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Screening for Organic Solvents in Hanford Waste Tanks Using Organic Vapor Concentrations

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MASTER

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Richland, Washington 99352

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. Due to the inhomogeneity of the waste, direct sampling of the tank waste to locate organic liquids may not conclusively demonstrate that a given tank is free of risk. 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 82 passively ventilated high-level radioactive waste tanks at the Hanford Site to identify those that might contain a significant amount of organic liquid waste. It includes seven tanks not addressed in the previous version of this report, *Screening for Organic Solvents in Hanford Waste Tanks Using Total Non-Methane Organic Compound Vapor Concentrations* (Huckaby et al. 1997).

The screening test is based on a simple model of the tank headspace that estimates the effective surface area of semivolatile organic liquid waste in a tank. Analyses by Cowley et al. (1997) 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. Thirteen tanks were identified as potentially containing at least that amount of semivolatile organic liquid based on conservative estimates. 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).

Tank headspace 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 upward in this study to reflect recent information obtained from hydrogen monitoring data and tracer studies.

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. Twenty-one tanks had an estimated area less than 1 m² and a 95% confidence limit value of area greater than 1 m².

In summary, given the screening model and assumptions regarding model input distributions and errors, 13 of the 82 tanks had estimated semivolatile organic liquid surface areas greater than one square meter, and there is a 95% confidence that 48 of the 82 tanks screened do not contain significant amounts of organic liquid waste.

References for Summary

Cowley WL, JM Grigsby, and AK Postma. 1997. *Organic Solvent Topical*. WHC-SD-WM-SARR-036 Rev. 1A, Duke Engineering Systems Hanford, Richland, Washington.

Huckaby JL, JA Glissmeyer, and DS Sklarew. 1997a. *Screening for Organic Solvents in Hanford Waste Tanks Using Total Non-Methane Organic Compound Vapor Concentrations*. PNNL-11490, Pacific Northwest National Laboratory, Richland, Washington.

Sederburg JP and JA Reddick. 1994. *TBP and Diluent Mass Balances in the PUREX Plant at Hanford 1955 - 1991*. WHC-MR-0483, Westinghouse Hanford Company, Richland, Washington.

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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 82 passively ventilated high-level radioactive waste tanks at the Hanford Site to determine which tanks might contain a significant amount of organic liquid waste. It includes seven tanks not addressed in the previous version of this report, *Screening for Organic Solvents in Hanford Waste Tanks Using Total Non-Methane Organic Compound Vapor Concentrations* (Huckaby et al. 1997a). Tank head space organic vapor concentrations and certain physical parameters required by the screening test (Cowley et al. 1997) 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 greatly reduced the inventory of organic liquid wastes in the tanks (Huckaby et al. 1996a), 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. 1997).

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 headspace, headspace organic vapor concentrations, and certain tank physical parameters (Cowley et al. 1997).

1.2 Quality Assurance

Collecting tank headspace 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 sample analytical results from the Oregon Graduate Institute of Science

and Technology (OGIST) and Oak Ridge National Laboratory (ORNL) before October 1995.^(a) 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.^(b) 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 used to estimate the surface area of semivolatile organic waste present in a tank. The data used for the screening process—temperature, headspace 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.

(a) Burnum ST. August 18, 1995. *Qualification of Reported WHC Vapor Program Data*. Letter 95-CHD-065 to President, Westinghouse Hanford Company. U.S. DOE, Richland, Washington.

(b) Hanford waste tanks are designated with the prefix 241- followed by the tank farm designation and individual tank number. In the spreadsheets, the prefix is not used, and the tanks are referred to only by their tank farm designation and the individual tank number, e.g., BY-109, U-204.

2.0 Screening Model

Screening for tanks that may have more than one square meter of surface area of semivolatile organic liquid waste is based on a simple model of tank headspace dynamics, headspace vapor sampling results, and selected headspace physical properties. The model assumes that the concentration of organic vapors in the tank headspace 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. Headspace 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. 1997), 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 headspace 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. (1997).

2.2 Model Description

The surface area of the organic liquid waste, A , was calculated by rearranging the expression given by Cowley et al. (1997) for the vapor concentration of semivolatile organic compounds in a vented headspace:

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

where

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

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

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

Here k is given in m/h when the tank headspace 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. (1997). The derivation of the equation is described in the appendix at the end of this 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:

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

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:

$$\log(p_i^*) = C_{i1} - \frac{C_{i2}}{(T + C_{i3})} \quad (2.4)$$

where C_{i1} , C_{i2} , and C_{i3} 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 headspace 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 headspace 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 headspace at the time samples were collected. The headspace ventilation rate, Q , and measurements of tank headspace 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 used in the model are temperature, pressure, ventilation rate, and organic vapor concentrations in the tank headspace. 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 headspace 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 headspace conditions. Tank headspace 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 headspace 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 headspace temperature, temperature readings were obtained from the permanently installed TC trees.

