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Screening for Organic Solvents in Hanford Waste Tanks Using Total Non-Methane Organic Compound Vapor Concentrations

J. L. Huckaby
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February 1997

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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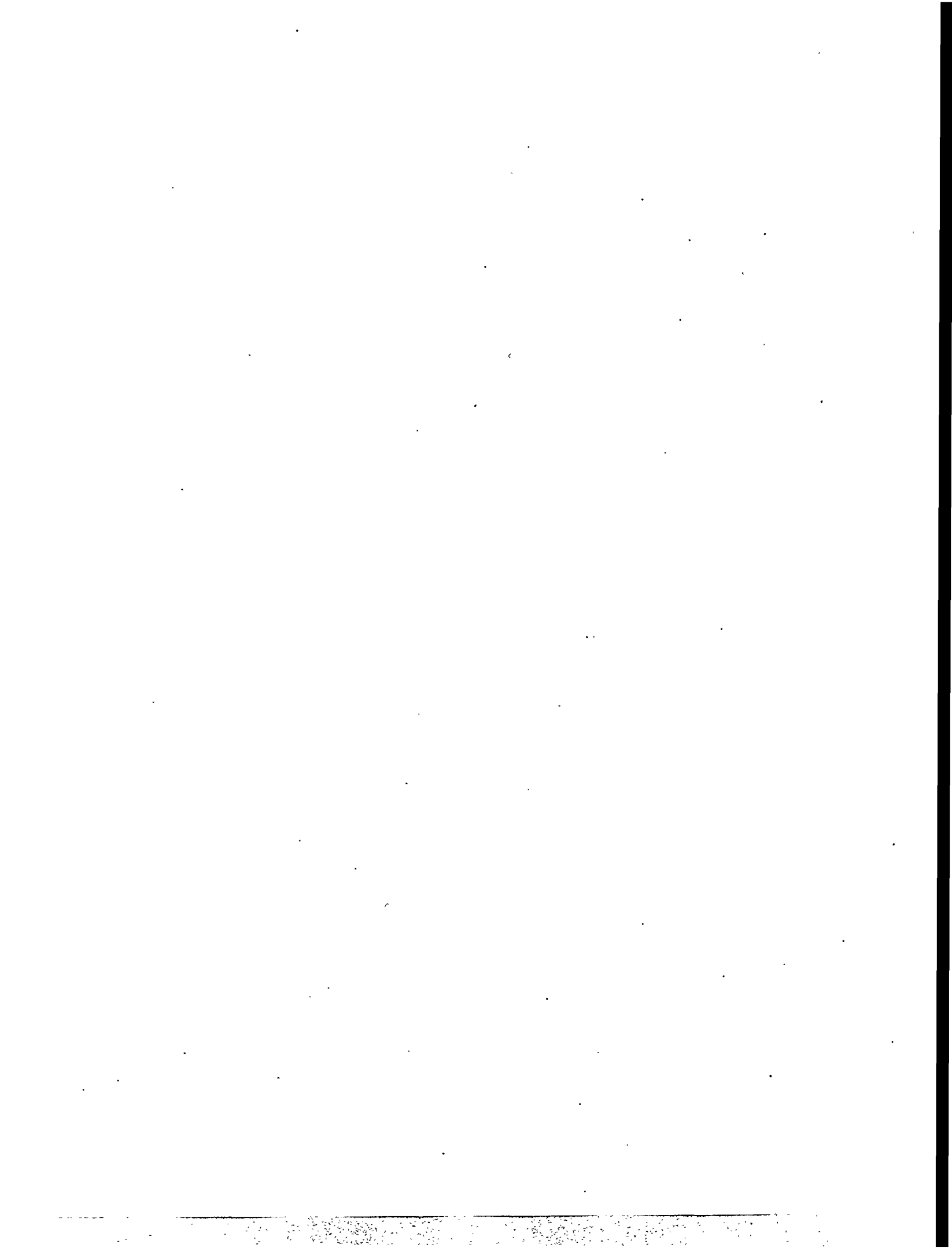
Summary

The potential ignition of organic liquids stored in the Hanford Site high-level radioactive waste tanks has been identified as a safety issue because expanding gases could potentially affect tank dome integrity. Organic liquid waste has been found in some of the waste tanks, but most are thought to contain only trace amounts. Direct sampling of the tank waste to locate organic liquids may not conclusively demonstrate that a given tank is free of risk due to the inhomogeneity of the waste. However, organic vapors present above the organic liquid waste can be detected with a high degree of confidence and can be used to identify problem tanks.

This report presents the results of a screening test that has been applied to 75 passively ventilated high-level radioactive waste tanks at the Hanford Site to determine those that might contain a significant amount of organic liquid waste. The screening test is based on a simple model of the tank headspace, headspace organic vapor concentrations, and certain tank physical parameters. Analyses indicate that damage to the tank dome is credible only if the organic liquid burn rate is above a threshold value, and this can occur only if the surface area of organic liquid in a tank is above a corresponding threshold value of about one square meter. Twelve tanks were identified as potentially containing at least that amount of semivolatile organic liquid based on conservative estimates.

Tank head space organic vapor concentrations and physical parameters required by the screening test have been compiled and are presented for each of the tanks studied. Estimates of the ventilation rates of the waste tanks have been revised in this study to reflect recent information obtained from hydrogen monitoring data.

A simple analysis of the uncertainty associated with the test results is also presented and applied to each of the tanks. This analysis suggests that the largest current uncertainty in the estimation of organic liquid surface area is that associated with knowledge of the tank ventilation rate. The uncertainty analysis is applied to determine 95% confidence limits for the estimated organic waste surface area in each tank.



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Acronyms and Abbreviations

EPA	U.S. Environmental Protection Agency
FID	flame ionization detection
FY	fiscal year
GC/FID	gas chromatography with flame ionization detection
GC/MS	gas chromatography with mass spectrometric detection
IL	impact level
ISVS	in situ vapor sampling
OGIST	Oregon Graduate Institute of Science and Technology
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
ppbv	parts per billion by volume
ppmv	parts per million by volume
QA	quality assurance
STP	standard temperature and pressure (0°C, 1.013×10^5 Pa)
SUMMA	process for chemically passivating stainless steel
TC	thermocouple
TNMOC	total non-methane organic compounds
TO-12	an EPA analytical protocol
TO-14	an EPA analytical protocol
TST	triple sorbent trap
VSS	vapor sampling system

1.0 Introduction

This report presents the results of a screening test that has been applied to 75 passively ventilated high-level radioactive waste tanks at the Hanford Site to determine which tanks might contain a significant amount of organic liquid waste. Tank head space organic vapor concentrations and certain physical parameters required by the screening test (Cowley et al. 1996) are compiled and presented for each of the tanks studied. A simple analysis of the uncertainty associated with the test results is also presented and applied to each of the tanks.

1.1 Background

Large quantities of organic extractants and solvents were used in chemical processes associated with past production of plutonium at the Hanford Site. While most of the organic liquid waste was disposed in other ways, some was sent as waste to the high-level radioactive waste storage tanks. Evaporation and chemical degradation have reduced the inventory of organic liquid wastes in the tanks, but some is known to remain.

Accidental ignition of these organic liquids followed by an open flame burn in the waste tanks has been identified as a safety issue. Safety analyses indicate that tank dome failure is credible only if the organic liquid burn rate is above a threshold value, and this could occur only if the surface area of organic liquid in a tank is above a corresponding threshold value of one square meter (Cowley et al. 1996).

The current strategy of the Organic Safety Project to resolve the organic liquid safety issue requires identification of all tanks that could contain a reservoir of organic liquid waste with a total surface area of 1 m² or greater (Meacham et al. 1997). However, records detailing the transfer of organic liquid waste to and between the tanks are incomplete, and the effects of aging and evaporation on the inventory of organic liquids cannot be determined with sufficient certainty for *a priori* identification of the tanks that might meet the 1-m² condition.

Direct sampling of tank waste to locate organic liquids may not conclusively demonstrate that a given tank is free of risk. Inhomogeneities in the waste and the technical difficulties of obtaining representative waste samples limit the effectiveness of that approach. However, organic vapors present above the organic liquid waste can be detected with a high degree of confidence and used to identify problem tanks. This approach has been used to develop a screening method based on a simple model of the tank head space, head space organic vapor concentrations, and certain tank physical parameters (Cowley et al. 1996).

1.2 Quality Assurance

Collecting tank head space characterization data suitable for organic liquid waste screening began in FY 1994, although the initial data were not specifically obtained for this purpose. Quality assurance (QA) documentation was incomplete for all sample analytical results from the Oregon Graduate Institute of Science and Technology (OGIST), and all results received from Oak Ridge National Laboratory (ORNL)

before October 1995 (Burnum 1995). However, these data provide valuable confirmation of other data, and their technical validity is comparable. Final organic vapor concentration data were obtained from the Tank Characterization Database (PNNL 1996).

Application of the screening method requires compiling the tank organic vapor data and physical parameters and performing a series of simple calculations for each tank. A computer spreadsheet has been created for this purpose. This report describes the sources of data used in the screening spreadsheet and measures taken to confirm their correctness and quality. Also, because the spreadsheet is used directly by the Organic Safety Project for safety-related decisions, its maintenance follows PNNL QA Impact Level II guidelines. Briefly, this means that data and calculations are independently verified and that changes to the spreadsheet are documented.

