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Potential Waste Tank Headspace Concentrations of DDE and 1-Naphthylamine

L.A. Mahoney

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

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Richland, WA 99352

Summary

Recent studies conducted for the Hanford Waste Treatment Plant (WTP) found that the centrifuged solids from tanks 241-AW-101, 241-AN-107, and 241-C-104 contained two carcinogenic chemicals, 1-naphthylamine and 2,2-bis(4-chlorophenyl)-1,1-dichloroethene (DDE), that had never been detected in tank headspaces. This report estimates the potential headspace concentrations associated with these two compounds.

The calculation was based on a comparison of headspace concentrations and waste concentrations for sixteen other organic compounds in the passively-ventilated tank 241-C-104. An approximate relation was found between the compounds' solubilities in water and their headspace concentrations (expressed as a fraction of the equilibrium concentration). This relation was usable only for sparingly soluble compounds. The relation was used to estimate the 241-C-104 headspace concentration of DDE that would result from the maximum measured waste concentration. The headspace concentration of 1-naphthylamine was calculated as that which would be in equilibrium with the minimum detection limit concentration in the liquid, there being no actual measurements of the compound in the liquid phase.

On the basis of the assumptions made in this report about organic compound transport and equilibration, the DDE concentration was estimated at well below one part per trillion, below standard analytical detection limits. 1-Naphthylamine could potentially be present in the headspace of a passively ventilated tank at the 0.2 ppb level. 1-Naphthylamine has only been detected in two double-shell tanks (241-AW-101 and 241-AN-107) which are actively ventilated. Active ventilation would most likely suppress and significantly dilute this concentration in the AN and AW exhaust stacks.

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1.0 Introduction

Recent studies conducted for the Hanford Waste Treatment Plant (WTP) have generated waste sample characterization data. The solids in the samples contained two carcinogenic chemicals, 1-naphthylamine (Chemical Abstracts Service, CAS, registry number 134-32-7) and 2,2-bis(4-chlorophenyl)-1,1-dichloroethene (dichlorodiphenyldichloroethylene, DDE, CAS 72-55-9) that had not been detected in tank headspaces. The molecular structure diagrams of these chemicals are given in Figures 1.1 and 1.2. These two chemicals were identified by Honeyman et al. (2004) as chemicals of potential concern because the chemicals could be present as vapors in the tank headspaces, and these vapors could be released into the workers' breathing zone. The purpose of this report is to assess what potential headspace concentrations might be associated with these two compounds.

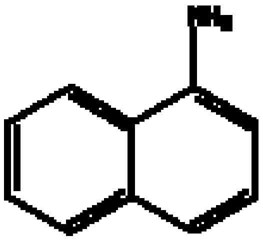

Figure 1.1. Structure of 1-Naphthylamine

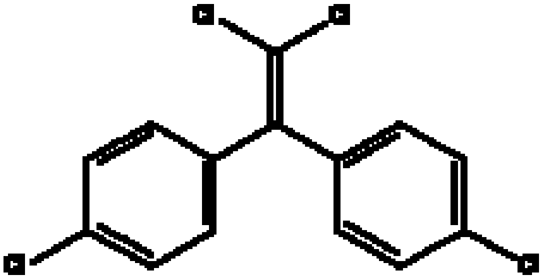

Figure 1.2. Structure of DDE

2.0 Background

Evans et al. (2001) made a homogenized composite of fourteen samples of waste from Hanford Tank 241-C-104 (hereafter referred to as C-104) and conducted regulatory analyses on representative sub-samples from both the centrifuged liquid and centrifuged solids. Similar studies were performed by Klinger et al. (2000) on two other composites; one made from thirty samples of waste from Tank 241-AW-101, and one made from seventeen samples of waste from Tank 241-AN-107.

