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VOC Transport in Vented Drums Containing Simulated Waste Sludge

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ABSTRACT

A model is developed to estimate the volatile organic compound (VOC) concentration in the headspace of the innermost layer of confinement in a lab-scale vented waste drum containing simulated waste sludge. The VOC transport model estimates the concentration using the measured VOC concentration beneath the drum lid and model parameters defined or estimated from process knowledge of drum contents and waste drum configuration. Model parameters include the VOC diffusion characteristic across the filter vent, VOC diffusivity in air, size of opening in the drum liner lid, the type and number of layers of polymer bags surrounding the waste, VOC permeability across the polymer, and the permeable surface area of the polymer bags. Comparison of model and experimental results indicates that the model can accurately estimate VOC concentration in the headspace of the innermost layer of confinement. The model may be useful in estimating the VOC concentration in actual waste drums.

EXECUTIVE SUMMARY

A test program is underway at the Idaho National Engineering Laboratory to determine if the drum headspace volatile organic compound (VOC) concentration is representative of the VOC concentration in the entire drum void space and demonstrate that the VOC concentration in the void space of each layer of confinement can be estimated using a model incorporating theoretical diffusive and permeative transport principles and limited waste drum sampling data. The test program consists of three stages. In the first stage, a model was developed to demonstrate that the unsteady-state VOC transport from vented lab-scale waste drums could be estimated based on measured or estimated transport parameters and prior knowledge of the initial VOC concentration inside the drum. In the second stage, a transport model was developed to estimate VOC concentration in the headspace of the innermost layer of confinement in lab-scale vented waste drums containing simulated waste sludge with a high VOC content. In the final stage, the model developed in the second stage will be used to estimate VOC concentrations in actual waste drums and determine if the drum headspace concentration is representative of the concentration throughout the drum. This report describes the results of the second stage of the test program.

A transport model was developed to estimate the VOC concentration throughout a lab-scale vented waste drum containing a simulated waste sludge based on the knowledge of drum headspace VOC concentration and waste drum configuration. Waste drum configuration describes the type of filter vent in the drum lid; the dimensions of the opening in the drum liner lid; and the type, number, and thickness of large and small polymer bags surrounding the waste. The model consisted of a series of material balance equations describing steady-state VOC transport across each layer of confinement. It was assumed that permeation is the primary transport mechanism across the polymer bags and diffusion is the primary transport mechanism across the drum liner headspace and drum headspace. In addition, it was assumed that an equilibrium exists between the vapor phase and any VOC-containing source in the innermost layer of confinement.

Two experiments were performed to measure the VOC concentration in lab-scale vented waste drums containing simulated waste sludge. In Trial 1, a simulated waste sludge containing methylene chloride, 1,1,1-trichloroethane (TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), carbon tetrachloride, and trichloroethylene (TCE) was placed inside a large polyethylene bag inside the waste drum. In Trial 2, a simulated waste sludge containing methanol, cyclohexane, TCA, toluene, and p-xylene was placed inside two small polyethylene bags located inside a large polyethylene bag. Two drums and drum liners were vented at the beginning of the Trial 2 test period and two drums were vented 31 days after the trial began.

Experimental results were expressed as a ratio between drum headspace VOC concentration and the VOC concentration inside the innermost polyethylene bag. The concentration ratio was calculated to minimize daily fluctuations that affected all measurements on a given day. The daily ratio also demonstrated when the transport rates were nearly equivalent. An average concentration ratio was calculated for all waste drums in a given trial. Most concentration ratios approached a constant value indicative of nearly equal transport rates from the innermost layer of confinement and the drum headspace. During Trial 1, the time required for the concentration ratio to reach a constant value varied between 10 to 50 days, depending on the VOC. During

Trial 2, the concentration ratio for toluene and p-xylene did not reach a constant value after 86 days. The time necessary to reach a near-constant value is a function of the filter vent diffusion characteristic, total number of layers of confinement, and the VOC vapor pressure. Model results for all VOCs, excluding toluene and p-xylene, were within a 95% confidence range of the experimental data.

Model equations were used to determine the effect of model parameters on the estimated concentration difference across a transport boundary, such as the liner lid or polymer bag. The VOC concentration difference across the drum liner will decrease with a larger cross-sectional area of the opening in the liner lid or a smaller VOC diffusion characteristic across the filter vent. The concentration difference across the polymer bag will decrease with a larger permeable surface area or a smaller polymer bag thickness. These variables are a function of the waste packaging configuration. In addition, a smaller VOC diffusion characteristic across the filter vent or a larger VOC permeability across the polymer bag will also decrease the concentration difference. All VOC permeabilities used in model calculations were measured at vapor concentrations less than measured during the lab-scale waste drum experiments. Vapor permeability coefficients generally increase with increasing vapor concentration. Depending on the waste drum configuration, the use of a larger permeability value could significantly reduce the estimated concentration difference across a polymer bag. Using a VOC permeability that was measured across an identical or similar polymer at a lower vapor concentration than exists under actual conditions will result in a conservative estimate of the concentration difference across the bag.

The VOC transport model has been demonstrated to accurately estimate the headspace concentration inside the innermost bag in a lab-scale vented waste drum containing simulated waste sludge. Model estimates of the inner bag concentrations are dependent on knowledge of drum headspace concentration at a given time. The model does not characterize the VOC transport rate as a function of time. In future experiments, the same model will be used to estimate the VOC concentration within actual waste drums at a given time.

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ACRONYMS

DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
STP	standard temperature and pressure
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
VOC	volatile organic compound
WIPP	Waste Isolation Pilot Plant

VOC Transport in Vented Drums Containing Simulated Waste Sludge

1. INTRODUCTION

Pretest waste characterization of waste drums for the bin-scale tests at the Waste Isolation Pilot Plant (WIPP) includes sampling for volatile organic compounds (VOCs) from three areas within drums (drum headspace, the 55-gal polymer bag headspace, and the innermost layer of confinement headspace) of transuranic waste.[1] The Department of Energy (DOE) must demonstrate to the Environmental Protection Agency (EPA) that a drum headspace sample is representative of the VOCs within the entire void space of the waste container in order to demonstrate compliance in the future when drums could be directly emplaced in the WIPP. The WIPP conditional no-migration determination specifies that the EPA expects that all layers of confinement in a container will have to be sampled until DOE can demonstrate, based on data collected, that sampling of all layers is either unnecessary or can be safely reduced.

A test program is underway at the Idaho National Engineering Laboratory to determine if the drum headspace VOC concentration is representative of the concentration in the entire drum void space and demonstrate that the VOC concentration in the void space of each layer of confinement can be estimated using a model incorporating theoretical diffusive and permeative transport principles and limited waste drum sampling data. The test program consists of three stages. In the first stage, a model was developed to demonstrate that the unsteady-state VOC transport from vented lab-scale waste drums could be calculated based on measured or estimated transport parameters and prior knowledge of the initial VOC concentration inside the drum.[2] The second stage involves development of a model to estimate VOC concentration in the headspace of the innermost layer of confinement in a lab-scale vented waste drum containing simulated waste sludge with a high VOC content. The final stage will use the model developed in the second stage to estimate VOC concentrations in actual waste drums. In each stage, a comparison of model estimates and experimentally measured VOC concentrations in lab-scale or actual waste drums were or will be made to validate model accuracy. A model capable of characterizing the VOC concentration in an actual waste drum will be useful in defining drum headspace representativeness and may more quickly eliminate the need to sample all inner layers of confinement which will result in lower worker radiation exposure, decreased bin loading times, and significant cost savings over the life of the WIPP test and operational phases.

This report describes model development and VOC transport experiments in lab-scale vented waste drums containing simulated waste sludges. Development of the VOC transport model is presented in Section 2. Section 3 contains a description of the experimental design for the VOC transport experiments and permeability measurements. The experimental and model results are presented and discussed in Section 4. The report conclusions are summarized in Section 5.

2. VOC TRANSPORT MODEL

A transport model was developed to estimate the VOC concentration in void volumes within a vented drum containing a waste that is a source of VOC emissions. Model parameters are defined from knowledge of drum headspace VOC concentration and waste drum configuration. A general schematic of a lab-scale waste drum configuration used in VOC transport experiments is shown in Figure 1. The waste drum configuration includes the type of filter vent in the drum lid; the dimensions of the opening the drum liner lid; and the type, number, and thickness of large and small polymer bags surrounding the waste. The model consists of a series of material balance equations describing steady-state VOC transport across each layer of confinement.

2.1 Model Equations

The innermost layer of confinement is referred to as the first void volume and is the headspace immediately surrounding the waste. This layer may be small bags or the large bag that lines the inside of the drum liner. The drum headspace is the final or n^{th} void volume. The average VOC transport rate from the innermost layer of confinement is primarily the result of VOC permeation and is defined by the equation

$$r_1 = \alpha_1 (c_1 - c_2) \quad , \tag{1}$$

where

r_1	=	VOC transport rate from innermost void volume, mol s^{-1}
α_1	=	$\psi \wp A_{p1} P/x_{p1}$, $m^3 s^{-1}$
ψ	=	ratio of gas volume at a given temperature and pressure to gas volume at standard temperature and pressure (STP) = 370.95 T/P
T	=	temperature, K
P	=	pressure, N m^{-2}
$\wp$	=	VOC permeability coefficient, m^3 (STP) m $N^{-1} s^{-1}$
A_{p1}	=	permeable surface area of innermost layer of confinement, m^2
x_{p1}	=	boundary thickness of innermost layer of confinement, m
c_i	=	VOC concentration within i^{th} void volume, mol m^{-3}.

In the case of **M** small bags containing all waste inside a drum, the model calculates only an average rate of VOC transport of r_1 from each bag. The total rate of VOC transport from all small bags is $\mathbf{M}r_1$. The VOC transport rate from the surrounding large bag into the drum liner headspace is defined, in general, as

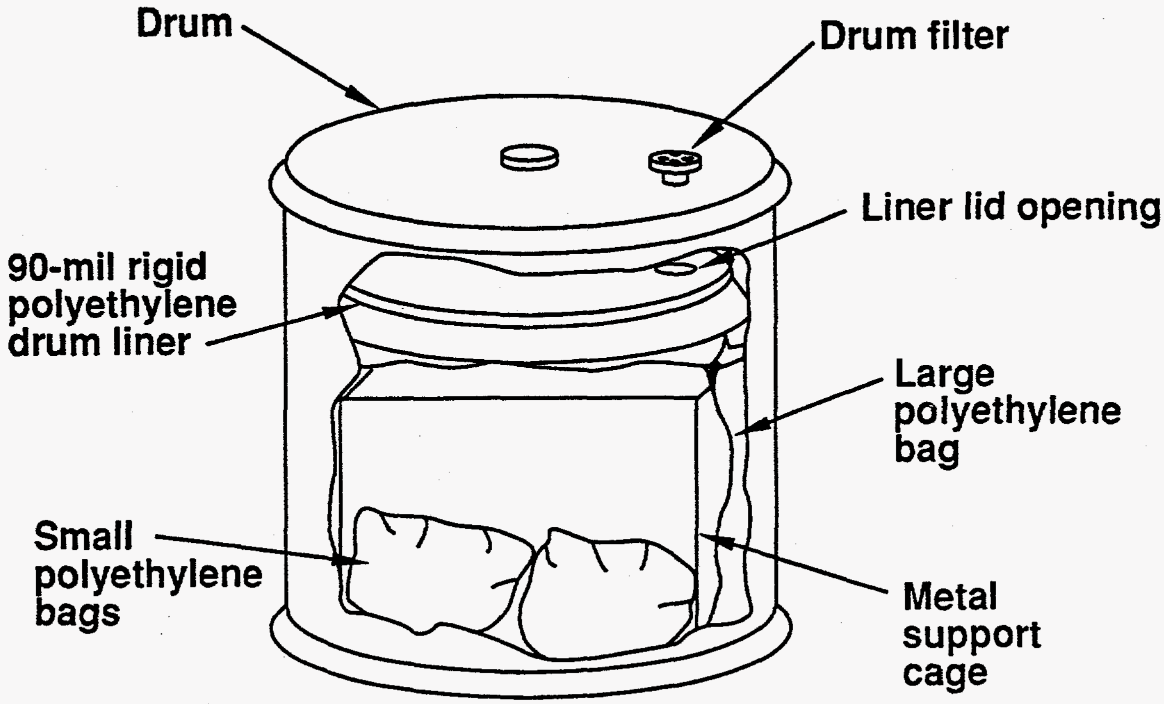

Figure 1. General schematic of lab-scale waste drum configuration.

$$r_{n-2} = \alpha_{n-2} \left(c_{n-2} - c_{n-1}\right) \quad , \tag{2}$$

which will be equivalent to Equation (1) if the large bag is the innermost layer of confinement.