Tank headspace temperatures were originally obtained from permanently installed TC trees for a correlation study of tank headspace characterization data (Palmer et al. 1996). Waste surface level data were used to determine which TC tree sensors were in the headspace, 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.

Headspace TC tree temperatures were verified by independently retrieving the surface level and TC tree data and recalculating average headspace 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 headspace (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 headspace, 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 headspace temperature was compared with the existing TC tree headspace temperature (obtained from Palmer et al. 1996). Adjustments were then made and documented.

Table 3.1 lists headspace temperature measurements from both the vapor sampling probe and TC tree sensors for each sampling event. The two independent measurements generally agree well. In 72 of the 92 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)	ORNL TST GC/MS	Total Non-Methane Organic Compound Concentration (mg/m ³)				Notes
							PNNL TST GC/MS	SAS SUMMA GC/MS	SAS TST	SAS SUMMA GC/FID	
A101	6/8/95	VSS ^(e)	37.0	35.4	9.89e+04	20	12	26	na ^(b)	na	na
A102	11/10/95	VSS	35.3	32.8	9.96e+04	3.8	na	na	na	na	5.0
A103	11/9/95	VSS	33.2	30	9.87e+04	6.4	na	na	na	na	7.8
A106	1/16/97	ISVS ^(e)	37.0	40.4	1.00e+05	na	na	na	4.8	2.4	1.1
AX101	6/15/95	VSS	25.6	30.4	9.83e+04	3.3	1.1	1.1	na	na	na
AX102	6/27/95	VSS	24.6	23.5	9.96e+04	8.2	7.8	12	na	na	na
AX103	6/21/95	VSS	32.8	32.2	9.92e+04	0.44	0.18	0.52	na	na	na
	3/3/97	ISVS	na	30.6	9.89e+04	na	na	na	na	na	0.89
AX104	1/23/97	ISVS	30.7	31.7	9.87e+04	na	na	na	1.1	0.075	0.34
B102	4/18/96	VSS	16.0	na	9.89e+04	na	na	na	na	na	4.2
B103	2/8/95	VSS	15.2	13.7	1.00e+05	10	na	14	na	na	na
	10/16/96	ISVS	19.0	19.5	9.96e+04	na	12	16	na	na	15
B105	7/30/96	ISVS	18.6	17.8	9.88e+04	na	3.8	2.6	na	na	1.5
B107	7/23/96	ISVS	18.6	15.8	9.92e+04	na	2.3	3.6	na	na	0.84
B202	7/18/96	ISVS	16.5	16	9.91e+04	na	na	na	na	na	0.87
BX102	7/31/96	ISVS	18.2	18.5	9.88e+04	na	7.9	1.1	na	na	0.87
BX103	8/1/96	ISVS	19.2	19.6	9.83e+04	na	42	55	na	na	52
	12/30/94	VSS	22.8	27.7	1.01e+05	85	na	49	na	na	na
	8/22/96	ISVS	22.5	na	9.94e+04	na	66	96	na	na	130
BX104	12/12/96	ISVS	22.3	na	9.90e+04	na	na	na	na	na	83
	2/6/97	ISVS	19.6	na	1.00e+05	na	na	na	na	na	84.7
	4/7/97	ISVS	19.1	na	9.90e+04	na	na	na	na	na	58.5
	6/10/97	ISVS	20.0	na	9.83e+04	na	na	na	na	na	86

Table 3.1 (contd)