Both studies conducted the same types of organic analyses:

- volatile organic analyses (VOA) were performed by mass spectrometry on volatiles that had been helium-purged from water-diluted samples of the composite
- semi-volatile organic analyses (SVOA) were conducted on concentrated methylene chloride ($MeCl_2$) or $MeCl_2$/acetone extracts of pH-adjusted samples, using a gas chromatograph/mass spectrometer (GC/MS)
- PCB and pesticide analysis used gas chromatography/electron capture detection (GC/ECD) on $MeCl_2$ or $MeCl_2$/acetone extracts after they had been cleaned using a Florisil cartridge.

DDE, a target analyte, was not measured in either phase of the AW-101 or AN-107 composites, where the minimum detection limits (MDLs) were 2 µg/L in the liquid and 20 µg/kg in the solids.(1) It also was not measured in the primary or duplicate samples of liquid centrifuged from the C-104 composite (MDL, 2 µg/L). It was measured at a concentration of 5.6 µg/kg in the primary sample of C-104 centrifuged bulk solids but was not measured in the duplicate (MDL, 4 µg/kg). Thus, it has been measured only at a concentration slightly above the MDL in the C-104 centrifuged solids and was not measured in the duplicate analysis of this same sample or in any liquid samples.

1-Naphthylamine was also a target analyte; it was determined by SVOA. It was not measured in the C-104 waste, where MDLs were 560 µg/L for liquid and 19,000 µg/kg for the centrifuged solids, nor in the AW-101 and AN-107 liquid samples (MDL 300 µg/L). In the AN-107 centrifuged solids, the measured 1-naphthylamine concentrations for primary and duplicate samples were 5400 and 2000 µg/kg compared to MDLs of 4300 and 4100 µg/kg. In the AW-101 centrifuged solids, the concentration was 1400 µg/kg in the primary sample compared to an MDL of 4800 µg/kg, but 1-naphthylamine was not measured in the duplicate where the MDL was 4300 µg/kg. Thus, 1-naphthylamine was reported in both the primary and duplicate analyses of the AN-107 solids samples and in the primary analysis of AW-101 solid samples. It was not measured in any liquid samples even though liquid MDLs were significantly lower than solid MDLs and the solubility of 1-naphthylamine in water is relatively high, 1700 mg/L

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(1) The MDL is a statistically-based QA value representing the lowest concentration at which the desired level of confidence in the measurement can be attained. Concentrations less than the MDL can often be detected and quantified but at a lower confidence level. Both Evans et al. (2001) and Klinger et al. (2000) reported concentrations of constituents whose concentrations were greater than 20% of the MDL, flagging those that were less than the MDL. Concentrations less than 20% of the MDL were detected for some constituents but were considered unquantifiable and not reported.

3.0 Headspace Concentration Observations

The relationship between the concentration of a compound as a vapor in the tank headspace and its concentration in the waste is complex. The headspace concentration is affected by the headspace ventilation rate, the solubility of the compound in the waste salt solution, the compound's diffusion rate in the waste liquid, the rate of circulation of the supernatant liquid, and the presence or absence of a crust on top of the supernatant. These factors are all tank-specific and waste-specific to some extent.

To make an order of magnitude estimate of the headspace concentration from the waste concentration, we reviewed data for a set of organics whose solubilities in water spanned a wide range. Their concentrations in the C-104 headspace were compared with their concentrations in the C-104 waste sample (Evans et al., 2001), and the resulting relationship was used to approximate the headspace concentrations of DDE and 1-naphthylamine under C-104 conditions.(2)

The compounds considered were 3-heptanone, butane, 2-pentanone, 2-methylpyridine, pentane, 2-heptanone, hexane, pyridine, octane, nonane, 4-heptanone, propanal, TBP, heptane, 2-hexanone, propyl nitrate, 2-propanone, and 2-butanone. These eighteen chemicals were the only ones present in both the TWINS headspace data for C-104 and the measurements from the C-104 waste sample analyses performed by Evans et al. (2001).