The rate of VOC transport from the drum liner is defined as

$$r_{n-1} = \beta_{n-1} \left(c_{n-1} - c_{n}\right) \quad , \tag{3}$$

where

β_{n-1}	=	$D\, A_{d,n-1}/x_{d,n-1}$
D	=	VOC-air diffusivity, $m^2\ s^{-1}$
$A_{d,n-1}$	=	cross-sectional area of opening in drum liner lid, m^2
$x_{d,n-1}$	=	diffusional length across opening in drum liner lid, m.

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

$$r_{n} = \frac{D^{*}}{c_{g}} \left(c_{n} - c_{n+1}\right) \quad , \tag{4}$$

where

D^* = VOC filter diffusion characteristic, mol s^{-1}

c_g = total gas concentration in waste drum, mol m^{-3}

c_{n+1} = VOC concentration outside drum, mol m^{-3}.

The total gas concentration can be estimated using the ideal gas law

$$c_g = \frac{RT}{P} \tag{5}$$

where R is the gas constant.

In the case where waste is contained in **M** small polymer bags, the VOC transport rates from all void volumes are assumed to be equal or nearly equal

$$Mr_1 = r_2 = r_3 = r_4 \ . \tag{6}$$

The VOC concentrations in the other void volumes are estimated using Equations (1) through (6) and knowledge of the drum headspace VOC concentration, c_4. The values of α and β are calculated based on process knowledge.

$$c_3 = c_4 + \frac{r_4}{\beta_3} \ , \tag{7}$$

$$c_2 = c_3 + \frac{r_4}{\alpha_2} \ , \tag{8}$$

$$c_1 = c_2 + \frac{(r_4/M)}{\alpha_1} \ . \tag{9}$$

2.2 Model Assumptions

The following assumptions were made in order to estimate the relationship between the VOC concentration measured in the drum headspace and the VOC concentrations in the other layers of confinement:

1. All VOC transport rates across the layers of confinement are at steady state.

2. The primary mechanisms for VOC transport are permeation across the polymer bags and diffusion across the drum liner and drum headspaces.

3. The VOC concentration throughout each void volume is uniform and is zero outside the waste drum.

4. The VOC concentrations in each small bag are equal.

5. All VOC properties and other model parameters remain constant.

6. An equilibrium exists between the vapor phase and the VOC source in the innermost layer of confinement.

3. VOC TRANSPORT EXPERIMENTS

3.1 Experimental Design

Lab-scale VOC transport experiments were developed to measure the VOC concentration in a vented waste drum containing simulated waste sludge with high VOC content. Two experimental trials were performed to demonstrate the influence of the type of VOC and the number of layers of confinement on VOC transport from vented drums. In the first trial, a simulated waste sludge containing methylene chloride, 1,1,1-trichloroethane (TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), carbon tetrachloride, and trichloroethylene (TCE) was placed inside a large polyethylene bag in the waste drum. In the second trial, a simulated waste sludge containing methanol, cyclohexane, TCA, toluene, and p-xylene was placed inside two smaller polyethylene bags that were placed inside a large polyethylene bag. In addition, two of the drums and drum liners were vented at the beginning of the Trial 2 test period and the other two drums were not vented until 31 days after the trial began to determine if there would be a difference between VOC concentrations in the headspaces of the vented and unvented drums containing similar waste matrices. The experimental design is summarized in Table 1.

Table 1. Experimental design for simulated waste drum VOC transport experiments.

Test period	Drum number	Sludge mixture[a]	Small bag	Liner
1	1	A	absent	open
	2	A	absent	open
	3	A	absent	open
	4	A	absent	open
2	1	B	present[b]	open
	2	B	present[b]	open
	3	B	present[b]	sealed[c]
	4	B	present[b]	sealed[c]

a. Sludge mixture A (~100 g each drum) contains approximately a 34% Regal Texaco oil, 4% methylene chloride, 25.5% carbon tetrachloride, 13% TCA, 5% TCE, 5% Freon-113, and 14% calcium silicate. Sludge mixture B (~200 g each drum) contains approximately a 34% Regal Texaco oil, 10% methanol, 10% cyclohexane, 10% TCA, 10% toluene, 10% p-xylene, and 15% calcium silicate.

b. Two small bags were present in each drum.

c. Sealed for the first 31 days of test period.

3.2 Automated Experimental Configuration

The same experimental configuration used for the automated sampling and analysis of VOC concentrations in unsteady-state VOC transport experiments[2] was used for these experiments and is shown in Figure 2. Each of the four lab-scale waste drums in the configuration was a scaled-down version of a DOT 17C 55-gal drum. Each waste drum contained a 90-mil high-density rigid polymer drum liner. The drum liner was a scaled-down Type III liner with a removable lid that was bolted on with a metal closure ring. A 0.375-in. hole was drilled in the drum lid so that a NFT-020 (Nuclear Filter Technology Corp.) carbon-composite filter could be screwed into the lid. In Trial 1, the filter vent was located 4.3 in. (10.8 cm) from the outside edge of the drum lid. In Trial 2, the filter vent was located 2 in. (5.1 cm) from the center of the drum. In both cases, a hole was drilled in the liner lid directly below the filter vent. Inside the drum liner was a large polyethylene bag supported by a wire cage that either contained simulated waste sludge or smaller polyethylene bags that contained the simulated waste sludge.

Headspace samples were collected by evacuating the manifold system to a vacuum and then back-filling the gas sampling loops. The gas sample flowed into the selected sampling loop until the pressure equilibrated to ambient pressure. Between samples, the automated gas sampling system evacuated the sampling manifold and gas sampling loops. Samples were transferred from the gas sampling loop to the gas chromatograph injector and analyzed by a flame ionization detector.

3.3 Experimental Procedures

A batch of simulated waste sludge with the composition listed in Table 2 was prepared for use in Trial 1 experiments. Calcium silicate was added to the solution until the solvents were

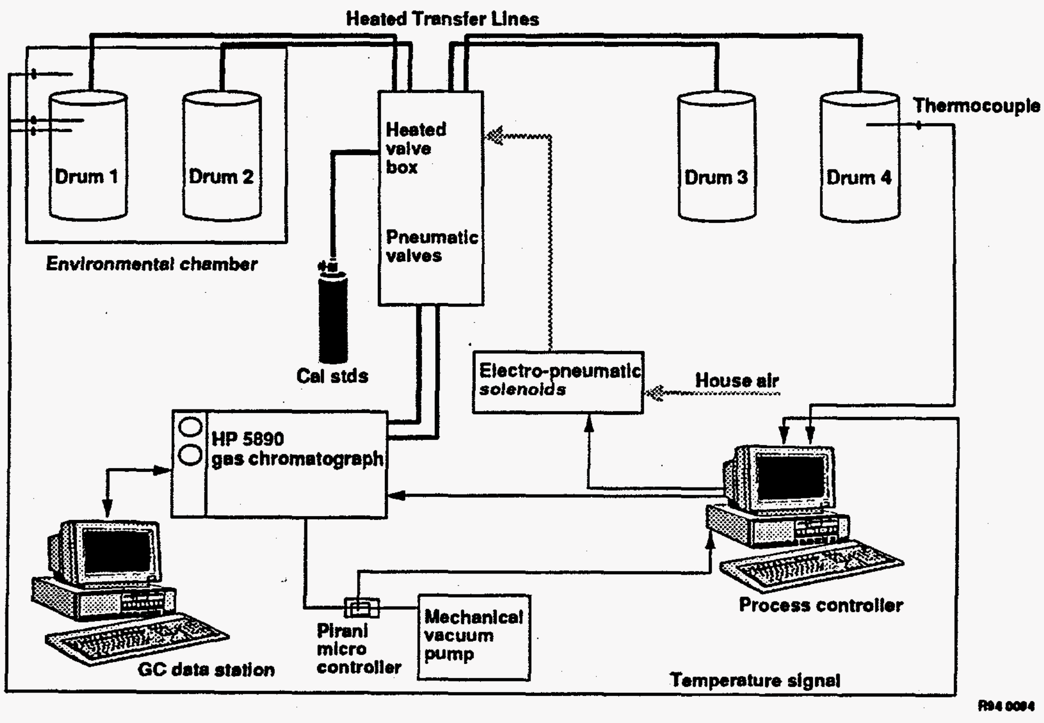

Figure 2. Automated VOC transport experimental configuration.

Table 2. Trial 1 sludge mixture.

Component	Weight (g)	Weight (%)
Regal Texaco oil	150.5	33.7
Methylene chloride	18.2	4.1
Carbon tetrachloride	113.9	25.5
1,1,1-trichloroethane	58.7	13.1
Trichloroethane	21.4	4.8
Freon 113	22.6	5.1
Calcium silicate	61.8	13.8

absorbed and the sludge formed a thick paste. The sludge was separated into four 500-ml glass jars that were capped with teflon-lined lids. Each jar contained approximately 100 g of sludge. One jar was opened and placed inside the large bag of each waste drum just before the bag was closed with a taped horsetail tie. A horsetail tie is formed by twisting together the open end of the bag and wrapping with tape. The same method was used for preparing horsetail ties in earlier VOC transport experiments.[2]

A batch of simulated waste sludge with the composition listed in the Table 3 was prepared for use in Trial 2 experiments. Calcium silicate was added to the solution until the solvents were completely absorbed and the sludge formed a thick paste. The sludge was separated into eight 500-ml glass jars and sealed with teflon lids. Each jar contained approximately 100 g of sludge. One jar was opened and placed in each small bag just before it was heat sealed and placed in a waste drum. Each bag was then filled with 3.5 liters of hydrocarbon-free air to prevent the bag

Table 3. Trial 2 sludge mixture.

