2 Water Condensate

In principle, dimethylmercury will also dissolve in water that has condensed in the cool region of an open riser, an open exhaust line, or an open transfer line. Although neither the solubility of dimethylmercury in water nor the Henry's Law constant for dimethylmercury in water have been reported, TR-2003-00238 reported the distribution coefficient for dimethylmercury between air and water is 0.31. The concentration in condensed water that is in equilibrium with the vapor in tank 241-C-104 can be directly calculated from this distribution coefficient.

$$\text{Concentration in water} = \left(\frac{1.1 \times 10^{-4}\,\text{mg}/\text{m}^3}{0.31}\right)\left(\frac{1\ \text{m}^3}{1000\ \text{L}}\right) = 3.5 \times 10^{-7}\,\text{mg}/\text{L}$$

This calculation indicates that the concentration would be about 0.00000035 mg/L. Results for the other waste tanks are summarized in Table 4.

Table 4. Concentration of Dimethylmercury in Water.

Tank	Dimethylmercury Headspace Concentration (mg/m^3)	Aqueous Phase Concentration* (mg/L)
241 C-103	4.0E-05	1.3E-07
241 C-103	4.2E-05	1.4E-07
241 C-104	1.1E-04	3.5E-07
241 C-104	1.1E-04	3.5E-07
241 C-107	<2.4E-06	<7.7E-09
241 C-107	<1.9E-06	<6.1E-09
241 C-107	<1.9E-06	<6.1E-09
241 C-109	<1.7E-06	<5.5E-09
241 C-109	<1.9E-06	<6.1E-09

Notes: *Calculated from using distribution coefficient as described in the text.

The concentrations in water range from less than 0.0000000055 to 0.00000035 mg/L. These concentrations are roughly three orders of magnitude lower than concentrations in the organic liquids (Table 3). This is because thermodynamic factors favor the dimethylmercury dissolution in an organic liquid rather than in water. The equilibrium approach implies that dimethylmercury will preferentially accumulate in the organic droplets. It is interesting to note that the drinking water standard for dimethylmercury is 0.002 mg/L, about 4 orders of magnitude higher than a hypothetical water droplet at equilibrium.

6.2 NON-EQUILIBRIUM

6.2.1 Organic Condensate

For the purposes of this calculation, it is assumed that the semivolatile compounds that are less volatile than dimethylmercury will selectively condense. Specifically, it is presumed that entire amount of dimethylmercury dissolved in 50 weight % of the headspace organic material. The concentration of dimethylmercury in the organic liquid can be calculated from the maximum observed concentrations of dimethylmercury and the average concentration of organic compounds as shown for tank 241-C-104 below. Results for all four C farm tanks are shown in Table 5.

$$\frac{1.1 \times 10^{-4}\,\text{mg/m}^3}{(0.5)(25\ \text{mg/m}^3)(1\ \text{g}/10^6\ \mu\text{g})} = 8.8\ \mu\text{g/g}$$

Table 5. Concentration of Dimethylmercury in a Condensed Organic Droplet.

Tank	Dimethylmercury Headspace Concentration (mg/m^3)	Organic Compounds Headspace Concentration[a] (mg/m^3)	Dimethyl Mercury Concentration in liquid[b] (μg/g)
241 C-103	4.0E-05	2139	3.7E-02
241 C-103	4.2E-05	2139	3.9E-02
241 C-104	1.1E-04	25	8.8E-00
241 C-104	1.1E-04	25	8.8E-00
241 C-107	<2.4E-06	5.6	<8.6E-01
241 C-107	<1.9E-06	5.6	<6.8E-01
241 C-107	<1.9E-06	5.6	<6.8E-01
241 C-109	<1.7E-06	0.9	<3.8E-00
241 C-109	<1.9E-06	0.9	<4.2E-00

Notes: [a]Data from the Tank Characterization Database access through TWINS on December 1, 2004.
[b]Calculated using 50% of the headspace organic concentration as described in the text.

The average estimated concentrations of dimethylmercury in the condensed organic liquid in tanks 241-C-103 and 241-C-104 are 0.042 and 8.8 μg/g of organic liquid. The difference arises not only because different amounts of dimethylmercury were measured in the headspace gas, but also because the amounts of organic material in the headspace gas differ. This complicates the interpretation of the results for tanks 241-C-107 and 241-C-109. The analytical work failed to detect dimethylmercury, but it was established that the concentration of dimethylmercury must be less than the detection limits shown in Table 5. The concentrations of organic material in the headspaces of these tanks are also very small. Consequently, the available information indicates that the concentration of dimethylmercury would be less than 0.68 to 4.2 μg/g of organic liquid, but the actual concentration might be considerably smaller than either of these values.

The concentration of dimethylmercury in a hypothetical organic condensate is larger than the concentration that would be realized under equilibrium conditions. For example, the average concentration of dimethylmercury in an organic liquid for tank 241-C-104 under equilibrium conditions was estimated to be 0.00035 µg/g (Table 3). The average concentration in a hypothetically condensed organic droplet under non-equilibrium conditions was 8.8 µg/g (Table 5).

The results displayed in the Table 5 show the amount of dimethylmercury dissolved in 1 g of liquid so that the values can be conveniently compared, but it is unreasonable to project the deposition of 1 g of organic material in a sealed riser or ventilation pipe. For example, the condensation of 50% of the organic material in a cubic meter of gas from tank 241-C-104 would provide about 0.0125 g of an organic liquid. The volume occupied by the liquid is about 0.03 mL and it would presumably be present as a film on the interior wall of the piping or on the surface of the water that simultaneously condensed from the gas. Moreover, the condensation of the organic material in the vapor would be accompanied by the condensation water as discussed in the next section.