Section 2 describes the screening model that detects the organic vapors in the tank headspaces. The data used for the screening process—temperature, head space pressure, ventilation rate, organic vapor concentration—are described in Section 3. Section 4 discusses the analysis of uncertainties used to establish confidence limits on the screening test results. Screening results are the subject of Section 5. References cited are listed in Section 6, and the appendix contains supporting documentation for the report.

2.0 Screening Model

Screening for tanks that may have more than one square meter of surface area of semivolatile organic liquid wastes is based on a simple model of tank head space dynamics, head space vapor sampling results, and selected head space physical properties. The model assumes that the concentration of organic vapors in the tank head space is the result of a steady-state balance between the rate at which organic waste liquids evaporate and the rate at which organic vapors are removed by exchange of air with the atmosphere. Head space temperature and ventilation rate are parameters in the model.

2.1 Model Bases

The model was used to estimate the surface area of semivolatile organic liquid waste using the measured concentration of total non-methane organic compounds (TNMOC). As specified in the safety analysis (Cowley et al. 1996), the organic liquid is assumed to have the composition of the organic liquid waste in Tank 241-C-103 (C-103) and to be at the measured tank head space temperature. The model cannot distinguish organic liquids present at the surface from liquids entrained in the waste, nor can it distinguish a single puddle of organic liquid from numerous small puddles. The bases and derivation of the model are given by Cowley et al. (1996).

2.2 Model Description

The surface area of the organic liquid waste, A , was calculated by rearranging the expression given by Cowley et al. (1996) for the vapor concentration of semivolatile organic compounds in a vented head space:

$$A = \frac{Q}{k} \left(\frac{C_{sat}}{C_{obs}} - 1 \right)^{-1} \quad (2.1)$$

where

- C_{obs} = observed head space vapor concentration of semivolatile organic compounds
- C_{sat} = saturated vapor concentration of semivolatile organic compounds
- k = mass transfer coefficient
- Q = head space ventilation rate.

The mass transfer coefficient, k , was calculated using the following correlation with head space temperature:

$$k = -0.248 + 0.0719T - 0.000497T^2 \quad (2.2)$$

Here k is given in m/h when the tank head space temperature, T , is given in °C. Equation (2.2) was derived by A. K. Postma and is based on the approximation described by Cowley et al. (1996). The derivation of the equation is described in the appendix at the end of the report.

The saturated vapor concentration of semivolatile organic compounds, C_{sat} was estimated from calculated partial pressures of the organic liquid waste currently stored in Tank C-103. The five semivolatile organic compounds that dominate the composition of the Tank C-103 organic liquid are n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, and tributyl phosphate (Pool and Bean 1994). Raoult's law was applied to estimate the composition of vapors in equilibrium with a solution of these five compounds. Specifically, C_{sat} was calculated using the following equation:

$$C_{sat} = \sum_{i=1}^5 \frac{x_i p_i^*(T) MW_i}{RT} \quad (2.3)$$

where

x_i = liquid phase mole fraction of i th component

$p_i^*(T)$ = vapor pressure of i th component (a function of temperature)

MW = molecular weight of i th component

T = temperature

R = ideal gas constant.

Liquid phase mole fractions of the five primary compounds were derived from analyses of the Tank C-103 organic liquid waste performed by Pool and Bean (1994). These are listed in Table 2.1 along with molecular weights for each compound.

Table 2.1. Semivolatile Organic Compounds in Tank C-103 Waste

Compound	Molecular Weight (g/mol)	Mole Fraction in Tank C-103 Waste	Antoine Constants		
			C_1	C_2	C_3
n-Dodecane	170.341	0.0564	7.3157	1830	198.3
n-Tridecane	184.368	0.2231	7.3147	1881.7	190.9
n-Tetradecane	198.395	0.1225	7.3143	1930.4	183.8
n-Pentadecane	212.422	0.0131	7.3123	1973.3	176.6
Tributyl phosphate	266.32	0.5845	8.916	3359	273.15

Vapor pressures were calculated for the five semivolatile compounds using equations of the Antoine form:

$$\log(p_i^*) = C_{11} - \frac{C_{12}}{(T + C_{13})} \quad (2.4)$$

where C_{11} , C_{12} , and C_{13} are the Antoine constants. The Antoine constants for the four alkanes were obtained from Dreisbach (1959) where they are described as being appropriate for temperatures as low as 25°C. These constants were applied even when tank head space temperatures were below 25°C, because none more suitable could be found. Antoine constants for tributyl phosphate were obtained from Schulz and Navratil (1984). Table 2.1 lists the Antoine constants used in screening calculations.

Analytical laboratories typically report measured head space vapor concentrations in parts per billion by volume (ppbv) or in the mass concentration units of mg/m³ for dry air at standard temperature and pressure (STP) (0°C and 1.013 × 10⁵ Pa). Concentrations given in ppbv were converted to mass concentrations using molecular weights and the ideal gas law and adjusted to tank conditions using the following equation:

$$C_{obs} = C_{STP} \left(\frac{273.15 \text{ K}}{T} \right) \left(\frac{P}{760 \text{ torr}} \right) \quad (2.5)$$

where C_{STP} is the mass concentration of TNMOC at STP, and T and P are the temperature and barometric pressure, respectively, of the tank head space at the time samples were collected. The head space ventilation rate, Q , and measurements of tank head space temperature and pressure at the time vapor samples were collected are discussed in Section 3.

Screening calculations were performed using an Excel spreadsheet. Spreadsheet calculations were reviewed for technical reasonableness and verified by independent hand calculations.

3.0 Screening Data

The parameters that are screened for use in the model are temperature, pressure, ventilation rate, and organic vapor concentrations in the tank head space. Measurement devices installed in the tanks provide the needed data. The instruments and the data thus obtained are described in the following sections.

3.1 Temperatures

Tank head space temperature is used in the model as an estimate of the organic liquid waste surface temperature, and also to adjust vapor concentrations from STP to actual head space conditions. Tank head space temperatures were routinely measured during the vapor sampling events using thermocouples (TCs) or resistance thermal devices incorporated into the vapor sampling probes. Some of the sampling events, however, were conducted using probes that lacked directly accessible temperature sensors, and, consequently, no head space temperature was given in the sampling event report. Also, because temperature sensors were not always recalibrated when a probe was moved from one tank to another, their reliability is sometimes questionable. For an independent verification of the head space temperature, temperature readings were obtained from the permanently installed TC trees.

Tank head space temperatures were originally obtained from permanently installed TC trees for a correlation study of tank head space characterization data (Palmer et al. 1996). Waste surface level data were used to determine which TC tree sensors were in the head space, and temperature readings for these sensors were obtained for the date that vapor samples were collected. If no TC tree readings were taken on the same day as the sampling event, the readings from the nearest dates were used. Because these data were collected and incorporated into the screening spreadsheet before PNNL QA Impact Level-II data review requirements were applied, the associated documentation is incomplete; this deficiency has been addressed by independently verifying all TC tree data.

Head space TC tree temperatures were verified by independently retrieving the surface level and TC tree data and recalculating average head space readings. The Tank Characterization Database was accessed first for surface level readings and then for collection sensor readings for each tank of interest (PNNL 1996). The surface level readings at the date closest to the time of sampling were used to determine which TC sensors were above the waste surface level. Surface level readings were given in inches (from the bottom of the tank) and, in most cases, the sensors were placed 61 cm (24 in.) apart. The number of the first sensor above the waste was compared with data obtained by Tran (1993). Where there was a discrepancy about which TC sensors were in the head space (most commonly because sensors were not 61 cm apart), the data from Tran (1993) were used.

Once it was determined which TC sensors were in the head space, the Tank Characterization Database was accessed for readings from these sensors for the sampling date (or the closest available dates) (PNNL 1996). These temperature readings were examined for consistency and an average calculated of all reasonable readings. This average head space temperature was compared with the existing TC tree head space temperature (obtained from Palmer et al. 1996). Adjustments were then made and documented.