The C-104 headspace data covered three samples, those taken on January 21, June 15, and September 21, 2004. All of the following types of data were removed as unsuitable:

- samples with a Result Type of Duplicate_Result, LCS_Standard, Matrix_Spike_Dup_Recovery, or Matrix_Spike_Recovery
- the QA samples
- samples with a Data Qualifier Code that included B, F, T, S, M, Q, and/or U.

The concentrations of each compound measured on each sample date were averaged to reduce the effects of short-term variation and, in some cases, of different sampling or analysis methods. Then the maximum of the averaged daily concentration was taken to represent a conservative concentration for the year 2004.

The waste sample concentration data for fifteen of the compounds came from the VOA, with the remaining three being taken from the SVOA. It should be noted the VOA results are likely to underestimate the true volatile compound concentrations because of losses occurring during compositing and sub-sampling (Klinger et al. 2000).

For all of the eighteen compounds except 2-methylpyridine and 2-propanone the concentrations were higher in the bulk solids than in the liquid, suggesting the compounds were stored in an organic liquid phase associated with the particles in the waste. The organic compounds are, therefore, thought to be present as microdroplets attached to the surfaces of individual particles.

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(2) Although 1-naphthylamine was observed in AW-101 and AN-107 waste, not in C-104 waste, there are no headspace organics concentration data in TWINS for AW-101 or AN-107 to allow the same kind of comparison for those tanks.

The concept of attached organic microdroplets is consistent with the history of the waste in the tanks. The in-tank degradation of the organic solvent and extractant waste originally placed in the tanks has produced species with a wide range of water solubility. The less soluble the species, the more it tends to reside in the organic droplet phase and the slower is its transport to the waste surface and headspace. The organic droplet phase could consist of both the original nonpolar organic waste itself (e.g., normal paraffinic hydrocarbon diluent, extractants, trace levels of DDE, etc.) and those degradation products whose low water solubility has prevented efficient transport to the waste surface.

In order to account for the complete inventory of each compound in C-104, an average concentration in the original waste was calculated from the concentrations in the centrifuged solids and the centrifuged liquid based on the assumption the sample composite represented the tank waste. The liquid density of 1.161 g/mL and the fraction of centrifuged solids in the composite, 82 wt%, measured by Evans et al. (2001) were used to calculate the average concentration of each compound in the composite using Equation (1). Phase concentrations that were not detected were treated as zero in this calculation.

$$m_{comp} = \left(1 - \omega_{centsol}\right)\frac{c_{centliq}}{\rho_{centliq}} + \omega_{centsol}\, m_{centsol} \qquad (1)$$

where m_{comp} = concentration of compound per unit mass composite
$\omega_{centsol}$ = weight fraction of centrifuged solids in the composite
$c_{centliq}$ = concentration of compound per unit volume centrifuged liquid
$\rho_{centliq}$ = density of the centrifuged liquid
$m_{centsol}$ = concentration of compound per unit mass centrifuged solids

The measured concentrations in the headspace, centrifuged liquid and centrifuged solids, and the calculated concentrations in the composite are shown in Table 3.1. The relatively high concentrations of the higher alkanes in the centrifuged liquid are surprising, since these compounds are only sparingly soluble. Possibly they were present as an unobserved organic liquid phase that was detached from the solids by centrifugation and therefore became disproportionately represented in the centrifuged liquid.

The next step compared the measured headspace concentration of each compound to the headspace concentration that would be expected if two conditions were met:

1. all the compound was in the form of a solute in the aqueous waste liquid

2. the headspace was in thermodynamic equilibrium with the aqueous solution of dilute organics, according to Henry's Law.

The first of these assumptions may not be accurate, as suggested by the fact many organics were found to be concentrated in the centrifuged solids rather than in the liquid. Nevertheless, the assumption reflects the physical fact the organics in the solids cannot be transported to the headspace except through the aqueous phase, making the aqueous solubility of the compounds an important physical feature. The second assumption depends on transport in the aqueous phase and on the rate of removal of the headspace contents by ventilation (which was passive in tank C-104 at the time the headspace samples were taken). This assumption is also a coarse approximation. However, the results prove to indicate a useful physical relationship, as will be shown.