Tank	Date Sampled	Sampling Method	Temperature from Vapor Probe (°C)	Temperature from TC Tre (°C)	Pressure (Pa)	Total Non-Methane Organic Compound Concentration (mg/m ³)					Notes
						ORNL TST GC/MS	PNNL TST GC/MS	PNNL SUMMA GC/MS	SAS TST	SAS SUMMA	
BX105	4/24/96	VSS	17.0	18.3	9.90e+04	na	na	na	na	na	4.4
BX106	8/15/96	ISVS	19.2	19.4	9.90e+04	na	na	na	na	na	2.0
BX107	11/17/95	VSS	19.8	21	9.92e+04	2.4	na	na	na	na	2.1
BX110	4/30/96	VSS	15.2	16.8	9.97e+04	na	2.0	4.9	na	na	2.0
BX111	8/27/96	ISVS	19.5	19.1	9.90e+04	na	10	11	na	na	3.3
BY101	8/29/96	ISVS	21.3	19.5	9.91e+04	na	48	47	na	na	57
BY102	11/21/95	VSS	23.4	na	9.94e+04	16	na	na	na	na	20
BY103	11/1/94	VSS	24.5	25.3	9.81e+04	12	na	6.5	na	na	na
BY104	6/24/94	VSS	26.0	26.8	9.96e+04	36	na	21	na	na	61
BY105	7/7/94	VSS	26.0	25.8	9.93e+04	12	na	5.3	na	na	0 ^e
BY106	4/23/97	ISVS	na	21.8	9.83e+04	na	na	na	na	na	13
BY107	7/8/94	VSS	27.0	29	9.87e+04	13	na	13	na	na	9.9
BY107	10/26/94	VSS	33.1	28	9.81e+04	160	na	70	na	na	na
BY108	10/27/94	VSS	25.7	30.5	9.84e+04	581	na	121	na	na	na
BY108	1/23/96	VSS	25.0	26.6	9.90e+04	na	na	na	na	na	222
BY108	3/28/96	VSS	24.4	25	9.88e+04	na	na	na	na	na	243
BY109	9/22/94	ISS ¹⁰	28.3	27.9	9.93e+04	na	na	na	na	na	306
BY110	11/14/96	ISVS	27.8	28	9.92e+04	na	na	na	na	na	311
BY110	1/30/97	ISVS	24.0	24.1	9.95e+04	na	na	na	na	na	215
BY111	11/16/94	VSS	24.0	25	9.76e+04	2.2	na	14	na	na	16
BY112	11/18/94	VSS	23.2	25.3	1.00e+05	6.3	na	50	na	na	0

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	PNNL SUMMA GC/MS	SAS TST	SAS SUMMA	
C101	9/1/94	VSS	34.0	35.1	9.86e+04	98	na	87	na	na	256
C102	8/23/94	VSS	25.8	26.5	9.90e+04	291	na	134	na	na	313
C103	May-94	VSS	38.0	38.8	9.87e+04	2139	na	na	na	na	520
	9/29/94	VSS	45.9	46.4	9.84e+04	4.4	na	7.1	na	na	3.6
	1/17/96	VSS	41.5	42.4	9.97e+04	na	na	na	na	na	3.6
C107	3/26/96	VSS	39.8	40.2	9.91e+04	na	na	na	na	na	2.8
	9/5/96	VSS	44.1	43.1	9.91e+04	na	na	na	na	na	3.4
	12/17/96	VSS	42.5	41.3	1.02e+05	na	na	na	na	na	3.8
	2/7/97	VSS	39.9	38.6	1.01e+05	na	na	na	na	na	3.7
C108	8/5/94	VSS	24.7	25	9.89e+04	na	1.4	0.37	na	na	0.4
C109	8/10/94	VSS	27.0	27.1	9.92e+04	1.8	na	0.4	na	na	0.65
C110	8/18/94	VSS	21.9	22.7	9.91e+04	28	na	5.6	na	na	22
C111	9/13/94	VSS	26.6	26.4	9.88e+04	1.2	na	0.59	na	na	0.18
C112	8/11/94	VSS	28.0	28.1	9.88e+04	6.3	na	3	na	na	3.4
C201	6/19/96	ISVS	15.2	16.1	9.91e+04	na	na	na	na	na	6.3
C202	6/25/96	ISVS	19.6	16.3	9.86e+04	na	na	na	na	na	2.5
C204	7/2/96	ISVS	17.8	na	9.81e+04	na	36	218	na	na	161
S101	6/6/96	ISVS	30.4	30.8	9.92e+04	na	13	15	na	na	8.3

