Characterization of Void Volume VOC Concentration in Vented TRU Waste Drums—Final Report

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ABSTRACT

A test program has been conducted at the Idaho National Engineering Laboratory to demonstrate that the concentration of volatile organic compounds within the innermost layer of confinement in a vented waste drum can be estimated using a model incorporating diffusion and permeation transport principles and limited waste drum sampling data. This final report summarizes the experimental measurements and model predictions for transuranic waste drums containing solidified sludges and solid waste.

EXECUTIVE SUMMARY

A test program was conducted at the Idaho National Engineering Laboratory to demonstrate that the VOC concentration within the innermost layer of confinement can be estimated using a model incorporating theoretical diffusion and permeation transport principles and limited waste drum sampling data. This report presents and evaluates a VOC transport model used to estimate the VOC concentration within the innermost layer of confinement of vented transuranic waste drums. The model consists of a series of material balance equations describing steady-state VOC transport from each distinct void volume in the drum. The primary model input is the measured drum headspace VOC concentration. Model parameters are determined or estimated based on available process knowledge.

The model effectiveness in estimating VOC concentration was examined for vented waste drums containing different waste types and configurations. Gas samples were collected from waste drums containing solidified sludge waste or solid waste. Sludge waste drums contained a maximum of 2 layers of polymer bags. The solid waste drums sampled had a maximum of 4 or 5 layers of polymer bags. Gas samples from 22 sludge waste drums were collected and analyzed at the Rocky Flats Environmental Technology Site. Gas sampling and waste characterization of 42 waste drums containing solid waste were performed at the Argonne National Laboratory-West.

In order to quantify the accuracy of the model results, the logarithm of the ratio of the predicted VOC concentration in the innermost layer of confinement, Y_{mod} , to the maximum VOC concentration measured in all bag headspaces, Y_{max} , was calculated

$$\psi = \log_{10} \left[\frac{Y_{\text{mod}}}{Y_{\text{max}}} \right] .$$

In the case where the model estimate and measured VOC concentrations are identical, ψ equals zero. The VOC transport model is considered to be accurate if the confidence limits bound the case of $\psi = 0$. Otherwise, the model is said to have a positive or negative bias. This means that model estimates of the maximum VOC concentration in a specific population of waste drums are consistently greater or less than the maximum measured VOC concentration. The transport model was used to estimate the concentration of 17 VOCs and the total VOC concentration in waste drums with a specific configuration characterized by the maximum number of layers of polymer bags. Model calculations were performed for two sets of VOCs. The first set consisted of VOCs in which most VOC-specific parameters, such as VOC permeability across the polyethylene bags and the drum filter vent VOC diffusion characteristic, were measured. Model calculations were performed for other VOCs using estimated values for VOC-specific parameters.

Model accuracy was determined for 13 of the 17 VOCs in which model calculations were performed. The transport model was accurate or conservatively estimated (positive bias) the maximum measured concentrations of 11 VOCs within vented waste drums. The model was accurate in estimating the total VOC concentration within the innermost layer of confinement for waste drums containing a maximum of 4 or 5 layers of polymer bags that were completely sampled within one day. The model exhibited a positive bias in estimating the total VOC concentration

within the innermost layer of confinement of waste drums containing a maximum of 2 layers of polymer bags. The model exhibited a negative bias for 2 VOCs.

The VOC transport model predicts, with 90% confidence, that the VOC concentration will not be less than 1/2 of the maximum measured VOC concentration in at least 90% of the waste drums for 8 VOCs and two of the waste drum configurations. The VOC transport model predicts that the VOC concentration will not be less than 1/3 of the maximum measured VOC concentration in at least 90% of the waste drums for 3 VOCs and waste drums with a maximum of four layers of polymer bags. For carbon tetrachloride and methanol, model estimates will not be less than 1/5 of the maximum measured VOC concentration in at least 90% of the waste drums.

The model results demonstrate that the maximum VOC concentration within the waste drum can be accurately or conservatively estimated using limited gas sampling data. Model applicability to other VOCs is expected since the VOCs investigated in this study exhibited a wide range of molecular weights, permeabilities in polyethylene, and vapor pressures.

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ACRONYMS AND ABBREVIATIONS

ANL-W	Argonne National Laboratory-West
DOE	U. S. Department of Energy
EPA	Environmental Protection Agency
Freon-113	1,1,2-trichloro-1,2,2-trifluoroethane
INEL	Idaho National Engineering Laboratory
NFT	Nuclear Filter Technology
NMD	no-migration determination
PRDL	program required detection limit
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Program Plan
QAPjP	Quality Assurance Project Plan
RFETS	Rocky Flats Environmental Technology Site
STP	standard temperature and pressure
TCA	trichloroethane
TCE	trichloroethylene
TRU	transuranic
VOC	volatile organic compound
WCC	Waste Characterization Chamber
WIPP	Waste Isolation Pilot Plant

Characterization of Void Volume VOC Concentration in Vented TRU Waste Drums

1. INTRODUCTION

In the final conditional Waste Isolation Pilot Plant (WIPP) No-Migration Determination (NMD), the Environmental Protection Agency (EPA) imposed several waste characterization requirements on the U. S. Department of Energy (DOE) specific to sampling and analyzing the headspace gases in waste containers to be emplaced in the WIPP facility.¹ The objectives of these requirements are to demonstrate that flammable gas mixtures or mixtures of gases that could become flammable when mixed with air do not exist within a container; to demonstrate that the waste received at the WIPP is comparable to that described in the DOE No-Migration Variance Petition; and to demonstrate that hazardous constituents will not exceed concentrations above health-based limits established by the EPA at the WIPP repository unit boundary. In order to comply with these requirements, the DOE must sample and analyze all layers of confinement (drum headspace, large polymer bag headspace, and innermost layer of confinement headspace) to ensure that data are representative of the VOCs within the entire void space within the waste container. The EPA expects that all layers of confinement in a container will have to be sampled until the DOE can demonstrate to the EPA, based on the data collected, that sampling of all layers is either unnecessary or can be safely reduced.

A test program was conducted at the Idaho National Engineering Laboratory (INEL) to demonstrate that the VOC concentration within the innermost layer of confinement can be estimated using a model incorporating theoretical diffusion and permeation transport principles and limited waste drum sampling data. The model and model validation results provide information that can be used to address the container headspace VOC concentration representativeness issue raised by the EPA. This report presents and evaluates a VOC transport model used to estimate the VOC concentration within the innermost layer of confinement of vented transuranic (TRU) waste drums. Primary model input is the measured drum headspace VOC concentration. Model parameters are determined or estimated based on available process knowledge.

2. VOC TRANSPORT MODEL

A transport model was developed to estimate the VOC concentration in void volumes within a vented drum containing waste contaminated with or containing VOCs. Model parameters are defined from knowledge of the waste drum configuration. A waste drum consists of a vented drum with a rigid drum liner that contains the waste inside one or two large polymer bags. The waste may have been placed directly in the innermost large bag or wrapped in one or more layers of smaller polymer bags, which were then placed inside the innermost large polymer bag. A small opening in the drum liner lid allows gas and vapor transport between the drum liner and drum headspaces. The waste drum configuration includes the type of filter vent in the drum lid, the dimensions of the opening in the drum liner lid, and the thickness of polymer bags surrounding the waste. The model, consisting of a series of material balance equations describing steady-state VOC transport from each distinct void volume in the drum, is presented in this section.

2.1 Model Equations

The primary mechanisms for steady-state gas transport across a polymer boundary are permeation across the polymer and diffusion across an opening in a layer of confinement. The steady-state gas transport via permeation across a polymer film is defined as

$$r = \left[\frac{\phi \rho A_p P}{x_p} \right] c \Delta y_p = K_p \Delta y_p \quad (1)$$

where

r = gas transport rate, mol s^{-1}

ϕ = $76 T / (273.15 P)$

T = gas temperature, K

P = gas pressure, cm Hg

ρ = gas permeability coefficient, $\text{cm}^3 (\text{STP}) \text{cm}^{-1} (\text{cm Hg})^{-1} \text{s}^{-1}$

A_p = polymer surface area across which gas permeates, cm^2

x_p = polymer boundary thickness, cm

c = total gas concentration = $P (RT)^{-1}$, mol cm^{-3}

R = $6236.6 \text{ cm}^3 (\text{cm Hg}) \text{mol}^{-1} \text{K}^{-1}$

Δy_p = gas mole fraction difference across polymer

K_p = gas permeation characteristic, $4.46 \times 10^{-5} \rho A_p P x_p^{-1}$, mol s^{-1} .

The steady-state gas transport across an opening in a layer of confinement via gas diffusion is defined as

$$r = \left[\frac{DA_d}{x_d} \right] c \Delta y_p = K_d \Delta y_p \quad (2)$$

where

D = gas diffusivity in air, $\text{cm}^2 \text{s}^{-1}$

A_d = cross-sectional area of opening across polymer boundary, cm^2

x_d = diffusional length across opening, cm

K_d = gas diffusion characteristic, $DA_dP (RTx_d)^{-1}$, mol s^{-1} .

2.1.1 Sludge Waste Drums

The large polymer bag immediately surrounding the sludge waste is the innermost layer of confinement and the headspace surrounding the waste is referred to as the first void volume. The drum liner headspace not included in the large bags and the drum headspace outside the drum liner are the second and third void volumes, respectively. The VOC transport rate from the innermost layer of confinement, r , is defined as

$$r = K_p (y_1 - y_2) \quad (3)$$

where y_i is the VOC mole fraction in the i^{th} void volume. The VOC transport rate from the drum liner is defined as

$$r = K_d (y_2 - y_3) \quad (4)$$

The VOC transport rate from the drum headspace across the drum filter vent is defined as

$$r = D_{VOC}^* (y_3 - y_\infty) \quad (5)$$

where

D_{VOC}^* = drum filter vent VOC diffusion characteristic, mol s^{-1}

y_∞ = VOC mole fraction outside waste drum.

The values of K_p and K_d are calculated based on process knowledge. The VOC mole fraction in the drum headspace, y_3 , is determined from analysis of gas samples collected below the filter vent.

Equation (5) is used to define the steady-state VOC transport rate in the waste drum. The VOC mole fractions in the other void volumes are calculated using Equations (3) and (4).

$$y_2 = y_3 + \frac{r}{K_d} \quad (6)$$

$$y_1 = y_2 + \frac{r}{K_p} \quad (7)$$

Combining Equations (5) through (7), the VOC mole fraction within the innermost layer of confinement can be defined directly in terms of the measured VOC mole fraction in the drum headspace

$$y_1 = y_3 + D_{VOC}^* y_3 \left[\frac{1}{K_p} + \frac{1}{K_d} \right] \quad (8)$$

Multiplying both sides of Equation (8) by a constant, the VOC concentration within the innermost layer of confinement is defined in terms of the drum headspace VOC concentration

$$Y_1 = Y_3 + D_{VOC}^* Y_3 \left[\frac{1}{K_p} + \frac{1}{K_d} \right] \quad (9)$$

where Y_i is the VOC concentration within the i^{th} layer of confinement in parts per million (ppm).

2.1.2 Solid Waste Drums

Most solid waste drums contain waste packaged in one or more layers of small polymer bags. These smaller bags are located inside a larger polymer bag. The polymer bag immediately surrounding the waste is the innermost layer of confinement and the headspace inside this layer of confinement is referred to as the first void volume. Large bag, drum liner, and drum headspaces are referred to as the second, third, and fourth void volumes, respectively. The VOC transport rate from the innermost layer of confinement of the i^{th} waste package wrapped in one or more polymer bags is defined by the equation

$$r_i = K_{p,1,i} (y_{1,i} - y_2) \quad (10)$$

where

$K_{p,1,i}$ = VOC permeation characteristic of first layer of confinement surrounding the i^{th} waste package, mol s^{-1}

$y_{1,i}$ = VOC mole fraction in headspace of i^{th} waste package.

The total VOC transport rate exiting the waste packages and entering the large bag headspace is equal to the sum of individual VOC transport rates from each waste package

$$r = \sum_{i=1}^N r_i \quad (11)$$

where N is the total number of small bags inside the drum. The VOC transport rate across the large polymer bags containing the waste packages is defined as

$$r = K_{p,2} (y_2 - y_3) \quad (12)$$

The VOC transport rate across the drum liner is defined as

$$r = K_d (y_3 - y_4) \quad (13)$$

The VOC transport rate from the drum headspace across the filter vent is defined as

$$r = D_{VOC}^* (y_4 - y_\infty) \quad (14)$$

Equation (14) is used to define the steady-state VOC transport rate in the drum. The VOC concentration in the drum liner headspace is calculated using Equation (13)

$$y_3 = y_4 + \frac{r}{K_d} \quad (15)$$

The VOC mole fraction in the large bag headspace is calculated using Equation (12)

$$y_2 = y_3 + \frac{r}{K_{p,2}} \quad (16)$$

Assuming that the VOC permeability characteristics of all waste packages are identical and that the VOC transport rates from all waste packages are identical, then the VOC mole fraction within the innermost layer of confinement of each waste package is the same and is calculated using Equations (10) and (11)

$$y_1 = y_2 + \frac{r}{NK_{p,1}} \quad (17)$$

The maximum model estimate of the VOC mole fraction in the innermost layer of confinement results if all VOC-contaminated waste is assumed to exist in one bag or $N = 1$. Using this assumption and combining Equations (14) through (17), the VOC concentration within the

innermost layer of confinement can be defined in terms of the measured VOC concentration in the drum headspace in an analogous form of Equation (9)

$$Y_1 = Y_4 + D_{VOC}^* Y_4 \left[\frac{1}{K_{p,1}} + \frac{1}{K_{p,2}} + \frac{1}{K_d} \right] \quad (18)$$

2.2 Model Assumptions

Model assumptions were made to minimize model complexity. Some assumptions were based on an understanding of the thermodynamic and kinetic nature of VOC transport in the waste drum. Other assumptions were based on process knowledge of the system. In cases where process knowledge was lacking, conservative assumptions that would result in higher model estimates of VOC concentration were made. Some of the model assumptions are listed below.

1. An equilibrium exists between the VOC-contaminated waste and the vapor phase in the innermost layer of confinement.
2. In waste drums containing solid waste, all VOC-contaminated waste is contained inside one waste package.
3. The VOC transport rates across all layers of confinement are equal and at steady state.
4. The primary mechanisms for VOC transport are permeation across the polymer bags and diffusion across the drum liner and drum filter vent.
5. A layer of confinement defined by multiple layers of polymer bags is considered a single polymer bag with a bag thickness equal to the sum of the bag thicknesses of the individual bags.
6. The VOC concentration throughout each void volume is uniform and is zero outside the waste drum.
7. All VOC properties and other model parameters remain constant.

2.3 Model Parameters

The permeability coefficients for 9 VOCs across polyethylene were measured at the INEL using a mixed-component chromatographic detection method. Carbon tetrachloride, 1,1,1-trichloroethane (TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), methylene chloride, and trichloroethylene (TCE) permeability values were measured using gas mixtures containing only one VOC in air as well as gas mixtures containing all five VOCs in air.² Earlier model calculations used permeability coefficients determined from one of these gas mixtures.^{2,3} In this report, an average value of previously reported permeabilities^{2,3} was used in model calculations. Permeability coefficients for toluene, methanol, cyclohexane, and p-xylene across polyethylene were measured using only single VOC-air mixtures.³ The values used in this report are summarized in Table 1.

Table 1. VOC permeability coefficients across polymer bags used in model calculations.

Compound	Permeability (Ba) ^a
Methylene chloride	260 ^b ± 26 ^c
Carbon tetrachloride	190 ^b ± 36
1,1,1-trichloroethane	140 ^b ± 12
Trichloroethylene	580 ^b ± 28
Freon-113	38 ^b ± 4.9
Methanol	135 ^d ± 35
Cyclohexane	12 ^d ± 1.7
Toluene	670 ^d ± 120
p-xylene	810 ^d ± 48

a. $Ba = 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} (\text{cm Hg})^{-1}$

b. Average value of results from permeability tests using single VOC-air and mixtures and multiple VOC-air mixtures

c. Standard deviation

d. Result from permeability test using single VOC-air mixture.

A similar experiment to measure VOC permeability across polyvinyl chloride (PVC) as a function of temperature and VOC concentration was conducted.^{a,b} Because of the low VOC concentrations used and the thicker polymer film, the experimental set-up was unable to detect the VOC on the permeate side of the PVC film for some compounds. From the limited data available, it appeared that VOC permeability across PVC was, in general, less but the same order of magnitude as the permeability across polyethylene. For these reasons, it was assumed that permeabilities of a specific VOC across polyethylene and PVC were the same for the purpose of model calculations.

When the measured VOC permeability across polyethylene was not known, it was calculated based on the estimated values of VOC diffusivity in polyethylene, $D_{\text{VOC-PE}}$, and VOC solubility in polyethylene, S ^{4,5}

a. Unpublished research results of VOC permeability tests across polyethylene and PVC, E.S. Peterson, EG&G Idaho, Inc. (June 1993).

b. Unpublished research results of VOC permeability tests across polyethylene and PVC, E. S. Peterson, Lockheed Idaho Technologies Co. (December 1994).

$$\rho = D_{VOC-PE} S \quad (19)$$

Methods used to estimate VOC diffusivity and solubility in polyethylene as well as estimated values of VOC permeability in polyethylene for a number of VOCs are presented in Appendix A.

The diffusivities of most VOCs in air at a given temperature and pressure were identified in the literature.⁶ In the case where diffusivity data were not identified, the VOC diffusivity in air was estimated using the equation⁷

$$D_{AB} = 2.745 \times 10^{-4} \frac{T^{1.823}}{\Pi} [p_{cA} p_{cB}]^{1/3} [T_{cA} T_{cB}]^{-1/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad (20)$$

where

D_{AB} = mass diffusivity for VOC(A)-air(B) system, $m^2 s^{-1}$

Π = pressure, atm

p_{ci} = critical pressure of species i, atm

T_{ci} = critical temperature of species i, K

M_i = molecular weight of species i.