Table 3.1. Concentrations of Selected Organic Compounds in C-104[a]

Chemical Name	**Chemical ID**	**Headspace conc. (ppm)**	**μg/L in centrifuged liquid**	**μg/kg in centrifuged solids**	**μg/kg in composite**
3-Heptanone	106-35-4	1.10	37.0	610	506
Butane	106-97-8	1.95	< MDL	2550	2091
2-Pentanone	107-87-9	0.29	< MDL	69.5	57
2-Methylpyridine [b]	109-06-8	0.0453	430	< MDL	67
Pentane	109-66-0	1.15	< MDL	6500	5330
2-Heptanone	110-43-0	0.15	48.5	605	504
Hexane	110-54-3	0.715	2500	8100	7030
Pyridine [b]	110-86-1	0.0445	2700	3250	3084
Octane	111-65-9	0.235	1900	4000	3575
Nonane	111-84-2	0.165	3100	3700	3515
4-Heptanone	123-19-3	0.082	< MDL	76	62
Propanal	123-38-6	0.15	< MDL	990	812
Tributyl phosphate [b]	126-73-8	0.00620	2050	53500	44188
Heptane	142-82-5	0.385	950	5750	4862
2-Hexanone	591-78-6	0.155	12.0	200	166
Propyl nitrate	627-13-4	0.353	< MDL	35	29
2-Propanone	67-64-1	1.75	500	310	332
2-Butanone	78-93-3	1.15	145	186	175

(a) The headspace concentrations are the maximum sample-event-averages for three sampling events in 2004 and are based on data from TWINS. The concentrations in the centrifuged liquid and solids taken from a C-104 waste composite are based on data in Evans et al. (2001). The concentrations in the composite were calculated using a liquid density of 1.161 g/mL and a centrifuged solids fraction of 82 wt% (Evans et al. 2001).

(b) The concentrations of these three compounds were based on SVOA measurements. All others came from VOA.

In the first step, the concentrations of organic compounds were put in terms of moles per volume of liquid phase, which includes both the centrifuged liquid and the liquid remaining in the centrifuged solids. The liquid fraction in the centrifuged solids was not measured or estimated by Evans et al. (2001) but can be calculated from data in that report. Formate, a very soluble organic anion, was found to be present at an average concentration of 2395 μg/mL in the centrifuged liquid and 1475 μg/g in the centrifuged solids. Assuming all the formate in the centrifuged solids was present as solute, the liquid weight fraction in the centrifuged solids can be calculated to be 0.715. The overall weight fraction of liquid phase in the composite was 0.766, counting the centrifuged liquid portion as shown in Equation (2), and that of solid phase is 0.234.

$$\omega_{liq,comp} = \left(1 - \omega_{centsol}\right) + \omega_{centsol}\left(\frac{c_{F,centsol}}{m_{F,centliq} / \rho_{centliq}}\right) \tag{2}$$

where $\omega_{liq,comp}$ = weight fraction of liquid phase in the composite
$c_{F,centsol}$ = concentration of formate per unit mass of centrifuged solids
$m_{F,centliq}$ = concentration of formate per unit volume of centrifuged liquid

The composite concentration, the overall liquid fraction, the measured liquid density, and the molecular weights were used to calculate mol/L liquid concentrations for all eighteen compounds. These concentrations were compared to the compounds' solubilities in pure water(3) as a check of reasonableness. Hexane, heptane, octane, and nonane were calculated to be present in the liquid phase in higher concentration than solubility would theoretically permit. This enhancement may have been due to the formation of a thin organic liquid phase at the surface of the centrifuged liquid samples.