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	PNNL SUMMA GC/MS	SAS TST	SAS SUMMA	SUMMA GC/FID	
	3/14/95	VSS	24.3	24.2	9.88e+04	10	na	21	na	na	na	
	1/26/96	VSS	19.0	25.8	9.98e+04	na	na	na	na	na	na	16
	4/4/96	VSS	23.1	24.1	1.00e+05	na	na	na	na	na	na	16
S102	9/19/96	VSS	28.5	29	9.93e+04	na	na	na	na	na	na	27.5
	1/21/96	VSS	26.3	26.5	1.00e+05	na	na	na	na	na	na	17
	2/11/97	VSS	22.5	23.9	9.99e+04	na	na	na	na	na	na	19.46
S103	6/12/96	ISVS	22.6	23.7	9.90e+04	na	13.0	7.2	na	na	na	2.7
S105	12/7/95	VSS	21.7	23	9.98e+04	2.7	na	na	na	na	na	2.5
S106	6/13/96	ISVS	19.1	19.4	9.87e+04	na	14	9.2	na	na	na	3.9
S107	6/18/96	ISVS	26.6	27.8	9.94e+04	na	na	na	na	na	na	7.1
S108	12/6/95	VSS	22.6	22.1	1.00e+05	0.96	na	na	na	na	na	2.6
S109	6/4/96	ISVS	20.5	18.8	9.89e+04	na	na	na	na	na	na	3.7
S110	12/5/95	VSS	26.2	27.7	9.98e+04	2.9	na	na	na	na	na	3.8
S111	3/21/95	VSS	23.0	21.4	9.75e+04	2	na	2	na	na	na	
S112	7/11/95	VSS	30.8	20	9.90e+04	na	5.0	5.9	na	na	na	8.2
T104	2/7/96	VSS	14.3	15.1	9.87e+04	na	na	1.9	na	na	na	1.9
T107	1/18/95	VSS	21.3	17.4	9.90e+04	1.5	na	3.9	na	na	na	
T110	8/31/95	VSS	18.6	19.9	9.93e+04	na	0.6	0.14	na	na	na	1.1
T111	1/20/95	VSS	15.4	16.1	9.96e+04	24	na	22	na	na	na	
TX104	5/5/97	ISVS	15.2	16.7	9.91e+04	na	na	0.786	1.5	0.21		
TX105	12/20/94	VSS	24.8	25.7	9.87e+04	1.3	na	5.2	na	na	na	
TX106	3/5/97	ISVS	18.1	19.9	9.95e+04	na	na	6.1	4.5	1.6		
TX111	10/12/95	VSS	22.6	19.6	9.99e+04	12	na	16	na	na	na	16

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	PNNL SUMMA GC/MS	SAS TST		
TX113	8/6/97	ISVS	na	19.1	1.01e+05	na	na	na	2.9	7.5	0.7
TX114	3/25/97	ISVS	16.4	na	9.93e+04	na	na	na	12	9.5	3
TX118	12/16/94	VSS	21.5	22	9.89e+04	6.4	na	11	na	na	9.2
TY101	4/6/95	VSS	15.6	16.6	9.83e+04	1.3	na	1.6	na	na	na
TY102	4/12/96	VSS	13.7	14.6	9.88e+04	na	0.97	0.96	na	na	0.35
TY103	4/11/95	VSS	15.9	16.4	9.94e+04	65	na	32	na	na	na
TY104	4/27/95	VSS	na	19.1	9.84e+04	na	12	84	na	na	46
U103	2/15/95	VSS	29.0	16.3	9.82e+04	3.1	na	1.7	na	na	na
U104	7/16/96	VSS	18.7	na	1.01e+05	na	na	11	na	na	na
U105	2/24/95	VSS	42.6	22.3	9.92e+04	4.8	na	3.1	na	na	na
U106	3/7/95	VSS	21.9	20.3	9.96e+04	10	na	13	na	na	na
U107	2/17/95	VSS	22.6	20.5	9.83e+04	6.6	na	16	na	na	na
U108	8/29/95	VSS	26.6	27.7	9.93e+04	na	9.5	6.1	na	na	12
U109	8/10/95	VSS	33.0	28.8	9.77e+04	na	12	6.6	na	na	9.2
U111	2/28/95	VSS	20.0	20.2	1.00e+05	9.3	na	4.2	na	na	na
U112	7/9/96	ISVS	18.3	18.4	9.83e+04	na	14	6.8	na	na	4.1
	12/6/96	ISVS	17.2	18.5	9.81e+04	na	na	na	na	na	2.63

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	PNNL SUMMA GC/MS	SAS TST	SAS SUMMA	
U203	8/9/95	VSS	17.7	17.8	9.90e+04	na	10	11	na	na	2.0
U204	8/8/95	VSS	17.8	13.8	9.95e+04	na	4.4	7.2	na	na	0.86

(a) VSS = Vapor sampling system.

(b) na = not available.

(c) ISVS = in situ vapor sampling [system]. Tank pressures for ISVS events were based on barometric pressure measurements from the Hanford Meteorological Station.

(d) P = preliminary data.

(e) O = total non-methane organic compound concentration given for SUMMA™ canister samples by GC/FID was determined by OGIST.

(f) 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 headspace 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 headspace temperature decreases the calculated saturation concentration of organic vapors, C_{sat} , which tends to increase the estimated surface area of organic liquid waste. For the purpose of assessing risk, using the lower temperature is more conservative.

3.2 Pressures

Tank headspace 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 (e.g., mg/m³) from standard pressure (1.013×10^5 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 headspace pressures for each of the sampling events. The sampling equipment did not include pressure instrumentation in certain recent sampling events, precluding direct measurement. In those cases, atmospheric pressure reported by the Hanford Meteorological Station for the date and time of sample collection was used to estimate the headspace pressure. These readings are included in the table.