The diffusion characteristic for specific VOCs across different drum filter vents was measured in experiments performed at the INEL.⁸ The drum filter vent VOC diffusion characteristic, D_{VOC}^* can be estimated using Equation (20) and process knowledge of the hydrogen (H_2) diffusion characteristic across the drum filter vent, $D_{H_2}^*$

$$D_{VOC}^* = \frac{D_{VOC-air}}{D_{H_2-air}} D_{H_2}^* \quad (21)$$

2.3.1 Sludge Waste Drums

Model parameters were measured or estimated from available process knowledge. The bag surface area was estimated to be $2,550 \text{ cm}^2$. This corresponds to the cross-sectional area of the drum liner lid. From process knowledge, two large polyethylene drum liner bags surround the sludge waste. Each bag was assumed to be 0.028 cm (11 mils) thick. The cross-sectional area of the opening in the drum liner lid is 5.07 cm^2 . The diffusion length across the drum liner⁹ was estimated to be 1.4 cm. The VOC diffusion characteristics across NFT-013 drum filter vents ranged from 9×10^{-7} to $2 \times 10^{-6} \text{ mol s}^{-1}$. The waste drums were maintained at ambient room temperature and pressure. A temperature of 25°C and a pressure of 61.0 cm Hg were used in model calculations.

2.3.2 Solid Waste Drums

All waste drums were assumed to have two polyethylene drum liner bags. Each bag was assumed to be 0.028 cm (11 mils) thick. Solid waste was assumed to be wrapped inside two or three layers of polymer bags. Small polyethylene bags were assumed to be 0.013 cm (5 mils) thick and PVC bags were assumed to be 0.028 cm (11 mils) thick. All small bags were assumed to be polyethylene unless process knowledge indicated the possible use of a PVC bag.¹⁰ The layers of polyethylene and PVC bags assumed in model calculations are summarized in Table 2. If the innermost layer of confinement was a polyethylene bottle, permeable surface area was assumed to equal 1,000 cm² and wall thickness of the bottle was assumed to be 0.25 cm (100 mils). The large bag surface area was estimated to be 2,550 cm². The cross-sectional area of the drum liner lid opening is 0.71 cm². The diffusion length across the drum liner lid³ was estimated to be 1.2 cm. The measured VOC diffusion characteristics across NFT-020 drum filter vents ranged from 2×10^{-7} to 6×10^{-7} mol s⁻¹. The waste drums were maintained at ambient room temperature and pressure. A temperature of 25°C and a pressure of 62.5 cm Hg were used in model calculations.

All model parameters, except the small bag surface area, can be estimated from process knowledge prior to characterization of waste drum contents. During waste characterization of solid waste drums, the operator estimated the bag shape (rectangular, triangular, elliptical, or cylindrical) of each bag gas sampled and measured the characteristic dimensions of the bag. Each bag shape and its characteristic dimensions are shown in Figure 1.

Table 2. Assumed small bag configuration in waste drums per waste identification code (IDC).

IDC ^a	Waste type	Number of bags		Total thickness (cm)
		PE ^b	PVC	
300	II.1A4	1	1	0.041
320	II.1A4	-	2	0.056
442	II.1A5	2	1	0.053
480	II.1A5	2	1	0.053
302	III.1A4	2	-	0.025
336	III.1A4	1	1	0.041
338	III.1A4	1	1	0.041
432	III.1A4	2	-	0.025
330	III.1A5	2	1	0.053
337	III.1A5	2	1	0.053

a. Drum contents per IDC described in Appendix B.

b. Polyethylene.

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Figure 1. Possible shapes and dimensions of small bags.

The surface area, A_s , of a rectangular-shaped bag was estimated using Equation (22)

$$A_s = 2[HL + LW + HW] \quad (22)$$

where H is bag height, L is length, and W is width as shown in Figure 1. The surface area of a triangular-shaped bag was estimated using Equation (23)

$$A_s = B\sqrt{0.5W^2} + 2\sqrt{\left(H - \frac{W}{2}\right)^2 + \left(\frac{W}{2}\right)^2} \sqrt{0.5W^2 + \left(\frac{B}{2}\right)^2} \quad (23)$$

where B is the length of the bag along its base as shown in Figure 1. The surface area of an elliptical-shaped bag was estimated using Equation (24)

$$A_s = 1.57 \left[W^2 + \frac{H^{2.25} W^{0.75}}{\sqrt{H^2 - W^2}} \sqrt{1 - \frac{W^2}{H^2}} \right] \quad (24)$$

The surface area of a cylindrical-shaped bag was calculated using Equation (25)

$$A_s = 3.14 \left[HD + \frac{D^2}{2} \right] \quad (25)$$

where D is the diameter of the bag as shown in Figure 1.

The minimum estimated small bag permeable surface area identified in each waste drum by waste type is summarized in Table 3. A histogram summarizing the distribution of the surface area for all small bags found in waste drums containing solid waste is shown in Figure 2. Based on this information, the small bag permeable surface area was assumed to be 500 cm² in all solid waste drums.

Table 3. Number of waste drums per waste type containing waste package with specific minimum estimated permeable surface area.

Waste Type	Minimum estimated surface area, cm ²					
	0-999	1,000-1,999	2,000-2,999	3,000-3,999	4,000-4,999	≥ 5,000
II.1A4	0	0	0	1	0	1
II.1A5	6	4	2	2	0	3
III.1A4	0	3	5	1	1	0
III.1A5	0	0	1	2	0	1
Total	6	7	8	6	1	5

Figure 2. Histogram of estimated permeable surface area of small bags characterized in Waste Type II and Waste Type III waste drums.

3. VOC TRANSPORT MODEL VALIDATION

3.1 Experimental Test Plan

The model effectiveness in estimating VOC concentration was examined for vented waste drums containing different waste types and configurations. Gas samples were collected from waste drums containing the following waste types:

Waste Type I—Solidified aqueous or homogeneous inorganic solids

Waste Type II—Solid inorganics

Waste Type III—Solid organics

Waste Type IV—Solidified organics.

Drums containing Waste Type I or Waste Type IV are referred to in this report as sludge waste drums. Drums containing Waste Type II or Waste Type III are referred to as solid waste drums. The original test plan called for the sampling of 22 drums each of Waste Types I, II, and III, with Waste Types II and III drums equally divided between drums containing 4 or 5 layers of polymer bags.¹¹ The final drum inventory, shown in Table 4, was determined by the availability of waste drums containing specific waste.

The definition of waste drum configuration includes the maximum number of layers of polymer bags expected in the waste drum. The waste type and maximum number of layers of polymer bags are identified by the shipping category code. Each shipping code begins with a Roman numeral indicating the waste type. A decimal point and Arabic numeral may follow indicating an effective G value which is only relevant for the issue of hydrogen generation. The next number indicates the maximum number of polymer bags in the drum. For example, a shipping category of I.1A4 indicates that the drum contains Waste Type I and no more than four layers of polymer bags surround the waste.

Table 4. Number of drums of each waste type sampled.

Waste type	Number of drums
I.2A2	9
II.1A4	5
II.1A5	17
III.1A4	13
III.1A5	7
IV.2AT	13

3.2 Drum Sampling and Analysis

Gas samples were collected from sludge waste drums and analyzed at the Rocky Flats Environmental Technology Site (RFETS). Gas sampling and waste characterization of all other waste drums were performed at the Argonne National Laboratory-West (ANL-W) at the INEL. All gas sampling and analysis were consistent with the methodology and quality assurance (QA)/quality control (QC) requirements specified in the Quality Assurance Program Plan (QAPP).¹² Task descriptions specific to obtaining data to determine VOC transport model accuracy in actual waste drums are listed in the Quality Assurance Project plan (QAPjP).¹¹ Data quality objectives specified in the QAPP and QAPjP were used at the RFETS and the INEL. Application of the same QA/QC program at the two sites ensured comparability of the data.

Drum headspace samples were initially collected from waste drums that had been vented for a minimum of 8 weeks to identify drums with detectable VOC concentrations. Drums with low concentrations of total VOCs (less than 10 ppm) were not sampled further or used to test the accuracy of the VOC transport model. Total vent times for waste drums used this study are listed in Appendices B and C.

3.2.1 Sludge Waste Drums

Gas sampling of waste sludge drums was performed in the RFETS Size-Reduction Vault Airlock. The sampling was conducted by laboratory technicians using a sample cart with SUMMA® passivated canisters, vacuum system, and pressure gauge. The gas sampling sequence also included a leak test of the system and a verification of sampling manifold cleanliness using a photoionization detector. Sample canister cleaning was performed in the analytical laboratory and was verified by gas chromatography/mass spectrometry.

Each sludge waste drum had a drum filter vent in the lid and a rigid polyethylene drum liner. The waste sludge was usually contained within two consecutive 55-gallon flat-bottomed polyethylene drum liner bags inside the drum liner. Drum headspace samples were collected by removing the top of the NFT-013 drum filter vent and inserting a sample needle into the carbon composite medium. After this sample was collected, the drum lid and drum liner lid were removed and a gas sample was collected from the innermost layer of confinement surrounding the waste sludge. The waste drum packaging configuration was documented on data sheets and recorded on videotape. The elapsed time for all samples to be collected from a drum was between 10 and 30 minutes.

3.2.2 Solid Waste Drums

Gas sampling and visual characterization of stored contact-handled TRU waste drums containing solid waste were performed in the ANL-W Hot Fuel Examination Facility Waste Characterization Chamber (WCC). The WCC gas sampling system is a semi-automated process. Operators were responsible for installing a passivated SUMMA® canister on the sample manifold and inserting the sample needle in the drum or bag headspace being sampled. The operator activated the computer-controlled process which opened and then automatically closed the sample line upon sample collection. Additional tasks automatically performed during the gas sampling sequence include system cleaning with separate helium and air gas streams, validation of system

cleanliness using a flame ionization detector, and a leak test of the sampling manifold. If detectable levels of VOCs were found, the cleaning sequence was repeated. The complete gas sampling sequence took approximately 20 minutes.

Each waste drum had a drum filter vent in the lid with a rigid drum liner inside. Two large polymer bags inside the drum liner contained waste packages wrapped inside one or more layers of smaller polymer bags. A drum headspace sample was collected by inserting the sample needle into the NFT-020 drum filter vent in the drum lid. After gas sample collection, the drum and drum liner lids were removed. A gas sample was collected from the headspace of the innermost layer of large polymer bags. The top of each large polymer liner bag was then removed to allow the removal of the smaller polymer bags. A gas sample from each separate bag was collected from the innermost layer of confinement that was not breached and contained at least 100 mL of void volume as decided by the operator. Gas samples were collected from some sealed polyethylene bottles. A small opening was formed by puncturing the lid of the bottle. The opening was immediately covered with tape to minimize the gas mass transfer rate from the bottle. A sample needle was inserted through the tape into the bottle headspace.

An effort was made to conduct the sampling of the drum headspace, the drum liner bag headspace, and the innermost layer of confinement of all small bags in one working day. In some cases, the drum and drum liner bag headspaces were sampled in one day and all small bags were sampled within the next 24 hours. In this case, the lids of the drum and drum liner were placed back on after gas sampling of the large bag and the drum liner bags were not opened until the second day. Visual characterization consisted of video and audio taping of gas sampling activities; estimating bag material and wall thickness; identifying bag shape; measuring linear dimensions of each bag; and describing waste contained in the bags.

3.3 Model Validation Results

Model calculations were performed for two sets of VOCs. The first set consisted of VOCs in which most VOC-specific parameters, such as VOC permeability across the polyethylene bags and the drum filter vent VOC diffusion characteristic, were measured. Model calculations were performed for other VOCs using estimated values for VOC-specific parameters. Model results are listed in Appendix D.

Model input included the measured VOC concentration in the drum headspace. If the drum headspace VOC concentration was reported to be undetected at a minimum concentration, this concentration was used as model input in those cases where a measurable quantity of VOC was observed in the bag headspaces. Model calculations were not performed where undetectable VOC concentrations were reported for the drum and bag headspaces. In the case where duplicate measurements were made, the higher VOC concentration was used as model input. Model estimates of VOC concentration within the innermost bag headspace were compared to the maximum measured VOC concentration in the bag headspaces. Model estimates of VOC concentration in the headspace of sealed polymer bottles were compared to the maximum measured VOC concentration in the bag and bottle headspaces. The estimated or measured total VOC concentration was the sum of the individual estimated or measured VOC concentrations.

3.3.1 VOCs with Measured Model Parameters

3.3.1.1 Polymer bags. The measured VOC concentrations within the drum headspace and all polymer bag headspaces in the waste drums containing solid waste are summarized in Appendix B. For most waste drums, detectable VOC concentrations ranged between 1 and 1,000 ppm. The measured VOC concentrations in the drum headspace and the innermost layer of confinement in sludge waste drums are listed in Appendix C. The primary constituents observed in the sludge waste drums were carbon tetrachloride, TCA, and Freon-113. In the majority of organic sludge waste drums, the concentration range for carbon tetrachloride was 1,000 to 100,000 ppm; for TCA, 100 to 100,000 ppm; and for Freon-113, 10 to 10,000 ppm. Five other VOCs (methylene chloride, toluene, m- and p-xylene, TCE, and methanol) were observed in the sludge waste drums. Analysis for xylenes can not distinguish m-xylene from p-xylene. The concentration range for the majority of these VOC measurements was 1 to 10,000 ppm.

In order to quantify the accuracy of the model results, the logarithm of the ratio of the predicted VOC concentration in the innermost layer of confinement, Y_{mod} , to the maximum VOC concentration measured in all bag headspaces, Y_{max} , was calculated

$$\psi = \log_{10} \left[\frac{Y_{\text{mod}}}{Y_{\text{max}}} \right] . \quad (26)$$

In the case where the model estimate and measured VOC concentrations are identical, ψ equals zero. A statistical test was developed to test the null hypothesis, H_0 , that the mean of ψ , μ_ψ , is equal and, therefore, the model is accurate. The alternative hypothesis, H_a , is that μ_ψ is not equal to zero

$$H_0: \mu_\psi = 0$$

$$H_a: \mu_\psi \neq 0 . \quad (27)$$

The VOC transport model is considered to be accurate if the confidence limits bound the case of $\psi = 0$. Otherwise, the model is said to have a positive or negative bias. This means that model estimates of the maximum VOC concentration in a specific population of waste drums are consistently greater or less than the maximum measured VOC concentration. The mean and standard deviation for ψ as well as the upper and lower 95% confidence limits for each waste drum configuration based on the maximum number of polymer bags and for each VOC in all waste drums are summarized in Table 5.

The plots of ψ for total VOC concentration in vented waste drums containing a maximum of two, four, or five layers of polymer bags are shown in Figures 3 through 5, respectively. In order to demonstrate that model estimates of total VOC concentration are not masking model deficiencies for individual VOCs, the values of ψ for individual VOCs are plotted as a function of the maximum measured VOC concentration and are shown in Figures 6 and 7. Error bars were assigned to each value of ψ . The method of calculating the model error is described in Appendix E.

Table 5. Mean, standard deviation, and 95%-confidence limits of ψ for total VOC concentration in drums by waste configuration and single VOCs in all waste drums.

Variable	Number of drums	Mean	St. deviation	Lower limit	Upper limit
Two bag layers	21	0.078	0.073	0.040	0.111
Four bag layers	12	-0.014	0.176	-0.125	0.097
Five bag layers	24	0.087	0.199	0.003	0.171
CCl ₄ ^a	21	-0.014	0.371	-0.182	0.154
Methanol	7	0.061	0.326	-0.241	0.363
CH ₂ Cl ₂ ^b	22	0.043	0.147	-0.022	0.108
TCA	51	0.118	0.150	0.077	0.159
TCE	24	-0.044	0.135	-0.101	0.013
Toluene	40	-0.044	0.150	-0.090	0.003
Freon-113	16	0.335	0.076	0.295	0.375
p-xylene	7	-0.092	0.093	-0.178	-0.006

a. Carbon tetrachloride.

b. Methylene chloride.

The lower tolerance limit for each variable in Table 5 was calculated to determine the value of ψ at which one can assert with 90% confidence that at least 90% percent of the drums from the same population will exceed.¹⁴ The lower tolerance limits and the ratio $Y_{\max}/Y_{\text{mod}}$ at the lower tolerance limit are listed in Table 6.

3.3.1.2 Polymer bottles. Sealed polymer bottles were observed in 9 waste drums. Although sampling of the bottles is not required, four bottles were sampled. Model calculations were performed to estimate the maximum VOC concentration in the sealed bottles. The ψ values for the polymer bottles are plotted as a function of the maximum measured VOC concentration in waste drums and are shown in Figure 8.

3.3.2 VOCs with Estimated Model Parameters

The values of ψ for 9 VOCs with estimated model parameters are plotted as a function of the maximum measured VOC concentration and are shown in Figure 9. The mean and standard deviation for ψ , the 95%-confidence limits, the 90% lower tolerance limit, and the ratio $Y_{\max}/Y_{\text{mod}}$ at the lower tolerance limit for 5 VOCs are listed in Table 7. Statistics were not calculated for the other VOCs because of the limited number of drums in which they were found.

Figure 3. Plot of ψ values for total VOC concentration in bag headspace of vented sludge waste drums containing a maximum of two layers of polymer bags.

Figure 4. Plot of ψ values for total VOC concentration in bag headspace of vented waste drums containing a maximum of four layers of polymer bags.

Figure 5. Plot of ψ values for total VOC concentration in bag headspace of waste drums containing a maximum of five layers of polymer bags.

Figure 6. Plot of ψ values for carbon tetrachloride, TCE, TCA, and toluene in bag headspace of all vented waste drums.

Figure 7. Plot of ψ values for Freon-113, methylene chloride, methanol, and p-xylene in bag headspace of all vented waste drums.

Table 6. 90%-confidence lower tolerance limit (LTL) for ψ and $Y_{\max}/Y_{\text{mod}}$ ratios at the LTL for total VOCs in specific waste drums and single VOCs in all waste drums.