Table 3.1 lists head space temperature measurements from both the vapor sampling probe and TC tree sensors for each sampling event. The two independent measurements generally agree well. In 61 of the 80 sampling events for which both vapor probe and TC tree temperature measurements are available,

Table 3.1. Measured Tank Physical Parameters and Organic Vapor Concentrations

Tank	Date Sampled	Sampling Method	Temperature from Vapor Probe (°C)	Temperature from TC Tree (°C)	Pressure (Pa)	Total Non-Methane Organic Compound Concentration (mg/m ³)				Notes
						ORNL TST GC/MS	PNNL TST GC/MS	SUMMA GC/MS	SUMMA GC/FID	
A-101	6/8/95	VSS ^(a)	37.0	35.4	9.893e+04	19	11.7	25.3	NA	
A-102	11/10/95	VSS	35.3	32.8	9.959e+04	3.6	NA	NA	4.98	
A-103	11/9/95	VSS	33.2	30	9.866e+04	5.8	NA	NA	7.82	
AX-101	6/15/95	VSS	25.6	30.4	9.830e+04	2.0	1	1.09	NA	
AX-102	6/27/95	VSS	24.6	23.5	9.959e+04	7.6	7.9	12.1	NA	
AX-103	6/21/95	VSS	32.8	32.2	9.919e+04	0.3	0.11	0.52	NA	
B-102	4/18/96	VSS	16.0	NA	9.887e+04	NA	NA	NA	4.2	
B-103	2/8/95	VSS	15.2	13.7	1.000e+05	9.8	NA	13.6	NA	
B-105	7/30/96	ISVS ^(b)	18.6	17.8	1.001e+05	NA	3.8	2.49	0.77	
B-107	7/23/96	ISVS	18.6	15.8	9.942e+04	NA	7.56	3.48	0.42	
B-202	7/18/96	ISVS	16.5	16	9.926e+04	NA	NA	NA	0.43	
BX-102	7/31/96	ISVS	18.2	18.5	9.861e+04	NA	7.63	1.06	0.43	
BX-103	8/1/96	ISVS	19.2	19.6	9.826e+04	NA	40.9	54.9	25.8	P ^(c)
BX-104	12/30/94	VSS	22.8	27.7	1.007e+05	85	NA	48.1	NA	
	8/22/96	ISVS	21.1	NA	9.919e+04	NA			65	P
BX-105	4/24/96	VSS	17.0	18.3	9.897e+04	NA	NA	NA	4.4	
BX-106	8/15/96	ISVS	19.2	19.4	9.885e+04	NA	NA	NA	1.0	
BX-107	11/17/95	VSS	19.8	21	9.919e+04	2.4	NA	NA	2.08	
BX-110	4/30/96	VSS	15.2	16.8	9.974e+04	NA	1.97	3.76	2	
BX-111	8/27/96	ISVS	19.5	19.1	9.797e+04	NA	11.3	11.45	1.66	P
BY-101	8/29/96	ISVS	21.3	19.5	9.887e+04	NA	7.63	48.7	28.6	P
BY-102	11/21/95	VSS	23.4	NA	9.939e+04	16	NA	NA	19.9	
BY-103	11/1/94	VSS	24.5	25.3	9.809e+04	12.1	NA	7.42	5.2	
BY-104	6/24/94	VSS	26.0	26.8	9.866e+04	32.1	NA	31.3	58.6	O ^(d)

Table 3.1 (contd)

Tank	Date Sampled	Sampling Method	Temperature from Vapor Probe (°C)	Temperature from TC Tree (°C)	Pressure (Pa)	Total Non-Methane Organic Compound Concentration (mg/m ³)				Notes
						ORNL TST GC/MS	PNNL TST GC/MS	SUMMA GC/MS	SUMMA GC/FID	
BY-105	7/7/94	VSS	26.0	25.8	9.959e+04	11.4	NA	6.8	15.2	O
BY-106	7/8/94	VSS	27.0	29	9.866e+04	12.7	NA	12.7	8.11	O
BY-107	10/26/94	VSS	33.1	28	9.809e+04	149.1	NA	68.8	173	
BY-108	10/27/94	VSS	25.7	30.5	9.835e+04	510	NA	92.4	594	
	1/23/96	VSS	25.0	26.6	9.901e+04	NA	NA	NA	205	
	3/28/96	VSS	24.4	25	9.881e+04	NA	NA	NA	243	
	9/10/96	VSS	28.3	27.9	9.873e+04	NA	NA	NA	153	P
	11/14/96	VSS	27.8	28	9.921e+04	NA	NA	NA	156	P
BY-109	9/22/94	ISS ^(e)	26.5	NA	9.906e+04	20.3	NA	14	16.1	O
BY-110	11/11/94	VSS	27.0	28.4	9.855e+04	28.8	NA	49.5	NA	
BY-111	11/16/94	VSS	27.0	25	9.759e+04	2.2	NA	8.21	9.6	
BY-112	11/18/94	VSS	23.2	25.3	1.001e+05	5.8	NA	13.8	NA	
C-101	9/1/94	VSS	34.0	35.1	9.862e+04	80.1	NA	84.7	256	O
C-102	8/23/94	VSS	25.8	26.5	9.902e+04	296	NA	134	313	O
C-103	May-94	VSS	38.0	38.8	9.933e+04	1238.5	NA	NA	520	O
C-107	9/29/94	VSS	46.0	46.4	9.835e+04	3.7	NA	6.4	3.6	
	1/17/96	VSS	41.5	42.4	9.971e+04	NA	NA	NA	3.6	
	3/26/96	VSS	39.8	40.2	9.909e+04	NA	NA	NA	4.2	
	9/5/96	VSS	44.1	43.1	9.869e+04	NA	NA	NA	1.72	P
C-108	8/5/94	VSS	25.0	25	9.893e+04	0.94	NA	NA	0.35	O
C-109	8/10/94	VSS	27.0	27.1	9.919e+04	1.57	NA	0.38	0.65	O
C-110	8/18/94	VSS	21.9	22.7	9.910e+04	22.6	NA	8.32	22.3	O
C-111	9/13/94	VSS	27.0	26.4	9.883e+04	1.1	NA	0.4	0.18	O
C-112	8/11/94	VSS	28.0	28.1	9.879e+04	6.1	NA	3	3.4	O

Table 3.1 (contd)

Tank	Date Sampled	Sampling Method	Temperature from Vapor Probe (°C)	Temperature from TC Tree (°C)	Pressure (Pa)	Total Non-Methane Organic Compound Concentration (mg/m ³)				Notes
						ORNL TST GC/MS	PNNL TST GC/MS	SUMMA GC/MS	SUMMA GC/FID	
C-201	6/20/96	ISVS	15.2	16.1	9.922e+04	NA	NA	NA	2.7	
C-202	6/25/96	ISVS	19.6	16.3	9.821e+04	NA	NA	NA	1.2	
C-204	7/2/96	ISVS	17.8	NA	9.825e+04	NA	36.8	128.6	80.2	
S-101	6/6/96	ISVS	30.4	30.8	1.005e+05	NA	13.3	14.6	8.3	
S-102	3/14/95	VSS	24.3	24.2	9.882e+04	9.4	NA	20.6	NA	
	1/26/96	VSS	19.0	25.8	9.982e+04	NA	NA	NA	16.5	
	4/4/96	VSS	23.1	24.1	1.004e+05	NA	NA	NA	15	
	9/19/96	VSS	28.5	29	9.898e+04	NA	NA	NA	13.8	P
S-103	6/12/96	ISVS	22.6	23.7	9.915e+04	NA	8.16	6.92	1.2	
S-105	12/7/95	VSS	21.7	23	9.978e+04	2	NA	NA	2.52	
S-106	6/13/96	ISVS	19.1	19.4	9.865e+04	NA	14.41	8.78	1.8	
S-107	6/18/96	ISVS	26.6	27.8	9.957e+04	NA	NA	NA	3.5	
S-108	12/6/95	VSS	22.6	22.1	1.001e+05	0.96	NA	NA	2.56	
S-109	6/4/96	ISVS	20.5	18.8	9.913e+04	NA	NA	NA	3.7	
S-110	12/5/95	VSS	26.2	27.7	9.983e+04	2.6	NA	NA	3.85	
S-111	3/21/95	VSS	23.0	21.4	9.749e+04	1.5	NA	2	NA	
S-112	7/11/95	VSS	30.8	20	9.905e+04	NA	5.00	5.87	8.22	
T-104	2/7/96	VSS	14.3	15.1	9.873e+04	NA	NA	1.93	1.93	
T-107	1/18/95	VSS	17.2	17.4	9.903e+04	1.4	NA	4.1	NA	
T-110	8/31/95	VSS	18.6	19.9	9.926e+04	NA	0.62	0.04	1.12	
T-111	1/20/95	VSS	15.4	16.1	9.961e+04	24.2	NA	21.7	NA	
TX-105	12/20/94	VSS	24.8	25.7	9.866e+04	1.2	NA	5.15	NA	
TX-111	10/12/95	VSS	22.6	19.6	9.993e+04	11	NA	15.78	16.31	
TX-118	12/16/94	VSS	21.5	22	9.893e+04	6.1	NA	11.8	9.2	

Table 3.1 (contd)

Tank	Date Sampled	Sampling Method	Temperature from Vapor Probe (°C)	Temperature from TC Tree (°C)	Pressure (Pa)	Total Non-Methane Organic Compound Concentration (mg/m ³)				Notes
						ORNL TST GC/MS	PNNL TST GC/MS	SUMMA GC/MS	SUMMA GC/FID	
TY-101	4/6/95	VSS	15.6	16.6	9.830e+04	1	NA	1.65	NA	
TY-102	4/12/96	VSS	13.7	14.6	9.883e+04	NA	0.85	0.77	0.35	
TY-103	4/11/95	VSS	15.9	16.4	9.945e+04	60	NA	31.9	NA	
TY-104	4/27/95	VSS	15.6	16.3	9.825e+04	3	NA	1.5	NA	
U-103	2/15/95	VSS	29.0	21.8	9.823e+04	7.2	NA	8.6	NA	
U-105	2/24/95	VSS	42.6	22.3	9.922e+04	4.4	NA	3	NA	
U-106	3/7/95	VSS	21.9	20.3	9.957e+04	10.1	NA	12.4	NA	
U-107	2/17/95	VSS	22.6	20.5	9.830e+04	6.4	NA	17.1	NA	
U-108	8/29/95	VSS	26.6	27.7	9.926e+04	NA	NA	6.08	12	
U-109	8/10/95	VSS	33.0	28.8	9.773e+04	NA	10.87	7.2	9.25	
U-111	2/28/95	VSS	20.0	20.2	1.004e+05	9.1	NA	4.3	NA	
U-112	7/9/96	ISVS	18.3	18.4	9.847e+04	NA	13.98	6.72	2	
U-203	8/9/95	VSS	17.7	17.8	9.898e+04	NA	14.6	10.6	1.98	
U-204	8/8/95	VSS	17.8	13.8	9.947e+04	NA	4.23	7	0.86	

(a) VSS = Vapor sampling system.
 (b) ISVS = in situ vapor sampling [system]. Tank pressures for ISVS events were based on barometric pressure measurements from the Hanford Meteorological Station.
 (c) P = prelimiNary data.
 (d) O = total non-methane organic compound concentration given for SUMMA™ canister samples by GC/FID was determined by OGIST.
 (e) ISS = in situ sampling [method]. Tank BY-109 organic vapor and temperature data were obtained using a prototype of the ISVS system. Tank pressure given was based on barometric pressure measurements from the Hanford Meteorological Station.

the difference between the measurements is less than 2°C. A notable exception to the generally good agreement is Tank U-105, which had head space temperatures of 42.6 and 22.3°C according to the vapor sampling probe and TC tree, respectively. In this case, the vapor sampling probe temperature reading appears to be in error.