Component	Weight (g)	Weight (%)
Regal Texaco oil	360.4	33.9
Methanol	107.5	10.1
Cyclohexane	106.3	10.0
1,1,1-trichloroethane	108.1	10.2
Toluene	109.8	10.3
p-xylene	107.9	10.2
Calcium silicate	163.3	15.4

from collapsing upon itself. At the beginning of the test period, two drums had a filter vent in the drum lid and an opening in the drum liner lid, while the other two drums had a long metal plug wrapped with teflon tape placed in the opening of the drum lid and drum liner. In this way, a sealed drum could be vented quickly by simply removing the plug. Gas samples from the headspace of each bag and from underneath the drum lid were generally collected from each drum twice a week. The total trial period lasted approximately 90 days.

3.4 Quality Control

3.4.1 Quality Control Samples

Initial calibration curves, continuing calibration standards, system blanks, and sample duplicates were part of the quality control procedures used to ensure the quality of the experimental data. An initial calibration curve plots the concentrations of the known analyte standard against the instrument response (area counts) to the analyte. A three-point five-replicate external calibration curve was prepared for each target compound before the start of each sampling day. The liquid standards were run randomly on the autosampler, and data were fitted to a curve by linear regression. At different times throughout the test period, the calibration range was modified accordingly so that all sample area counts were within the calibration curve. Sample duplicates were collected for each waste drum from one of the headspaces on each sampling day. The percent recovery for each sample duplicate was calculated to evaluate the precision of the automated sampling and analytical system. The percent recovery is defined as the ratio of the duplicate concentration to sample concentration multiplied by 100.

3.4.2 Additional Quality Checks

The following baseline checks were made to ensure that the system performed as designed:

1. The process controller block configuration controlling the pneumatic solenoids was confirmed to verify that a specified valve opened and closed when actuated.

2. Sequential timing was verified to ensure quantitative sample transfer before any sample analysis.

3. The maximum attainable vacuum pressures for an open and closed manifold system were determined. Pressure set points were based on these measurements and were modified slightly as needed to ensure correct sequencing.

4. Temperature thermocouples were standardized using a calibrated thermocouple and thermometer. At the beginning of each test period and randomly throughout the experiments, the temperatures of the heated transfer lines and manifold valve box were checked.

5. During the preparation of the polyethylene bags, the bulkhead feedthroughs were attached to the bag and leak tested before the bag was placed in the waste drum.

4. EXPERIMENTAL AND MODEL RESULTS

4.1 VOC Transport Experiments

The TCA concentrations measured in the drum and large bag headspaces for each drum in Trial 1 are shown in Figure 3. The TCA concentrations measured in the drum and small bag headspaces for each drum in Trial 2 are shown in Figure 4. The rate of change in the VOC concentration during Trial 2 was less than in Trial 1 because of the larger quantity of simulated sludge placed in the drums. These trends were observed for other VOCs. The other measured VOC concentrations from Trials 1 and 2 are listed in Appendix A.

In Trial 1, the gas sampling lines in Drum 1 pulled out of the drum and large bag bulkhead feedthroughs. Correction of the problem required opening all layers of confinement; therefore, data collection from the drum was discontinued. At the completion of each trial, all drums were disassembled to determine if any of the layers of confinement had been damaged or compromised. The drum lid seals, drum feedthrough septa, large bag feedthrough septa, large bags, and small bags remained intact throughout both trials. During both trials, small amounts of the simulated waste sludge spilled from the jars and came in contact with the surrounding polyethylene bag. During Trial 2, the horsetail ties on the large bags in Drums 3 and 4 became loose. The piece of tape folded over the end of the horsetail had come undone, and part of the horsetail had unwound. The tape at the base of the horsetail was still intact.

During Trial 1, the relative standard deviation for the initial calibration standards was less than 15% with only a few exceptions. During Trial 2, the relative standard deviation never exceeded 15%. The coefficient of determination, r^2, is a measure of linearity. An absolute value of unity is indicative of perfect linearity. During Trial 1, the values of r^2 for the initial calibration curves exceeded 0.99 in most cases. During Trial 2, the values of r^2 exceeded 0.98 in most cases. On two occasions, initial calibration curves for cyclohexane had an r^2 less than 0.96. Precision was assessed through the analysis of sample duplicates and expressed as the percent recovery. Percent recoveries were generally between 95% and 105% during Trial 1 and were generally between 90% and 110% during Trial 2. The percent recovery for p-xylene during Trial 2 ranged between 80% and 120%.

4.2 Model Calculations

The VOC concentrations throughout a waste drum were estimated using the model equations presented in Section 2. Model parameters were measured or estimated from available process knowledge.

4.2.1 Surface Areas

The large bag dimensions were 33 in. (83.8 cm) wide and 36 in. (91.4 cm) long. Allowing for approximately 6 in. (15.2 cm) of material to form the horsetail, the resulting maximum surface area was estimated to be 1,980 $in.^2$ (12,800 cm^2). The dimensions of the heat-sealed small bags were 12 in. (30.5 cm) by 18 in. (45.7 cm). The maximum surface area of each small bag was

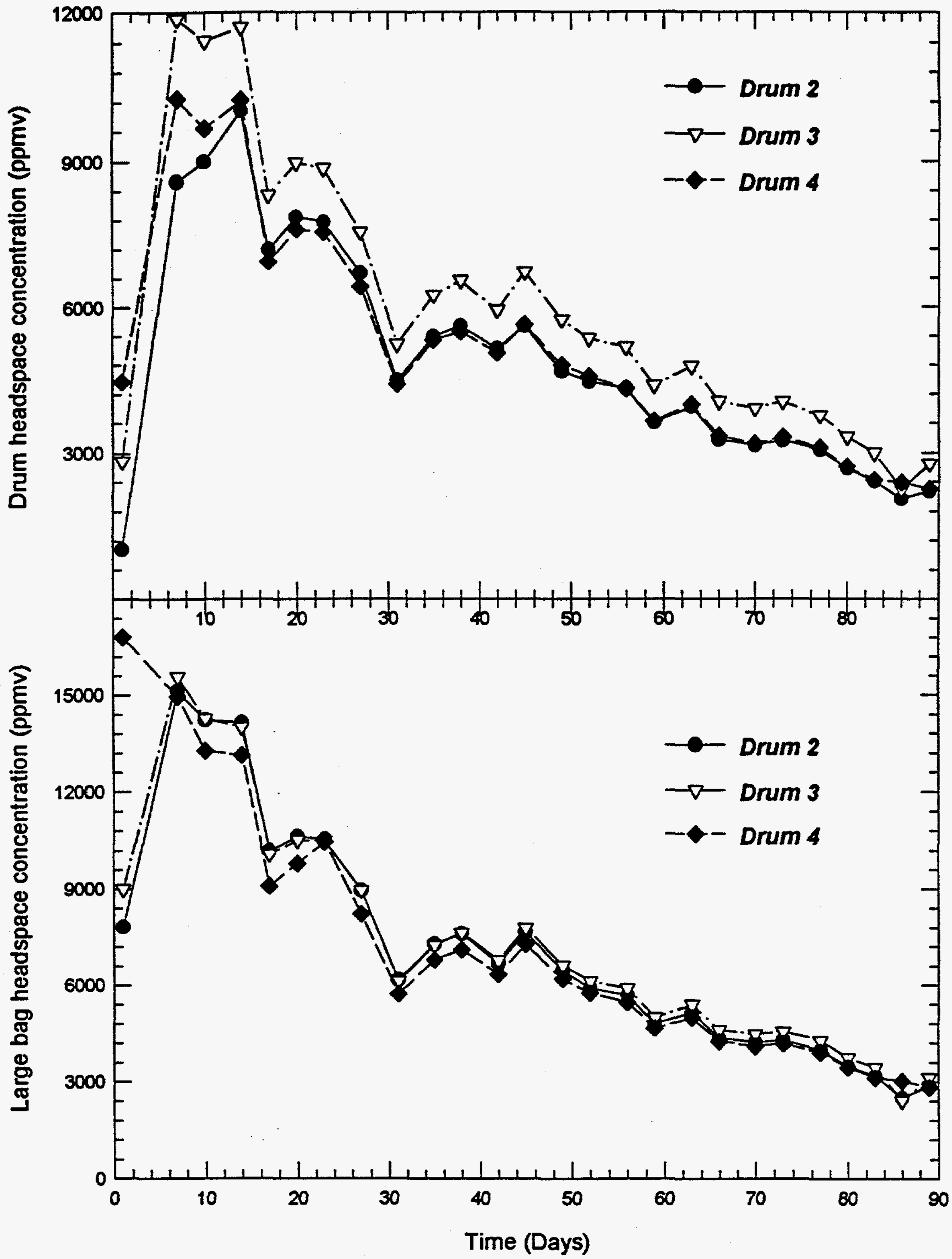

Figure 3. The measured TCA concentration within drum headspace and large bag headspace of lab-scale waste drums during Trial 1.

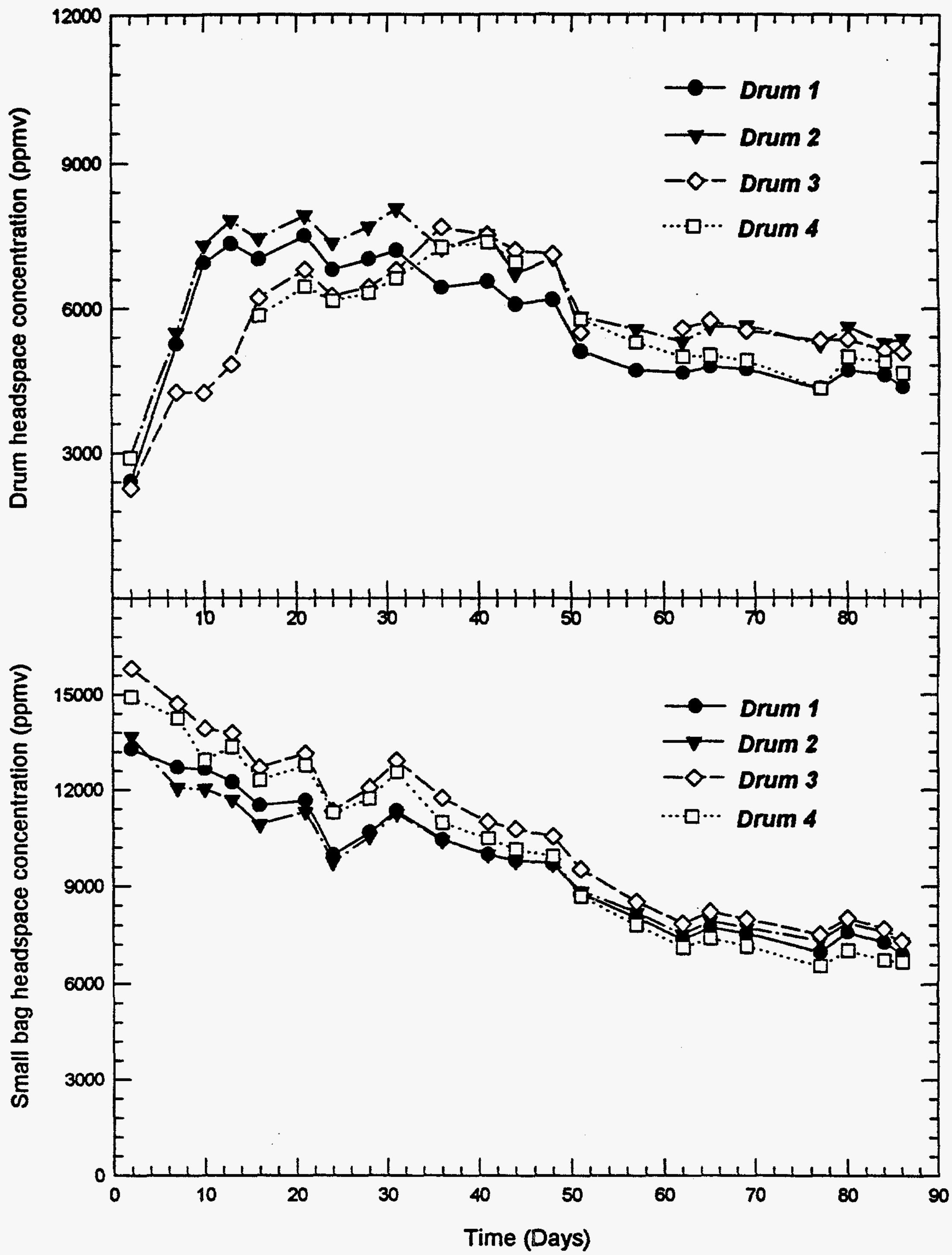

Figure 4. The measured TCA concentration within drum headspace and small bag headspace of lab-scale waste drums during Trial 2.