Tank headspace 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 headspace and barometric pressure are relatively small.

3.3 Ventilation Rates

The tank headspace ventilation rate is a key parameter in the model. The guidelines of the current safety documentation, *Organic Solvent Topical* (Cowley et al. 1997), 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 headspace 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 m³/h (50 ft³/h) on tanks with certain automatic level gauges. The corresponding estimated ventilation rate can therefore be expressed as

$$Q = 1.416 + 0.0001875 * V \quad (3.1)$$

where Q is the ventilation rate in m³/h, and V is the tank headspace volume in m³. For the tanks considered in this report, this estimate provides a maximum value for Q of about 2.3 m³/h. (Tank AX-102 has the largest headspace volume, which Palmer et al. [1996] estimate to be 4,686 m³.)

Recent studies of passively ventilated tanks using helium and sulfur hexafluoride as tracer gases indicate actual ventilation rates are higher than those predicted by Equation (3.1) (Huckaby et al. 1997b). Table 3.2 lists the eight tanks studied, the average ventilation rates measured, and the ventilation rate predicted by Equation (3.1) using headspace volumes given by Palmer et al. (1996). Except for Tank C-107, measured ventilation rates are consistently higher, and sometimes much higher, than rates predicted by Equation (3.1).

Ventilation rates have also been estimated recently by Wilkins et al. (1996) for seven passively ventilated tanks by measuring the rates at which hydrogen concentrations decrease after gas release events. Table 3.3 summarizes the data for the seven tanks. All of the ventilation rates given in Table 3.3 are higher than the highest rate ($2.3 \text{ m}^3/\text{h}$) predicted by Cowley et al. (1997). These discrepancies are among ventilation rate estimates and measurements to be addressed in a revision of *Organic Solvent Topical*, and it is anticipated that the revision will adopt $17 \text{ m}^3/\text{h}$ as a conservative estimate of the passive ventilation rate. To be consistent, this value was also adopted for this report. Using this value, which is higher than that found or estimated in most tanks, tends to increase the estimated surface area of organic liquid waste. For the purpose of assessing risk, using a higher ventilation rate is more conservative. Therefore, when measured ventilation rates have exceeded $17 \text{ m}^3/\text{h}$ in Tanks AX-103 and BY-105, screening calculations employed the measured ventilation rates for these tanks.

Table 3.2. Ventilation Rates from Tracer Gas Measurements

Tank	Tracer Gas	Dates	Measured Ventilation Rate (m^3/h)	Equation (3.1) Ventilation Rate (m^3/h)
A-101	Helium	July 9–July 15, 1997	17	1.6
AX-102	Helium	August 28–September 8, 1997	28	2.3
AX-103	Helium	February 25–March 3, 1997	42	2.2
BY-105	Sulfur Hexafluoride	April 17–May 8, 1997	27	1.8
C-107	Helium	February 21–March 21, 1997	1.9	1.9
S-102	Sulfur Hexafluoride	September 24, 1996–February 11, 1997	3.8	1.8
U-103	Helium	July 23–August 13, 1997	2.7	1.7
	Sulfur Hexafluoride	February 27–July 22, 1997	3.0	1.7
U-105	Helium	July 18–August 15, 1997	8.5	1.7

Table 3.3. Ventilation Rates from Hydrogen Monitoring Data

Tank	Date	Ventilation Rate (ft ³ /min) ^(a)	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).				

3.4 Organic Vapor Concentrations

Headspace organic vapor concentrations were determined by sampling each tank headspace 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 headspace gases and vapors.

The VSS transports air from the tank headspace to sampling media located in a mobile laboratory above the tank. Transport losses of headspace constituents are minimized by extensively purging the system with headspace 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 headspace 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 headspace sampling have been described by Mahon et al. (1997). Huckaby et al. (1996b) 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).

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 headspaces. 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.

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

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 headspace. 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:

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

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. Cowley et al. (1997) 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 headspace 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 five targeted semivolatile compounds were above instrument detection limits in these two tanks. 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 headspaces. 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.

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. (1997) 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. (1997).

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 headspace 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 estimated by assuming that passive ventilation rates are normally distributed about a mean of 17 m³/h, and that 95% of all passive ventilation rates are below 34 m³/h. It follows from the properties of normally distributed variables that

$$\sigma^2(Q) = 107 \text{ m}^6/\text{h}^2.$$

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. 1996b).