In all cases in which both vapor sampling probe and TC tree temperatures were available, screening calculations were performed using the lower temperature. Using the lower head space temperature decreases the calculated saturation concentration of organic vapors, C_{sat} , which tends to increase the estimated surface area of organic liquid waste (i.e., from the perspective of assessing risk, using the lower temperature is more conservative).

3.2 Pressures

Tank head space pressures were routinely measured at the start of each sampling event. Measured values were used in screening calculations to adjust pressure dependent organic vapor concentrations (mg/m^3) from standard pressure ($1.013 \times 10^5 \text{ Pa}$) to the measured pressure of the tank at the time of sampling. This adjustment is necessary to place measured organic vapor concentrations and those estimated by the model on a consistent basis.

Table 3.1 lists tank head space pressures for each of the sampling events. The sampling equipment did not include pressure instrumentation in certain recent sampling events, so no direct measurement of the tank head space pressure was made. In those cases, atmospheric pressure reported by the Hanford Meteorological Station for the date and time of sample collection was used to estimate the head space pressure. These readings are noted in the table.

Tank head space pressures were reviewed for reasonableness and verified against values in the Tank Characterization Database (PNNL 1996). Pressure is used only to make a minor adjustment of vapor concentrations from STP to tank conditions (typically the adjustment due to pressure is less than 3% of the concentration), and variations in head space and barometric pressure are relatively small.

3.3 Ventilation Rates

The tank head space ventilation rate is a key parameter in the model. The guidelines of the current safety documentation (Cowley et al. 1996) estimate the ventilation rate of the passively ventilated single-shell tanks to be the arithmetic sum of 1) ventilation due to barometric pressure fluctuations and 2) ventilation due to an air purge used to protect certain instruments (instrument air). In the absence of other factors, barometric pressure fluctuations would cause an average 0.45% of a tank head space volume to be exchanged with the atmosphere each day (Crippen 1993). Operating specifications for the instrument air allowed purge rates as high as $1.4 \text{ m}^3/\text{h}$ ($50 \text{ ft}^3/\text{h}$) on tanks with certain automatic level gauges. The corresponding estimated ventilation rate can therefore be expressed as

$$Q = 1.416 + 0.0001875 * V$$

where Q is the ventilation rate in m^3/h , and V is the tank head space volume in m^3 . For the tanks considered in this report, this estimate provides a maximum value for Q of about $2.3 \text{ m}^3/\text{h}$. (Tank AX-102 has the largest head space volume, which Palmer et al. [1996] estimate to be $4,686 \text{ m}^3$.)

Ventilation rates were recently estimated by Wilkins et al. (1996) for seven passively ventilated tanks by measuring the rates at which hydrogen concentrations decrease after gas release events. Table 3.2 summarizes the data for the seven tanks. All of the ventilation rates given in Table 3.2 are higher than the

Table 3.2. Ventilation Rates from Hydrogen Monitoring Data

Tank	Date	Ventilation Rate (ft ³ /min)	Ventilation Rate (m ³ /h)	Average (m ³ /h)
S-111	November 1995	2	3.4	6.0
	December 1995	4	6.8	
	December 1995	4	6.8	
	February 1996	4	6.8	
S-112	January 1996	4	6.8	6.8
U-103	October 1995	2.5	4.3	9.6
	November 1995	7	12	
	December 1995	2	3.4	
	February 1995	11	19	
U-105	December 1995	9	15	12
	February 1996	5	8.5	
U-107	December 1995	4.5	7.7	6.4
	February 1996	3	5.1	
U-108	October 1995	3	5.1	5.7
	November 1995	4	6.8	
	December 1995	3	5.1	
U-109	September 1995	4	6.8	6.2
	October 1995	5	8.5	
	December 1995	2	3.4	
Column Average		4.4	7.4	7.5
(a) Values in ft ³ /min are reported directly from Wilkins et al. (1996).				

highest rate (2.3 m³/h) predicted by Cowley et al.(1996). Because underestimating the ventilation rate could result in incorrectly concluding that a tank does not contain a significant amount of organic liquid waste (when it actually does), the ventilation rate used in the screening test was based on the estimates given by Wilkins et al. (1996).

The individual ventilation rate measurements in Table 3.2 vary significantly. Tank U-103, for example, had measured rates ranging from 3.4 to 19 m³/h, which follow a low-high-low-high sequence over the four-month period they were measured. Given the variability of the measurements, it was decided that the average of tank-averaged values represented the best estimate of the passive ventilation rate. Specifically, it was assumed that

$$Q = 7.5 \text{ m}^3/\text{h}$$

for all tanks (even those for which measurements of Q are available), as given in the last column of Table 3.2.

3.4 Organic Vapor Concentrations

Head space organic vapor concentrations were determined by sampling each tank head space and analyzing the samples at analytical laboratories. Two different sampling methods were used to collect samples, and two different sampling media were used. Available results are given in Table 3.1.

3.4.1 Vapor Sampling Methods

The vapor phase data used in this report are based on samples collected using either the vapor sampling system (VSS) method or the in-situ vapor sampling (ISVS) method. Both methods provide means for exposing sampling media to the tank head space gases and vapors.

The VSS transports air from the tank head space to sampling media located in a mobile laboratory above the tank. Transport losses of head space constituents are minimized by extensively purging the system with head space air and by heating all transfer tubing and the sampling manifold. The ISVS method treats the two sampling media differently; sorbent trap sampling media are lowered into the tank head space to avoid sample transport losses, and SUMMA^(a) canister samples are collected using a purged (but unheated) transfer tube that allows the bulky canisters to remain outside the tank.

Testing and validation of the VSS for tank head space sampling have been described by Mahon et al. (1997). Huckaby et al. (1996) describe both methods and the results of tests that compared the performance of the two methods. The comparison tests indicated that the methods were equivalent for organic liquid waste screening.

3.4.2 Vapor Sampling Media

Both the VSS and ISVS methods allow collection of samples using two different sampling media, evacuated SUMMA canisters and triple sorbent traps (TSTs).

(a) SUMMA is a registered trade mark of Molectrics, Inc., Cleveland, Ohio.

SUMMA canisters are stainless steel vessels whose internal surfaces have been prepared by the SUMMA process, which passivates active sites on the canister walls to minimize the adsorption of gases and vapors. SUMMA canisters used for waste tank sampling are cleaned, tested for contaminants, and evacuated at an analytical laboratory before use. The evacuated canisters are filled with air from the tank through a valve, which is then closed to seal the sample inside. SUMMA canister samples are then sent to an analytical laboratory for analysis. SUMMA technology is generally accepted by analytical air chemists for collection of organic vapors in air and is specifically cited in the U.S. Environmental Protection Agency (EPA) TO-12 and TO-14 methods for air analysis (EPA 1988).

The TSTs, which are small glass or stainless steel tubes that contain three beds of different sorbent material, are also used to sample organic vapors in waste tank head spaces. A known amount of sample gas is passed through the tube, which traps (by adsorption) virtually all of the organic vapors. Unlike SUMMA canisters, TSTs concentrate organic vapors by selectively removing them from the air sample, and other constituents of the air (oxygen, nitrogen, argon, etc.) are not collected. After sampling is complete, TSTs are sealed and sent to a laboratory for analysis.

3.4.3 Vapor Sample Analyses

Samples from both SUMMA canisters and TSTs are transferred and concentrated for analysis. SUMMA canister samples are transferred by cryogenically concentrating the organic vapors present in a subsample of the air in the canister. Adsorbed organic vapors in TST samples are thermally desorbed from the sorbent media and cryogenically concentrated.

The concentrated organic compounds are then analyzed either by gas chromatography with mass spectrometric detection (GC/MS) or by gas chromatography with flame ionization detection (GC/FID). GC/MS is used to identify individual organic constituents in both TST and SUMMA canister samples and provides quantitative concentration information on targeted species and estimated concentration information on non-targeted species. The SUMMA canister GC/MS method is a modification of the EPA TO-14. GC/FID analysis is applied to SUMMA canister samples to measure the concentration of TNMOC using EPA TO-12.