432 in.^{2} (2,790 cm^2). The cross-sectional area of the opening in the drum liner lid was calculated to be 0.11 in.^{2} (0.71 cm^2) in Trial 1 and 0.09 in.^{2} (0.60 cm^2) in Trial 2.

4.2.2. Transport Lengths

All polyethylene bags were 0.004 in. (0.01 cm) thick. The average thickness of the liner lid where the opening was located was 0.19 in. (0.47 cm). The diffusional length across the drum liner lid was assumed equal to the sum of the opening diameter and lid thickness.

4.2.3 VOC Transport Properties

The VOC permeability coefficients were measured using a mixed-component chromatographic detection method[2] and are listed in Table 4. The diffusivities of most VOCs in air at a given temperature and pressure were identified in the literature.[3] In the case where diffusivity data could not be identified, the VOC diffusivity in air was estimated using the Slattery equation[4]

$$D_{AB} = 2.745 \times 10^{-8} \frac{T^{1.823}}{\Pi} \left[p_{cA}\, p_{cB}\right]^{1/3} \left[T_{cA}\, T_{cB}\right]^{-0.495} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2} \qquad (10)$$

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 same equation was used to correct for any difference in temperature and pressure observed in the experiments. The VOC diffusion characteristic across a NFT-020 filter vent has been determined for all VOCs used in the two trials.[5] An empirical correlation was developed based on these results that estimated the VOC diffusion characteristic from the estimated ratio of hydrogen-to-VOC diffusivity at given conditions and the hydrogen diffusion characteristic across a NFT-020 filter vent

$$D_{voc}^* = \gamma D_{H_2}^* \left(\frac{V_{c,H_2}}{V_{c,voc}}\right)^{0.333} \left[\frac{D_{voc-air}}{D_{H_2-air}}\right] \qquad (11)$$

Table 4. Vapor permeability coefficient across a polyethylene bag at 25°C at a specific VOC concentration in air.

Compound	Concentration (ppmv)	Permeability: Ba[a]	Permeability: $[m^3(STP)\ m/(N\ s)]$ ($\times 10^{15}$)
Methylene chloride	1006	232 ± 15[b]	1.74 ± 0.11
Carbon tetrachloride	295	181 ± 39	1.36 ± 0.29
1,1,1-trichloroethane	994	83.1 ± 3.4	0.62 ± 0.03
Trichloroethylene	300	660 ± 15	4.95 ± 0.11
Freon-113	1010	34.3 ± 1.3	0.26 ± 0.01
Methanol	100	135 ± 35	1.01 ± 0.26
Cyclohexane	745	12.4 ± 1.7	0.093 ± 0.013
Toluene	501	668 ± 121	5.01 ± 0.91
p-xylene	501	811 ± 48	6.08 ± 0.36

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

b. Standard deviation.

where

D_i^* = diffusion characteristic for species i across filter vent, mol s^{-1}

γ = empirical parameter = 1.2

$V_{c,i}$ = critical volume of species i, $m^3\ mol^{-1}$

$D_{i\text{-}air}$ = diffusivity of species i in air, $m^2\ s^{-1}$.

4.2.4 Temperature and Pressure

The waste drums were maintained at ambient room temperature and pressure. A constant temperature of 76.5°F (24.7°C) and a constant pressure of 644.8 torr were used in all model calculations.

4.3 Model Results

Model calculations were performed using the computer program listed in Appendix B. The program was run on an IBM PS/2 Model 70 using a Lahey FORTRAN compiler. In Figures 5 and 6, the daily average concentration ratios from vented drums are compared with model estimates of the concentration ratio during Trials 1 and 2, respectively. The absolute value of the error bar assigned above and below the daily concentration ratio is equal to twice the pooled estimate of the standard error of the mean. There is approximately a 95% certainty that the actual VOC concentration ratio lies within the region covered by the error bars. Assuming that the daily variance between the experimental concentration ratios in all the lab-scale waste drums is approximately the same for each day, the pooled estimate of the standard error of the mean, S_x, was defined as

$$S_x = \sqrt{\frac{\sum_{i=1}^{N} s_i^2 \,/\, N}{n}} \qquad (12)$$

where

s_i^2 = sample variance for i^{th} test day

N = total number of test days

n = total number of drums.

In Trial 1, three drums were used to calculate the daily sample variance. During Trial 2, two pooled estimates were calculated. The two drums vented at the beginning of the test period were used to calculate the sample mean and variance over the first 31 days. After 31 days, the other waste drums were vented. All four drums were used to calculate the pooled estimate of the standard error of the mean for the time period beginning after day 31. The concentration ratio in the unvented drums quickly approached the values in the vented drums upon removal of the plug.

Model predictions of the concentration ratios were calculated using experimental and estimated values for the VOC diffusion characteristic across the NFT-020 filter vent. A comparison of the two model results shows that the higher estimated concentration ratio is associated with a lower VOC diffusion characteristic. The difference between model results was less than one standard deviation associated with the experimental average concentration ratio. The ratio of the drum headspace concentration to the innermost layer of confinement concentration was calculated to minimize daily fluctuations that affected all measurements on a given day, as well as demonstrate when the transport rates were nearly equivalent. Most concentration ratios approached a constant value indicative of nearly equal transport rates from the innermost layer of confinement and the drum headspace. During Trial 1, the time required for the concentration ratio to reach a constant value varied between 10 and 50 days, depending on the VOC. During Trial 2, it took much longer for the concentration ratio for toluene and p-xylene to reach a constant value. Given sufficient time, a maximum and near-constant concentration ratio should be achieved for all VOCs. The time it took to reach a near-constant

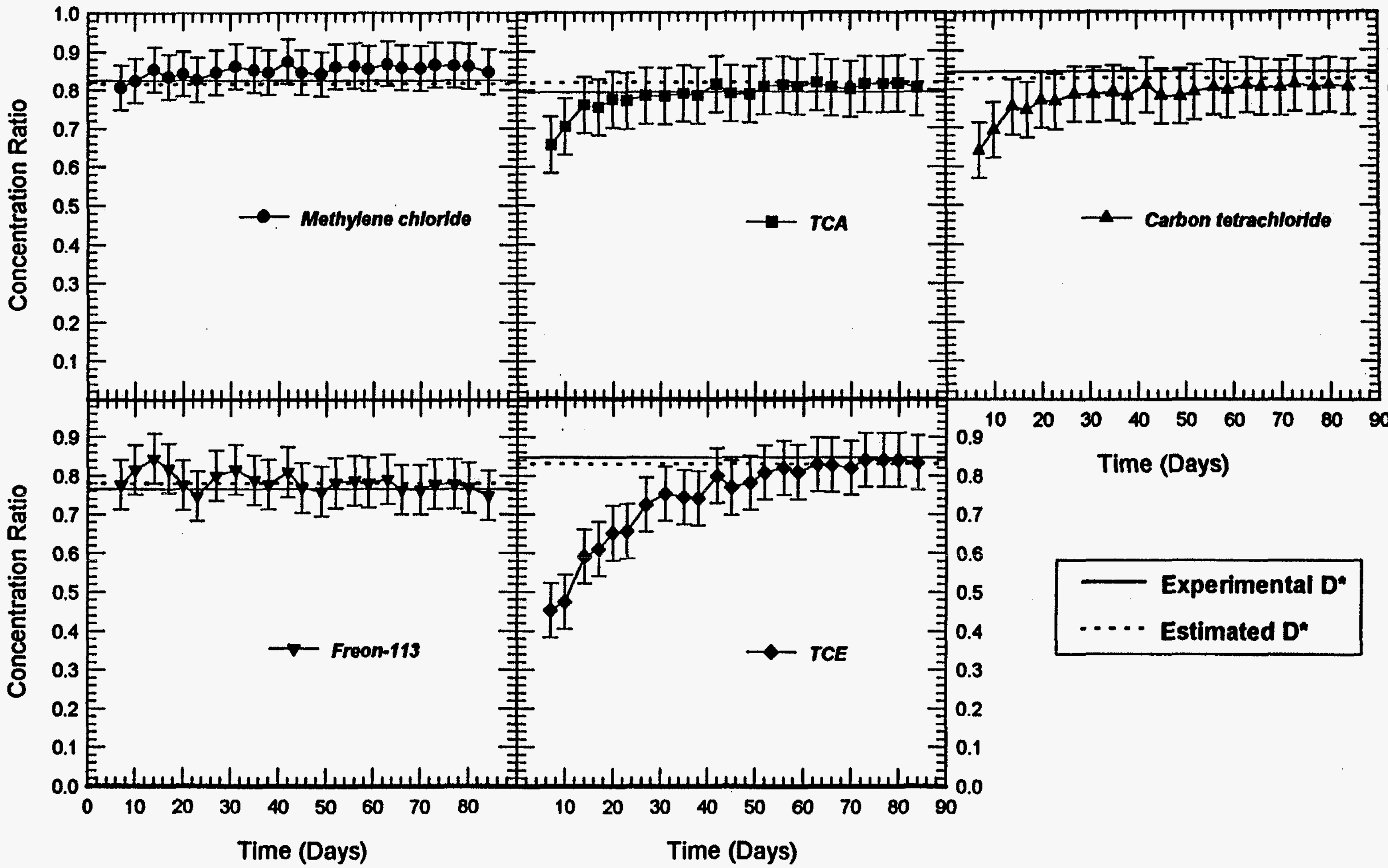

Figure 5. Daily average drum headspace-to-large bag headspace VOC concentration ratio and model predictions during Trial 1.