Finally, the equilibrium concentrations in the gas phase were calculated from the liquid-phase concentrations by using Henry's Law(4) and were ratioed to the measured concentrations in the headspace. Table 3.2 shows the concentrations in the liquid phase, the compound properties, and the ratio of the calculated equilibrium headspace concentration to the actual concentration.

The ratio can be generally regarded as the fractional approach to equilibrium, although for several highly-soluble compounds the "approach" is greater than 100%, a result of the approximating assumptions that were made. There is a trend of increasing fraction of equilibrium as the solubility increases. The consistency of the trend can be clearly seen in Figure 3.1, in which the fractional approach to equilibrium of each compound is plotted versus its solubility.

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(3) The solubilities at 25°C were obtained in January 2006 from the database maintained by Syracuse Research Corp. at http://www.syrres.com/esc/physdemo.htm.

(4) The Henry's Law coefficients at 25°C were obtained in January 2006 from the database at http://www.syrres.com/esc/physdemo.htm.

Table 3.2 Calculated Liquid- and Gas-Phase Concentrations for Selected Organic Compounds in C-104

Chemical Name	Molecular Weight (g/gmol)	mol/L in liquid phase	Implied dissolved mg/L liq	Solubility (mg/L H_2O)	Henry's Law Constant (atm/(mol/m^3))	Gas phase: ppm actual / equil. ppm
3-Heptanone	114.19	6.71E-06	0.767	4300	9.08E-05	1.80
Butane	58.12	5.45E-05	3.17	61.2	0.95	3.77E-05
2-Pentanone	86.13	1.00E-06	0.086	43000	8.36E-05	3.46
2-Methylpyridine (a)	93.13	1.08E-06	0.101	1.00E+06	9.96E-06	4.19
Pentane	72.15	1.12E-04	8.08	38	1.25	8.22E-06
2-Heptanone	114.19	6.68E-06	0.763	4300	1.69E-04	0.133
Hexane	86.18	1.24E-04	10.7	9.5	1.8	3.21E-06
Pyridine (a)	79.10	5.91E-05	4.67	1.00E+06	1.10E-05	0.068
Octane	114.23	4.74E-05	5.42	0.66	3.21	1.54E-06
Nonane	128.26	4.15E-05	5.32	0.22	3.4	1.17E-06
4-Heptanone	114.19	8.27E-07	0.094	3200	5.49E-05	1.81
Propanal	58.08	2.12E-05	1.23	306000	7.34E-05	0.097
Tributyl phosphate (a)	266.32	2.51E-04	66.9	280	1.41E-06	0.017
Heptane	100.21	7.35E-05	7.37	3.4	2	2.62E-06
2-Hexanone	100.16	2.51E-06	0.251	17500	9.32E-05	0.663
Propyl nitrate	105.09	4.14E-07	0.043	3290	1.27E-03	0.672
2-Propanone	58.08	8.65E-06	0.503	1.00E+06	3.97E-05	5.09
2-Butanone	72.11	3.68E-06	0.265	223000	5.69E-05	5.50

The concentrations in the waste are calculated from measurements presented in Evans et al. (2001).

(a) The headspace concentrations are the maximum sample-event-averages for three sampling events in 2004 and are based on data from TWINS. The concentrations in the centrifuged liquid and solids taken from a C-104 waste composite are based on data in Evans et al. (2001). The concentrations in the composite were calculated using a liquid density of 1.161 g/mL and a centrifuged solids fraction of 82 wt% (Evans et al. 2001).