Variable	LTL	$Y_{\max}/Y_{\text{mod}}$ at LTL
Two bag layers	-0.050	1.12
Four bag	-0.360	2.29
Five bag layers	-0.254	1.80
CCl_4^{a}	-0.663	4.60
Methanol	-0.700	5.01
$\text{CH}_2\text{Cl}_2^{\text{b}}$	-0.212	1.63
TCA	-0.115	1.30
TCE	-0.275	1.88
Toluene	-0.284	1.92
Freon-113	0.195	0.64
p-xylene	-0.309	2.04

a. Carbon tetrachloride.

b. Methylene chloride.

Figure 8. Plot of ψ values for total VOC concentration within sealed polymer bottles in vented solid waste drums.

Figure 9. Plot of ψ values for VOCs with estimated model parameters within all vented waste drums.

Table 7. Mean, standard deviation, 95%-confidence limits, and 90% lower tolerance limit (LTL) of ψ for VOCs with estimated model parameters.

VOC	Number of drums	Mean	Standard deviation	Lower conf. limit	Upper conf. limit	LTL	$Y_{\max}/Y_{\text{mod}}$ at LTL
Acetone	15	-0.085	0.110	-0.146	-0.024	-0.290	1.95
1,1-dichloroethane	6	0.055	0.102	-0.047	0.157	-0.199	1.58
Chloroform	8	-0.097	0.157	-0.225	0.031	-0.445	2.79
1,1-dichloroethene	7	0.124	0.094	0.040	0.208	-0.095	1.25
Tetrachloroethene	5	-0.016	0.116	-0.149	0.117	-0.334	2.16

4. DISCUSSION

4.1 Model Assumptions

Model assumptions that VOC transport rates across all layers of confinement are equal and that the primary means of VOC transport are permeation across the polymer bags and diffusion across the drum liner lid and drum vent were confirmed in lab-scale experiments.³ A minimum vent time of 8 weeks was specified in order for the drum headspace concentration to approach a constant value. The total vent time for most waste drums exceeded 100 days.

Some model assumptions were made to simplify model calculations. These assumptions included uniform VOC concentration throughout a given void volume, a series of polymer bags represented as a single bag with wall thickness equal to the sum of the wall thicknesses of the individual bags, and equal VOC permeability across polyethylene and PVC. The use of a diffusion length across the drum liner greater than the actual drum thickness was a simple way of accounting for concentration gradients near the drum liner opening. Equation (18) can be used to demonstrate that wall thicknesses are summed together for a series of bags with the same VOC permeability and approximately the same permeable surface area. The assumption of equal VOC permeability across all polymers were made because most large and small polymer bags were made of polyethylene and there were limited VOC permeability data available for PVC. The mean and standard deviation of ψ for total VOC concentration in 15 waste drums identified as containing PVC bags were 0.003 and 0.186, respectively. The inclusion of $\psi = 0$ within a 95%-confidence interval indicates that the assumption is valid.

It is anticipated that some model parameters can never be known without complete characterization of waste drum contents. Conservative assumptions that were applicable to all or most waste drums, thus eliminating the need for detailed waste characterization, were made for a number of model parameters. Conservative assumptions inherently result in a higher estimated VOC concentration within the innermost layer of confinement. Assumptions concerning total bag thickness and the permeable surface area of large and small polymer bags are considered to be conservative. The maximum number of layers of polymer bags was assumed in each waste drum. The large bag surface area only gives credit to the top of the large bag. A survey of nearly 40 waste drums containing different waste types indicated that nearly all drums contained small polymer bags with a total permeable surface area greater than 500 cm². Other conservative assumptions included a VOC concentration of zero outside the waste drum, maximum bag thicknesses, and the placement of all VOC-contaminated waste inside one small bag.

4.2 Sensitivity Analysis

Sensitivity analysis identifies the magnitude of change in a dependent variable for a given change in an independent variable. The percent change in the model estimate of VOC concentration within the innermost layer of confinement given a 1% increase in model parameter or variable x is defined as

$$\% \Delta Y_1 = \left(\frac{\partial Y_1}{\partial x} \right) \frac{x}{Y_1} \quad (28)$$

Equation (28) was used to evaluate the sensitivity of model results for Freon-113, carbon tetrachloride, and TCE in waste drums containing different waste types. These VOCs represent the low-, mid-, and high-end of the permeability range for the VOCs. Examples of the sensitivity of Y_1 for a 1% increase in the magnitude of a model parameter or variable are summarized in Table 8. Model results are most sensitive to changes in the drum headspace concentration. Model results are also sensitive to changes in gas pressure, drum filter vent VOC diffusion characteristic, bag thickness, and permeable surface area of the innermost layer of confinement. The dependency of the estimated VOC concentration within the innermost layer of confinement on these parameters is shown graphically in Figure 10. Model results are not as sensitive to changes in other parameters (thickness and surface area of outer polymer bag layers, gas diffusivity and temperature, diffusion length across drum liner lid opening, and cross-sectional area of drum liner lid opening).

The combination of this sensitivity analysis and knowledge of the variance of model parameters can identify which parameters significantly affect model results. Of those variables or parameters having the greatest effect on model results; VOC permeability, drum filter vent VOC diffusion characteristic, and permeable surface area of the innermost layer of confinement have the greatest variability. There is little variability in gas pressure during measurements.

4.3 Model Validation

Model results were compared to the maximum measured VOC concentration in all bag headspaces. It is expected that the maximum concentration will be within the innermost layer of confinement that contains VOC-contaminated waste. However, a number of drums had the highest VOC concentrations measured in the large bag headspace. The VOC concentration in the large bag headspace is expected to be similar but less than the maximum concentration within one of the waste packages. Although most solid waste drums were completely sampled in one day, seven drums were sampled over two days. It was assumed that sample results would not be significantly different. The mean and standard deviation of ψ for total VOC concentration in these waste drums sampled over two days were 0.185 and 0.156, respectively. The 95%-confidence limits were both greater than $\psi = 0$ indicating a positive model bias. This suggests that longer sampling time may have resulted in lower measured VOC concentration in the small bags. Despite reasonable precautions, the VOC concentration within small bags may decrease before they are sampled. A gas sample can be collected from the large bag headspace more quickly after drum lid removal than can be collected from most waste packages after the large bags are opened. In this case, it is reasonable then to use the VOC concentration measured in the large bag headspace if it the highest reported concentration.

Table 8. Examples of percent change in model estimate of VOC concentration within innermost layer of confinement given a 1% increase in model variable or parameter.

VOC	Waste type	Model Variables			Model Parameters								
		Y_{DH}	P	T	ρ	$x_{p,1}$	$A_{p,1}$	$x_{p,2}$	$A_{p,2}$	D	x_d	A_d	D^*_{VOC}
Freon-113 ($\rho = 40$ Ba)	I.2A2	1.01	-0.68	0.05	-0.83	0.83	-0.83	—	—	-0.02	0.02	-0.02	0.68
	III.1A4	1.02	-0.73	0.08	-0.65	0.45	-0.45	0.20	-0.20	-0.08	0.08	-0.08	0.73
	III.1A5	1.01	-0.82	0.05	-0.76	0.63	-0.63	0.13	-0.13	-0.05	0.05	-0.05	0.82
	IV.2AT	1.01	-0.68	0.05	-0.63	0.63	-0.63	—	—	-0.05	0.05	-0.05	0.68
CCl ₄ ^a ($\rho = 190$ Ba)	I.2A2	1.02	-0.35	0.07	-0.28	0.28	-0.28	—	—	-0.07	-0.07	-0.07	0.35
	II.1A5	1.02	-0.49	0.10	-0.39	0.32	-0.32	0.07	-0.07	-0.10	0.10	-0.10	0.49
	III.1A5	1.02	-0.49	0.10	-0.39	0.32	-0.32	0.07	-0.07	-0.10	0.10	-0.10	0.49
	IV.2AT	1.02	-0.35	0.07	-0.28	0.28	-0.28	—	—	-0.07	0.07	-0.07	0.35
Toluene ($\rho = 670$ Ba)	I.2A2	1.02	-0.21	0.10	-0.11	0.11	-0.11	—	—	-0.10	0.10	-0.10	0.21
	II.1A5	1.03	-0.33	0.15	-0.18	0.15	-0.15	0.03	-0.03	-0.15	0.15	-0.15	0.33
	III.1A5	1.03	-0.33	0.15	-0.18	0.15	-0.15	0.03	-0.03	-0.15	0.15	-0.15	0.33
	IV.2AT	1.02	-0.21	0.10	-0.11	0.11	-0.11	—	—	-0.10	0.10	-0.10	0.21

a. Carbon tetrachloride.

Figure 10. Sensitivity of VOC concentration within innermost layer of confinement of vented solid waste drum to key model parameters.

4.3.1 VOCs with Measured Model Parameters

The model was accurate in estimating the total VOC concentration within waste drums with a maximum of four layers of polymer bags as well as the concentration of carbon tetrachloride, methanol, methylene chloride, TCE, and toluene. The model exhibited a positive bias for waste drums with a maximum of two layers of polymer bags (sludge waste drums), waste drums with a maximum of five layers of polymer bags, and in estimating the concentration within the innermost layer of confinement of TCA and Freon-113. The model exhibited a negative bias in the case of p-xylene.

Model bias in estimating the concentration of individual VOCs is attributed to the values of VOC-specific parameters used in model calculations, specifically VOC permeability. In the case of TCA and Freon-113, model results would approach measured VOC concentrations with increasing values of VOC permeability. Most sludge waste drums contained TCA, Freon-113, and carbon tetrachloride. Carbon tetrachloride plasticization of polyethylene results in an increase in amorphous fractional free volume.¹³ In Appendix A, a method for estimating VOC permeability in polyethylene shows how VOC permeability will increase with an increasing amorphous polymer volume fraction. Thus, the VOC permeability measured in unplasticized polyethylene will be less than VOC permeability in plasticized polyethylene. The negative model bias in predicting p-xylene concentrations suggests a smaller permeability value would result in more accurate model results. The highest VOC permeability measured in polyethylene bags was for p-xylene (810 Ba). Although the model was deemed accurate in estimating TCE and toluene concentrations, the upper confidence limits for these compounds were closest to zero. The permeability of TCE (580 Ba) and toluene (670 Ba) were similar in magnitude to that of p-xylene.

The positive bias in model results for sludge waste drums is attributed to the bias in estimating TCA concentration, since TCA is a primary constituent in the waste drums. Although a model bias was detected for waste drums with a maximum of five layers of polymer bags, the lower confidence limit was only 0.003. The 7 drums that were sampled over two days were listed as having a maximum of 5 layers. Excluding the waste drums sampled over two days, the mean and standard deviation of ψ for total VOC concentration in 17 waste drums containing a maximum of five layers of polymer bags were 0.057 and 0.198, respectively. The inclusion of $\psi = 0$ within a 95%-confidence interval indicates that the model is accurate for these waste drums that were completely sampled within one day.

Model precision was characterized by the lower tolerance limit defined by the mean and standard deviation of ψ for the sampled waste drums. In this case, one can be 90% confident that the calculated value of ψ will exceed the lower tolerance limit in at least 90% of waste drums sampled from the same population of waste drums. This limit is assumed to represent a worst-case situation since waste drums with small or negligible VOC concentrations were screened from this test program. The ratio $Y_{\max}/Y_{\text{mod}}$ at the lower tolerance limit indicates the maximum VOC concentration in the waste drums not be exceeded in at least 90% of the waste drums. In most cases, the ratio does not exceed 3 and in many cases is less than two. For carbon tetrachloride and methanol, the ratio is approximately 5.

Values of ψ were calculated for the 4 waste drums in which sealed polymer bottles were sampled. No statistical tests were performed because of the limited sample size. Preliminary results suggest the model may be useful; however, since the model will predict higher VOC

concentrations within sealed polymer bottles than in polymer bags, its use should be limited to drums where it is reasonable to assume that sealed bottles contain VOC-contaminated waste.

4.3.2 VOCs with Estimated Model Parameters

The model was accurate in estimating the concentration of 1,1-dichloroethane, chloroform, and tetrachloroethene. The model exhibited a positive bias in estimating the concentration of 1,1-dichloroethene. The model exhibited a negative bias in the case of acetone. As in the case of negative bias for p-xylene, a large value for acetone permeability (6,600 Ba) was used in model calculations. The values of ψ for ethyl benzene, o-xylene, benzene, and 1,1,2,2-tetrachloroethane found in one or two waste drums were calculated near or greater than zero in all cases. The ratio of the maximum measured VOC concentration to the model estimate at the lower tolerance limit for the 5 VOCs did not exceed 3 in any case.

4.4 Data Quality

All QA/QC requirements for gas sampling and analysis at the RFETS were met. All QA/QC requirements for gas sampling and analysis at the INEL were met except for duplicate samples. A total of 17 duplicate samples were collected from the drum headspace. The QA/QC requirements states that the relative percent difference can not exceed 25%.¹² The relative percent difference limit was exceeded in only 3 drums. In addition, the higher measured VOC concentration in the drum headspace was used as model input. As a result, this discrepancy in the QA/QC requirement is not expected to significantly affect model results and conclusions.

A total of 64 waste drums were sampled. Several waste drums were not used in model validation. One sludge waste drum was rejected because of insufficient venting time before gas sampling. Three waste drums containing solid waste could not be used because all bags in the drum were breached. As a result, no bag headspace samples were collected. Three waste drums sampled at ANL-W were identified as possibly having gas sample results that were in error. Gas sample results from three waste drums sampled at ANL-W (Drum ID 00613, 10216, and 24107) were identified as unusual. In drums 10216 and 24107, the measured drum headspace concentration was at least 20 times less than the measured VOC concentration in the innermost layers of confinement. This discrepancy was not observed in any other drums. The drum headspace gas sampling step was reviewed on videotape. Improper insertion of the sampling needle was the most probable cause for the low VOC concentrations. Both the needle insertion and needle removal steps were studied to determine the depth of needle penetration into the filter media. In both cases, no noticeable penetration was observed. This would result in the undesired intake of the ambient air into the sample canister and the dilution of the drum headspace gas. Gas sampling of several other drums in which a representative sample of the drum headspace was believed to be collected was also re-examined. Noticeable needle penetration was observed in those drums.

In drum 00613, no appreciable concentration of VOCs was detected in the large or small bag although 27 ppm TCA was measured in the drum headspace. No obvious explanation for this discrepancy is apparent, however; because any model results will be approximately two orders of magnitude greater than the reported concentration in the small bag, inclusion of data from this

drum may result in the overestimation of model accuracy. For this reason, the gas sample results of this waste drum were not used.

4.5 Model Applicability

The compounds for which VOC-specific model parameters were measured were selected because the compounds represented the range of physical properties observed in the 29 VOCs that are analyzed for in gas samples collected from all TRU waste drums intended for placement at the WIPP facility. These VOCs also represent the most common compounds observed in actual waste drums. Molecular weights ranged from methanol (MW = 32) to Freon-113 (MW = 187). Compounds included those with high permeability across polyethylene (i.e., p-xylene, TCE, toluene) and low permeability (Freon-113, cyclohexane). Methanol is a polar compound while carbon tetrachloride is nonpolar. Para-xylene and trichloroethylene exert a low vapor pressure while methylene chloride exerts a high vapor pressure. The properties of 9 VOCs in which model parameters were estimated also covered a wide range. Molecular weights ranged from acetone (MW = 58) to tetrachloroethene (MW = 166). Compounds included those with high permeability across polyethylene (i.e., 1,1,2,2-tetrachloroethane, acetone) and low permeability (benzene).

5. CONCLUSIONS

The objective of this study was to demonstrate that the VOC concentration within the innermost layer of confinement can be estimated using a model incorporating diffusion and permeation transport principles and limited waste drum sampling data. The following conclusions can be made:

1. The VOC transport model was accurate in estimating the VOC concentration within the innermost layer of confinement for 8 VOCs. The VOC-specific model parameters for 5 compounds (carbon tetrachloride, TCE, toluene, methylene chloride, and methanol) were measured. The VOC-specific model parameters for 3 compounds (1,1-dichloroethane, chloroform, and tetrachloroethene) were estimated.
2. The VOC transport model was accurate in estimating the total VOC concentration within the innermost layer of confinement for waste drums containing a maximum of 4 or 5 layers of polymer bags that were completely sampled within one day.
3. The VOC transport model exhibited a positive bias in estimating the VOC concentration within the innermost layer of confinement for 3 VOCs. The VOC-specific model parameters for 2 compounds (TCA and Freon-113) were measured. The VOC-specific model parameters for 1,1-dichloroethene were estimated. The bias is the result of using VOC permeability values in model calculations that are lower than actual values. Permeabilities of TCA and Freon-113 in polyethylene in actual waste drums are believed to be greater than values measured under laboratory conditions due to solvent plasticization which increases the volume fraction of amorphous polymer.
4. The VOC transport model exhibited a positive bias in estimating the total VOC concentration within the innermost layer of confinement for sludge waste drums containing a maximum of 2 layers of polymer bags that were sampled within one day. It is believed that the bias is related to model bias in estimating TCA and Freon-113 concentrations which are primary constituents in sludge waste drum headspace.
5. The VOC transport model exhibited a negative bias in estimating the VOC concentration within the innermost layer of confinement for 2 VOCs. The VOC-specific model parameters for p-xylene were measured. The VOC-specific model parameters for acetone were estimated.
6. The VOC transport model predicts, with 90% confidence, a VOC concentration not less than 1/2 of the maximum measured VOC concentration in at least 90% of the waste drums for 8 VOCs and two of the waste drum configurations. The VOC transport model predicts a VOC concentration not less than 1/3 of the maximum measured VOC concentration in at least 90% of the waste drums for 3 VOCs and waste drums with a maximum of four layers of polymer bags. For carbon tetrachloride and methanol, model estimates are not less than 1/5 of the maximum measured VOC concentration in at least 90% of the waste drums.