The three analyses (TO-12 and TO-14 of SUMMA canisters and GC/MS of TSTs) should provide comparable measurements of the TNMOC concentration. However, because there are differences in both the sampling media and analyses, some discrepancies are expected. For example, for GC/MS analyses of SUMMA and TST samples, the concentration of TNMOC is determined by summing the concentrations of the individual species. The concentrations of the non-targeted species can only be estimated, and in those tanks that have a preponderance of non-targeted species present, the error may be relatively high. In addition, mass spectral quantitation is not as linear as FID quantitation, introducing additional errors. If the organic constituents are complex and separation is relatively poor, quantitation is also less accurate. On the other hand, TO-12 quantitation is based on a propane calibration, and if all constituents are hydrocarbons, it is quite accurate. Compounds to which the FID is insensitive (e.g., perchlorinated compounds) or to which the FID responds poorly (e.g., highly oxidized compounds) are not properly represented in the TO-12 TNMOC concentration.

Generally, for tanks with low organic concentrations, the GC/MS and GC/FID TNMOC results may differ by an order of magnitude because individual species often dominate the measurement. However, because the concentrations are so low, these discrepancies have a negligible effect on the assessment of

risk. For higher concentrations of TNMOC, differences between the GC/MS and GC/FID results are well under an order of magnitude, typically being within a factor of two or three.

3.4.4 Adjustment for Volatile Organic Compounds

The TNMOC concentration includes all detectable organic vapors, including many volatile species. Because of this, the TNMOC concentration is an inherently high estimate of the semivolatile compound vapors present. To avoid misidentifying a tank as possibly having a significant quantity of organic liquid waste when in fact it does not, available organic speciation data have been used to adjust TNMOC concentrations for the presence of volatile species. The adjustment was unnecessary for most tanks because, even when all the TNMOC are assumed to be semivolatile compounds, the screening calculations indicate the tank has less than a 1-m² surface area of semivolatile organic liquid waste.

To account for the volatile species included in TNMOC measurements, organic speciation data from GC/MS analyses were used to calculate the mass concentration fraction of semivolatile species. The TNMOC concentration was then multiplied by this factor to estimate the actual concentration of semivolatile species in the tank head space. n-Decane and all compounds that eluted after n-decane in the gas chromatogram were considered to be semivolatile. The mass concentration fraction of semivolatile species, X , was calculated for each tank using the following formula:

$$X = \frac{\sum_{i > \text{decane}} \bar{c}_i}{\sum_{i > \text{methane}} \bar{c}_i} \quad (3.1)$$

where \bar{c}_i is the reported average concentration of the i th species.

Values of X were calculated for both SUMMA canister and TST samples (when GS/MS data were available). The TNMOC concentration was then multiplied by the larger value of X , and this product was used instead of the unadjusted TNMOC concentration in all screening calculations (see Table 3.1). Cowley et al. (1996) employed a similar approach when performing their uncertainty analysis on Tank BY-104 results.

The need for this correction of the TNMOC value can be seen by considering Tanks U-203 and U-204. Both of these tanks appear to have organic liquid waste surface areas of more than 1 m² when the unadjusted TNMOC concentrations are used in the screening calculations. However, results of the GC/MS analyses of head space samples indicate that the mass concentration fraction of semivolatile species is only 0.03 in Tank U-203 and 0.01 in Tank U-204. In fact, the reported TNMOC concentration (by GC/MS) in both of these tanks was dominated by a single halocarbon refrigerant (trichlorofluoromethane), and none of the Tank C-103 semivolatile compounds were above instrument detection limits. At the same time, semivolatile compounds dominate the TNMOC concentrations of other tanks, including T-111 and TY-103, in which the mass concentration fractions of semivolatile species were 0.93 and 0.97, respectively.

Tanks BX-104, BY-108, C-107, and S-102 have been sampled recently for a study on the effects of seasonal variations of the tank head spaces. Because the study addresses only a selected list of targeted analytes and does not include estimates of tentatively identified compound concentrations, no mass

concentration fraction of semivolatile species can be calculated for these events. In these instances, the mass concentration fraction of semivolatile species estimated from previous sampling events was used to correct the TNMOC values.

3.4.5 Verification of Vapor Data in Spreadsheet

Concentrations of TNMOC were obtained directly from reports on TST analyses by PNNL and ORNL, SUMMA canister GC/MS analyses by PNNL, and SUMMA canister GC/FID analyses by PNNL and OGIST. Values obtained from the analytical reports were compared with the values obtained from the Tank Characterization Database to verify that the information was correct (PNNL 1996). Differences were generally attributable to the number of significant figures used in the calculations. All TO-12 results have been verified, but a small number of GC/MS results remain unverified because the Tank Characterization Database has not yet been populated with all of the early data.

4.0 Analysis of Uncertainties

An analysis of uncertainties was performed to establish confidence limits on the screening test results. Specifically, the objective was to determine, with 95% confidence, the largest surface area of organic liquid waste that might exist in each tank.

Cowley et al. (1996) performed a Monte Carlo method sensitivity and uncertainty analysis on the data and results for Tank BY-104. Because the Monte Carlo method involves a large number of calculations and does not lend itself to incorporation into an Excel spreadsheet, a different approach to estimating uncertainties has been adopted here. However, when practicable, the current analysis employs probability distributions for the independent variables that are the same as or similar to those developed by Cowley et al. (1996).

4.1 Variance of Organic Liquid Waste Surface Area

The uncertainty of the calculated surface area, A , of organic liquid waste was estimated by assuming that it is normally distributed with a mean corresponding to its true value. It was also assumed that the variance of A is due to random errors in the independent variables.

A standard treatment of random error propagation was used that estimates the variance of a function using partial differentials of the function and estimated variances of the dependent variables. As described in Section 2.2, the surface area of organic liquid waste, A , is a function of the ventilation rate, Q , the mass transfer coefficient, k , the saturation concentration of semivolatile organic vapors, C_{sat} , and the observed head space concentration of semivolatile organic vapors, C_{obs} . The equation for variance of A is given by

$$\sigma^2(A) = \left(\frac{\partial A}{\partial Q}\right)^2 \sigma^2(Q) + \left(\frac{\partial A}{\partial C_{obs}}\right)^2 \sigma^2(C_{obs}) + \left(\frac{\partial A}{\partial C_{sat}}\right)^2 \sigma^2(C_{sat}) + \left(\frac{\partial A}{\partial k}\right)^2 \sigma^2(k) \quad (4.1)$$

where $\sigma^2(Y)$ is the variance of the parameter Y .

The partial differential terms in this equation were derived from the expression for A and evaluated directly for each tank. Subsections 4.1.1 through 4.1.4 describe the bases for estimation of independent variable variances.

4.1.1 Variance of Ventilation Rate

The variance of the ventilation rate, $\sigma^2(Q)$, was determined from data in Table 3.2. Because the value of Q used in calculations is the average of individual tank averages (and not the simple average of all measurements), the variance of Q depends on the variances of data associated with each tank. The variance, following an analogous situation discussed by Hogg and Ledolter (1992, p. 275), is given by the following:

$$\sigma^2(Q) = \frac{1}{N} \sum_{i=1}^N \sigma_i^2(Q) + \frac{1}{N} \sum_{i=1}^N \left(\bar{Q}_i - \frac{1}{N} \sum_{i=1}^N \bar{Q}_i \right)^2 \quad (4.2)$$

Here

N = number of tanks

$\sigma_i^2(Q)$ = variance of ventilation rate data for i th tank

\bar{Q}_i = mean ventilation rate of i th tank.

For the ventilation rates given in Table 3.2, and assigning the variance of the single measurement for Tank S-112 to be zero, the above equation yields

$$\sigma^2(Q) = 17.33 \text{ m}^6/\text{h}^2$$

4.1.2 Variance of Observed Organic Vapor Concentration

The TNMOC concentrations reported by the analytical laboratories were subject to both sampling and analytical errors. Errors have been addressed by employing two different types of sampling media (SUMMA canisters and TSTs), using different analytical laboratories, and performing comparison tests of the VSS and ISVS methods (Huckaby et al. 1996).

Agreement between results from the two types of sampling media and results from independent laboratories can be determined by considering the TNMOC data presented in Table 3.1. The independent values agree fairly well, and there is no apparent bias suggesting that higher TNMOC values tend to come from either sampling medium or from either of the analytical laboratories. Biases that might cause an underestimation of tank head space TNMOC concentrations have been reduced by using the largest of the average concentrations reported to calculate organic liquid waste surface area.

Comparison tests of the VSS and ISVS methods demonstrated that these two significantly different sampling methods provided very similar results. Though SUMMA canister samples collected with the ISVS method did exhibit losses of semivolatile organic compounds, these losses were minor even for samples from a tank with a very high TNMOC concentration and where sampling was conducted under very adverse conditions. It is noteworthy that the precision of final analytical measurements (e.g., relative standard deviation for a given type of sample) are usually as good as can be expected from the analytical method, suggesting that random sampling errors are small compared with random analytical errors.

The variance of head space TNMOC concentrations was estimated from a general assessment of the analytical accuracy expected for GC/MS. Specifically, it was assumed that there is a 95% confidence that

the reported TNMOC values are correct to within 30% of the true value, and that the values are normally distributed about the true mean. From a table of the standard normal distribution, this means

$$2 \sigma(C_{STP}) \approx 0.30 C_{STP}$$

where C_{STP} is the reported TNMOC concentration at STP, and $\sigma(C_{STP})$ is the standard deviation of the reported concentration. It was assumed that this estimate of variance includes random errors associated with determining and applying the mass concentration fraction of semivolatile species described in Section 3.4.4.