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 headspace 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 headspace 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 headspace 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 headspace 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. (1997) 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. [1997], 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. (1997) 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. The estimated variance of A is dominated by the variance assigned to C_{sat} for the first five 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 0.11 for all tanks.

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.

Table 4.1. Evaluated Terms of Equation (2.1)

Tank	Sample Date	$\sigma^2(A) = \left(\frac{\partial A}{\partial Q}\right)^2 \sigma^2(Q) + \left(\frac{\partial A}{\partial C_{obs}}\right)^2 \sigma^2(C_{obs}) + \left(\frac{\partial A}{\partial C_{sat}}\right)^2 \sigma^2(C_{sat}) + \left(\frac{\partial A}{\partial k}\right)^2 \sigma^2(k)$		
		$\left(\frac{\partial Q}{\partial A}\right)^2 \sigma^2(Q)$	$\left(\frac{\partial A}{\partial C_{obs}}\right)^2 \sigma^2(C_{obs})$	$\left(\frac{\partial A}{\partial C_{sat}}\right)^2 \sigma^2(C_{sat})$
BY108	10/27/94	9.5e+04	8.7e+06	5.4e+07
C102	8/23/94	6.7e+02	7.1e+02	4.4e+03
C204	7/2/96	1.0e+03	1.8e+02	1.1e+03
TY103	4/11/95	5.5e+02	2.5e+02	1.5e+03
BX104	8/22/96	6.4e+01	1.3e+01	8.3e+01
C103	May-94	1.0e+02	3.1e+00	1.9e+01
C101	9/1/94	1.8e+01	3.1e+00	1.9e+01
T111	1/20/95	1.9e+01	2.0e+00	1.2e+01
BX103	8/1/96	7.1e+00	6.6e-01	4.1e+00
BY107	10/26/94	3.7e+00	3.5e-01	2.2e+00
B103	2/8/95	3.5e+00	2.7e-01	1.7e+00
C110	8/18/94	1.3e+00	9.5e-02	5.9e-01
C201	6/19/96	1.1e+00	7.4e-02	4.6e-01
B103	10/16/96	7.6e-01	5.4e-02	3.3e-01

5.0 Screening Results

Screening calculations were performed using data from 107 tank headspace vapor sampling events from 82 passively ventilated waste tanks. Key parameters of the screening calculations and estimated organic liquid waste surface areas for each of the 107 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 m² for 13 tanks, as indicated by "Yes" in the ninth column of the table, and greater than 5 m² for eight tanks (Tanks BX-104, BY-108, C-101, C-102, C-103, C-204, T-111 and TY-103). Of the 13 tanks for which $A > 1$ m², six are in the 241-C tank farm, and two 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 $A > 1$ m² (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 $A > 1$ m².

Two tanks, C-103 and C-204, were determined to have a negative value for A because $C_{sat} < C_{obs}$ for these tanks (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 those tanks with very large $\sigma^2(A)$. Twenty-one tanks had an estimated A less than 1 m² and a 95% confidence limit value of A greater than 1 m².

In summary, given the screening model and assumptions regarding model input distributions and errors, there is 95% confidence that 1) 48 of the 82 tanks screened do not contain significant amounts of organic liquid waste, and 2) 13 of the remaining 34 tanks have a surface area of semivolatile organic waste greater than 1 m².

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	A101	6/8/95	na ^(a)	495	22.47	1.7	0.48		1.10	
2	A102	11/10/95	na	402	4.37	1.6	0.12		0.27	
3	A103	11/9/95	na	319	6.86	1.5	0.26		0.58	
4	A106	1/16/97	na	561	4.19	1.7	0.07		0.17	
5	AX101	6/15/95	na	220	2.93	1.3	0.18		0.41	
6	AX102	6/27/95	na	184	10.86	1.2	0.92		2.08	
7	AX103	6/21/95	na	383	0.46	1.6	0.01		0.03	
8	AX104	3/3/97 ^(b)	na	336	0.78	1.5	0.07		0.12	
9	B102	4/18/96	na	93	3.87	0.8	0.95		2.16	
10	B103	2/8/95	0.61	75	7.80	0.6	3.07	Yes	7.05	
		10/16/96	0.61	123	8.97	0.9	1.43	Yes	3.26	
11	B105	7/30/96	na	110	3.48	0.9	0.63		1.44	
12	B107	7/23/96	0.16	91	0.53	0.8	0.13		0.29	
13	B202	7/18/96	na	93	0.80	0.8	0.19		0.43	
14	BX102	7/31/96	0.14	114	1.01	0.9	0.17		0.38	
15	BX103	8/1/96	0.49	125	24.41	0.9	4.3	Yes	10.19	