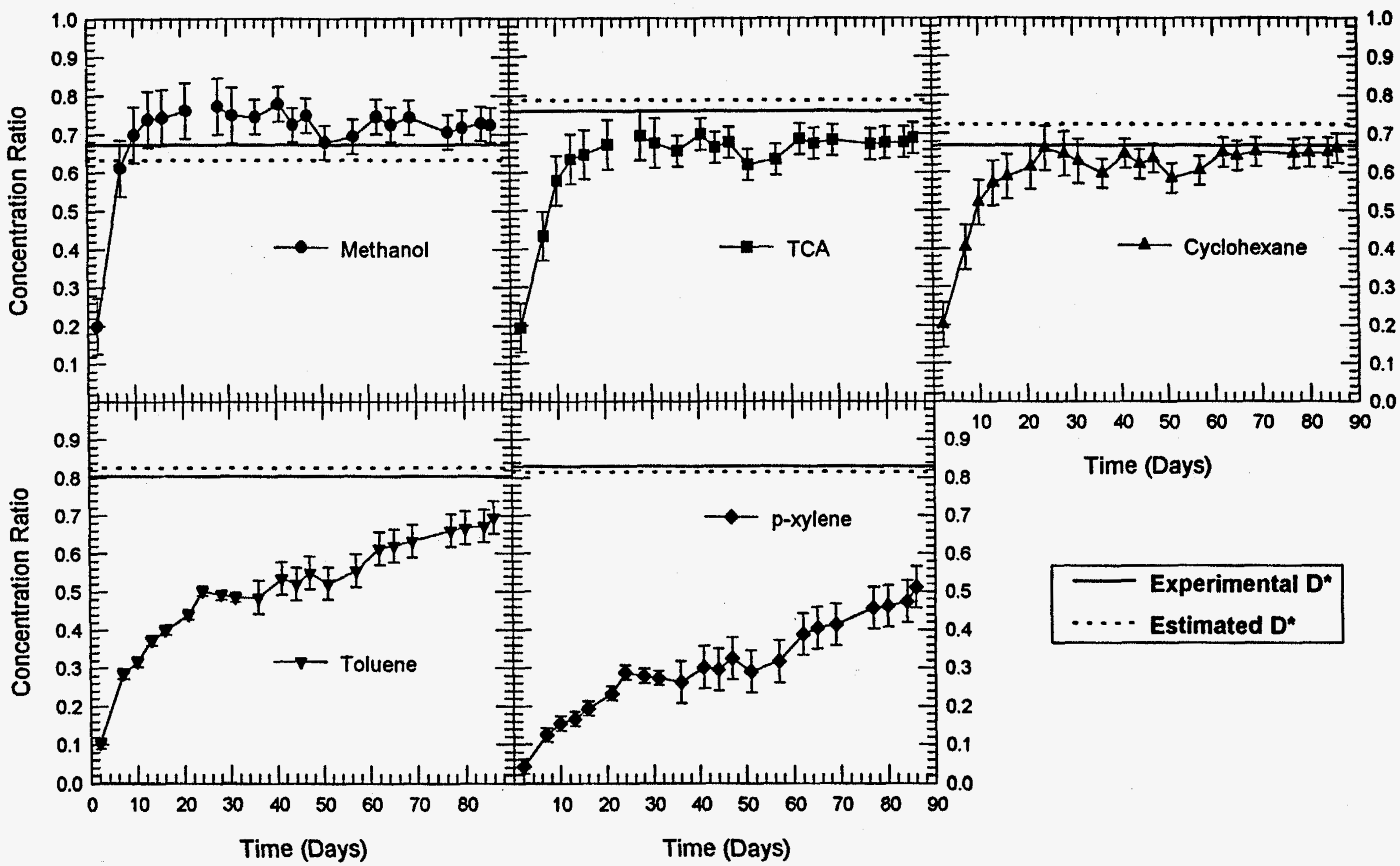

Figure 6. Daily average drum headspace-to-small bag headspace VOC concentration ratio and model predictions during Trial 2.

value was a function of the waste drum configuration and the VOC source. Tables 5 and 6 show that the time decreased with increasing VOC vapor pressure. The VOC vapor pressure was estimated using the Antoine equation.[6,7]

The drum headspace-to-small bag concentration ratio curves in Figure 6 indicate that VOCs entered the drum headspace of Drums 3 and 4 even when the drum liner were not vented. It is possible that the taped pin used to seal the drum and drum liner lids did not achieve a perfect seal. It is more probable that the VOCs diffused through the butadiene-styrene gasket on the drum liner lid. In addition, while the concentration ratio in the unvented drums was less than in the vented drums, the ratios in the unvented quickly approached the values in the other drums after the pin was removed. This fact suggests if an opening in the liner lid and a filter vent can be installed without removing the drum lid, then the drum could be sampled shortly after vent installation. However, a drum that requires the lid to be removed to insert an opening in the liner lid should be treated as a newly packaged drum. In this case, a minimum waiting period must pass before gas samples taken from the vented drums can be considered representative of the gas concentration throughout the void volume of the drum. The minimum waiting time

Table 5. Comparison of VOC vapor pressure and approximate average time when near-constant drum-headspace-to-large-bag VOC concentration ratio was reached during Trial 1.

Compound	Vapor pressure (mm Hg)	Time (days)
Methylene chloride	430.5	14
Freon-113	334.4	18
1,1,1-TCA	133.5	52
Carbon tetrachloride	115.2	55
TCE	69.1	62

Table 6. Comparison of VOC vapor pressure and approximate average time when near-constant drum-headspace-to-small-bag VOC concentration ratio was reached during Trial 2.

Compound	Vapor pressure (mm Hg)	Time (days)
1,1,1-TCA	133.5	14
Methanol	126.4	14
Cyclohexane	97.6	24
Toluene	28.4	>86
p-xylene	8.8	>86

before sampling can take place is a function of the VOCs in the waste, the amount of VOCs in the waste matrix, and the waste drum configuration.

4.4 Effect of Parameter Values on Model Results

4.4.1 VOC Diffusion

By combining Equations (3) and (4) and recalling the assumption of no VOCs outside the drum, the relative concentration difference between the drum headspace and the drum liner headspace as compared with the drum headspace concentration is defined as

$$\frac{\Delta c_{n-1}}{c_n} = \frac{D^*}{D}\,\frac{\Delta x_d\,RT}{A_d\,P}\ . \qquad (13)$$

The concentration difference will decrease as the VOC diffusion characteristic across the filter vent decreases. The latter can be accomplished by changing the filter vent design. The assumed diffusion length across the liner lid increases linearly as the opening diameter increases. However, because the cross-sectional area is a linear function of the square of the opening diameter, the concentration difference will decrease as the opening diameter increases.

Comparison of model calculations using actual and estimated values for the VOC diffusion characteristic indicate some difference in the predicted concentration ratio. The smaller value resulted in a higher estimate of the VOC concentration ratio. The measured VOC diffusion characteristic was an average value determined for six filter vents of similar design.[5] Variance about the average value resulted from the design of the filter vent and filter medium. Model estimates for both trials were calculated using the mean VOC diffusion characteristic as well as values that were two standard deviations above and below the mean and are shown in Figures 7 and 8. The effect on the estimated VOC concentration ratio is dependent upon the relative size of the standard deviation. When the diffusion characteristic standard deviation was greater than 15% of the mean, the difference between model results using the mean and the bounding value for the diffusion characteristic was generally greater than twice the pooled estimate of the standard error. The VOCs that fall in this category are methanol, cyclohexane, and p-xylene. In the future, smaller variances in the measured VOC diffusion characteristic may result by simply sampling a larger population of filter vents.

4.4.2 VOC Permeation

The relative difference between the concentration in the inner bag headspace and the drum headspace is defined by combining Equations (1) and (4)

$$\frac{\Delta c_1}{c_n} = \frac{D^* RT/P}{\rho A_p P/\Delta x_p} = \left(\frac{D^*}{\rho}\right)\left(\frac{\Delta x_p RT}{A_p P^2}\right)\ . \qquad (14)$$

The concentration difference across the inner bag will decrease with increasing permeable surface area or decreasing bag thickness. These variables are a function of the waste packaging

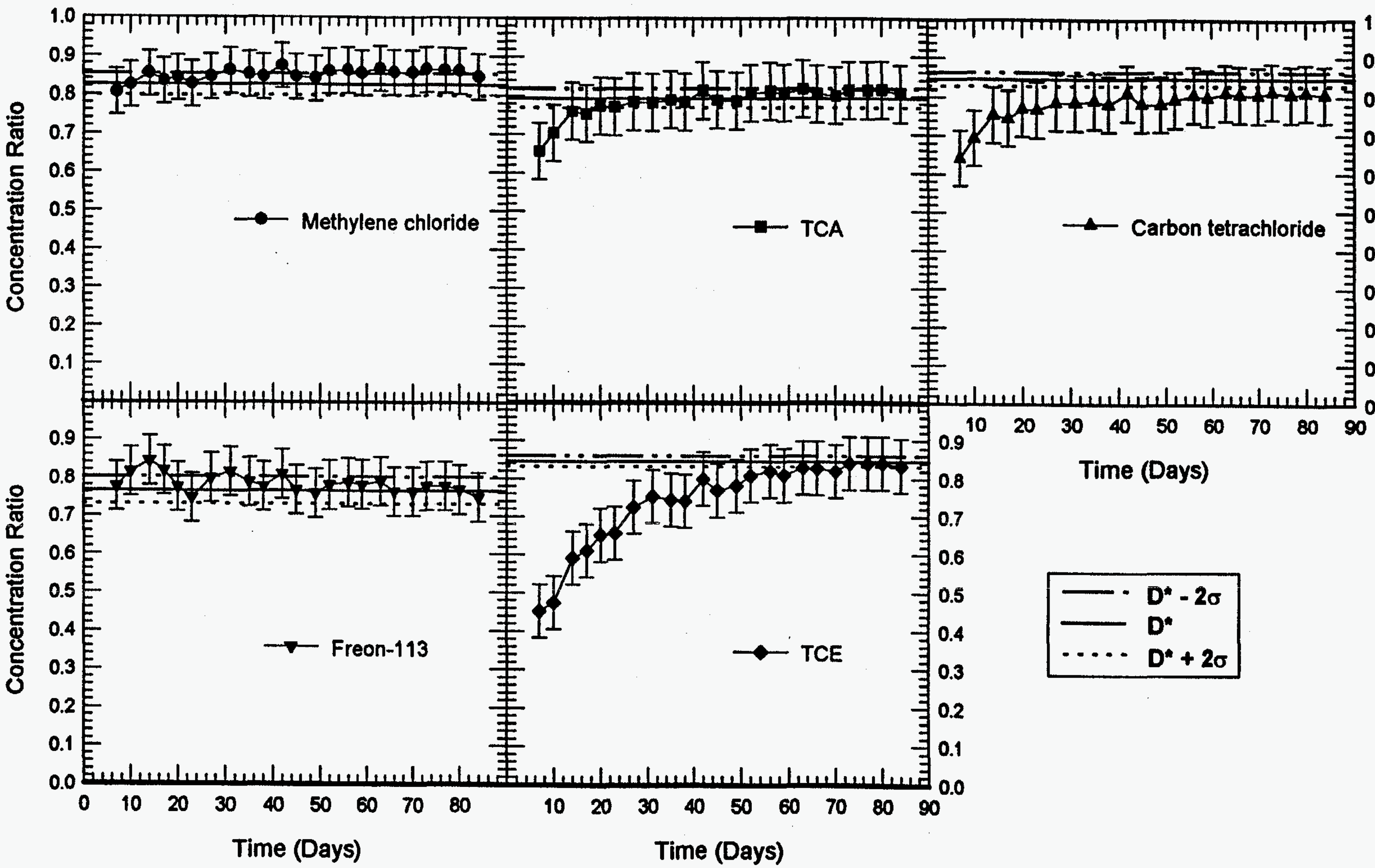

Figure 7. Predicted VOC concentration ratios in Trial 1 using a VOC diffusion characteristic defined by the mean value, D*, and the standard deviation about the mean, σ.