The reported TNMOC concentration at STP is adjusted to tank temperature and pressure, and C_{obs} is calculated using the following equation:

$$C_{obs} = C_{STP} \left(\frac{273.15 \text{ K}}{T} \right) \left(\frac{P}{760 \text{ torr}} \right)$$

The variance in C_{obs} can now be related to the variances in C_{STP} , T , and P using the same propagation-of-random-errors rule as adopted in Section 4.1:

$$\sigma^2(C_{obs}) = \left(\frac{\partial C_{obs}}{\partial C_{STP}} \right)^2 \sigma^2(C_{STP}) + \left(\frac{\partial C_{obs}}{\partial T} \right)^2 \sigma^2(T) + \left(\frac{\partial C_{obs}}{\partial P} \right)^2 \sigma^2(P) \quad (4.3)$$

Where $\sigma^2(T)$ and $\sigma^2(P)$ are the variances of the measured tank temperature and pressure, respectively. The partial differential terms were derived from the expression for C_{obs} and evaluated within the spreadsheet. Measurements of tank temperatures and pressures were assumed to be affected by random errors, and the reported values were normally distributed with means corresponding to their true values. Temperatures were assumed to have a standard deviation of 2°C [i.e., $\sigma^2(T) = 4^\circ\text{C}^2$], and pressures were assumed to have a standard deviation of $6.7 \times 10^2 \text{ Pa}$ (5 torr) [i.e., $\sigma^2(P) = 4.4 \times 10^5 \text{ Pa}^2$].

4.1.3 Variance of Saturated Organic Vapor Concentration

The saturation vapor concentration of semivolatile organic compounds, C_{sat} , was calculated for each tank as a function of the head space temperature. The uncertainty of this variable is not, however, determined by the uncertainty in temperature measurement. Instead, the estimation of component vapor pressures at the head space temperature and the assumption that organic waste liquids would have the same composition as that in Tank C-103 probably introduced much greater uncertainties.

In their sensitivity analysis, Cowley et al. (1996) assumed the calculated C_{sat} was correct to within a factor of four and assigned equal probability to the true value as being between $0.25C_{sat}$ and $4C_{sat}$. However, that distribution does not lend itself to the propagation-of-random-errors treatment applied in this report. Here a normal distribution for C_{sat} was assigned with a variance of

$$\sigma^2(C_{sat}) = \frac{9}{64} C_{sat}^2$$

This distribution and variance correspond to those assuming that the 95% confidence limits on the true C_{sat} value are at $0.25C_{sat}$ and $1.75C_{sat}$.

Note that to meet the objective of this uncertainty analysis (i.e., determine the largest value of A for which there is a 95% confidence that the true value is less than A), only errors that result in overestimating C_{sat} are of concern. Thus, though the normal distribution for C_{sat} adopted here results in very low probabilities for values above about $1.75 C_{sat}$ (unlike the distribution of Cowley et al. [1996], which is uniform between $0.25C_{sat}$ and $4C_{sat}$), this region of the distribution is not of interest.

4.1.4 Variance of Mass Transfer Coefficient

Cowley et al. (1996) used a normal distribution for the mass transfer coefficient, k , and assigned it a standard deviation of 20% of k . This distribution and standard deviation were adopted in this study so that

$$\sigma^2(k) = 0.04 k^2$$

4.1.5 Comparison of Variance Terms

Table 4.1 lists calculated values of $\sigma^2(A)$ and the terms on the right hand side of Equation (4.1) for the 14 tanks with the highest $\sigma^2(A)$ values. Tanks are listed in the order of decreasing values of $\sigma^2(A)$. The highest $\sigma^2(A)$ values (at the top of the table) are associated with very large C_{sat} and C_{obs} variance terms. These variance terms are very large because the term

$$\left(\frac{C_{sat}}{C_{obs}} - 1 \right)$$

in Equation (2.1) is small (or even negative, as in the case of Tank C-103). The estimated variance of A is dominated by the variance assigned to C_{sat} for the first seven tanks in Table 4.1 but tends to be dominated by the variance assigned to the ventilation flow rate, Q , for all other tanks, including all tanks not listed in the table.

The variance term associated with the mass transfer coefficient, k , is small compared with other terms in Equation (4.1). Because they differ only by constants, the ratio of the mass transfer coefficient variance term (column six in Table 4.1) to the ventilation flow rate variance term (column three in the table) is 0.13 for all tanks.

Table 4.1. Evaluated Terms of Equation (2.1)

Tank	Sample Date	$\sigma^2(A) = \left(\frac{\partial A}{\partial Q}\right)^2 \sigma^2(Q) + \left(\frac{\partial A}{\partial C_{obs}}\right)^2 \sigma^2(C_{obs}) + \left(\frac{\partial A}{\partial C_{sat}}\right)^2 \sigma^2(C_{sat}) + \left(\frac{\partial A}{\partial k}\right)^2 \sigma^2(k)$				
		$\left(\frac{\partial Q}{\partial A}\right)^2 \sigma^2(Q)$	$\left(\frac{\partial A}{\partial C_{obs}}\right)^2 \sigma^2(C_{obs})$	$\left(\frac{\partial A}{\partial C_{sat}}\right)^2 \sigma^2(C_{sat})$	$\left(\frac{\partial A}{\partial k}\right)^2 \sigma^2(k)$	$\sigma^2(A)$
BY-108	10/27/94	6.70e+05	3.10e+09	1.90e+10	8.60e+04	2.20e+10
C-204	7/2/96	4,943	90,395	562,637	643	660,000
C-102	8/23/94	107	137	855	14	1,100
C-103	May-94	66	30	184	9	290
TY-103	4/11/95	58	25	155	8	250
BY-101	8/29/96	5.2	0.9	5.5	0.7	12.2
C-101	9/1/94	2.9	0.6	3.7	0.4	7.6
T-111	1/20/95	3.1	0.4	2.4	0.4	6.3
BX-104	12/30/94	2.4	0.4	2.3	0.3	5.4
BX-103	8/1/96	1.1	0.1	0.8	0.1	2.2
BY-107	10/26/94	0.72	0.09	0.54	0.09	1.40
B-103	2/8/95	0.56	0.05	0.32	0.07	1.00
C-110	8/18/94	0.13	0.01	0.07	0.02	0.22
S-112	7/11/95	0.061	0.005	0.031	0.008	0.110

4.5

4.2 95% Confidence Limit for Organic Liquid Waste Surface Area

An upper confidence limit for the value of A was established using the variance calculated with Equation (4.1) and estimated variances of the independent variables described in Sections 4.1.1 through 4.1.4. Assuming that A is normally distributed, there is a 95% probability that its value is less than $A + 1.65 \sigma(A)$. Section 5 presents the calculated 95% confidence values for A and discusses their role in interpreting screening results.

5.0 Screening Results

Screening calculations were performed using data from 86 tank head space vapor sampling events from 75 passively ventilated waste tanks. Key parameters of the screening calculations and estimated organic liquid waste surface areas for each of the 86 sampling events are listed in Table 5.1. Calculations were performed with an Excel spreadsheet program, version 5.0, on a personal computer. All parameters and constants were imbedded in the cell calculations. Entries in Table 5.1 were left blank when data were not available but are anticipated. Except when indicated as preliminary with a "P" in the last column, all data associated with each sampling event are considered final. Entries are marked "NA" when data were not available, for example, when the measurement or analysis was not performed.

The estimated organic liquid waste surface area, A , is greater than 1 m^2 for 12 tanks, as indicated by "Yes" in the ninth column of the table, and greater than 5 m^2 for five tanks (Tanks BY-108, C-102, C-103, C-204, and TY-103). Of the 12 tanks for which $A > 1 \text{ m}^2$, four are in the 241-C tank farm, and three are in the 241-BY farm. Most of the tanks identified as containing potentially significant quantities of organic liquid waste are in the 241-BY and 241-C tank farms, which agrees qualitatively with the fact that these tank farms received the majority of the PUREX process organic wash waste and waste organic liquids (Sederburg and Reddick 1994). Over 25% of the passively ventilated tanks in these two farms were indicated to have $A > 1 \text{ m}^2$ (all tanks in the 241-BY and 241-C farms have been vapor sampled and screened except for Tank C-203), while only about 10% of tanks outside of the 241-BY and 241-C farms were found to have $A > 1 \text{ m}^2$.

One tank, C-103, was determined to have a negative value for A because $C_{sat} < C_{obs}$ for this tank (see Table 5.1, columns five and six, and Equation 2.3). Because the true C_{sat} must be greater than C_{obs} , either the estimated C_{sat} value is too low and/or the estimated C_{obs} value is too high. Both these biases tend to cause a conservative identification of tanks as having potentially significant amounts of organic liquid waste.

Table 5.1 also lists estimated 95% confidence limit values for A for each sampling event in the tenth column. These values are generally about twice as large as the best estimate of A except for the five tanks with a very large $\sigma^2(A)$. Only one tank, C-110, has an estimated A less than 1 m^2 and a 95% confidence limit value of A greater than 1 m^2 . Though the screening model itself does not indicate that Tank C-110 has a significant amount of organic liquid waste, this cannot be said with 95% confidence.