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Appendix A

Estimation of VOC Permeability in Polyethylene

Appendix A

Estimation of VOC Permeability in Polyethylene

If the solubility of a gas in polyethylene is proportional to pressure (Henry's law is applicable) and the gas diffusion constant is independent of pressure, then the gas permeability in polyethylene is defined as¹

$$\rho = D_{v-p} S \quad (\text{A-1})$$

where

$$\rho = \text{VOC permeability in polyethylene, cm}^3 \text{ (STP) cm}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$$

$$D_{v-p} = \text{VOC diffusivity in polyethylene, cm}^2 \text{ s}^{-1}$$

$$S = \text{VOC solubility coefficient in polyethylene, cm}^3 \text{ (STP) cm}^{-3} \text{ atm}^{-1}$$

The VOC permeability in polyethylene can be estimated using known or estimated values for D_{v-p} and S . Solubility coefficients were correlated with the Lennard-Jones force constants for the solubilized permeating vapor.¹ The VOC solubility coefficient is estimated to be

$$S = \alpha S_0 \quad (\text{A-2})$$

where,

$$\alpha = \text{Volume fraction of amorphous polymer.}$$

$$S_0 = \text{Solubility coefficient in completely amorphous polyethylene (cm}^3 \text{ (STP) cm}^{-3} \text{ atm).}$$

The value of α may range from 0 to 1.0. An average value of $\alpha = 0.5$ was used in the calculations. The value of S_0 is estimated as:

$$S_0 = e^{0.022\epsilon/\kappa - 5.07} \quad (\text{A-3})$$

where ϵ/κ is the force constant in the Lennard-Jones (6-12) potential field equation (K).

Diffusion coefficients were estimated based on a correlation with the molecular diameter of the permeating molecule.² The diffusion coefficient of a permeant in polyethylene is estimated by the equation

$$D_{v-p} = \frac{D_0}{\tau \beta} \quad (\text{A-4})$$

where

D_o = Diffusion coefficient in completely amorphous polyethylene (cm^2/s)

τ = Geometric impedance factor.

β = Chain immobilization factor.

The geometric impedance factor accounts for the reduction in the diffusion coefficient due to the necessity of molecules to bypass crystallites and move through amorphous regions of nonuniform cross-sectional area. The chain immobilization factor takes into account the reduction in amorphous chain segment mobility due to the proximity of crystallites. A correlation to estimate D_o at 25°C is

$$\ln\left(\frac{D_o}{d^2}\right) = 3.66 - 1.32[d - 0.5\phi^{0.5}] \quad (\text{A-5})$$

where d is the gas molecule diameter in $\text{\AA}$ and the quantity $0.5\phi^{0.5}$ is the mean unoccupied distance between two chain segments in the amorphous polymer and is assumed to equal $0.9 \text{ \AA}$ in all calculations. The gas molecular diameter is estimated from kinetic theory using experimentally determined viscosities or suitable approximations. The term D_o/d^2 is expressed in 10^9 sec^{-1} .

A correlation for β at 25°C is

$$\beta = e^{\gamma[d-0.5\phi^{0.5}]^2} \quad (\text{A-6})$$

where γ is a constant and is characteristic of the polymer and the volume fraction of crystallinity.

A correlation for τ is

$$\tau = \alpha^{-n} \quad (\text{A-7})$$

where n is a constant. For linear polyethylenes prepared from Ziegler catalysts and branched, high pressure polyethylenes, $n=1.88$. For linear polyethylenes prepared from Phillips catalysts and hydrogenated polybutadiene, $n=1.25$. An average value of $n = 1.565$ was used in the estimations.

Values of d and ϵ/κ were obtained from available sources.³ In cases where known values were not available, the values of d and ϵ/κ were obtained through correlations.⁴

$$d = (2.3551 - 0.087 \omega) \left(\frac{T_c}{P_c} \right)^{1/3} \quad (\text{A-8})$$

and

$$\epsilon/k = (0.7915 + 0.1693 \omega) T_c \quad (\text{A-9})$$

where

$$\begin{aligned} P_c &= \text{Critical pressure (atm)} \\ T_c &= \text{Critical temperature (K)} \\ \omega &= \text{Acentric factor.} \end{aligned}$$

In the absence of tabulated acentric factors, the values of d and ϵ/k were estimated using the Chung method³

$$d = 0.809 V_c^{1/3} \quad (\text{A-10})$$

where V_c is the critical molar volume (cm^3/mol), and

$$\epsilon/k = \frac{T_c}{1.2593} \quad (\text{A-11})$$

Measured VOC permeabilities across polyethylene were used to define several equation parameters. A value of $\gamma = 0.079$ minimized the error between estimated and experimentally determined permeability values. This value of γ was within reported range of values.² The estimated and measured VOC permeabilities are listed in Table A-1. The method calculated permeability values that were the same order of magnitude as experimental values except for carbon tetrachloride, methylene chloride, and methanol. All three compounds are one-carbon molecules.

The estimated VOC permeabilities for 9 other VOCs are listed in Table A-2. Because of the deficiency of the method for one-carbon molecules, the permeability of chloroform in polyethylene was approximated using both measured and estimated permeabilities of carbon tetrachloride and methylene chloride. The permeability of chloroform, a molecule containing one hydrogen atom, is assumed to be between the permeability of carbon tetrachloride (no hydrogen atoms) and methylene chloride (two hydrogen atoms). A linear relationship was assumed

$$P_{CHCl_3} = \left[\frac{P_{CHCl_3}^{est} - P_{CCl_4}^{est}}{P_{CH_2Cl_2}^{est} - P_{CCl_4}^{est}} \right] (P_{CH_2Cl_2}^{meas} - P_{CCl_4}^{meas}) + P_{CCl_4}^{meas} \quad (\text{A-12})$$

where

$$\begin{aligned} \rho^{est} &= \text{Estimated permeability listed in Table A-1} \\ \rho^{meas} &= \text{Measured permeability listed in Table A-1.} \end{aligned}$$

Table A-1. Measured and estimated VOC permeability across polyethylene bag.

VOC	$P_{\text{meas}}(\text{Ba})^a$	$P_{\text{est}}(\text{Ba})$
CH_2Cl_2^b	260	48
CCl_4^c	190	4
TCA	140	154
TCE	580	347
Methanol	135	4,357
Cyclohexane	15	1
Toluene	670	268
p-xylene	810	287
Freon-113 ^d	40	40

a. $\text{Ba} = 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} (\text{cm Hg})^{-1}$.

b. Methylene chloride.

c. Carbon tetrachloride.

d. 1,1,2-trichloro-1,2,2-trifluoroethane.

Table A-2. Estimated permeability of different VOCs across polyethylene bag using method outlined in this appendix.

VOC	$P_{est} (Ba)^a$
Benzene	80
Ethylbenzene	250
PCA ^b	2,000
DCE ^c	140
Chloroform	15
o-xylene	360
Acetone	6,635
DCA ^d	195
PCE ^e	460

a. $Ba = 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} (\text{cm Hg})^{-1}$

b. 1,1,2,2-Tetrachloroethane.

c. 1,1-dichloroethene.

d. 1,1-dichloroethane.

e. Tetrachloroethene.

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Appendix B

**Measured VOC Concentrations Inside
Vented Waste Drums Containing solid Waste**

Appendix B

Measured VOC Concentrations Inside Vented Waste Drums Containing Solid Waste

The measured VOC concentrations in the drum, large bag, and small bag headspaces in vented waste drums containing solid waste are listed in this appendix. The waste type is listed for each drum: Waste Type II contains inorganic solid waste and Waste Type III contains primarily organic solid waste. The final Arabic numeral indicates the maximum number of layers of polymer bags expected inside the drum. Waste drums containing the same waste type do not necessarily contain the same waste forms. These waste forms are identified by an INEL identification code (IDC). The IDCs seen in the waste drums are summarized below.

INEL IDC	Waste Type	Description
300	II	Graphite molds
320	II	Heavy nonspecial source metals
336	II	Paper and rags - moist
442	II	Unleached Raschig rings
480	II	Unleached light non-special source metals
337	III	Plastic (Teflon, PVC, etc.) and nonleaded rubber
338	III	Insulation and CWS filter media
432	III	Resin, leached and cemented

Table B-1. Total vent time, measured VOC concentrations, and estimated bag surface area in waste drum (Drum ID 00613).

Total vent time: 872 days			INEL IDC: 300						
Waste type: II.1A4			VOC concentration (ppm)						
Canister ID	Headspace	Number of bags	Surface area (cm ²)	CCl ₄ ^a	CH ₂ Cl ₂ ^b	Toluene	TCA ^c	TCE ^d	CHCl ₃ ^e
EI756	DH ^f	—	—	0.32J ^g	0.30U ^h	3.0	26	1.2J	5.0
EI530	LB ⁱ	1	2,550	0.03U	0.08J	0.04U	0.4	0.03U	0.03U
EI588	SB ^j	1	3,000	0.03U	0.18J	0.04U	0.13J	0.03U	0.03U

a. Carbon tetrachloride.

b. Methylene chloride.

c. 1,1,1-trichloroethane.

d. Trichloroethylene.

e. Chloroform.

f. Drum headspace.

g. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

h. U-Analyte undetected at this concentration.

i. LB-Large bag.

j. SB-Small bag.

Table B-2. Total vent time, measured VOC concentrations, and estimated surface area in waste drum (Drum ID 01667).

Total vent time: 863 days			INEL IDC: 300			
Waste Type: II.1A4			VOC concentration (ppm)			
Canister ID	Headspace	Number of bags	Surface area (cm ²)	CH ₂ Cl ₂ ^a	Toluene	TCA ^b
EI	DH ^c	—	—	0.11J ^d	0.09J	0.23J
EI	LB ^e	2	2,550	0.05U ^f	0.06J	0.11J
EI	LB-D ^g	—	—	0.05U	0.05J	0.16J

a. Methylene chloride.

b. 1,1,1-trichloroethane.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. LB-Large bag.

f. U-Analyte undetected at this concentration.

g. D-Duplicate.

Table B-3. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 17491).

Total vent time: 503 days			INEL IDC: 300					
Waste Type: IL1A4			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	CH ₂ Cl ₂ ^a	Toluene	TCA ^b	TCE ^c	CHCl ₃ ^d
EI467	DH ^e	—	—	0.8J ^f	0.7J	15	0.4J	0.1J
EI782	LB ^g	2	2,550	3.1J	1.6J	49	0.7J	0.5J
EI774	SB ^h	1	10,330	2.6J	1.8J	48	0.7J	0.5J

a. Methylene chloride.

b. 1,1,1-trichloroethane.

c. Trichloroethylene.

d. Chloroform.

e. Drum headspace.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. LB-Large bag.

h. SB-Small bag.

Table B-4. Total vent time, measure VOC concentration and estimated bag surface area in waste drum (Drum ID 22922).

Total vent time: 2,085 days			INEL IDC: 300			
Waste Type: II.1A4			VOC concentration (ppm)			
Canister ID	Headspace	Number of bags	Surface area (cm ²)	CH ₂ Cl ₂ ^a	TCA ^b	Acetone
EI	DH ^c	—	—	1.8	11	17U ^d
EI	LB ^e	1	2,550	4.3	21	25J ^f

a. Methylene chloride.

b. 1,1,1-trichloroethane.

c. Drum headspace.

d. U-Analyte undetected at this concentration.

e. LB-Large bag.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

Table B-5. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 01754).

Total vent time: 743 days			INEL IDC: 320		
Waste type: II.1A4			VOC concentration (ppm)		
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	p-xylene
EI	DH ^a	—	—	17	1.6
EI	LB ^b	1	2,550	21	2.1

a. Drum headspace.

b. LB-Large bag.

Table B-6. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 22072).

Total vent time: 2,087 days			INEL IDC: 442					
Waste Type: IL1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	MeOH ^c	Acetone
EI223	DH ^d	—	—	21	71	19	180J ^e	17U ^f
EI274	DH-D ^g	—	—	23	80	21	220J	19J
EI423 ^h	LB ⁱ	1	2,550	21	66	18	320	22J
EI485 ^h	SB-1 ^j	3	5,800	28	91	27	220J	24J
EI468 ^h	SB-2	3	5,800	25	85B ^k	23	220J	24J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Methanol.

d. DH-Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. U-Analyte undetected at this concentration.

g. D-Duplicate.

h. Samples taken one day after DH sample was collected.

i. LB-Large bag.

j. SB-Small bag.

k. B-Analyte detected in the blank.

Table B-7. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 23664).

Total vent time: 2,087 days			INEL IDC: 442		
Waste type: II.IA5			VOC concentration (ppm)		
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	CH ₂ Cl ₂ ^b
EI275	DH ^c	—	—	310	25
EI756	LB ^d	1	2,550	230	20
EI757 ^e	LB	—	—	180B ^f	14J ^g
EI759 ^e	LB-D ^h	—	—	150B	12J
EI589 ^e	SB-1 ⁱ	1	6,500	280	25
EI617 ^e	SB-1D	—	—	320B	30

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Drum headspace.

d. LB-Large bag.

e. Sample taken one day after DH sample was collected.

f. B-Analyte detected in blank.

g. J-Analyte less than program required detection limit and greater than or equal to the method detection limit.

h. D-Duplicate.

i. SB-Small bag.

Table B-8. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 08878).

Total vent time: 818 days			INEL IDC: 480			
Waste type: II.1A5			VOC concentration (ppm)			
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	Ccl ₄ ^b	CHCl ₃ ^c
EI754	DH ^d	—	—	1,400	8.8U ^e	9.1U
EI773	DH-Dup ^f	—	—	1,400	9.0U	9.3U
EI429	LB- ^g	1	2,550	170	—	—
EI767	SB-1 ^h	2	2,700	77	—	—
EI616	SB-2	2	4,470	1,900	14J ⁱ	—
EI522	SB-3	2	2,170	1,900	—	—
EI774	SB-4	2	3,030	1,700	—	—
EI382 ^j	PB-1 ^k	1	1,530	6,200	—	—
EI082 ^j	PB-2	1	1,530	4,400	—	24J
EI459	PB-3	1	1,530	1,900	—	—
EI051 ^j	PB-4	1	1,530	2,500	31J	25J

a. 1,1,1-trichloroethane.

b. Carbon tetrachloride.

c. Chloroform.

d. Drum headspace.

e. U-Analyte undetected at this concentration.

f. Dup-Duplicate.

g. LB-Large bag.

h. SB-Small bag.

i. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

j. 100 mL sample collected from innermost layer of confinement.

k. PB—Sealed polymer bottle.

Table B-9. Total vent time, measured concentration of most common VOCs and estimated bag surface area in waste drum (Drum ID 11415).

Total vent time: 1,316 days			INEL IDC: 480				
Waste Type: II.1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	Acetone
EI275	DH ^c	—	—	28	73	260	60J ^d
EI936	LB ^e	1	2,550	38	84	360	82J
EI391	SB-1 ^f	1	960	33	66	290	63J
EI470	SB-2	2	2,740	52	120	500	100J
EI928	SB-3	2	3,830	43	91	410	89J
EI424	SB-4	1	2,350	50	100	470	98J
EI765	SB-5	2	2,800	36	82	360	86J
EI296	SB-6	1	2,580	36	78	330	75J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. LB-Large bag.

f. SB-Small bag.

Table B-10. Total vent time, measured concentration of other VOCs and estimated bag surface area in waste drum (Drum ID 11415).

Total vent time: 1,316 days			INEL IDC: 480					
Waste type: II.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	C ₂ H ₄ Cl ₂ ^a	Xylene ^b	Methanol	EB ^c	C ₂ Cl ₄ ^d
EI275	DH ^e	—	—	4.4J ^f	24	54J	5.6J	1.5J
EI936	LB ^g	1	2,550	5.7J	35	91J	7.8J	2.0J
EI391	SB-1 ^h	1	960	4.3J	29	62J	6.8J	1.8J
EI470	SB-2	2	2,740	7.9J	45	110J	10J	2.7J
EI928	SB-3	2	3,830	6.3J	38	86J	8.7J	2.2J
EI424	SB-4	1	2,350	7.1J	46	97J	10J	2.6J
EI765	SB-5	2	2,800	5.5J	33	82J	7.6J	1.9J
EI296	SB-6	1	2,580	5.1J	36	74J	7.9J	1.9J

a. 1,1-dichloroethane.

b. m-, p-xylene.

c. Ethyl benzene.

d. Tetrachloroethene.

e. Drum headspace.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. LB-Large bag.

h. SB-Small bag.

Table B-11. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 12215).

Total vent time: 2,392 days			INEL IDC: 480					
Waste Type: II.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	Xylene ^a	TCA ^b	TCE ^c	Acetone
EI474	DH ^d	—	—	5.1J ^e	0.5U ^f	51	6.1	32J
EI473	DH-Dup ^g	—	—	6.8D ^h	0.5DJ	71D	8.1D	32J
EI227	LB ⁱ	2	2,550	13	0.9J	120	17	42J
EI387	SB-1 ^j	2	3,850	11	0.7J	110	15	37J
EI617	SB-2	2	4,100	9.3	0.7J	83	12	31J
EI757	SB-3	2	4,140	12	0.8J	110	15	37J
EI483	SB-4	2	3,050	11	—	110	13	36J
EI493	SB-5	2	4,170	10	0.7J	97	12	34J
EI482	SB-6	2	6,020	9.1	—	93	11	33J

a. m-, p-xylene

b. 1,1,1-trichloroethane.

c. Trichloroethylene.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. U-Analyte undetected at this concentration.

g. Dup-Duplicate

h. D-Dilution.

i. LB-Large bag.

j. SB-Small bag.

Table B-12. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 12878).

Total vent time: 1,317 days			INEL IDC: 480					
Waste Type: IL1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	Acetone	C ₂ Cl ₄ ^c
EI224	DH ^d	—	—	3.2J ^e	72	270	85J	2.0J
EI755	DH-Dup ^f	—	—	3.9J	78	290	86J	2.0J
EI866	LB ^g	1	2,550	3.7J	67	300	87J	2.0J
EI861	SB-1 ^h	2	3,050	3.4J	60	280	81J	1.9J
EI759	SB-2	2	4,460	4.2J	80	350	100J	2.3J
EI425	SB-3	2	2,940	3.7J	84	330	110J	2.0J
EI232	SB-4	2	2,640	4.4J	90	360	110J	2.3J
EI256	SB-5	2	2,190	3.9J	87	340	110J	2.1J
EI150	SB-6	2	1,960	5.1J	97	430	110J	2.9J
EI272	SB-7	2	2,720	4.4J	91	390	100J	2.4J
EI205	SB-8	2	4,520	3.2J	71	280	110J	1.7J
EI181	SB-9	2	4,520	4.9J	110	400	110J	2.7J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Tetrachloroethene.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. Dup-Duplicate.

g. LB-Large bag.

h. SB-Small bag.