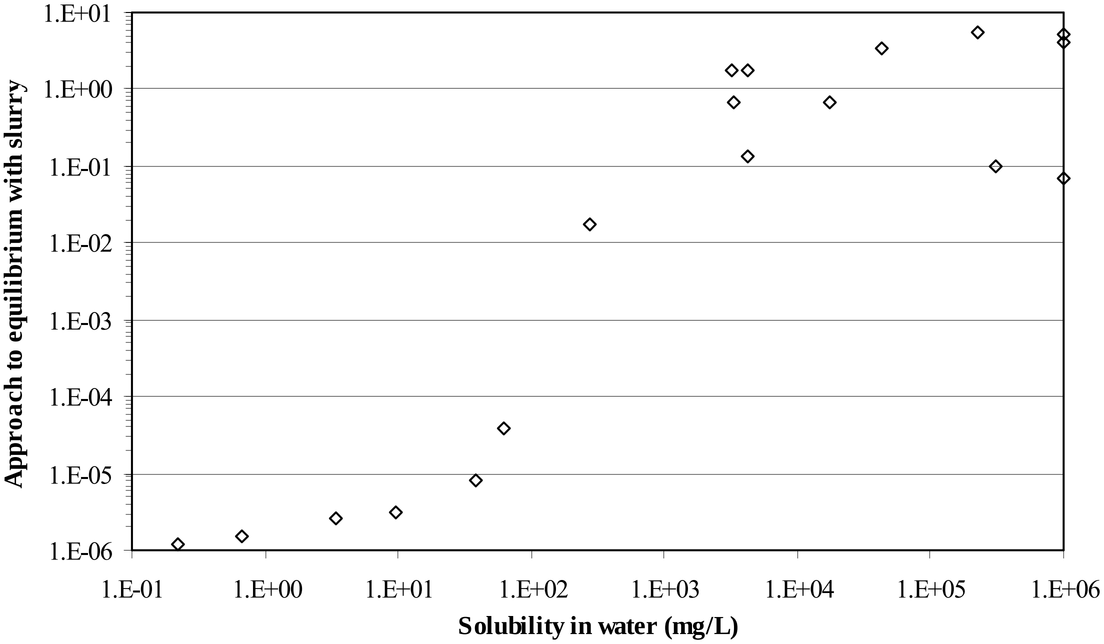

Figure 3.1. Relationship between Approach to Gas-Phase Equilibrium and Solubility in the Liquid, for Selected Organic Compounds in C-104

The compounds whose solubilities in water are less than 100 mg/L (i.e., the alkanes) have headspace concentrations that are less than 5 x 10^{-5} of the equilibrium gas-phase concentration. At higher solubilities the trend shows more scatter with the fractional approach varying from about 0.1 to 5.5. In this range, an upward trend with solubility is suggested but is not clear. Based on the results in the figure, the approximations in the transport model results in an overestimation of at least a factor of 5 that makes the relationship between the approach to equilibrium and the solubility unusable for high solubilities. Accordingly, this relation is applied only to sparingly soluble organics.

4.0 Headspace Concentration Estimation

Headspace concentration calculations were carried out for DDE using the measured concentrations and known properties as well as the relationship between aqueous solubility and fractional approach to equilibrium found from the C-104 data. The resulting estimate of DDE headspace concentration is specific to the conditions in tank C-104. It may have some applicability to other passively ventilated tanks whose waste might contain equal concentrations of the two compounds, but it would overestimate the headspace concentrations in actively-ventilated tanks.

Table 4.1 shows the concentrations, properties, and sequence of calculations that lead to the approximate predictions of the headspace concentration of DDE under C-104 conditions. The estimate of the fractional approach to headspace equilibrium is based on the upper-bound fraction for the solubility ranges in which the compound falls (per Figure 1.1). The compound DDE is in the low-solubility range (like the alkanes) where the upper-bound fraction is 5 x 10^{-5}.