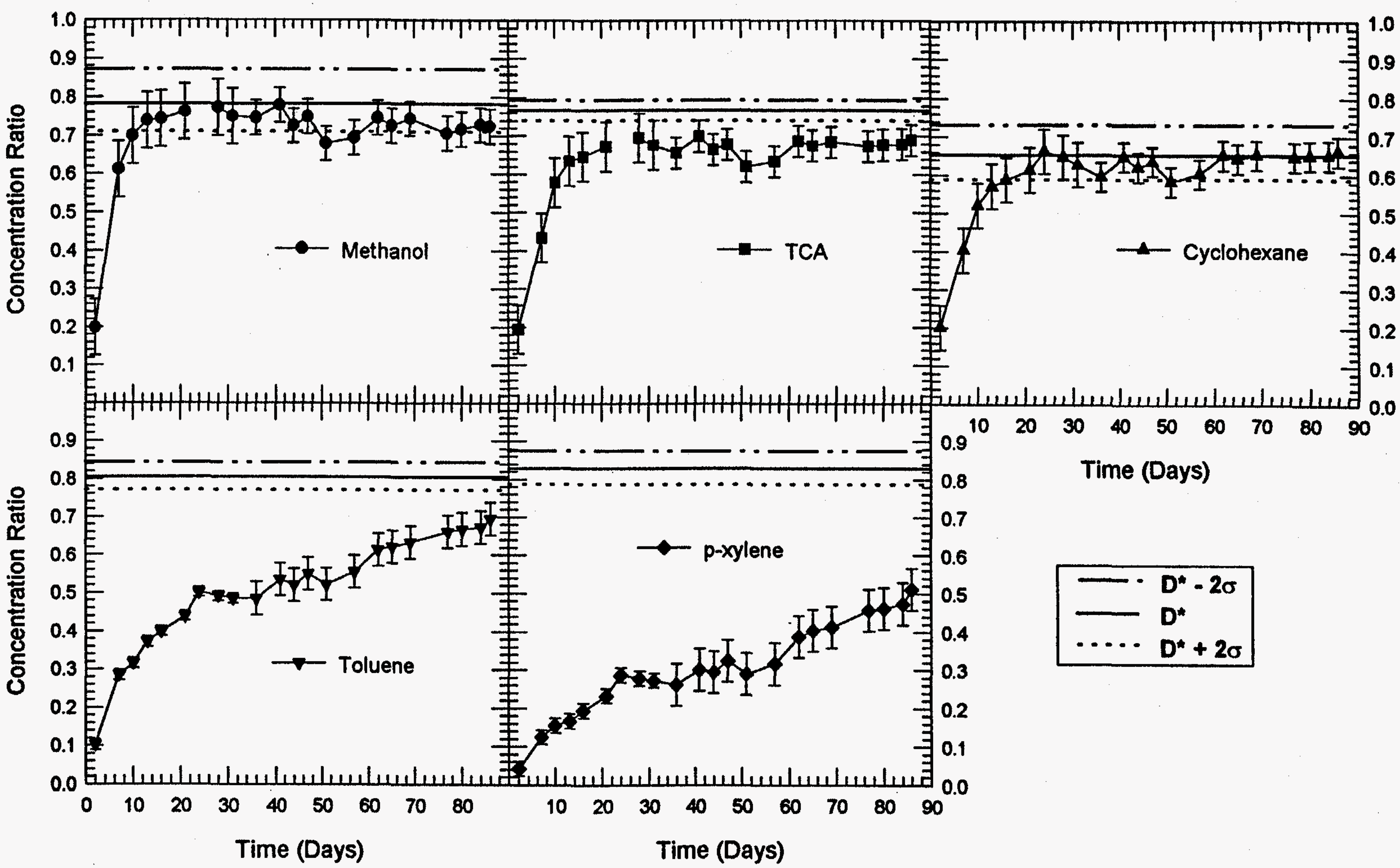

Figure 8. Predicted VOC concentration ratios in Trial 2 using a VOC diffusion characteristic defined by the mean value, D*, and the standard deviation about the mean, σ.

configuration and will vary from drum to drum. In addition, a decreasing VOC diffusion characteristic across the filter vent or increasing VOC permeability across the polymer bag will lead to a decrease in the concentration difference. For a given filter vent design, these two parameters are a function of the VOC in the waste drum. Because the range of VOC diffusion characteristics across a filter vent is relatively narrow, one can estimate the permeability value where the concentration difference becomes insignificant. Temperature and pressure affect the concentration difference, but there is little control over these parameters.

Vapor permeability coefficients generally increase with increasing vapor concentration. All VOC permeabilities listed in Table 4 and used in model calculations were measured at vapor concentrations less than those measured during the lab-scale waste drum experiments. Thus, the predicted concentration difference across a polymer bag was assumed to be equal to or greater than the actual. Equation (14) can be used to estimate the change in the concentration difference with increasing VOC permeability. In the case where the estimated concentration difference is small, an increase in the permeability value will decrease an already small value. For low-permeability VOCs, the permeability may be two or three times larger at higher vapor concentrations. Depending on the waste drum configuration, the use of a larger permeability value could significantly reduce the estimated concentration difference. The use of a VOC permeability measured across an identical or similar polymer bag at VOC vapor concentrations less than those that exist under actual conditions will result in a conservative estimate of the actual concentration difference across the bag.

Equation (14) can demonstrate the impact of assumed permeable surface area. In the experiments, the maximum surface area of the small and large bags are known by direct measurement. In actual waste drums, the surface area will be estimated from process knowledge or indirectly observed by real-time radiography. Because the estimated concentration difference is inversely proportional to the available surface area, a conservative approach would assume the smallest likely value.

4.5 Experimental and Model Refinements

The presence of multiple layers of small or large polymer bags is probable. For model calculations, the multiple layers will be assumed to be equivalent to a single layer with a thickness equal to the sum of all the individual layers. This assumption will be investigated during the gas sampling and waste characterization of actual vented waste drums.

A conservative application of the transport model to actual waste drums would be to give less than full credit for the total permeable surface area of the bags.

5. CONCLUSIONS

A VOC transport model accurately estimated the VOC concentration in the headspace of the innermost layer of confinement of a lab-scale vented waste drum containing simulated waste sludge. The model estimates the VOC concentration in the drum based on the measured VOC concentration beneath the drum lid and other model parameters that are determined or estimated from process knowledge of the drum contents and the waste drum configuration. These model parameters include the VOC diffusion characteristic across the filter vent, VOC diffusivity in air, size of opening in the drum liner lid, the type and number of layers of polymer bags surrounding the waste, VOC permeability across the polymer, and the permeable surface area of the polymer bags. Model equations indicate that knowledge of some parameters is not important in cases where the estimated concentration difference between layers is expected to be small.

6. REFERENCES

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Appendix A

Measured VOC Concentrations in Lab-scale Waste Drums

Table A-1. Measured VOC concentration (ppmv) in Drum 2 headspaces during Trial 1.

	Methylene chloride		Freon-113		1,1,1-trichloroethane		Carbon tetrachloride		Trichloroethylene	
Day	DH[a]	LB[b]	DH	LB	DH	LB	DH	LB	DH	LB
7	4930	6550	3961	5695	8594	15132	10190	19529	861.5	2939
10	4551	5796	4122	5333	9011	14237	10563	18143	878	2132.5
14	4825	5883	4721	5779	10035	14154	6472	9755	1397.8	2782.2
17	3000	3747	3581	4553	7199	10207	6594	9826	1155	2194.2
20	3166	3877	2942	3919	7870	10628	9573	13843	974.8	1698.2
23	2667	3323	2582	3582	7766	10531	8874	12734	817.7	1402.4
27	2428	2944	2703	3470	6711	8956	8281	11409	926	1396.8
31	2305	2786	2918	3754	4484	6161	8192	11277	924.7	1337.5
35	1925	2365	1768	2381	5385	7282	6981	9662	729.4	1071.2
38	1899	2344	1695	2312	5607	7609	6904	9562	728.9	1069.2
42	1764	2098	1795	2335	5131	6677	6991	9104	789.3	1049.8
45	1814	2262	1495	2090	5603	7658	6767	9383	776.9	1096.5
49	1516	1925	1271	1828	4672	6465	6071	8515	699.2	973.1
52	1514	1845	1319	1805	4458	5918	5928	8099	702.9	929.6
56	1495	1806	1258	1685	4319	5679	5644	7564	705	916.2
59	1244	1519	1119	1515	3618	4800	4811	6471	582.6	766.1
63	1321	1595	1107	1484	3949	5151	5230	6922	659.4	848.5
66	1055	1296	788	1108	3270	4359	4343	5798	558.1	717.4
70	1009	1245	756	1050	3151	4209	4189	5578	550.7	717.9
73	1045	1270	774	1055	3245	4283	4327	5695	591.4	746.7
77	974	1169	753	1011	3055	3970	4207	5616	536.1	671.8
80	831	1004	588	809	2681	3480	3695	4829	510.8	637.7
83	692	855	483	682	2420	3191	3161	4190	460.4	593.8
87	613	702	408	528	2052	2500	2286	2865	404.3	474.5
90	758	925	522	727	2206	2882	3437	4505	507.9	631.3
93	777	930	565	770	2540	3271	3574	4610	550.8	676.9

a. Drum headspace.

b. Large bag headspace.

Table A-2. Measured VOC concentration (ppmv) in Drum 3 headspaces during Trial 1.