Table B-13. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 13751).

Total vent time: 1,318 days			INEL IDC: 480					
Waste Type: II.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	C ₂ Cl ₄ ^c	Acetone
EI259	DH ^d	—	—	3.6J ^e	210	360	10.J	61J
EI854	DH-Dup ^f	—	—	3.2J	200	330	9.1J	61J
EI007	LB ^g	1	2,550	3.2J	170	330	9.1J	58J
EI852	SB-1 ^h	2	1,130	4.8J	240	510	14.J	54J
EI287	SB-2	2	400	0.9J	86	81	2.9J	31J
EI040 ⁱ	SB-3	2	750	—	140	100	3.3J	51J
EI486	SB-4	2	380	—	—	—	—	—
EI488	SB-5	2	280	—	71	34	1.8J	21J
EI077	PB-1 ^j	2	2,050	1.0J	55	74	4.2	24J
EI050 ⁱ	SB-6	2	260	0.6J	37	37	2.5J	—
EI045 ⁱ	SB-7	2	160	—	79	20	1.9J	31J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Tetrachloroethene.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. Dup-Duplicate.

g. LB-Large bag.

h. SB-Small bag.

i. 100 mL sample collected from innermost layer of confinement.

j. PB-Polymer bottle.

Table B-14. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 21952).

Total vent time: 2,065 days			INEL IDC: 480			
Waste type: II.1A5			VOC concentration (ppm)			
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CCl ₄ ^b
EI084	DH ^c	—	—	8.8	100	0.7J ^d
EI247	DH-Dup ^e	—	—	7.4	97	0.8J
EI489 ^{f,g}	LB ^h	1	2,550	6.3	49	0.4J
EI236 ^{f,g}	SB ⁱ	2	8,320	8.9	100	1.2J

a. 1,1,1-trichloroethane.

b. Carbon tetrachloride.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. Dup-Duplicate.

f. Bag breached before sample collected.

g. Sample taken one day after DH sample was collected.

h. LB—Large bag.

i. SB—Small bag.

Table B-15. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 22249).

Total vent time: 2,008 days			INEL IDC: 480				
Waste type: IL1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	MeOH ^b	Acetone
EI457	DH ^c	—	—	12J ^d	1,500	17U ^e	17U
EI592	LB ^f	2	2,550	11U	1,100	—	20J
EI530	LB-Dup ^g	—	—	11J	1,300	—	22J
EI532	SB-1 ^h	2	2,820	13J	1,300	22J	27J
EI772	SB-2	2	1,840	12J	1,400	—	22J
EI620	SB-3	2	1,800	14J	1,500	—	22J
EI465	SB-4	2	4,030	11U	1,200	—	22J
EI782	SB-5	2	2,300	11U	1,300	—	21J

a. 1,1,1-trichloroethane.

b. Methanol.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. U-Analyte undetected at this concentration.

f. LB-Large bag.

g. Dup-Duplicate.

h. SB-Small bag.

Table B-16. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 22293).

Total vent time: 2,154 days			INEL IDC: 480				
Waste Type: II.1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	Toluene	CH ₂ Cl ₂ ^b	Acetone
EI489	DH ^c	—	—	320 ^d	15J ^d	15J	17U ^e
EI828	LB ^f	2	2,550	910	31J	38J	24J
EI466	SB-1 ^g	2	640	660	23J	28J	20J
EI080	SB-2	2	10,700	830	31J	36J	23J
EI389	SB-3	2	3,140	950	35J	40J	26J
EI831	SB-4	2	1,370	710	23J	28J	22J
EI247	SB-5	2	4,490	460	20J	14J	—
EI823	SB-6	1	2,840	720	18J	21J	—
EI236	SB-7	2	1,550	770	27J	22J	19J
EI557 ^h	SB-8	1	860	270	8.5J	8.7J	—
EI250	SB-9	2	2,690	460	21J	11J	—
EI212	SB-10	1	1,290	330	20J	10J	—
EI497	SB-11	2	2,090	670	23J	21J	—
EI211	SB-12	1	1,470	700	23J	23J	20J
EI380 ^h	SB-13	2	440	570	13J	20J	20J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. U-Analyte undetected at this concentration.

f. LB-Large bag.

g. SB-Small bag.

h. 100 mL sample collected from innermost layer of confinement.

Table B-17. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 22549).

Total vent time: 2,031 days			INEL IDC: 480				
Waste Type: II.1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	Acetone	C ₂ Cl ₄ ^b
EI471	DH ^c	—	—	13J ^d	980	17U ^e	9.2J
EI460	DH-Dup ^f	—	—	12J	900	17U	10U
EI195	LB ^g	2	2,550	16J	1,400	23J	12U
EI619	SB-1 ^h	2	2,590	18J	1,300	23J	12U
EI204	SB-2	2	2,290	15J	1,300	23J	15U
EI221	SB-3	2	3,230	16J	1,400	24J	15U
EI182	SB-4	2	4,850	14J	1,500	22J	16U
EI209	SB-5	2	730	12J	1,100	21J	12U

a. 1,1,1-trichloroethane.

b. Tetrachloroethene.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. U-Analyte undetected at this concentration.

f. Dup-Duplicate.

g. LB-Large bag.

h. SB-Small bag.

Table B-18. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 22557).

Total vent time: 2,078 days			INEL IDC: 480					
Waste type: II.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CCl ₄ ^b	CH ₂ Cl ₂ ^c	Acetone
EI390	DH ^d	—	—	22	150	1.3J ^e	3.3J	20J
EI831	LB ^f	1	2,550	30	210	1.8J	5.2J	25J
EI212 ^g	SB-1 ^h	2	3,680	25	170	1.8J	4.0J	22J
EI936 ^g	SB-2	2	905	15	110	1.0J	1.9J	17U ⁱ
EI752 ^g	SB-3	1	1,520	3.4	78	0.7J	0.9J	17U
EI383 ^{g,j}	SB-4	2	840	26	170	1.7J	3.4J	18U
EI823 ^g	SB-5	2	1,880	26	190	1.7J	4.4J	24J
EI533 ^g	SB-6	2	2,200	24	180	1.5J	4.3J	23J
EI472 ^g	SB-7	2	4,500	24	170	1.4J	3.3J	22J
EI209 ^g	SB-8	2	2,330	27	190	1.8J	4.2J	24J
EI460 ^g	SB-9	2	1,880	26	200	1.8J	4.5J	24J
EI204 ^g	SB-10	2	2,280	23	100	1.0J	1.0U	17U
EI619 ^g	SB-11	2	1,880	26	190	2.2J	3.9J	23J
EI389 ^g	SB-12	2	1,140	24	160	1.2J	3.2J	21J

a. 1,1,1-trichloroethane.

b. Carbon tetrachloride.

c. Methylene chloride.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. LB-Large bag.

g. Samples taken one day after DH sample was collected.

h. SB-Small bag.

i. U-Analyte undetected at this concentration.

j. 100 mL sample collected from innermost layer of confinement.

Table B-19. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 22944).

Total vent time: 2,085 days			INEL IDC: 480		
Waste type: II.1A5			VOC concentration (ppm)		
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	CH ₂ Cl ₂ ^b
EI772	DH ^c	—	—	91	4.9J ^d
EI782	LB ^e	2	2,550	80	4.3J
EI620	SB-1 ^f	1	1,700	160	7.8J
EI754	SB-2	2	870	92	4.5J
EI774	SB-3	2	960	110	5.7J
EI290 ^g	SB-4	1	2,590	0.55J	0.1U ^h
EI054 ^g	SB-5	2	540	20	0.6J
EI830	SB-6	2	1,400	58	2.4J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. LB-Large bag.

f. SB-Small bag.

g. 100 mL sample collected from innermost layer of confinement.

h. U-Analyte undetected at this concentration.

Table B-20. Total vent time, measure concentration of three VOCs and estimated bag surface area in waste drum (Drum ID 23020).

Total vent time: 2,036 days			INEL IDC: 480			
Waste Type: II.1A5			VOC concentration (ppm)			
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	CH ₂ Cl ₂ ^b	Toluene
EI494	DH ^c	—	—	550	4.9U ^d	6.0J ^e
EI859	DH-Dup ^f	—	—	590	4.8U	6.5J
EI433	LB ^g	2	2,550	630	6.2U	7.1J
EI458	SB-1 ^h	2	3,670	580	4.9U	6.5J
EI527	SB-2	2	3,890	700	6.5U	7.4J
EI076 ^h	PB-1 ^j	0	1,580	930	12J	9.6J
EI039 ⁱ	SB-3	2	3,250	690	7.1U	7.6J
EI079 ⁱ	SB-4	2	3,315	620	5.7U	6.8J
EI042 ⁱ	SB-5	2	3,815	640	6.2U	7.0J
EI044 ⁱ	PB-2	0	1,580	5,500D ^k	99	14.J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Drum headspace.

d. U-Analyte undetected at this concentration.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. Dup-Duplicate.

g. LB-Large bag.

h. SB-Small bag.

i. 100 mL sample collected from innermost layer of confinement.

j. PB-Sealed polymer bottle.

k. D-Dilution.

Table B-21. Total vent time, measured concentration of four VOCs and estimated bag surface area in waste drum (Drum ID 23020).

Total vent time: 2,036 days			INEL IDC: 480				
Waste Type: II.1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Xylene ^a	C ₂ H ₄ Cl ₂ ^b	C ₂ H ₂ Cl ₂ ^c	EB ^d
EI494	DH ^e	—	—	3.1U ^f	4.2U	5.2U	3.1U
EI859	DH-Dup ^g	—	—	3.1U	4.2U	5.1U	3.1U
EI433	LB ^h	2	2,550	4.0U	5.3U	6.5U	4.0U
EI458	SB-1 ⁱ	2	3,670	3.1U	4.2U	5.2U	3.1U
EI527	SB-2	2	3,890	4.2U	5.6U	6.9U	4.2U
EI076 ^j	PB-1 ^k	0	1,580	6.2U	8.3U	10.U	6.2U
EI039 ^j	SB-3	2	3,250	4.5U	6.1U	7.4U	4.5U
EI079 ^j	SB-4	2	3,315	3.7U	4.9U	6.0U	3.7U
EI042 ^j	SB-5	2	3,815	4.0U	5.3U	6.5U	4.0U
EI044 ^j	PB-2	0	1,580	8.7J ^l	27J	7.1J	3.6J

a. m-, p-xylene.

b. 1,1-dichloroethane.

c. 1,1-dichloroethene.

d. Ethyl benzene.

e. Drum headspace.

f. U-Analyte undetected at this concentration.

g. Dup-Duplicate.

h. LB-Large bag.

i. SB-Small bag.

j. 100 mL sample collected from innermost layer of confinement.

k. PB-Sealed polymer bottle.

l. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

Table B-22. Total vent time, measure VOC concentration and estimated bag surface area in waste drum (Drum ID 23312).

Total vent time: 2,146 days			INEL IDC: 480				
Waste Type: IL1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CH ₂ Cl ₂ ^b	Acetone
EI473	DH ^c	—	—	7.2J ^d	470	9.7J	46J
EI470	LB ^e	2	2,550	11. J	680	15J	72J
EI475 ^f	SB-1 ^g	2	3,070	8.9J	730	15J	63J
EI482 ^f	SB-2	2	2,650	8.0J	600	14J	65J
EI474 ^f	SB-3	2	3,160	10. J	630	14J	66J
EI483 ^f	SB-4	2	3,800	9.1J	670	14J	80J
EI467 ^f	SB-5	2	4,220	9.9J	570	13J	51J
EI524 ^f	SB-6	2	2,720	8.8J	640	12J	65J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. LB-Large bag.

f. Samples taken one day after DH sample was collected.

g. SB-Small bag.

Table B-23. Total vent time, measure VOC concentration and estimated bag surface area in waste drum (Drum ID 24765).

Total vent time: 2,036 days			INEL IDC: 480					
Waste Type: II.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	Xylene ^a	TCA ^b	CCl ₄ ^c	CH ₂ Cl ₂ ^d
EI768	DH ^e	—	—	14	0.5J ^f	52	0.3U ^g	3.6J
EI859	LB ^h	2	2,550	33	0.9J	130	—	9.0
EI857	LB-D ⁱ	—	—	32	1.0J	120	—	8.5
EI527 ^j	SB-1 ^k	2	3,880	25	0.8J	110	—	8.2
EI819 ^j	SB-2	2	4,350	30	1.0J	160	1.2J	8.5J
EI497 ^j	SB-3	2	6,770	25	0.7U	110	—	7.2J
EI765 ^j	SB-4	1	4,330	21	0.7J	76	—	5.7
EI751 ^j	SB-5	2	2,630	24	0.9J	97	—	5.9J
EI452 ^{j,l}	PB-1 ^m	0	1,530	0.5J	0.1U	6.9	—	0.8J

a. m-, p-xylene.

b. 1,1,1-trichloroethane.

c. Carbon tetrachloride.

d. Methylene chloride.

e. Drum headspace.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. U-Analyte undetected at this concentration.

h. LB-Large bag.

i. D-Duplicate.

j. Samples taken one day after DH sample was collected.

k. SB-Small bag.

l. 100 ml sample collected.

m. PB-Sealed polymer bottle.

Table B-24. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 24786).

Total vent time: 1,920 days			INEL IDC: 480				
Waste Type: II.1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CH ₂ Cl ₂ ^b	CHCl ₃ ^c
EI388	DH ^d	—	—	4.6J ^e	63	4.6J	0.5J
EI432	LB ^f	2	2,550	7.1J	120	10	1.1J
EI222	SB-1 ^g	2	1,400	2.9	14	1.2	0.2J
EI456	SB-2	2	1,325	1.8	14	1.2	0.2J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Chloroform.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. LB-Large bag.

g. SB-Small bag.

Table B-25. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 01677).

Total vent time: 840 days			INEL IDC: 302								
Waste type: III.1A4			VOC concentration (ppm)								
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	TCE ^b	Tol ^c	Acet ^d	MeOH ^e	Bz ^f	C ₂ Cl ₄ ^g	CHCl ₃ ^h
EI091	DH ⁱ	—	—	51	150	12	20J ^j	273	1.5J	0.9J	2.7J
EI	LB ^{k,l}	1	2,550	—	—	—	—	—	—	—	—

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Toluene.

d. Acetone.

e. Methanol.

f. Benzene.

g. Tetrachloroethene.

h. Chloroform.

i. Drum headspace.

j. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

k. LB-Large bag.

l. Bag was not sampled because it was breached.

Table B-26. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 14466).

Total vent time: 839 days			INEL IDC: 302				
Waste type: III.1A4)			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	C ₂ Cl ₄ ^c
EI476	DH ^d	—	—	6.6J ^e	65	99	2.7J
EI421	DH-Dup ^f	—	—	7.6J	67	100	3.1J
EI	LB ^{g,h}	—	2,550	—	—	—	—

a. 1,1,1-trichloroethane.

b. Trichloroethene.

c. Tetrachloroethene.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. Dup-Duplicate.

g. LB-Large bag.

h. Bag was not sampled because it was breached.

Table B-27. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 24098).

Total vent time: 2,136 days			INEL IDC: 336				
Waste Type: III.1A4			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	CH ₂ Cl ₂ ^b	Toluene	TCE ^c
EI192	DH ^d	—	—	110	1.4J ^e	12	4.8J
EI210	DH-Dup	—	—	110	1.4J	12	5.0J
EI618	LB ^g	2	2,550	170	2.1J	16	6.6J
EI234	SB-1 ^h	2	4,690	190	2.4J	19	7.5J
EI061 ⁱ	SB-2	2	3,050	220	2.9J	20	8.3J
EI280	SB-3	1	2,270	120	1.5J	12	5.0J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Trichloroethylene.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. Dup-Duplicate.

g. LB-Large bag.

h. SB-Small bag.

i. 100 mL sample collected from innermost layer of confinement.

Table B-28. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 24107).

Total vent time: 2,064 days			INEL IDC: 336				
Waste Type: III.1A4			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	Xylene ^c
EI492	DH ^d	—	—	3.2	2.9	0.8	0.1J ^e
EI276	LB ^f	2	2,550	15	55	6.7	0.4U ^g
EI255 ⁱ	SB-1 ^h	2	4,250	15	52	6.6	0.4U
EI254 ⁱ	SB-2	2	2,590	19	64	8.0	0.6J
EI495 ⁱ	SB-3	2	2,620	19	65	8.0	0.5J
EI386 ⁱ	SB-4	2	7,550	180	560	73	5.5J
EI281 ⁱ	SB-5	2	2,610	18	62	7.9	0.5J
EI269 ^{i,j}	SB-6	2	2,640	20	72	11	0.5J
EI201 ⁱ	SB-7	2	2,430	20	65	8.2	0.7J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. m-, p-xylene.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. LB-Large bag.

g. U-Analyte undetected at this concentration.

h. SB-Small bag.

i. Sample taken one day after DH sample was collected.

j. 100 mL sample collected from innermost layer of confinement.

Table B-29. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 24214).

Total vent time: 2,121 days			INEL IDC: 336						
Waste type: III.1A4			VOC concentration (ppm)						
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	Xylene ^a	TCA ^b	CCl ₄ ^c	TCE ^d	CH ₂ Cl ₂ ^e
EI768	DH ^f	—	—	7.8	21	98	0.5U ^g	2.4J ^h	11
EI751	LB ⁱ	2	2,550	9.6	27	130	0.8J	3.2J	14
EI819	SB-1 ^j	1	4,160	7.7J	19	120	4.3J	4.5J	12
EI856	SB-2	1	5,380	9.0	24	130	4.5J	4.9J	13
EI858	SB-3	1	7,940	9.7	26	130	0.7U	3.0J	13

a. m-,p-xylene.

b. 1,1,1-trichloroethane.

c. Carbon tetrachloride.

d. Trichloroethylene.

e. Methylene chloride.

f. Drum headspace.

g. U-Analyte undetected at this concentration.

h. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

i. LB-Large bag.

j. SB-Small bag.