In summary, given the screening model and assumptions regarding model input distributions and errors, there is 95% confidence that 1) 62 of the 75 tanks screened do not contain significant amounts of organic liquid waste and 2) 12 of the remaining 13 tanks have a surface area of semivolatile organic waste greater than 1 m^2 .

Table 5.1. Screening Inputs and Results

	Tank	Date Sampled	Fraction of Semivolatile species, X	Saturation Conc. of Semivolatile Species, C_{sat} (mg/m ³)	Observed Conc. of Semivolatile Species, C_{obs} (mg/m ³)	Mass Transfer Coeff., k (m/h)	Organic Liquid Waste Surface Area, A (m ²)	Is $A > 1$ m ² ?	95% Confidence Limit for A (m ²)	Notes
1	A-101	6/8/95	NA	495	22	1.68	0.21		0.45	
2	A-102	11/10/95	NA	402	4.4	1.58	0.05		0.11	
3	A-103	11/9/95	NA	319	6.9	1.46	0.11		0.25	
4	AX-101	6/15/95	NA	220	1.8	1.27	0.05		0.10	
5	AX-102	6/27/95	NA	184	11	1.17	0.41		0.90	
6	AX-103	6/21/95	NA	383	0.46	1.55	0.01		0.01	
7	B-102	4/18/96	NA	93	3.9	0.78	0.42		0.92	
8	B-103	2/8/95	0.61	75	7.8	0.64	1.4	Yes	3.0	
9	B-105	7/30/96	NA	110	3.5	0.87	0.28		0.62	
10	B-107	7/23/96	0.16	91	1.1	0.76	0.12		0.27	
11	B-202	7/18/96	NA	93	0.40	0.78	0.04		0.09	
12	BX-102	7/31/96	0.14	114	1.0	0.90	0.07		0.2	
13	BX-103	8/1/96	0.49	125	24	0.95	1.9	Yes	4.4	P
14	BX-104	12/30/94	0.66	173	51	1.13	2.8	Yes	6.6	
		8/22/96	0.66	148	39	1.05	2.6	Yes	5.9	P
15	BX-105	4/24/96	NA	102	4.0	0.83	0.37		0.82	
16	BX-106	8/15/96	NA	125	0.91	0.95	0.06		0.13	
17	BX-107	11/17/95	NA	132	2.2	0.98	0.13		0.28	
18	BX-110	4/30/96	NA	86	3.5	0.73	0.43		0.95	
19	BX-111	8/27/96	0.11	124	1.1	0.94	0.07		0.2	P
20	BY-101	8/29/96	NA	129	44	0.97	4.1	Yes	9.9	P

Table 5.1 (contd)

	Tank	Date Sampled	Fraction of Semivolatile species, X	Saturation Conc. of Semivolatile Species, C_{sat} (mg/m ³)	Observed Conc. of Semivolatile Species, C_{obs} (mg/m ³)	Mass Transfer Coeff., k (m/h)	Organic Liquid Waste Surface Area, A (m ²)	Is $A > 1$ m ² ?	95% Confidence Limit for A (m ²)	Notes
21	BY-102	11/21/95	0.18	182	3.2	1.16	0.12		0.25	
22	BY-103	11/1/94	NA	200	11	1.22	0.35		0.77	
23	BY-104	6/24/94	0.19	228	9.9	1.29	0.26		0.58	
24	BY-105	7/7/94	NA	224	14	1.28	0.38		0.84	
25	BY-106	7/8/94	NA	248	11	1.33	0.27		0.59	
26	BY-107	10/26/94	0.39	270	59	1.38	1.5	Yes	3.5	
27	BY-108	10/27/94	0.42	222	221	1.27	1470	Yes	246884	
		1/23/96	0.42	209	77	1.24	3.5	Yes	8.6	
		3/28/96	0.42	199	91	1.21	5.3	Yes	14	
		9/10/96	0.42	268	57	1.37	1.5	Yes	3.4	P
		11/14/96	0.42	266	58	1.37	1.5	Yes	3.5	P
28	BY-109	9/22/94	0.49	238	7.0	1.31	0.17		0.38	
29	BY-110	11/11/94	0.20	248	8.8	1.33	0.21		0.45	
30	BY-111	11/16/94	NA	209	8.5	1.24	0.26		0.56	
31	BY-112	11/18/94	0.15	179	1.9	1.15	0.07		0.15	
32	C-101	9/1/94	0.80	443	177	1.62	3.1	Yes	7.7	
33	C-102	8/23/94	0.61	224	170	1.28	19	Yes	74	
34	C-103	May-94	0.80	606	853	1.77	-15	Yes	13	
35	C-107	9/29/94	NA	1105	5.3	2.01	0.02		0.04	
		1/17/96	NA	792	3.1	1.88	0.02		0.03	
		3/26/96	NA	696	3.6	1.83	0.02		0.05	
		9/5/96	NA	893	1.4	1.93	0.01		0.01	P

Table 5.1 (contd)

	Tank	Date Sampled	Fraction of Semivolatile species, X	Saturation Conc. of Semivolatile Species, C_{sat} (mg/m ³)	Observed Conc. of Semivolatile Species, C_{obs} (mg/m ³)	Mass Transfer Coeff., k (m/h)	Organic Liquid Waste Surface Area, A (m ²)	Is $A > 1$ m ² ?	95% Confidence Limit for A (m ²)	Notes
36	C-108	8/5/94	NA	209	0.84	1.24	0.02		0.05	
37	C-109	8/10/94	NA	248	1.4	1.33	0.03		0.07	
38	C-110	8/18/94	0.66	159	14	1.09	0.64		1.4	
39	C-111	9/13/94	NA	236	1.0	1.30	0.02		0.05	
40	C-112	8/11/94	NA	270	5.4	1.38	0.11		0.24	
41	C-201	6/20/96	NA	86	2.5	0.73	0.31		0.67	
42	C-202	6/25/96	NA	96	1.1	0.79	0.11		0.24	
43	C-204	7/2/96	0.88	110	103	0.87	127	Yes	1466	
44	S-101	6/6/96	NA	330	13	1.48	0.21		0.46	
45	S-102	3/14/95	0.03	195	0.55	1.20	0.02		0.04	
		1/26/96	0.03	123	0.46	0.94	0.03		0.06	
		4/4/96	0.03	177	0.41	1.15	0.02		0.03	
		9/19/96	0.03	282	0.36	1.40	0.01		0.02	P
46	S-103	6/12/96	NA	170	7.4	1.12	0.30		0.67	
47	S-105	12/7/95	NA	157	2.3	1.08	0.10		0.23	
48	S-106	6/13/96	0.15	124	2.0	0.94	0.13		0.28	
49	S-107	6/18/96	NA	240	3.1	1.31	0.08		0.17	
50	S-108	12/6/95	NA	162	2.3	1.10	0.10		0.22	
51	S-109	6/4/96	NA	121	3.4	0.93	0.23		0.51	
52	S-110	12/5/95	NA	232	3.5	1.30	0.09		0.19	
53	S-111	3/21/95	NA	152	1.8	1.06	0.08		0.18	
54	S-112	7/11/95	NA	134	7.5	0.99	0.45		0.98	

Table 5.1 (contd)

	Tank	Date Sampled	Fraction of Semivolatile species, X	Saturation Conc. of Semivolatile Species, C_{sat} (mg/m ³)	Observed Conc. of Semivolatile Species, C_{obs} (mg/m ³)	Mass Transfer Coeff., k (m/h)	Organic Liquid Waste Surface Area, A (m ²)	Is $A > 1$ m ² ?	95% Confidence Limit for A (m ²)	Notes
55	T-104	2/7/96	NA	79	1.8	0.68	0.25		0.56	
56	T-107	1/18/95	NA	104	3.8	0.84	0.33		0.73	
57	T-110	8/31/95	NA	118	1.0	0.92	0.07		0.16	
58	T-111	1/20/95	0.93	88	21	0.74	3.2	Yes	7.29	
59	TX-105	12/20/94	NA	206	4.6	1.23	0.14		0.31	
60	TX-111	10/12/95	0.04	130	0.60	0.97	0.04		0.08	
61	TX-118	12/16/94	0.13	154	1.4	1.07	0.06		0.14	
62	TY-101	4/6/95	NA	90	1.5	0.75	0.17		0.37	
63	TY-102	4/12/96	NA	75	0.79	0.64	0.12		0.27	
64	TY-103	4/11/95	0.97	92	54	0.77	14	Yes	40	
65	TY-104	4/27/95	NA	90	2.8	0.75	0.32		0.69	
66	U-103	2/15/95	NA	158	7.7	1.08	0.36		0.78	
67	U-105	2/24/95	NA	165	4.0	1.11	0.17		0.37	
68	U-106	3/7/95	0.06	138	0.68	1.01	0.04		0.08	
69	U-107	2/17/95	0.05	141	0.77	1.02	0.04		0.09	
70	U-108	8/29/95	NA	240	11	1.31	0.27		0.59	
71	U-109	8/10/95	NA	289	9.5	1.41	0.18		0.40	
72	U-111	2/28/95	0.04	134	0.34	0.99	0.02		0.04	
73	U-112	7/9/96	0.11	115	1.4	0.90	0.10		0.22	
74	U-203	8/9/95	0.03	109	0.40	0.87	0.03		0.07	
75	U-204	8/8/95	0.01	76	0.07	0.65	0.01		0.02	

P = preliminary data were used in calculations.