Table 4.1. Estimation of the Headspace Concentrations of DDE under C-104 Conditions

	DDE
Maximum concentration measured in centrifuged solids, μg compound/kg (Evans et al., 2001, Klinger et al., 2000)	5.6
Weight fraction of centrifuged solids in C-104 composite (Evans et al., 2001)	0.82
Concentration, μg compound/kg composite (calculated assuming zero concentration in liquid phase, because the measured concentration was not detected)	4.6
Density of C-104 centrifuged liquid, kg/L (Evans et al., 2001)	1.161
Volume fraction of solid phase in C-104 composite (calculated from formate data in Evans et al. [2001])	0.234
Concentration, μg compound/L of liquid phase in composite	7.0
Molecular weight, g/mol	318.03
Concentration, mol/L liquid	2.19E-08
Henry's Law constant of compound, atm/(mol/m^3)	4.16E-05
Equilibrium headspace concentration based on Henry's Law, ppm	0.00091
Solubility, mg compound/L water	4.00E-02
Conservative estimate of fractional approach to headspace equilibrium under C-104 conditions	5.00E-05
Approximate headspace concentration under C-104 conditions, ppm	**5E-08**

Because of the low water solubility of DDE, its estimated concentration in the C-104 headspace is well below one part per trillion and, therefore, is below standard analytical detection limits.

1-Naphthylamine has relatively high solubility in water, so the approach applied to DDE cannot be used on 1-naphthylamine without making an estimate of its headspace concentration that exceeds its equilibrium value. Therefore another approach is applied, one in which the maximum liquid concentration of 1-naphthylamine that can be inferred from measurements is considered to be in equilibrium with the headspace. This approach would overestimate the headspace concentration in even a passively ventilated tank.

The only tanks in whose waste 1-naphthylamine has been measured, to date, were the DSTs AW-101 and AN-107. The compound was measured only in the centrifuged solids; none was measured in the centrifuged liquids, where the MDL was 300 μg/L. To bound the headspace concentration under passive ventilation conditions, assume the headspace vapor is in equilibrium with liquid whose concentration of 1-naphthylamine is equal to 300 μg/L. The Henry's Law constant for the compound is 1.11 x 10^{-7} atm/(mol/m^3) and its molecular weight is 143.19 g/mol.(5) The equilibrium headspace concentration is therefore

$$= \frac{3\,x\,10^{-4}\ g/L}{143.19\ g/mol}\ \frac{1000\ L}{m^3}\ \frac{1.11\,x\,10^{-7}\ atm}{mol/m^3}\ \frac{10^9\ \ ppb}{atm} = \ 0.23\text{ ppb}$$

This is the bounding headspace concentration of 1-naphthylamine that would be present if this chemical was at the analytical MDL at the waste surface and the headspace was not ventilated. Stack concentrations of 1-naphthylamine would be expected to be significantly lower than the 0.23 ppb estimate because the liquid waste was not at the MDL (and may have been less than 20% of the MDL based on actual reporting limits used in the analytical reports), the headspaces of AW-101 and AN-107 are actively ventilated, and emissions from these tanks are automatically diluted by roughly a factor of 6 by mixing with the air from other tanks in the farm.

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(5) All properties were obtained in January 2006 from the database at http://www.syrres.com/esc/physdemo.htm.

5.0 References

Evans JC, JA Campbell, FV Hoppes, EW Hoppe, GS Klinger, GM Mong, AK Sharma, MJ Steele, RT Steele, MW Urie. 2001. *Organic Analysis of C-104 Tank Waste*, WTP-RPT-008, Rev. 1, Battelle, Pacific Northwest Division, Richland, Washington.

Honeyman JO, JE Meacham, RJ Cash, AM Sastry, and JL Huckaby. 2004. *Industrial Hygiene Chemical Vapor Technical Basis,* RPP-22491 Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

Klinger GS, MW Urie, JA Campbell, SA Clauss, TW Clauss, EW Hoppe, GM Mong, and AK Sharma. 2000. *Organic Analysis of AW-101 and AN-107 Tank Waste*, PNWD-2461, Rev. 1, Battelle, Pacific Northwest Division, Richland, Washington.

Stock, LM and JL Huckaby. 2004. *A Survey of Vapors in the Headspaces of Single-Shell Waste Tanks,* PNNL-13366, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.