	Methylene chloride		Freon-113		1,1,1-trichloroethane		Carbon tetrachloride		Trichloroethylene	
Day	DH[a]	LB[b]	DH	LB	DH	LB	DH	LB	DH	LB
7	5418	6081	4577	5307	11875	15575	14740	20538	1435.3	2611.5
10	4852	5459	4388	6033	11437	14287	14141	18572	1368.4	2263.5
14	5022	5592	4798	5479	11708	14004	7891	9771	1945	2822.6
17	3131	3561	3658	4304	8326	10092	7896	9832	1565.2	2199.8
20	3317	3703	3034	3662	8987	10516	11383	13710	1274.9	1691.6
23	2807	3188	2676	3346	8874	10493	10531	12761	1069.9	1408.4
27	2507	2834	2730	3272	7563	8959	9652	11528	1134.1	1402.8
31	2455	2685	3077	3562	5226	6125	9666	11339	1127.7	1340.7
35	2066	2279	1901	2240	6252	7246	8285	9683	896.6	1075.8
38	2056	2282	1850	2206	6550	7639	8195	9637	899.4	1083
42	1902	2062	1947	2251	5934	6768	8165	9388	935.1	1068.5
45	2016	2226	1691	2024	6728	7791	8248	9608	960.4	1122.4
49	1735	1910	1495	1788	5738	6631	7601	8814	871.5	1004.5
52	1691	1853	1509	1786	5351	6123	7346	8506	854.7	967.9
56	1664	1821	1430	1683	5177	5896	6884	7848	848.8	952.9
59	1404	1537	1281	1519	4379	4997	5903	6766	708.9	801.6
63	1493	1621	1281	1499	4770	5385	6400	7257	795.4	887.9
66	1221	1330	950	1130	4052	4602	5390	6120	680.3	756.7
70	1170	1286	909	1085	3906	4463	5175	5895	674.9	755.1
73	1218	1317	934	1095	4044	4551	5406	6090	723.3	794.1
77	1118	1221	892	1063	3756	4267	5302	6038	648.7	718.2
80	967	1053	717	855	3316	3747	4597	5195	616.5	681.2
83	806	896	592	723	2998	3440	3946	4517	557.4	623.4
87	636	668	436	500	2249	2413	2566	2745	432.4	451.7
90	901	976	655	776	2776	3117	4330	4865	615.5	674.8
93	920	995	709	835	3199	3585	4501	5045	669.3	729.3

a. Drum headspace.

b. Large bag headspace.

Table A-3. Measured VOC concentration (ppmv) in Drum 4 headspaces during Trial 1.

	Methylene chloride		Freon-113		1,1,1-trichloroethane		Carbon tetrachloride		Trichloroethylene	
Day	DH[a]	LB[b]	DH	LB	DH	LB	DH	LB	DH	LB
7	4489	5773	3871	5022	10271	14968	12854	20058	1208	2690
10	4105	5129	3794	4717	9678	13276	11888	17312	1068	2129
14	4450	5276	4348	5170	10250	13149	6830	9156	1545	2635
17	2644	3206	3174	3875	6952	9096	6619	9057	1174	1974
20	2809	3439	2491	3342	7615	9799	9443	12728	987.4	1575
23	2373	2963	2190	3046	7562	10476	8816	11919	830.7	1407
27	2164	2614	2374	3015	6435	8220	7998	10365	919.1	1306
31	2118	2505	2685	3333	4400	5725	8194	10591	930	1277
35	1771	2110	1597	2063	5313	6788	7017	9105	739.2	1071
38	1736	2100	1528	2016	5486	7111	6810	8958	724.2	1030
42	1634	1902	1635	2065	5055	6343	7024	8855	791.9	1024
45	1700	2046	1380	1833	5634	7284	6957	9069	800.3	1077
49	1454	1751	1194	1605	4803	6197	6396	8319	730.7	966.4
52	1450	1707	1240	1610	4570	5751	6332	8103	735.5	935.2
56	1404	1658	1143	1497	4322	5460	5754	7315	730.1	914
59	1183	1414	1045	1366	3658	4665	4962	6369	605.1	770.7
63	1259	1475	1019	1326	3990	4988	5385	6788	685.4	849.1
66	1016	1207	731.9	987.6	3346	4256	4521	5746	586.9	726.9
70	968	1158	686.1	934.7	3189	4097	4298	5485	579.6	725.6
73	1005	1184	707	939.6	3311	4179	4536	5717	624.3	761
77	929	1101	680.4	907.8	3094	3906	4421	5596	567.2	689.3
80	795	946	531.1	719.7	2715	3441	3854	4917	537.4	657.9
83	663	797	428.6	595.6	2451	3119	3293	4178	488.6	595.9
87	693	831	448.3	617.2	2393	3010	2482	3136	489.7	594.8
90	736	871	477.9	641.4	2258	2833	3596	4517	538.9	647.8

a. Drum headspace.

b. Large bag headspace.

Table A-4. Measured VOC concentration (ppmv) in Drum 1 headspaces during Trial 2.

	Methanol			Cyclohexane			1,1,1-TCA			Toluene			p-xylene		
Day	DH[a]	LB[b]	SB[c]	DH	LB	SB	DH	LB	SB	DH	LB	SB	DH	LB	SB
2	16780	60723	93110	3185	14735	17128	2407	11418	13829	—	—	—	28.9	725	785
7	47410	76547	81487	6195	15797	16050	5250	12452	12705	1057	3701	3753	92.0	751	774
10	53145	76754	80242	7998	15847	16100	6940	12413	12651	2267	7040	7173	157.6	1011	1046
13	53065	73483	75969	8339	15245	15433	7337	12058	12235	2519	6688	6787	169.5	1020	1046
16	50397	70657	72312	7899	14155	14289	7018	11393	11506	2529	6322	6402	188.3	985	1008
21	51870	70494	70837	8590	14545	14614	7502	11608	11660	1917	4344	4379	241.2	1056	1075
24	42404	55352	56007	7636	12048	12146	6800	9865	9956	1877	3758	3792	260.8	922	942
28	42957	58225	58579	—	13226	12736	7024	10596	10664	1975	4056	4087	277.1	1035	1053
31	40507	57627	57493	8238	13883	13927	7192	11284	11326	2067	4312	4332	303.0	1150	1167
36	32588	47513	47739	7331	12654	12709	6427	10395	10436	1991	4074	4099	301.7	1115	1132
41	30879	41589	42438	7661	12221	12373	6547	9843	9981	2130	4036	4072	336.6	1130	1154
44	26165	38316	39729	7194	12122	12246	6080	9695	9788	2011	3966	4004	327.0	1146	1166
48	24435	34539	34559	7419	12252	12250	6174	9686	9710	2100	4061	4058	348.3	1215	1222
51	17992	28220	28724	6251	11146	11247	5098	8668	8753	1900	3998	3822	306.7	1147	1163
57	14105	22195	22491	5791	10234	10318	4702	7990	8041	1825	3605	3628	298.8	1123	1140
62	13276	18984	19242	5582	9140	9204	4645	7288	7345	1768	3168	3183	332.6	1003	1015
65	13634	20244	20428	5812	9772	9822	4773	7690	7729	1886	3367	3379	359.8	1058	1070
69	12627	18158	18452	5941	9717	9823	4726	7449	7540	1966	3418	3444	378.4	1093	1110
77	8440	12815	13187	5481	9131	9131	4311	6949	6973	1998	3403	3205	395.1	1108	904
80	9459	13915	14115	5695	9426	9495	4698	7523	7579	2086	3463	3479	441.4	1155	1167
84	8802	12800	12028	5603	9145	9186	4592	7226	7267	2059	3362	3369	444.6	1126	1134
86	8124	11855	12049	5219	8546	8610	4355	6878	6927	1965	3165	3178	429.5	1062	1072

a. Drum headspace.

b. Large bag headspace.

c. Small bag headspace.

Table A-5. Measured VOC concentration (ppmv) in Drum 2 headspaces during Trial 2.

	Methanol			Cyclohexane			1,1,1-TCA			Toluene			p-xylene		
Day	DH[a]	LB[b]	SB[c]	DH	LB	SB	DH	LB	SB	DH	LB	SB	DH	LB	SB
2	19510	62370	94943	3632	14493	16806	2932	11450	13668	—	—	—	58.0	1033	1157
7	46627	72916	76179	6190	14327	14714	5487	11722	12055	1055	3555	3637	121.1	888	924
10	55505	73439	75474	8030	14447	14713	7301	11776	12017	2108	6490	6635	187.1	1119	1168
13	56565	70600	72644	8505	13966	14162	7818	11522	11688	2311	6052	6157	192.0	1084	1118
16	54242	67368	68782	8232	13134	13213	7444	10828	10906	2317	5652	5704	210.6	1020	1042
21	55295	69349	69887	8715	13543	13594	7924	11280	11310	1676	3771	3799	249.8	1021	1035
24	47033	55720	56501	7913	11321	11384	7361	9697	9745	1673	3263	3285	259.2	859	874
28	49606	60476	60920	8571	12496	12570	7685	10462	10518	1762	3497	3523	277.1	935	948
31	48767	60709	61389	8758	13056	13163	8053	11167	11246	1843	3683	3724	295.0	1007	1025
36	40495	51773	52482	7811	11972	12075	7233	10341	10406	1807	3529	3560	295.7	958	970
41	38985	45933	46840	8339	11689	11787	7521	9877	9975	2015	3542	3549	333.6	948	954
44	32814	42992	43488	7505	11523	11689	6706	9735	9786	1833	3474	3484	313.0	944	952
48	31458	38627	39089	7933	11471	11573	7043	9632	9706	1967	3531	3556	339.0	971	979
51	24640	32860	33462	6645	10567	10650	5827	8768	8842	1755	3359	3371	287.6	914	919
57	20090	26435	26794	6318	9709	9776	5563	8134	8184	1762	3232	3250	290.2	881	887
62	17270	22241	22643	5921	8724	8774	5294	7470	7509	1725	2899	2896	323.7	801	794
65	18445	23706	24141	6336	9297	9377	5603	7873	7933	1887	3095	3110	359.7	846	846
69	17331	21586	21952	6543	9293	9349	5643	7670	7713	1988	3183	3179	377.0	877	864
77	12220	15817	16174	6085	8786	8853	5230	7263	7321	2056	3238	3240	392.3	898	889
80	12807	16664	17012	6274	9057	9121	5612	7830	7883	2169	3305	3314	445.9	941	938
84	11719	15379	15707	5917	8783	8833	5266	7538	7579	2069	3226	3232	428.6	926	920
86	11314	14227	14575	5900	8219	8279	5357	7189	7273	2080	3046	3056	437.1	877	875

a. Drum headspace.

b. Large bag headspace.

c. Small bag headspace.

Table A-6. Measured VOC concentration (ppmv) in Drum 3 headspaces during Trial 2.

	Methanol			Cyclohexane			1,1,1-TCA			Toluene			p-xylene		
Day	DH[a]	LB[b]	SB[c]	DH	LB	SB	DH	LB	SB	DH	LB	SB	DH	LB	SB
2	11039	82861	97923	2730	18441	19583	2276	14538	15823	—	—	—	40.6	1447	1523
7	37754	89641	91678	4112	18067	18296	4243	14529	14705	986	4680	4721	107.6	1231	1251
10	—	87603	84983	3971	17677	16970	4234	14252	13916	1499	8659	8214	130.3	1564	1501
13	40795	82585	84866	4542	16788	16899	4837	13672	13783	1817	8036	8087	147.5	1496	1516
16	47277	78215	80121	5891	15561	15598	6213	12664	12700	2354	7537	7558	205.7	1432	1443
21	51097	80260	81027	6404	15997	16019	6800	13129	13151	1771	5029	5042	255.2	1454	1454
24	43360	65966	65334	5904	13725	13459	6256	11527	11335	1712	4388	4298	260.6	1260	1234
28	43940	68617	68617	6267	14529	14614	6438	11990	12065	1816	4511	4324	281.5	1335	1335
31	43903	69721	71077	6402	15341	15349	6793	12895	12929	1955	4763	4468	316.0	1462	—
36	43978	56862	57640	8012	13774	13867	7672	11681	11743	2210	4452	4451	378.3	1402	1396
41	37974	48876	49889	8226	13118	13182	7506	10926	10981	2328	4309	4254	417.4	1362	1362
44	33276	44870	45795	7944	12812	12953	7190	10655	10760	2276	4192	4190	424.0	1362	1329
48	30515	39634	40480	8001	12731	12764	7112	10498	10545	2384	4218	3987	467.7	1406	—
51	—	33232	33786	6272	11619	11682	5492	9485	9534	2037	3925	—	398.1	1303	1264
57	26093	26093	26053	6133	10621	10266	—	8714	8513	—	3718	3608	—	1252	1216
62	16696	21460	21833	6261	9308	9366	5580	7812	7855	2127	3208	3189	471.9	—	1047
65	17071	22617	22950	6564	9885	9914	5744	8184	8216	2296	3401	3384	517.4	1127	1102
69	15407	20315	20633	6489	9834	9887	5528	7942	7987	2325	3449	3428	532.3	1148	1113
77	10941	14414	14797	6295	9246	9323	5316	7441	7506	2493	3467	3448	593.3	1155	1120
80	10869	15248	15541	6087	9472	9527	5342	7977	8020	2448	3511	3505	616.7	1187	1170
84	10218	13918	14236	5872	9148	9210	5106	7632	7684	2397	3407	3403	618.7	1149	1134
86	9549	12846	13166	5733	8551	8606	5090	7272	7316	2343	3210	3010	601.9	1080	1069

a. Drum headspace.

b. Large bag headspace.

c. Small bag headspace.