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Appendix

Mass Transfer Coefficient for Solvent Evaporation

A. K. Postma

Appendix

Mass Transfer Coefficient for Solvent Evaporation

The evaporation rate of solvent from a pool into a tank head space can be expressed as the product of mass transfer coefficient, concentration driving force, and pool area:

$$SER = k_c(C_s - C_b)A \quad (A.1)$$

where

- SER = solvent evaporation rate, kg/s
- k_c = mass transfer coefficient, m/s
- C_s = solvent vapor concentration at pool interface, kg/m³
- C_b = solvent vapor concentration in bulk head space air, kg/m³
- A = pool interfacial area, m².

Numerical values of k_c applicable to waste tanks were estimated using the Chilton-Colburn mass transfer-heat transfer analogy (Sherwood et al. 1975) and a natural convection heat transfer correlation applicable to horizontal heated surfaces facing upward (McAdams 1954). The Chilton-Colburn analogy relates the mass transfer coefficient to heat transfer coefficient and fluid properties as follows:

$$k_c = \frac{h_c D_{AB}}{k} \left(\frac{Sc}{Pr} \right)^{1/2} \quad (A.2)$$

where

- k_c = mass transfer coefficient, m/s
- h_c = heat transfer coefficient, W/m²·K
- D_{AB} = diffusivity of solvent vapor, m²/s
- k = thermal conductivity of gas, W/m·K
- Sc = Schmidt number, dimensionless
- Pr = Prandtl number, dimensionless.

Schmidt and Prandtl numbers are defined as follows:

$$Sc = \frac{\nu}{D_{AB}} \quad (A.3)$$

where ν = kinematic viscosity of gas, m²/s, and

$$Pr = \frac{c_p \mu}{k}$$

where

- C_p = heat capacity of gas, J/kg·K
- μ = dynamic viscosity of gas, kg/m·s
- k = thermal conductivity of gas, W/m·K.

Heat transfer coefficients applicable to heated planar surfaces facing upward can be correlated with the product of Grashov and Prandtl numbers (McAdams 1954). A simplified form of this correlation that applies to large Grashov numbers (large surfaces) and normal air temperatures and pressures is presented as the following dimensional equation (McAdams 1954):

$$h_c = 1.52 \Delta T^{1/2} \quad (\text{A.4})$$

where

- h_c = convective heat transfer coefficient, W/m²·K
- ΔT = temperature difference between surface and bulk air (K).

As is evident from Equation (A.4), the magnitude of h_c depends on the temperature difference across the boundary layer of air over the pool. This ΔT can be estimated from the decay heat load in a tank. The heat flux in soil overburden caused by decay heat may be related to head space air temperature, atmospheric air temperature, and the properties of soil overburden (Crowe et al. 1993):

$$\frac{q}{A} = \frac{k_s(T_{vap} - T_{air})}{\Delta Z} \quad (\text{A.5})$$

where

- $\frac{q}{A}$ = heat flux (W/m²)
- T_{vap} = annual average bulk head space air temperature (K)
- T_{air} = annual average atmospheric temperature (K)
- k_s = thermal conductivity of soil overburden, W/m·K
- ΔZ = average depth of soil overburden, m.

The formulation expressed in Equation (A.5) neglects the small temperature differences that would exist from head space air to dome and from soil surface to atmospheric air. The temperature difference (waste surface to tank dome surface) that is associated with the heat flux quantified in Equation (A.5) may be computed by dividing the flux by an overall heat transfer coefficient. The flux is equal to the overall coefficient multiplied by a temperature difference:

$$\frac{q}{A} = (h_c + h_r)\Delta T_{SD} \quad (\text{A.6})$$

where

- h_c = convection heat transfer coefficient, W/m²·K
 h_r = radiation heat transfer coefficient, W/m²·K
 ΔT_{SD} = temperature difference between waste surface and tank dome (K).

Radiation heat transfer from waste surface to tank dome was studied by Crowe et al. (1993), and it was shown that the transfer rate could be expressed as

$$q_{SD} = A_s F_{SD} \sigma (T_s^4 - T_D^4) \quad (\text{A.7})$$

where

- q_{SD} = radiation heat transport rate from waste surface to tank dome, W
 A_s = surface area of waste, m²
 F_{SD} = radiation factor, dimensionless
 σ = Stefan-Boltzmann constant, W/m²·K⁴
 T_s = waste surface temperature (K)
 T_D = tank dome surface temperature (K).

The radiation factor, F_{SD} , was estimated from surface and geometry considerations to be approximately 0.62 by Crowe et al. (1993). The heat transfer coefficient, h_r , appearing in Equation (A.6) can be derived by dividing q_{SD} [Equation (A.7)] by surface area, A_s , and temperature difference, $(T_s - T_D)$. The resulting value of h_r is

$$h_r = F_{SD} \sigma (4T_A^3 + T_A \Delta T_{SD}^2) \quad (\text{A.8})$$

where T_A = average temperature, $(T_s + T_D)/2$.

Mass transfer coefficients may be evaluated as a function of head space air temperature using Equation (A.2), with h_r predicted from Equation (A.4). A calculational scheme using the formulae presented in this appendix is described as follows:

1. Specify a head space air temperature of interest.
2. Compute a heat flux from Equation (A.5). Constants in this equation are assigned values on the basis of information presented by Crowe et al. 1993: k_s , the soil thermal conductivity is ~0.1 W/m·K; T_{AIR} , the annual average atmospheric air temperature is ~286.7·K; ΔZ , the soil overburden depth is ~4.02 m.
3. Compute ΔT_{SD} from Equation (A.6). Because h_c and h_r depend on temperature, an iterative procedure is used to simultaneously solve the equation for ΔT_{SD} and those for radiation heat transfer (A.8) and convective heat transfer (A.4).

4. Compute the temperature drop from waste surface to bulk air by dividing the overall temperature drop, ΔT_{SD} , by two.
5. Compute h_c from Equation (A.4) using the temperature difference calculated in step 4.
6. Compute k_c , the mass transfer coefficient, from Equation (A.2). Simplification used to quantify the parameters of Equation (A.2) include the following:
 - Pr is assigned a constant value of 0.71, a value applicable to air (McAdams 1954).
 - D_{AB} is evaluated for the tetradecane-air pair. This is done with a handbook equation (Perry 1950). Because tetradecane has a higher molecular weight than most components of the solvent, and because predicted diffusivities decrease with increasing molecular weight, the predicted k_c will be lower than would be predicted for solvents having an average molecular weight lower than that of tetradecane.
 - Viscosity and thermal conductivity of the gas are assigned values applicable to air at the temperature of the gas film (average of head space air and waste surface temperatures).

Numerical values of k_c predicted by means of the above described methodology are listed as a function of head space air temperature in Table A.1. A simple means for relating k_c to head space temperature was devised by fitting a quadratic equation in temperature to the data of the table. The form of the equation is

$$k_c = A + BT + CT^2 \quad (\text{A.9})$$

where

$$\begin{aligned} k_c &= \text{mass transfer coefficient, m/h} \\ T &= \text{head space air temperature, } ^\circ\text{C} \\ A, B, C &= \text{fitting constants.} \end{aligned}$$

Because three constants allow curve fit at three points, the fitting constants were chosen so that the quadratic equation agreed with k_c values listed in Table A.1 at temperatures of 14, 42, and 72°C. These temperatures represent the two extremes and the midpoint for the data set listed in the table. Numerical values of A , B , and C were found to be -0.248, 0.072, and 4.97E-4, respectively. Thus the k_c data of Table A.1 may be approximately correlated by

$$k_c = -0.248 + 0.072 T - 4.97E-4 T^2 \quad (\text{A.10})$$

where

$$\begin{aligned} k_c &= \text{mass transfer coefficient, m/h} \\ T &= \text{head space air temperature, } ^\circ\text{C.} \end{aligned}$$

Table A.1. Predicted Mass Transfer Coefficients

Head Space Air Temperature (°C)	Mass Transfer Coefficient (m/h)
14.0	0.66
16.0	0.89
18.0	1.07
20.0	1.20
22.0	1.30
24.0	1.39
26.0	1.47
28.0	1.54
30.0	1.60
32.0	1.66
34.0	1.71
36.0	1.76
38.0	1.81
40.0	1.85
42.0	1.89
44.0	1.93
46.0	1.97
48.0	2.01
50.0	2.04
52.0	2.07
54.0	2.11
56.0	2.14
58.0	2.17
60.0	2.19
62.0	2.22
64.0	2.25
66.0	2.28
68.0	2.30
70.0	2.33
72.0	2.35

Equation (A.10) may be used in preliminary evaluations where a rough approximation of k_c is adequate. Equation (A.10) underpredicts k_c values in Table A.1 by 0 to 20% for temperatures in the range of 14 to 42°C and overpredicts k_c values in the table by 0 to 4% for temperatures in the range of 42 to 72°C. For an improved fit of k_c - temperature data, numerical interpolation of the data of Table A.1 is advised. Alternatively, the solution procedure used to generate the k_c values listed in the table may be implemented to eliminate errors in k_c caused by the imperfect fit of data by Equation (A.10).

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