6.2.2 Water Condensate

For completeness, the amount of dimethylmercury that would condense in water in an enclosed riser or ventilation pipe was also considered. If the vapor pressure of water in the warm headspace gas was 25 torr (the vapor pressure of water at about 25 °C) and the vapor pressure of water in the cooled closed riser or pipe was 15 torr (the vapor pressure of water at 15 °C), then approximately 0.5 mole (9 g) of water would condense from a cubic meter of headspace gas that migrated into the cool region. There are 0.00011 milligrams of dimethylmercury per cubic meter in the vapor from tank 241-C-104, its condensation together with water in the same volume of gas would produce a solution that contained

$$\frac{\left(1.1 \text{ x } 10^{-4} \text{mg/m}^3\right)}{\left(9 \text{ g/m}^3\right)\left(1 \text{ L/1000 g}\right)} = 0.012 \text{ mg/L.}$$

For comparison, the Environmental Protection Agency specification for dimethylmercury in drinking water is 0.002 mg/L (Internal Memo TBSP04RJC02, "Meeting Report: Televideo Conference with Savannah River Concerning Mercury and Dimethylmercury"). Table 6 shows the concentration of dimethyl mercury in a hypothetically condensed water droplet for the four C Farm tanks for which data are now available.

Table 6. Concentration of Dimethylmercury in a Condensed Water Droplet.

Tank	Dimethylmercury Headspace Concentration (mg/m^3)	Dimethyl Mercury Concentration in Water* (mg/L)
241 C-103	4.0E-05	4.4E-03
241 C-103	4.2E-05	4.7E-03
241 C-104	1.1E-04	1.2E-02
241 C-104	1.1E-04	1.2E-02
241 C-107	<2.4E-06	<2.7E-04
241 C-107	<1.9E-06	<2.1E-04
241 C-107	<1.9E-06	<2.1E-04
241 C-109	<1.7E-06	<1.9E-04
241 C-109	<1.9E-06	<2.1E-04

Notes: *Calculated using water partial pressure as described in the text.

This calculation implies that the concentration of dimethylmercury in a hypothetically condensed water droplet would be much smaller than the concentrations of dimethylmercury in organic droplets that had been condensed under the same circumstances.

6.3 SAVANNAH RIVER SITE RESULTS

Work on the concentrations of mercury and dimethylmercury at the Savannah River Site was recently discussed during a conference call (Internal Memo TBSP-04-RJC-02) and was reported in TR-2003-00238. Investigations at the Savannah River Site indicate that there are relatively high concentrations of mercury and dimethylmercury at several locations (Internal Memo TBSP04RJC02). The concentrations of dimethylmercury in the low level liquid wastes in the Effluent Treatment Facility range from 0.000023 to 0.097 mg/L in the liquid phase and from 0.00002 to 0.18 mg/m^3 in the associated vapor. Concentrations range up to 0.36 mg/m^3 in the vapor in their 3H evaporator and up to 14 mg/L in the water condensate from the evaporator. The high concentrations in the evaporator vapor and the evaporator condensate apparently result from heating mercury and organic compounds in the evaporator at temperatures in excess of 100 °C. The volatile dimethylmercury distills and is condensed with the water.

7.0 CONCLUSIONS

The amounts of dimethylmercury that would be present in condensed water and condensed organic liquids have been evaluated for two different situations. One model is applicable for the condensation of dimethylmercury in liquid droplets of water or of organic compounds in risers and ventilation lines in which equilibrium can be achieved between dimethylmercury in the vapor and the liquid. The other model bounds the maximum dimethylmercury concentration by assuming that a volume of headspace air is condensed to form an organic or water droplet.

The equilibrium model is based on a conventional engineering approach for the estimation of the distribution of organic materials between liquid and vapor phases. Active ventilation has the immediate effect of diluting the organic constituents in the headspace vapor and deterring their condensation. The approach that is used here is most applicable for tanks that are passively ventilated. Natural variations in temperature from summer to winter will alter the results, but the variations will not be large because of compensating effects. A decrease in temperature will decrease the concentration and pressure, p, of dimethylmercury in the headspace and also require the adoption of a smaller value for the vapor pressure of the pure dimethylmercury, p^0. These terms appear in the numerator and denominator of Raoult's Law.

The model that is used for the estimation of the concentration of dimethylmercury under non-equilibrium conditions is necessarily arbitrary. However, the approach is reasonable for the calculation of the limiting concentration of dimethylmercury in such condensates since it considers the deposition of the entire amount of dimethylmercury that is in the vapor into 50 % of the organic liquid that is present in the same vapor. This approach predicts larger concentrations of dimethylmercury in organic droplets or films than would be obtained under equilibrium conditions.

The results for the equilibrium and the non-equilibrium situations indicate that dimethylmercury will preferentially accumulate in the organic condensate rather than in condensed water. To illustrate, the results for tank 241-C-104 imply that the concentration of dimethylmercury in an organic droplet is about 1000 times higher than the concentration of the compound in an associated droplet of water under equilibrium conditions. The difference was smaller in the non-equilibrium calculation.

The limited results that are now available for the four C farm tanks indicate that the dimethylmercury concentration in an organic or water droplet is small. The concentration in a water droplet at equilibrium is four orders of magnitude below the drinking water standard. The equilibrium dimethylmercury concentration in an organic droplet was also extremely low.

Finally, it is pertinent that the samples from C farm were collected because this farm has relatively high concentrations of organic materials and inorganic mercury compounds. Samples designated for the analysis of mercury and dimethylmercury have recently been collected from the U Farm tanks. These new analytical results should provide a much better perspective on the distribution of these substances at the Hanford Site.

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