Table B-30. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 32529).

Total vent time: 1,840 days			INEL IDC: 336					
Waste type: III.1A4			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CCl ₄ ^b	TCE ^c	CH ₂ Cl ₂ ^d
EI769	DH ^e	—	—	39	250	1.4U ^f	1.3U	35
EI863	DH-Dup ^g	—	—	34	220	—	—	32
EI428	LB ^h	1	2,550	14	58	—	—	7
EI585	SB-1 ⁱ	1	4,000	38	260	—	—	31
EI243	SB-2	1	3,270	44	310	—	—	36
EI485	SB-3	1	2,570	42	330	—	—	39
EI860	SB-4	1	3,860	17	93	3.0J ^j	1.5J	11

a. 1,1,1-trichloroethane.

b. Carbon tetrachloride.

c. Trichloroethylene.

d. Methylene chloride.

e. Drum headspace.

f. U-Analyte undetected at this concentration.

g. Dup-Duplicate.

h. LB-Large bag.

i. SB-Small bag.

j. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

Table B-31. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 10216).

Total vent time: 1,408 days			INEL IDC: 338						
Waste type: III.1A4			VOC concentration (ppm)						
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CCl ₄ ^b	TCE ^c	C ₂ Cl ₄ ^d	C ₂ H ₂ Cl ₂ ^e
EI468	DH ^f	—	—	0.3U ^g	11	0.5J ^h	39	0.5J	1.2J
EI177	LB ⁱ	1	2,550	4.8U	270	14J	810	11J	31J
EI274	SB-1 ^j	1	— ^k	—	240	12J	740	10J	28J
EI476	SB-2	2	5,800	3.0J	220	11J	710D ^l	8.9J	25
EI253	SB-3	2	5,570	—	240	12J	690	9.6J	28J
EI972	SB-4	2	5,950	3.0J	220	12J	600D	8.8J	23
EI423	SB-5	2	2,780	—	290	14J	880	12J	33J
EI421	SB-6	2	1,930	—	280	14J	840	12J	32J
EI426	SB-7	2	1,540	—	280	13J	790	12J	29J

a. 1,1,1-trichloroethane.

b. Carbon tetrachloride.

c. Trichloroethylene.

d. Tetrachloroethene.

e. 1,1-Dichloroethene

f. Drum headspace.

g. U-Analyte undetected at this concentration.

h. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

i. LB-Large bag.

j. SB-Small bag.

k. Unable to determine.

l. D-Dilution.

Table B-32. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 02678).

Total vent time: 113 days			INEL IDC: 432					
Waste type: III.1A4			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	C ₂ Cl ₄ ^c	C ₂ H ₄ Cl ₂ ^d
EI008	DH ^e	—	—	10J ^f	190	320	26	3.0U ^g
EI009	LB ^h	1	2,550	14J	330	460	36	4.5J
EI197	PB ⁱ	0	2,750	10J	230	320	26	3.3J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Tetrachloroethylene.

d. 1,1-dichloroethane.

e. Drum headspace.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. U-Analyte undetected at this concentration.

h. LB-Large bag.

i. PB-Sealed polymer bottle.

Table B-33. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 10578).

Total vent time: 1,360 days			INEL IDC: 432					
Waste type: III.1A4			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	Freon ^c	C ₂ H ₂ Cl ₄ ^d
EI856	DH ^e	—	—	12J ^f	84	190	22	1.3J
EI495	LB ^g	1	2,550	0.4J	3.2	7.6	1.0	0.06U ^h
EI003	SB-1 ⁱ	1	1,700	15J	87	220	19	1.5J
EI831	SB-2	1	1,820	11J	71	180	16	1.2J
EI060 ^j	SB-3	1	1,580	11J	69	170	20	1.3J
EI019 ^j	SB-4	1	1,760	15J	95	210	26	1.6J
EI052 ^j	SB-5	1	1,630	16J	100	240	30	1.7J
EI025 ^j	SB-6	1	1,630	14J	95	200	26	1.5J
EI022 ^j	SB-7	1	2,870	17J	110	220	26	1.8J
EI059 ^j	SB-8	1	1,630	14J	95	180	25	1.5J
EI055 ^j	SB-9	1	1,820	14J	94	190	20	1.5J
EI020 ^j	SB-10	1	1,760	11J	69	140	13	1.2J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. 1,1,2-trichloro-1,2,2-trifluoroethane.

d. Tetrachloroethane.

e. Drum headspace.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. LB-Large bag.

h. U-Analyte undetected at this concentration.

i. SB-Small bag.

j. 100 mL sample collected from innermost layer of confinement.

Table B-34. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 12875).

Total vent time: 1,359 days			INEL IDC: 432					
Waste type: III.1A4			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	C ₂ H ₄ Cl ₂ ^c	C ₂ Cl ₄ ^d
EI280	DH ^e	—	—	5.3J ^f	180	370	5.7J	1.8J
EI255	LB ^g	—	2,550	12.J	420	860	15.J	4.5U ^h
EI472	SB-1 ⁱ	—	3,600	11.J	320	720	11.J	4.2U
EI386	SB-2	—	5,570	10.J	300	640	9.9J	3.5U
EI858	SB-3	—	4,700	13.J	450	810	14.J	4.3J
EI250	SB-4	—	3,400	12.J	370	700	12.J	4.0J

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. 1,1-dichloroethane.

d. Tetrachloroethene.

e. Drum headspace.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. LB-Large bag.

h. U-Analyte undetected at this concentration.

i. SB-Small bag.

Table B-35. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 17756).

Total vent time: 846 days			INEL IDC: 432						
Waste type: III.1A4			VOC concentration (ppm)						
Canister ID	Headspace	Number of bags	Surface area (cm ²)	TCA ^a	CH ₂ Cl ₂ ^b	Toluene	TCE ^c	C ₂ H ₂ Cl ₂ ^d	C ₂ H ₄ Cl ₂ ^e
EI826	DH ^f	—	—	350	16.J ^g	9.3J	2.3J	220	3.5J
EI862	DH-Dup ^h	—	—	350	16.J	9.9J	2.2J	210	3.3J
EI855	LB ⁱ	2	2,550	500	21.J	13.J	2.5U ⁱ	300	4.4J
EI867	SB-1 ^k	2	1,760	440	19.J	14.J	2.7J	230	3.8J
EI863	SB-2	2	1,760	480	20.J	13.J	2.4J	260	4.3J
EI865	SB-3	2	1,760	460	19.J	11.J	2.1J	250	4.4J
EI868	SB-4	2	1,760	510	20.J	11.J	2.6U	280	4.4J
EI829	SB-5	2	1,760	330	14.J	9.8J	1.7J	150	2.9J
EI860	SB-6	2	1,760	430	17.J	12.J	2.1J	190	3.9J
EI764	SB-7	2	1,760	490	20.J	11.J	2.5U	240	4.4J
EI869	SB-8	2	1,760	170	7.7J	7.7J	1.1J	66	1.6J
EI853	SB-9	2	1,760	470	20.J	10.J	2.5U	230	4.2U
EI864	SB-10	2	1,760	340	16.J	11.J	1.9J	160	3.3J
EI177	SB-11	2	1,760	260	8.6J	8.8J	2.0J	82	2.1U
EI092	SB-12	2	1,760	190	6.7J	6.7J	0.9U	70	1.6J
EI196	SB-13	2	1,760	140	4.8J	6.9J	0.9J	38	1.1J

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. Trichloroethylene.

d. 1,1-dichloroethene.

e. 1,1-dichloroethane.

f. Drum headspace.

g. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

h. Dup-Duplicate.

i. LB-Large bag.

j. U-Analyte undetected at this concentration.

k. SB-Small bag.

Table B-36. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 17759).

Total vent time: 833 days			INEL IDC: 432				
Waste Type: III.1A4			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CH ₂ Cl ₂ ^b	C ₂ H ₂ Cl ₂ ^c
EI385	DH ^d	—	—	12.DJ ^{e,f}	290D	21.DJ	130D
EI273	LB ^g	—	2,550	19J	500	35J	240
EI215	SB-1 ^h	—	2,750	12J	290	14J	98
EI174	SB-2	—	2,850	9.7J	210	12J	68
EI184	SB-3	—	3,000	11J	310	14J	100
EI089	SB-4	—	3,650	5.5J	93	5.5J	33
EI282	SB-5	—	3,750	12J	330	20J	130
EI536	SB-6	—	3,400	7.9J	200	10J	60
EI248	SB-7	—	3,150	7.4J	180	8.7J	52
EI203	SB-8	—	2,340	7.3J	240	12J	63
EI423	SB-9	—	3,660	7.4J	240	11J	62
EI549 ⁱ	SB-10	—	4,100	11J	360	19J	110
EI081 ⁱ	SB-11	—	3,570	5.8J	190	9.6J	53
EI068 ⁱ	SB-12	—	3,240	2.9J	44	2.1J	44
EI072 ⁱ	SB-13	—	2,630	5.7J	150	7.2J	35
EI070 ⁱ	SB-14	—	3,400	9.9J	210	11J	46
EI074 ⁱ	SB-15	—	3,570	8.2J	240	11J	68
EI554 ⁱ	SB-16	—	3,400	7.5J	240	11J	56

a. 1,1,1-trichloroethane.

b. Methylene chloride.

c. 1,1-dichloroethene.

d. Drum headspace.

e. D-Dilution.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. LB-Large bag.

h. SB-Small bag.

i. 100 mL sample collected from innermost layer of confinement.

Table B-37. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 13229).

Total vent time: 118 days			INEL IDC: 432	
Waste type: III.1A4			VOC concentration (ppm)	
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene
EI827	DH ^a	—	—	10
EI769	LB ^b	1	2,550	34
EI	SB-1 ^{c,d}	2	3,050	—
EI	SB-2 ^d	2	3,050	—
EI	SB-3 ^d	2	2,200	—
EI	SB-4 ^d	2	3,050	—

a. Drum headspace.

b. LB-Large bag.

c. SB-Small bag.

d. Bag not sampled because all layers were breached.

Table B-38. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 11433).

Total vent time: 1,318 days			INEL IDC: 330				
Waste type: III.1A5			VOC concentration (ppm)				
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	CCl ₄ ^b	TCE ^c
EI195	DH ^d	—	—	9.3DJ ^{e,f}	200D	2.0DJ	330D
EI185	DH-Dup ^g	—	—	1.9J	40	0.5DJ	68
EI003	LB ^h	2	2,550	10.DJ	220D	2.5DJ	370D
EI250 ⁱ	SB-1 ^j	1	2,370	10.J	210	2.0J	340
EI828 ⁱ	SB-2	3	6,360	9.7J	210	2.2J	350
EI211 ⁱ	SB-2	3	—	10.J	200	2.0J	350
EI471 ⁱ	SB-3	2	4,920	7.8U	150	1.5J	250

a. 1,1,1-trichloroethane.

b. Carbon tetrachloride.

c. Trichloroethylene

d. Drum headspace.

e. D-Dilution.

f. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

g. Dup-Duplicate.

h. LB-Large bag.

i. Sample taken one day after DH sample was collected.

j. SB-Small bag.

Table B-39. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 23901).

Total vent time: 1,976 days		INEL IDC: 330			
Waste type: III.1A5		VOC concentration (ppm)			
Canister ID	Headspace	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b
EI205	DH ^c	—	9.2J ^d	340	93
EI256	LB ^e	2,550	4.8J	64	37
EI181	SB ^f	23,000	9.8J	280	88

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. LB-Large bag.

f. SB—Small bag.

Table B-40. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 07170).

Total vent time: 1,408 days			INEL IDC: 337					
Waste type: III.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	Acetone	C ₂ H ₄ Cl ₂ ^c
EI273	DH ^d	—	—	3.6J ^e	150	240	62	27
EI385	DH-Dup ^f	—	—	3.3J	140	240	62	27
EI259	LB ^g	1	2,550	7.2J	310	490	110	60

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. 1,1-dichloroethane.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. Dup-Duplicate.

g. LB-Large bag.

Table B-41. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 10663).

Total vent time: 1,318 days			INEL IDC: 337			
Waste type: III.1A5			VOC concentration (ppm)			
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b
EI278	DH ^c	—	—	5.4J ^d	140	210
EI232	LB ^e	1	2,550	5.8J	150	220

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Drum headspace.

d. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

e. LB-Large bag.

Table B-42. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 24092).

Total vent time: 2,133 days				INEL IDC: 337						
Waste type: III.1A5				VOC concentration (ppm)						
Canister ID	Headspace	Number of bags	Surface area (cm ²)	CCl ₄ ^a	CH ₂ Cl ₂ ^b	Toluene	TCA ^c	TCE ^d	Freon ^e	CHCl ₃ ^f
EI535	DH ^g	—	—	48	1.1J ^h	5.3	63	1.1J	0.6J	3.5J
EI465	DH-Dup ⁱ	—	—	51	1.0J	5.6	68	1.0J	0.6J	3.6J
EI830	LB ^j	—	2,500	150	3.0J	14J	200	2.3J	1.8J	10J
EI857	SB ^k	—	3,000	140	3.1J	16	200	2.4J	1.8J	10J

a. Carbon tetrachloride.

b. Methylene chloride.

c. 1,1,1-trichloroethane.

d. Trichloroethylene.

e. 1,1,2-trichloro-1,2,2-trifluoroethane.

f. Chloroform.

g. Drum headspace.

h. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

i. Dup-Duplicate.

j. LB-Large bag.

k. SB-Small bag.

Table B-43. Total vent time, measured VOC concentration and estimated bag surface area in waste drum (Drum ID 07034).

Total vent time: $\approx$ 1,000 days		INEL IDC: 337					
Waste type: III.1A5		VOC concentration (ppm)					
Canister ID	Headspace	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	CHCl ₃ ^c	Acetone
EI522	DH ^d	—	2.2J ^e	170	210	100	29
EI772	LB ^f	2,550	6.1J	580	640	340	63
EI824	SB ^g	3,000	5.6DJ ^h	470D	550D	290D	55

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Chloroform.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. LB-Large bag.

g. S-Small bag.

h. D-Dilution.

Table B-44. Total vent time, assured VOC concentration and estimated bag surface area in waste drum (Drum ID 09435).

Total vent time: 152 days			INEL IDC: 337					
Waste type: III.1A5			VOC concentration (ppm)					
Canister ID	Headspace	Number of bags	Surface area (cm ²)	Toluene	TCA ^a	TCE ^b	Methanol	CHCl ₃ ^c
EI206	DH ^d	—	—	2.7	21	0.3J ^e	17U ^f	3.9
EI192	LB ^g	1	2,550	7.4	71	0.45	37J	13

a. 1,1,1-trichloroethane.

b. Trichloroethylene.

c. Chloroform.

d. Drum headspace.

e. J-Analyte less than program required detection limit and greater than or equal to method detection limit.

f. U-Analyte undetected at this concentration.

g. LB-Large bag.

Appendix C

Measured VOC Concentrations In Vented Sludge Waste Drums

Table C-1. Total drum vent time and measured concentrations (ppm) of TCA, carbon tetrachloride, and Freon-113 in sludge waste drums.

Drum ID	Waste type	Total vent time (days)	TCA ^a		CCl ₄ ^b		Freon-113 ^c	
			DH ^d	LB ^e	DH	LB	DH	LB
76142	I.2A2	70	18.9	24.6	—	—	1.4J	2.3J ^f
76144	I.2A2	126	120.1	155	1.3U ^g	18.6	—	—
76182	I.2A2	0	0.7U	3.8J	1.0J	6.1J	4.1J	15
76189	I.2A2	232	130	164	—	—	—	—
76206	I.2A2	126	58	86	—	—	0.8J	1.1J
76282	I.2A2	162	271	414	1,401	1,925	86.J	141.J
76287	I.2A2	146	429J	614J	2,266	3,074	86.J	142.J
76303	I.2A2	146	65	84	—	—	2.4J	4.4J
71022	IVA2T	210	51,287	58,376	69,969	82,309	6,700.J	7,337.J
71932	IVA2T	189		108,830	77,686	135,540	6,363	8,919
71940	IVA2T	91	40,620	61,377	109,990	183,750	9,305	13,401
71941	IVA2T	181	48,701	58,741	143,230	171,660	11,602	12,291
72128	IVA2T	189	—	—	—	—	188J	150U
72623	IVA2T	205	8.8	11.2	3.8	0.6J	—	—
76135	IVA2T	232	709	928	4,139	5,508	73.J	89.J
76196	IVA2T	110	2,471J	2,856J	25,4109	29,752	2,822.J	3,947.J
76200	IVA2T	233	7,588J	10,257J	66,903	93,545	10,962.J	15,224
76203	IVA2T	233	18,212	17,812	60,360	55,580	1,859.J	2,018.J
76283	IVA2T	232	5,024	6,122	20,977	24,588	809.J	1,114.J

a. 1,1,1—Trichloroethane.

b. Carbon tetrachloride.

c. 1,1,2-trichloro-1,2,2-trifluoroethane.

d. Drum headspace.

e. Large bag.

f. J—Analyte less than program required detection limit and greater than or equal to method detection limit.

g. U—Analyte undetected at this concentration.

Table C-2. Total drum vent time and measured VOC concentrations (ppm) in sludge waste drums.