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 $A > 1 \text{ m}^2$?	95% Confidence Limit for A (m ²)	Notes
16	BX104	12/30/94	0.66	173	51.44	1.1	6.4	Yes	15.43	
		8/22/96	0.66	168	77.78	1.1	13.1	Yes	34.44	
		12/12/96	0.66	165	49.46	1.1	6.6	Yes	15.90	P ^(e)
		2/6/97	0.66	130	51.73	1.0	11.62	Yes	29.47	P
		4/7/97	0.66	124	35.22	0.9	7.15	Yes	17.24	P
		6/10/97	0.66	134	51.29	1.0	10.57	Yes	26.57	P
		4/24/96	na	102	4.05	0.8	0.84		1.91	
17	BX105	8/15/96	na	125	1.83	0.9	0.27		0.60	
18	BX106	11/17/95	na	132	2.19	1.0	0.29		0.66	
19	BX107	4/30/96	0.08	86	0.36	0.7	0.10		0.22	
20	BX110	8/27/96	0.11	124	1.15	0.9	0.17		0.38	
21	BX111	8/29/96	0.02	129	1.10	1.0	0.2		0.34	
22	BY101	11/21/95	0.18	182	3.23	1.2	0.26		0.60	
23	BY102	11/1/94	na	200	10.75	1.2	0.79		1.80	
24	BY103	6/24/94	0.19	228	10.37	1.3	0.63		1.43	
25	BY104	7/7/94	0.26	224	2.95	1.3	0.18		0.40	
26	BY105	4/23/97 ^(d)	0.26	158	2.25	1.1	0.45		0.86	
27	BY106	7/8/94	na	248	11.52	1.3	0.62		1.41	
28	BY107	10/26/94	0.39	270	54.79	1.4	3.1	Yes	7.4	

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
29	BY108	10/27/94	0.42	222	216.49	1.3	505	Yes	13562	
		1/23/96	0.42	209	83.47	1.2	9.1	Yes	23.1	
		3/28/96	0.42	199	91.36	1.2	12.0	Yes	31	
		9/10/96	0.42	268	114.43	1.4	9.2	Yes	24	
		11/14/96	0.42	266	116.10	1.4	9.6	Yes	25	
		1/30/97	0.42	192	81.33	1.2	10.50	Yes	26.99	P
		9/22/94	0.49	238	8.86	1.3	0.50		1.14	
		11/11/94	0.20	248	8.76	1.3	0.47		1.06	
		11/16/94	na	192	7.44	1.2	0.58		1.31	
		11/18/94	0.15	179	1.88	1.2	0.16		0.35	
30	C101	9/1/94	0.80	443	177.27	1.6	7.0	Yes	17.8	
32	C102	8/23/94	0.61	224	170.48	1.3	42	Yes	168	
34	C103	May-94	0.80	606	1462.72	1.8	-16	Yes	3	
		9/29/94	na	1097	5.90	2.0	0.05		0.10	
37	C107	1/17/96	na	792	3.08	1.9	0.04		0.08	
		3/26/96	na	696	2.39	1.8	0.03		0.07	
		9/15/96	na	893	2.91	1.9	0.03		0.06	
		12/17/96	na	780	3.32	1.9	0.04		0.09	
		2/7/97	na	635	3.22	1.8	0.05		0.11	P
		8/5/94	na	204	1.25	1.2	0.09		0.19	
		8/10/94	na	248	1.60	1.3	0.08		0.19	
38	C108	8/18/94	0.66	159	16.73	1.1	1.83	Yes	4.2	
39	C109									
40	C110									

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 $A > 1 \text{ m}^2$?	95% Confidence Limit for A (m ²)	Notes
41	C111	9/13/94	na	236	1.07	1.3	0.06		0.13	
42	C112	8/11/94	na	270	5.57	1.4	0.26		0.59	
43	C201	6/19/96	na	86	5.83	0.7	1.7	Yes	3.8	
44	C202	6/25/96	na	96	2.30	0.8	0.53		1.19	
45	C204	7/2/96	0.88	110	174.32	0.9	-53	Yes	29.43	
46	S101	6/6/96	na	330	12.86	1.5	0.47		1.06	
		3/14/95	0.03	195	0.55	1.2	0.040		0.09	
		1/26/96	0.03	123	0.44	0.9	0.065		0.15	
47	S102	4/4/96	0.03	177	0.44	1.1	0.037		0.08	
		9/19/96	0.03	282	0.73	1.4	0.032		0.07	
		12/19/96	0.03	234	0.46	1.3	0.026		0.06	
		2/11/97	0.03	168	0.53	1.1	0.048		0.11	
48	S103	6/12/96	0.07	170	0.77	1.1	0.07		0.16	
49	S105	12/7/95	na	157	2.46	1.1	0.25		0.57	
50	S106	6/13/96	0.15	124	1.97	0.9	0.29		0.66	
51	S107	6/18/96	na	240	6.34	1.3	0.35		0.80	
52	S108	12/6/95	na	162	2.36	1.1	0.23		0.52	
53	S109	6/4/96	na	121	3.38	0.9	0.53		1.20	
54	S110	12/5/95	na	232	3.42	1.3	0.20		0.44	
55	S111	3/21/95	na	152	1.78	1.1	0.19		0.43	
56	S112	7/11/95	0.01	134	0.07	1.0	0.01		0.02	
57	T104	2/7/96	na	79	1.79	0.7	0.58		1.31	

Table 5.1 (contd)

Tank	Date Sampled	Fraction of Semivolatile species, χ	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)	I_s $A > 1$ m ² ?	95% Confidence Limit for A (m ²)	Notes
58	T107	1/18/95	na	106	3.58	0.9	0.70		1.58
59	T110	8/31/95	na	118	1.03	0.9	0.16		0.37
60	T111	1/20/95	0.93	88	20.94	0.7	7.2	Yes	17.02
61	TX104	5/5/97	na	86	1.39	0.7	0.381		0.86
62	TX105	12/20/94	na	206	4.60	1.2	0.32		0.71
63	TX106	3/5/97	na	113	5.62	0.9	1.00		2.27
64	TX111	10/12/95	0.04	130	0.60	1.0	0.08		0.18
64	TX113	8/6/97	0.01	124	0.07	0.9	0.01		P
65	TX114	3/25/97	0.11	97	1.26	0.8	0.28		0.64
66	TX118	12/16/94	0.13	154	1.29	1.1	0.13		0.30
67	TY101	4/6/95	na	90	1.47	0.8	0.38		0.85
68	TY102	4/12/96	na	75	0.90	0.6	0.32		0.73
69	TY103	4/11/95	0.97	92	58.48	0.8	38	Yes	119.00
		11/22/96	0.97	117	74.11	0.9	32	Yes	99.03
70	TY104	4/27/95	na	96	2.84	0.8	0.66		1.48
71	U103	2/15/95	0.04	158	0.42	1.1	0.04		0.09
72	U104	7/16/96	na	119	0.55	0.9	0.09		0.19
73	U105	2/24/95	na	165	4.35	1.1	0.41		0.94
74	U106	3/7/95	0.06	138	0.71	1.0	0.09		0.20
75	U107	2/17/95	0.05	141	0.72	1.0	0.09		0.19
76	U108	8/29/95	na	240	10.71	1.3	0.60		1.37
77	U109	8/10/95	na	289	10.47	1.4	0.45		1.03

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 $A > 1 \text{ m}^2$?	95% Confidence Limit for A (m ²)	Notes
78	U111	2/28/95	0.04	134	0.34	1.0	0.04	0.10	P
		7/9/96	0.11	115	1.40	0.9	0.23		
79	U112	12/6/96	na	104	2.40	0.8	0.48	1.08	
80	U203	8/9/95	0.03	109	0.29	0.9	0.05	0.12	
81	U204	8/8/95	0.01	76	0.07	0.6	0.02	0.05	

(a) na = not available.

(b) The measured ventilation rate of 42.5 m³/h was used with the March 1997 Tank AX-103 organic vapor data.

(c) P = preliminary data were used in calculations.

(d) The measured ventilation rate of 34 m³/h was used with the Tank BY-105 April 1997 organic vapor data.

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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 headspace 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 headspace 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):

$$h_c = 1.52 \Delta T^{1/6} \quad (A.4)$$

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 headspace air temperature, atmospheric air temperature, and the properties of soil overburden (Crowe et al. 1993):

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

where

$\frac{q}{A}$ = heat flux (W/m²)

T_{vap} = annual average bulk headspace air temperature (K)

T_{air} = annual average atmospheric temperature (K)

k_s = thermal conductivity of soil overburden, W/m·K

ΔT = average depth of soil overburden, m.

The formulation expressed in Equation (A.5) neglects the small temperature differences that would exist from headspace 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:

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

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

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

where

δ_{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

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

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

Mass transfer coefficients may be evaluated as a function of headspace 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 headspace 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 headspace air and waste surface temperatures).

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

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

where

k_c = mass transfer coefficient, m/h
 T = headspace air temperature, °C
 A, B, C = fitting constants.

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

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

where

k_c = mass transfer coefficient, m/h
 T = headspace air temperature, °C.

Table A.1. Predicted Mass Transfer Coefficients

Headspace 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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