Drum ID	Waste type	Total vent time (days)	TCE ^a		CH ₂ Cl ₂ ^b		MeOH ^c		Toluene		Xylene ^d	
			DH ^e	LB ^f	DH	LB	DH	LB	DH	LB	DH	LB
76142	I.2A2	70	—	—	—	—	—	—	4.3	5.1	19	25
76144	I.2A2	126	7.6	8.5	3.1J ^g	3.9J	—	—	—	—	—	—
76182 ^h	I.2A2	0	—	—	—	—	13U ⁱ	34J	71	121	38	58
76189	I.2A2	232	7.3J	9.4J	11.5J	14.0J	—	—	1.9J	2.0U	—	—
76206	I.2A2	126	1.6J	2.2J	7.0	9.6	—	—	2.0	2.6	—	—
76302	I.2A2	126	—	—	—	—	30	57	48	64	439	558
76303	I.2A2	146	1.6J	1.7J	4.6J	4.2J	—	—	2.4J	3.0J	—	—
71940	IVA2T	91	—	—	—	—	46,232U	58,914	—	—	—	—
72128	IVA2T	189	—	—	1,298J	1,289J	—	—	11,408	10,347	—	—
72132	IVA2T	221	—	—	86,284	98,077	—	—	10,428	11,389	—	—
72139	IVA2T	189	3.0J	3.0U	8.6J	10.3J	—	—	169	178	—	—
72623	IVA2T	205	23.7	31.5	—	—	6.1J	38J	9.0	7.6	—	—

a. Trichlorethylene.

b. Methylene chloride.

c. Methanol

d. m-, p-xylene

e. Drum headspace

f. Large bag

g. J—Analyte less than program required detection limit and greater than or equal to method detection limit.

h. Also contains cyclohexane DH-0.7U; LB-10.6.

i. U—Analyte undetected at this concentration.

Appendix D

Model Predictions of VOC Concentration in Vented Waste Drums

Table D-1. Model estimate of total VOC concentration within the innermost layer of confinement of vented waste drums with maximum of 2 layers of polymer bags.

Drum ID	Concentration (ppm)
76142	63
76144	213
76282	2,816
76287	4,380
76302	640
76189	239
76206	112
76303	126
71022	209,614
71932	234,810
71940	332,170
71941	330,866
72128	162,370
72132	151,250
72139	224
72623	71
76135	7,632
76196	50,892
76200	146,370
76203	126,629
76283	42,030

Table D-2. Model estimate of total VOC concentration within the innermost layer of confinement of vented waste drums with maximum of 4 layers of polymer bags.

Drum ID	Concentration (ppm)
17491	35
01754	27
22922	27
24098	261
24214	272
32529	654
02678	778
10578	463
12875	818
17756	688
17759	586
13229	13

Table D-3. Model estimate of total VOC concentration within the innermost layer of confinement of vented waste drums with maximum of 5 layers of polymer bags.

Drum ID	Concentration (ppm)
22072	804
23664	692
08878	3,320
11415	754
12215	137
12878	554
13751	1,010
21952	251
22249	3,590
22293	807
22549	2,335
22557	396
22994	225
23020	1,400
23312	1,142
24765	151
24786	165
11433	809
23901	770
07170	590
10663	535
24092	204
07034	588
09435	109

Table D-4. Model estimate of total VOC concentration within the innermost layer of confinement of vented waste drums with sealed polymer bottles.

Drum ID	Concentration (ppm)
23020	2,353
02678	1,328
24765	243
08878	5,537

Table D-5. Model estimate of carbon tetrachloride concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)
76144	2.0
76287	3,423
76282	2,116
08878	17
21952	1.3
22557	2.4
24765	0.5
24214	0.9
32529	2.4
11433	3.8
24092	9.0
76283	31,390
76196	38,380
71932	117,350
71940	166,150
71941	216,410
76200	101,060
76203	91,180
71022	105,690
72623	5.7
76135	6,252

Table D-6. Model estimate of methanol concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)
22072	58
11415	174
22249	55
09435	55
71940	71,655
72623	9.5
76302	46

Table D-7. Model estimate of methylene chloride concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)
76144	5.0
76189	18
76206	11
76303	7.4
72128	2,080
72132	138,300
72139	14
23644	44
22293	29
22557	6.5
22944	9.6
23312	19
24765	7.0
24786	9.0
17491	1.4
22922	3.3
24098	2.5
24214	20
32529	63
17756	26
17759	34
24092	2.2

Table D-8. Model estimate of TCA concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)	Drum ID	Concentration (ppm)
76144	196	22072	168
76287	700	23664	647
76282	443	08878	3,310
76142	31	11415	170
76189	212	12215	121
76206	94	12878	173
76303	106	13751	497
76283	8,212	21952	237
76196	4,040	22249	3,547
71932	98,330	22293	757
71940	66,395	22549	2,320
71941	79,605	22557	355
76200	12,400	22944	215
76203	29,877	23020	1,395
71022	83,830	23312	1,113
72623	14.4	24765	123
76135	1,160	24786	149
17491	32	24214	210
22922	24	32529	537
23901	805	24098	235
10663	330	12875	333
07170	355	10578	155
11443	473	02678	351
24092	150	17756	647
07034	400	17759	536
09435	50		

Table D-9. Model estimate of TCE concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)
76144	9.7
76189	9.4
76206	2.1
76303	2.1
72623	30
22072	27
11415	365
12215	8.6
12878	379
13751	505
24098	6.5
24214	3.3
32529	1.8
02678	414
10578	246
12875	479
17756	3.0
11433	463
23901	131
07170	337
10663	295
24092	1.5
07034	295
09435	0.5

Table D-10. Model estimate of toluene concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)	Drum ID	Concentration (ppm)
76302	59	23020	9.3
76142	5.3	23312	10
76206	2.5	24765	20
76303	3.0	24786	6.6
72128	14,160	24214	11
72132	12,940	32529	54
72139	210	24098	17
72623	11	10578	16
17491	1.0	12875	7.0
01754	25	02678	13
22072	30	17756	12
11415	40	23901	13
12215	7.3	10663	7.7
12878	4.6	07170	5.1
13751	5.1	11433	13
21952	13	09435	3.9
22249	17	07034	3.1
22293	21	24092	7.6
22549	19	13229	13
22557	31	17759	16

Table D-11. Model estimate of Freon-113 concentration within the innermost layer of confinement of vented waste drums.

Drum ID	Concentration (ppm)
76287	257
76282	257
76142	4.2
76206	2.4
76303	7.2
76283	2,430
76196	8,474
71932	19,110
71940	27,940
71941	34,840
76200	32,920
76203	5,582
71022	20,120
76135	220
10578	76
24092	3.1

Table D-12. Model estimate of p-xylene and acetone concentrations within the innermost layer of confinement of vented waste drums.

VOC	Drum ID	Concentration (ppm)
p-xylene	76302	535
	76142	23
	01754	2.1
	11415	31
	12215	0.6
	24765	0.6
	24214	26
Acetone	76303	21
	72623	18
	22922	21
	22072	24
	11415	74
	12215	40
	12878	105
	13751	75
	22249	21
	22293	21
	22549	21
	22557	25
	23312	57
	07034	36
	07170	77

Table D-13. Model estimate of VOC concentrations within the innermost layer of confinement of vented waste drums.

VOC	Drum ID	Concentration (ppm)
Chloroform	76282	37
	76135	101
	17491	0.2
	08878	21
	24786	1.1
	07034	226
	09435	8.8
	24092	7.9
DCE ^a	76144	3.5
	76282	35
	76189	8.5
	76206	3.5
	76303	9.9
	17756	467
	17759	276
DCA ^b	72623	0.5
	11415	11
	02678	5.6
	12875	11
	17756	6.5
	07170	64
PCE ^c	72623	0.6
	12875	2.6
	02678	38
	12878	3.3
	13751	16

Table D-13. (continued).

VOC	Drum ID	Concentration (ppm)
o-xylene	76302	47
	24214	15
Ethyl benzene	76302	166
	11415	11
Benzene	76144	4.1
PCA ^d	10578	1.6

a. 1,1-dichloroethene.

b. 1,1-dichloroethane.

c. Tetrachloroethene.

d. 1,1,2,2-tetrachloroethane.

Appendix E

Calculation of Experimental and Model Error

Appendix E

Calculation of Experimental and Model Error

The function, ψ , is the ratio of the predicted VOC concentration in the innermost layer of confinement, Y_{mod} , to the maximum measured VOC concentration in the bag headspaces, Y_{max} , for a single VOC

$$\psi = \log_{10} \left(\frac{Y_{\text{mod}}}{Y_{\text{max}}} \right) \quad (\text{E-1})$$

The variance, σ_{ψ}^2 , of the function ψ is defined as

$$\sigma_{\psi}^2 = \left(\frac{\partial \psi}{\partial Y_{\text{mod}}} \right)^2 \sigma_{\text{mod}}^2 + \left(\frac{\partial \psi}{\partial Y_{\text{max}}} \right)^2 \sigma_{\text{max}}^2 \quad (\text{E-2})$$

where σ_{mod}^2 and σ_{max}^2 are the variance of Y_{mod} and Y_{max} , respectively

Inserting Equation (E-1) into Equation (E-2) yields

$$\sigma_{\psi}^2 = 0.189 \left[\left(\frac{\sigma_{\text{mod}}}{Y_{\text{mod}}} \right)^2 + \left(\frac{\sigma_{\text{max}}}{Y_{\text{max}}} \right)^2 \right] \quad (\text{E-3})$$

The ratios in Equation (E-3) are the relative standard deviation of the predicted and measured VOC concentration in the bag headspace, respectively.

Precision of analytical methods used to determine VOC concentration in a sample is expressed as the percent relative standard deviation (%RSD) between replicate measurements. The reported %RSD is applicable to concentrations exceeding the program required detection limit (PRDL). In some cases, VOC concentrations were below the PRDL but greater than or equal to the method detection limit. Since error generally increases with decreasing VOC concentration and the method detection limit is approximately an order of magnitude less than the PRDL, concentrations less than the PRDL were assumed to have a %RSD ten times greater than the %RSD for measurements exceeding the PRDL or a maximum acceptable value of 25% as specified in the QAPP, whichever was less.

The variance of the model estimate is estimated based on the known or estimated variances of the model variables and parameters

$$\sigma_{\text{mod}}^2 = \sum_{m=1}^M \sum_{j=1}^{J_m} \left(\frac{\partial A_m}{\partial x_{m,j}} \right)^2 \sigma_{x_{m,j}}^2 \quad (\text{E-4})$$

where

$$\begin{aligned} M &= \text{total number of layers of confinement} \\ J_m &= \text{total number of variables defining function } A_m \\ x_{m,j} &= j^{\text{th}} \text{ variable in function } A_m \end{aligned}$$

In the case where $M = 4$,

$$\begin{aligned} A_1 &= Y_4 \\ A_2 &= D^*Y_4/K_{p,1} = 22,400 D^*Y_4x_{p,1}/(\rho A_{p,1}P) \\ A_3 &= D^*Y_4/K_{p,2} = 22,400 D^*Y_4x_{p,2}/(\rho A_{p,2}P) \\ A_4 &= D^*Y_4/K_d = D^*Y_4RTx_d/(DA_dP) \end{aligned}$$

In the case where $M = 3$,

$$\begin{aligned} A_1 &= Y_3 \\ A_2 &= D^*Y_3/K_p = 22,400 D^*Y_3x_p/(\rho A_pP) \\ A_3 &= D^*Y_3/K_d = D^*Y_3RTx_d/(DA_dP) \end{aligned}$$

When the function A_i is proportional or inversely proportional to the variable $x_{i,j}$, then

$$\left(\frac{\partial A_m}{\partial x_{m,j}} \right)^2 = \left(\frac{A_m}{x_{m,j}} \right)^2 \quad (\text{E-5})$$

Inserting Equation (E-5) into Equation (E-4) yields

$$\sigma_{\text{mod}}^2 = \sum_{m=1}^M \sum_{j=1}^{J_m} A_m^2 \left(\frac{\sigma_{x_{m,j}}}{x_{m,j}} \right)^2 \quad (\text{E-6})$$

Thus, in order to define the total variance of the model result, the relative standard deviation for each variable or parameter must be known or estimated. The relative standard deviation associated with VOC concentration measurements in waste drums and VOC-specific model parameters have been determined experimentally and are listed in Table E-1. The relative standard deviation of other model parameters and variables are listed in Table E-2.

Table E-1. Measured relative standard deviation for measured VOC concentration, drum filter vent VOC diffusion characteristic, and VOC permeability in polyethylene bags.

VOC	σ_{Y3}/Y_3^a	σ_{Y4}/Y_4^b	σ_{D^*}/D^{*a}	σ_{D^*}/D^{*b}	σ_p/ρ
CCl_4^c	0.01	0.05	0.05	0.07	0.19
Methanol	0.02	0.06	0.09	0.23	0.26
CH_2Cl_2^d	0.04	0.06	0.05	0.09	0.10
TCA	0.01	0.04	0.06	0.09	0.09
TCE	0.01	0.05	0.13	0.06	0.05
Toluene	0.02	0.04	0.19	0.12	0.18
Freon-113	0.01	0.06	0.06	0.10	0.13
p-xylene	0.01	0.05	0.20	0.15	0.06

a. Specific to the RFETS.

b. Specific to the INEL.

c. Carbon tetrachloride.

d. Methylene chloride.

Table E-2. Estimated standard deviation of other model parameters and variables.

Parameter	Relative standard deviation
Bag thickness	0.05
Small bag area	0.20
Large bag area	0.20
Diffusion	0.05
Diffusion area	0.05
Diffusion length	0.05
Pressure	0.01
Temperature	0.01

The function, ψ_{tot} , is the ratio of the total predicted VOC concentration in the innermost layer of confinement, Y_{mod}^* , to the total maximum measured VOC concentration in the bag headspaces, Y_{max}^*

$$\psi_{tot} = \log_{10} \left[\frac{Y_{mod}^*}{Y_{max}^*} \right] \quad (E-7)$$

The values of Y_{mod}^* and Y_{max}^* are defined as

$$Y_{mod}^* = \sum_{i=1}^N Y_{mod, i} \quad (E-8)$$

$$Y_{max}^* = \sum_{i=1}^N Y_{max, i} \quad (E-9)$$

where

$Y_{mod, i}$ = predicted concentration of i^{th} VOC in waste drum, ppm

$Y_{max, i}$ = maximum measured concentration of i^{th} VOC in bag headspaces, ppm

N = total number of VOCs in waste drum

The variance, $\sigma_{\psi, tot}^2$, of the function ψ_{tot} is defined as

$$\sigma_{\psi, tot}^2 = 0.189 \left[\frac{\sum_{i=1}^N \sigma_{mod, i}^2}{(Y_{mod}^*)^2} + \frac{\sum_{i=1}^N \sigma_{max, i}^2}{(Y_{max}^*)^2} \right] \quad (E-10)$$

Appendix F

VOC Transport Model Computer Program FORTRAN Code

Appendix F

VOC Transport Model Computer Program FORTRAN Code

```
c This computer program resulted from work developed under Government Contract No. DE-AC07-94ID13223 at the
c Idaho National Engineering Laboratory and is subject to a Limited Government License. Neither the
c United States nor the United States Department of Energy, nor any of its employees, makes any warranty,
c express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or
c usefulness of any information, apparatus, product, or process disclosed, or represents that its use would
c not infringe privately-owned rights.
c
c program estimates VOC concentration in innermost layer of confinement in a vented waste drum at the
c Idaho National Engineering Laboratory (INEL) or at Rocky Flats (RFP) given VOC concentration in drum headspace.
c Program user specifies the VOC, its concentration in the drum headspace beneath the drum lid, and other
c model parameters.
c-----
c model assumes constant drum temperature
c-----
c
c declaration of variables
  character*21 vocid(20),ifname,ofname
  real ap(3),ad(3),xp(3),xd(3),y(20,4),temp,pHg,dch2
  real amw,pm,df,b,c,atc,apc,avc
  real a(4),adcvoc,test
  integer n(20)
c
c-----
c User provided input
c-----
c
c nvoc - number of VOCs in drum
c layer - number of layers of confinement
c y(n,m) - n-th VOC conc'n in m-th layer of confinement (ppmv)
c      m=1, average concentration in headspace of each small bag
c      m=1 or m=2, large bag headspace
c      m=2 or m=3, drum liner headspace
c      m=3 or m=4, drum headspace
c ap(m) - permeation surface area around m-th layer of confinement (cm2)
c ad(m) - cross sectional area for diffusion out of m-th layer
c      of confinement (cm2)
c xp(m) - thickness of permeable surface (cm)
c xd(m) - length of diffusional path between layers of confinement (cm)
c dch2 - diffusion characteristic of H2 (mol/mol fraction/s)
c
c*****
c vocid(n) - VOC identification number
c   1 - CCl4   2 - cyclohexane   3 - methanol   4 - CH2Cl2
c   5 - Toluene   6 - TCA   7 - TCE   8 - Freon-113   9 - p-xylene
c  10 - Benzene  11 - Ethylbenzene  12 - 1,1,2,2-tetrachloroethane
c  15 - 1,1-dichloroethene  16 - chloroform  17 - o-xylene
c  18 - acetone  19 - 1,1-dichloroethane  20 - tetrachloroethene
c*****
c
c      vocid(1)='carbon tetrachloride'
c      vocid(2)='cyclohexane'
```



```

vocid(3)='methanol
vocid(4)='methylene chloride
vocid(5)='toluene
vocid(6)='1,1,1-trichloroethane'
vocid(7)='trichloroethylene
vocid(8)='Freon-113
vocid(9)='p-xylene
vocid(10)='benzene
vocid(11)='ethylbenzene
vocid(12)='1,1,2,2-C2H2Cl4
vocid(15)='1,1-dichloroethene
vocid(16)='chloroform
vocid(17)='o-xylene
vocid(18)='acetone
vocid(19)='1,1-dichloroethane
vocid(20)='tetrachloroethene

c
c-----
c---Input initial conditions from a file---
c-----
c
  write(*,5)
5  format(1x,'Enter name of input file: ')
  read(*,*)ifname
  write(*,12)
12 format(1x,'Specify drum number ')
  read(*,*)test
  open(unit=3,file=ifname,status='unknown')
  read(3,*)ofname,layer
  open(unit=2,file=ofname,status='unknown')
c temp - drum temperature, C
c pHg - ambient pressure, cm Hg
c n - VOC identification number
  read(3,*)(ap(m),ad(m),xp(m),xd(m),m=1,layer-1)
  read(3,*)dch2,temp,pHg,njc
c-----
c---Specify VOC ID code, conc (ppm) in drum headspace
c-----
  read(3,*)ntot
  do 15 in=1,ntot
    read(3,*)n(in),y(n(in),layer)
15 continue
c
c-----
c---Output headings-----
c-----
  call preout(layer,ap,ad,xp,xd,test)
c
c-----
c Computation of concentrations
c-----
c
  do 20 iz=1,ntot
    call vprop(n(iz),dch2,amw,pm,df,b,c,atc,apc,avc,
      $adcvoc,temp,pHg)
c a(x) = alpha(x) or abeta(x)
  do 26 l=1,layer-1
    if(1.le.(layer-2))then
c calculates term to estimate permeation rate from polymer bag
      call alpha(pm,ap(l),xp(l),temp,pHg,a(l),b,c)

```

```

      else
c calculates term to estimate diffusion rate out of drum liner
      call beta(df,ad(l),xd(l),a(l),temp,pHg)
      end if
26  continue
      call conc(layer,a,adcvoc,y,n(iz),pHg,temp,c0)
      call output(layer,y,n(iz),volid(n(iz)))
20  continue
      call postout(pHg,temp,dch2)
      end

c ***** Subroutine assigns values specifies VOC properties *****
      subroutine vprop(n,dh2,amw,pm,df,b,c,atc,apc,avc,dvoc,temp,pHg)
      real amw,pm,df,b,c,atc,apc,avc
      integer n
      real mw(20),p(20),d(20),vpb(20)
      real vpc(20),tc(20),pc(20),vc(20),dv(20)

c
c mw(i) - molecular weight of compound i
c p(i) - VOC i permeability across polyethylene at 25C, cm3 cm/cm2 s cm Hg
c d(i) - diffusivity of VOC i in air at 25 C (cm2/sec)
c vpb(i) - Antoine equation coefficient, B, for i-th component
c vpc(i) - Antoine equation coefficient, C (K), for i-th component
c tc(i) - critical temperature for i-th component (K)
c pc(i) - critical pressure for i-th component (atm)
c vc(i) - critical volume for i-th component (cm3/mol)
c dv(i) - VOC diffusion characteristic across NFT-020 filter vent, mol/s
c
c amw,pm,df,b,c,atc,apc,avc correspond to properties
c of designated VOC each time through the loop
c
c-----
c properties of H2, air used to estimate VOC diffusion characteristic
c-----
c pch,tch - critical pressure (atm), temperature (K) of hydrogen
c pca,tca - critical pressure (atm), temperature (K) of air
c h2mw,airmw - molecular weight of hydrogen, air
      pch=12.8
      tch=33.3
      pca=36.4
      tca=132.
      h2mw=2.016
      airmw=29.
      smw=1./airmw+1./h2mw
c t - temperature (K), pr - gas pressure (atm)
      t=temp+273.2
      pr=pHg/76.
c define constant, c0
      c0=2.745e-4*(t**1.823/pr)
c
c-----
c
c 1 = carbon tetrachloride
c
      mw(1)=153.82
      p(1)=190.e-10
      d(1)=0.0828
      vpb(1)=1242.43
      vpc(1)=-43.15

```

```

tc(1)=556.4
pc(1)=45.0
vc(1)=276.
if(dh2.eq.115.e-7)dv(1)=1.10e-6
if(dh2.eq.44.e-7)dv(1)=3.03e-7
c
c 2 = cyclohexane
c
mw(2)=84.1
p(2)=15.e-10
d(2)=0.0750
vpb(2)=1203.526
vpc(2)=-50.287
tc(2)=553.4
pc(2)=40.2
vc(2)=308.
if(dh2.eq.115.e-7)dv(2)=1.08e-6
if(dh2.eq.44.e-7)dv(2)=4.43e-7
c
c 3 = methanol
c
mw(3)=32.0
p(3)=135.e-10
d(3)=0.152
vpb(3)=1473.11
vpc(3)=-43.15
tc(3)=512.6
pc(3)=79.9
vc(3)=118.
if(dh2.eq.115.e-7)dv(3)=9.43e-7
if(dh2.eq.44.e-7)dv(3)=6.05e-7
c
c 4 = methylene chloride
c
mw(4)=84.9
p(4)=260.e-10
d(4)=0.104
vpb(4)=1325.9
vpc(4)=-20.55
tc(4)=510.
pc(4)=60.
vc(4)=193.
if(dh2.eq.115.e-7)dv(4)=1.75e-6
if(dh2.eq.44.e-7)dv(4)=4.43e-7
c
c 5 = toluene
c
mw(5)=92.1
p(5)=670.e-10
d(5)=0.0849
vpb(5)=1343.943
vpc(5)=-53.773
tc(5)=591.7
pc(5)=40.6
vc(5)=316.
if(dh2.eq.115.e-7)dv(5)=1.28e-6
if(dh2.eq.44.e-7)dv(5)=3.66e-7
c
c 6 = TCA
c

```

```

mw(6)=133.4
p(6)=140.e-10
d(6)=0.0794
vpb(6)=2136.6
vpc(6)=29.65
tc(6)=545.
pc(6)=42.4
vc(6)=281.
if(dh2.eq.115.e-7)dv(6)=1.05e-6
if(dh2.eq.44.e-7)dv(6)=3.60e-7
c
c 7 = TCE
c
mw(7)=131.4
p(7)=580.e-10
d(7)=0.0875
vpb(7)=1018.6
vpc(7)=-80.45
tc(7)=571.
pc(7)=48.5
vc(7)=256.
if(dh2.eq.115.e-7)dv(7)=1.39e-6
if(dh2.eq.44.e-7)dv(7)=3.20e-7
c
c 8 = Freon-113
c
mw(8)=187.4
p(8)=40.e-10
c estimated diffusivity (Wilke-Lee eqn)
d(8)=0.062
vpb(8)=1099.9
vpc(8)=-45.65
tc(8)=487.2
pc(8)=33.7
vc(8)=304.
if(dh2.eq.115.e-7)dv(8)=1.04e-6
if(dh2.eq.44.e-7)dv(8)=3.45e-7
c
c 9 = p-xylene
c
mw(9)=106.2
p(9)=810.e-10
d(9)=0.0670
vpb(9)=1453.43
vpc(9)=-57.840
tc(9)=616.2
pc(9)=34.7
vc(9)=379.
if(dh2.eq.115.e-7)dv(9)=1.15e-6
if(dh2.eq.44.e-7)dv(9)=2.51e-7
c
c 10 = benzene
c
mw(10)=78.11
p(10)=80.e-10
vpb(10)=1211.033
vpc(10)=-52.36
tc(10)=562.1
pc(10)=47.67
vc(10)=259.

```

```

samw=sqrt(1./airmw+1./mw(10))
sqmw=samw/sqrt(smw)
d(10)=c0*(pc(10)*pca)**(1./3.)*samw/sqrt(tca*tc(10))
dv(10)=dh2*((pc(10)/pch)**(1./3.)*(tc(10)/tch)**(-0.5)*sqmw)
c
c 11 = ethylbenzene
c
mw(11)=106.2
p(11)=250.e-10
vpb(11)=1424.25
vpc(11)=-59.944
tc(11)=617.1
pc(11)=35.13
vc(11)=374.
samw=sqrt(1./airmw+1./mw(11))
sqmw=samw/sqrt(smw)
d(11)=c0*(pc(11)*pca)**(1./3.)*samw/sqrt(tca*tc(11))
dv(11)=dh2*((pc(11)/pch)**(1./3.)*(tc(11)/tch)**(-0.5)*sqmw)
c
c 12 = 1,1,2,2-tetrachloroethane
c
mw(12)=167.9
p(12)=2000.e-10
vpb(12)=1228.1
vpc(12)=-93.3
tc(12)=661.2
pc(12)=57.64
vc(12)=338.
samw=sqrt(1./airmw+1./mw(12))
sqmw=samw/sqrt(smw)
d(12)=c0*(pc(12)*pca)**(1./3.)*samw/sqrt(tca*tc(12))
dv(12)=dh2*((pc(12)/pch)**(1./3.)*(tc(12)/tch)**(-0.5)*sqmw)
c
c 15 = 1,1-dichloroethene
c
mw(15)=96.9
p(15)=140.e-10
vpb(15)=1099.4
vpc(15)=-35.95
tc(15)=513.
pc(15)=47.5
vc(15)=227.4
samw=sqrt(1./airmw+1./mw(15))
sqmw=samw/sqrt(smw)
d(15)=c0*(pc(15)*pca)**(1./3.)*samw/sqrt(tca*tc(15))
dv(15)=dh2*((pc(15)/pch)**(1./3.)*(tc(15)/tch)**(-0.5)*sqmw)
c
c 16 = chloroform
c
mw(16)=119.4
p(16)=210.e-10
vpb(16)=1163.03
vpc(16)=-45.75
tc(16)=536.4
pc(16)=53.
vc(16)=238.9
samw=sqrt(1./airmw+1./mw(16))
sqmw=samw/sqrt(smw)
d(16)=c0*(pc(16)*pca)**(1./3.)*samw/sqrt(tca*tc(16))
dv(16)=dh2*((pc(16)/pch)**(1./3.)*(tc(16)/tch)**(-0.5)*sqmw)

```

```

c
c 17 = o-xylene
c
mw(17)=106.1
p(17)=360.e-10
vpb(17)=1474.679
vpc(17)=-59.46
tc(17)=630.3
pc(17)=36.8
vc(17)=369.
samw=sqrt(1./airmw+1./mw(17))
sqmw=samw/sqrt(smw)
d(17)=c0*(pc(17)*pca)**(1./3.)*samw/sqrt(tca*tc(17))
dv(17)=dh2*((pc(17)/pch)**(1./3.)*(tc(17)/tch)**(-0.5)*sqmw)
c
c 18 = acetone
c
mw(18)=58.1
p(18)=6640.e-10
vpb(18)=1161.
vpc(18)=-49.15
tc(18)=508.1
pc(18)=46.4
vc(18)=209.
samw=sqrt(1./airmw+1./mw(18))
sqmw=samw/sqrt(smw)
d(18)=c0*(pc(18)*pca)**(1./3.)*samw/sqrt(tca*tc(18))
dv(18)=dh2*((pc(18)/pch)**(1./3.)*(tc(18)/tch)**(-0.5)*sqmw)
c
c 19 = 1,1-dichloroethane
c
mw(19)=99.0
p(19)=195.e-10
vpb(19)=1174.02
vpc(19)=-44.09
tc(19)=523.
pc(19)=50.
vc(19)=236.
samw=sqrt(1./airmw+1./mw(19))
sqmw=samw/sqrt(smw)
d(19)=c0*(pc(19)*pca)**(1./3.)*samw/sqrt(tca*tc(19))
dv(19)=dh2*((pc(19)/pch)**(1./3.)*(tc(19)/tch)**(-0.5)*sqmw)
c
c 20 = tetrachloroethene
c
mw(20)=165.8
p(20)=460.e-10
vpb(20)=1415.492
vpc(20)=-52.15
tc(20)=620.2
pc(20)=47.
vc(20)=289.6
samw=sqrt(1./airmw+1./mw(20))
sqmw=samw/sqrt(smw)
d(20)=c0*(pc(20)*pca)**(1./3.)*samw/sqrt(tca*tc(20))
dv(20)=dh2*((pc(20)/pch)**(1./3.)*(tc(20)/tch)**(-0.5)*sqmw)
c
c assigns values to variables for designated VOC
c
amw=mw(n)

```

```

pm=p(n)
df=d(n)
b=vpb(n)
c=vpc(n)
atc=tc(n)
apc=pc(n)
avc=vc(n)
dvoc=dv(n)
return
end

```

c ***** Subroutine solves for constant alpha *****

```

subroutine alpha(pm,ap,yp,temp,pHg,aalpha,b,c)

```

c Correction of permeability coefficient for drum temperature.

c Assume temperature inside poly bags and drum liner are same

c for polyethylene: $\log P_f = K - 0.22 c_0$

c $K = c_1 - c_2/T, T(K)$

c $c_0, c_1, c_2 = \text{constants}; c_2 = 3700$

c for liquids: $P = P_f/P_{vap}(\text{sat'd})$

c Therefore $(P_1/P_2) = [P_f/P_{vap}(\text{sat'd})]_1/[P_f/P_{vap}(\text{sat'd})]_2$

c

c Assume same ratio relationship describes temp. effect for VOC gases

c VOC vapor pressure estimated using Antoine equation

c current permeability, diffusivity data for 25 C = 298.15 K

c

c td - drum temperature, K

td=temp+273.2

c to - reference temperature, K

to=298.15

c ptk - permeability coefficient at temperature td

p1=10.**(-3700./td+b/(c+td))

p2=10.**(-3700./to+b/(c+to))

ptk=(p1/p2)*pm

c cstp - P/T at standard temp (273.12 K) and pressure (1 atm = 76 cm Hg)

cstp=76./273.15

c aalpha - computed value of alpha (cm³/s)

aalpha=ptk*(ap/yp)*pHg*(cstp*td/pHg)

return

end

c ***** Subroutine solves for constant beta *****

```

subroutine beta(df,ad,xd,abeta,temp,pHg)

```

```

real df,dtk,td,patm

```

c Correction of diffusion coefficient for drum temp.

c Assume diffusivity is proportional to $T^{1.823}/P, T(K) P(\text{atm})$

c td - drum temperature, K

td=temp+273.2

c to - reference temperature, K

to=298.15

c patm - atmospheric pressure (atm)

patm=pHg/76.0

dtk=df*(1./patm)*(td/to)**1.823

abeta=dtk*ad/xd

return

end

c ***** Subroutine calculates concentrations *****

```

c -----Equations used before manipulation-----
c Q1 = (alpha+beta)1 * (c2-c1)
c Q2 = [(alpha+beta)2 * (c3-c2)]
c Q3 = [(alpha+beta)3 * (c4-c3)]
c Q4 = - [(D*) * y4]
c Due to quasi steady-state assumption, Q1=Q2=Q3=Q4=Q
c -----
      subroutine conc(l,a,advoc,y,n,pHg,temp,co)
      real a(4),advoc,y(20,4),q,yy(20,4),pHg,temp
      real patm,co,ro,td
      integer n,k
c Converts concentration in drum headspace from ppmv to mol/cm3
c y has units ppmv (mole fraction)
c yy has units mol/cm3 (mole concentration)
c patm - atmospheric pressure (atm)
      patm=pHg/76.0
c td - drum temperature (K)
      td=temp+273.15
c ro - gas constant (cm3 atm / mol K)
      ro=82.06
c co - initial gas concentration in each layer of confinement (mol/cm3)
      co=patm/(ro*td)
      yy(n,l)=y(n,l)*co*1.e-6
      q=-advoc*y(n,l)*1.e-6
c * Computes actual concentrations *
      yy(n,l-1)=yy(n,l)-q/a(l-1)
      yy(n,l-2)=yy(n,l-1)-q/a(l-2)
      if(l.eq.4)yy(n,1)=yy(n,2)-q/a(1)
c Converts predicted concentrations in mol/cm3 to ppm
      do 130 k=1,l
          y(n,k)=yy(n,k)/co*1.e+6
130  continue
      end

      subroutine preout(ly,ap,ad,xp,xd,test)
      real ap(3),ad(3),xp(3),xd(3),test
      write(2,150)test
150  format(1x,'Drum ID number:',1x,f6.0)
      write(2,*)' '
      write(2,152)
152  format(1x,'Model parameters:')
      write(2,154)
154  format(19x,'ap(cm2)',9x,'ad(cm2)',8x,'xp(cm)',9x,'xd(cm)')
      write(2,156)
156  format(19x,'-----',9x,'-----',8x,'-----',9x,'-----')
      if(ly.eq.4)then
          write(2,158)ap(ly-3),ad(ly-3),xp(ly-3),xd(ly-3)
158  format(1x,'2 small bags',7x,f6.0,10x,f4.2,11x,f4.2,11x,f5.2)
      else
          end if
          write(2,160)ap(ly-2),ad(ly-2),xp(ly-2),xd(ly-2)
160  format(1x,'Large bag',10x,f6.0,10x,f4.2,11x,f4.2,11x,f5.2)
          write(2,162)ap(ly-1),ad(ly-1),xp(ly-1),xd(ly-1)
162  format(1x,'Drum liner',9x,f6.0,10x,f4.2,11x,f4.2,11x,f5.2)
          write(2,*)' '
          write(2,*)'Predicted VOC concentrations (ppmv) in headspace of:'
          write(2,*)' '
          if(ly.eq.4)then
              write(2,164)

```



```

164  format(1x,'Compound',15x,'Drum*',3x,'Drum Liner',2x,'Large Bag',
      # 2x,'Small bags',4x,'DH/SB')
      write(2,166)
166  format('-----',15x,'-----',2x,'-----',2x,'-----',2x,
      # '-----')
      else
      write(2,264)
264  format(1x,'Compound',15x,'Drum*',3x,'Drum Liner',2x,'Large Bag',
      # 4x,'DH/LB')
      write(2,266)
266  format('-----',15x,'-----',2x,'-----',2x,'-----')
      end if
      return
      end

```

c ***** subroutine prints output to file *****

```

      subroutine output(ly,y,n,vocid)
      real y(20,4)
      character*21 vocid
      ratio=y(n,ly)/y(n,1)
      if(ly.eq.4)then
        write(2,168)vocid,y(n,4),y(n,3),y(n,2),y(n,1),ratio
168  format(1x,a21,f8.1,2x,f8.1,3x,f8.1,3x,f8.1,6x,f5.3)
      else
        write(2,268)vocid,y(n,3),y(n,2),y(n,1),ratio
268  format(1x,a21,f8.1,2x,f8.1,3x,f8.1,6x,f5.3)
      end if
      return
      end

```

```

      subroutine postout(pHg,temp,dch2)
      write(2,*) '
      write(2,170)temp
170  format(1x,'Drum temperature (C):',2x,f4.1)
      write(2,172)pHg
172  format(1x,'Ambient pressure (cm Hg):',2x,f4.1)
      write(2,174)dch2
174  format(1x,'Hydrogen filter diffusion characteristic (mol/mol frac
      #tion/s):',e12.5)
      return
      end

```