Table A-7. Measured VOC concentration (ppmv) in Drum 4 headspaces during Trial 2.

	Methanol			Cyclohexane			1,1,1-TCA			Toluene			p-xylene		
Day	DH[a]	LB[b]	SB[c]	DH	LB	SB	DH	LB	SB	DH	LB	SB	DH	LB	SB
2	16983	93725	85669	3441	18662	18947	2899	14914	15066	—	—	—	44.8	1438	1435
7	—	87774	88968	—	17587	17994	—	14241	14581	—	4498	4571	—	1188	1195
10	—	79599	82842	—	15678	16254	—	12936	13436	—	7525	7800	—	1378	1428
13	57398	80811	83924	5651	16254	16873	—	13344	13860	1871	7668	7951	119.3	1436	1481
16	53888	76710	79659	5327	14920	15502	5852	12292	12776	1778	7095	7359	126.7	1348	1392
21	58084	80225	83573	5863	15335	15914	6443	12774	13259	1353	4737	4920	156.3	1368	1419
24	50101	67039	67850	5604	12842	13170	6148	10984	11274	1400	4000	4141	179.1	1181	1181
28	53466	72359	75368	5935	14501	14501	6317	11713	12178	1476	4246	4414	188.7	1297	1297
31	54215	75010	78663	5956	14641	15359	6615	12544	13156	1554	4453	4675	200.3	1359	1425
36	46649	60909	64110	7448	12702	13534	7250	10958	11675	1833	4048	4321	259.6	1269	1355
41	41495	52119	53702	7904	12346	12800	7357	10473	10846	2023	3993	4154	303.1	1255	1304
44	34745	46855	48327	7611	12000	12400	6947	10130	10473	2007	3999	4040	315.0	1266	1306
48	—	39903	42726	—	11867	12632	—	9918	10558	—	—	3524	—	1305	1389
51	23020	32012	34050	6482	10478	11149	5766	8676	9226	1960	3555	3787	317.6	1183	1256
57	17204	23332	25089	5954	9430	10039	5278	7806	8329	1952	3314	3532	325.6	1116	1190
62	14736	19208	20354	5535	8397	8881	4984	7111	7519	1863	2919	3095	360.1	982	1038
65	14486	19859	21021	5687	8855	9385	5010	7387	7839	1983	3081	3282	392.5	1023	1088
69	13106	17313	18492	5706	8782	9349	4908	7149	7614	2052	3117	3332	411.2	1036	1108
77	7805	11323	12171	5080	8081	8647	4309	6544	7002	2063	3086	3316	431.3	1026	1103
80	9039	12147	12830	5640	8310	8799	4978	7027	7445	2255	3147	3348	497.8	1064	1134
84	8329	10844	11487	5541	8037	8533	4872	6735	7148	2256	3068	3274	509.2	1033	1103
86	7573	10531	10451	5179	7809	7940	4634	6678	6775	2142	2858	3077	487.8	834	1037

a. Drum headspace.

b. Large bag headspace.

c. Small bag headspace.

Appendix B

Computer Program to Estimate VOC Concentration Ratio in Vented Waste Drums Containing VOC Source

```
c
c
c program calculates the steady state VOC concentration in a
c lab-scale vented waste drum containing simulated waste sludge.
c-----------------------------------------------------------
c model assumes constant drum temperature
c-----------------------------------------------------------
c declaration of variables
      character*21 vocid(9),ifname,ofname
      integer nvoc,n,i,m
      real ap(3),ad(3),xp(3),xd(3),y(9,4),temp,pHg,dch2
      real amw,pm,df,b,c,atc,apc,avc
      real a(4),advocair,adcvoc,test
c-----------------------------------------------------------
c User provided input
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   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*************************************************************
      vocid(1)='carbon tetrachloride '
      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             '
c-----------------------------------------------------------
c----Input initial conditions from a file-----
c-----------------------------------------------------------
      write(*,5)
5     format(1x,'Enter name of input file:  ')
      read(*,*)ifname
      open(unit=3,file=ifname,status='unknown')
      read(3,*)test,ofname
      open(unit=2,file=ofname,status='unknown')
      read(3,*)nvoc,layer
c   temp - drum temperature, C
c   pHg - ambient pressure, cm Hg
c   njc - counter (1 = actual D*,voc; 2 = estimated D*,voc
```

```
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
      do 30 i=1,nvoc
        read(3,*)n,y(n,layer)
c-----------------------------------------------------
c Computation of concentrations
c-----------------------------------------------------
        call vprop(n,amw,pm,df,b,c,atc,apc,avc,adcvoc)
c a(x) = alpha(x) or abeta(x)
        do 26 l=1,layer-1
          if(l.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
c accounts for presence of two small bags
        if(layer.eq.4)a(1)=2.*a(1)
c estimate VOC diffusion characteristic if njc=2
        if(njc.eq.2)then
          call dvocair(apc,atc,amw,advocair)
          call dcvoc(avc,advocair,dch2,adcvoc)
        else
        end if
        call conc(layer,a,adcvoc,y,n,pHg,temp,c0)
 30   continue
      call output(layer,y,vocid,ap,ad,xp,xd,pHg,temp,dch2,test)
      end
c
c ***** Subroutine assigns values to each volatile's properties *****
      subroutine vprop(n,amw,pm,df,b,c,atc,apc,avc,dvoc)
      real amw,pm,df,b,c,atc,apc,avc
      integer n
      real mw(9),p(9),d(9),vpb(9)
      real vpc(9),tc(9),pc(9),vc(9),dv(9)
c mw(i) - molecular weight of compound i
c p(i) - VOC i permeability across polye at 25C, cm3 cm/cm2 s cm Hg
c d(i) - diffusion 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   amw,pm,df,b,c,atc,apc,avc correspond to properties
c   of designated VOC each time through the loop
c-----------------------------------------------------
c 1 = carbon tetrachloride
      mw(1)=153.82
      p(1)=161.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.
    dv(1)=3.0e-7
c 2 = cyclohexane
    mw(2)=84.1
    p(2)=12.4e-10
    d(2)=0.0750
    vpb(2)=1203.526
    vpc(2)=-50.287
    tc(2)=553.4
    pc(2)=40.2
    vc(2)=308.
    dv(2)=4.4e-7
c 3 = methanol
    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.
    dv(3)=6.05e-7
c 4 = methylene chloride
    mw(4)=84.9
    p(4)=244.e-10
    d(4)=0.104
    vpb(4)=1325.9
    vpc(4)=-20.55
    tc(4)=510.
    pc(4)=60.
    vc(4)=193.
    dv(4)=4.4e-7
c 5 = toluene
    mw(5)=92.1
    p(5)=668.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.
    dv(5)=3.7e-7
c 6 = TCA
    mw(6)=133.4
    p(6)=83.e-10
    d(6)=0.0794
    vpb(6)=2136.6
    vpc(6)=29.65
    tc(6)=545.
    pc(6)=42.4
    vc(6)=281.
    dv(6)=4.0e-7
```

```
c 7 = TCE
      mw(7)=131.4
      p(7)=311.e-10
      d(7)=0.0875
      vpb(7)=1018.6
      vpc(7)=-80.45
      tc(7)=571.
      pc(7)=48.5
      vc(7)=256.
      dv(7)=3.2e-7
c 8 = Freon-113
      mw(8)=187.4
      p(8)=27.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.
      dv(8)=3.45e-7
c 9 = p-xylene
      mw(9)=106.2
      p(9)=811.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.
      dv(9)=2.5e-7
c assigns values to variables for designated VOC
      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
c ***** Subroutine solves for constant alpha *****
      subroutine alpha(pm,ap,xp,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 Pf = K - 0.22 c0
c                    K = c1 - c2/T,  T(K)
c                    c0,c1,c2 = constants;     c2=3700
c for liquids:   P=Pf/Pvap(sat'd)
c Therefore  (P1/P2) = [Pf/Pvap(sat'd)]1/[Pf/Pvap(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/xp)*pHg*(cstp*td/pHg)
      return
      end
c
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(atm)
c td - drum temperature, K
      td=temp+273.2
c tO - reference temperature, K
      t0=298.15
c patm - atmospheric pressure (atm)
      patm=pHg/76.0
      dtk=df*(1./patm)*(td/t0)**1.823
      abeta=dtk*ad/xd
      return
      end

c ***** Subroutine calculates the ratio of Dvoc-air/DH2-Air  *****
      subroutine dvocair(apc,atc,amw,advocair)
      real apc,atc,amw,advocair,mwair,mwh2
c mwair, mwh2 - molecular weights of air, H2 (g/mol)
      mwh2=2.
      mwair=29.
c pch2, tch2 are critical temperature (K) and pressure (atm) of H2
      tch2=33.3
      pch2=12.8
c variables used for intermediate calculations start with a r
      rpc=(apc/pch2)**0.3333
      rtc=(atc/tch2)**(-0.495)
      rmw=((1./mwair+1./amw)/(1./mwair+1./mwh2))**0.5
c  advocair - Dvoc-air/DH2-air  (dimensionless)
      advocair=rpc*rtc*rmw
      return
      end

c ***** Subroutine calculates voc diffusion characteristic *****
      subroutine dcvoc(avc,advocair,dch2,adcvoc)
      real gamma,avc,advocair,dch2,rvc,vch2,adcvoc
```

```
c  gamma is a parameter indicating the distribution of pore
c  sizes in the filter (see EDF RWMC-643).
c  Value was determined based on experimental results.
      gamma=1.2
c vch2 is the critical volume of H2 (m3/kmol)
      vch2=65.
c  adcvoc - voc diffusion characteristic, D*voc, (mol/mol fraction/s)
      rvc=(vch2/avc)**0.333
      adcvoc=gamma*rvc*advocair*dch2
      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,adcvoc,y,n,pHg,temp,co)
      real a(4),adcvoc,y(9,4),q,yy(9,4),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=-adcvoc*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/(2.*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

c ***** subroutine prints output to file *****
      subroutine output(ly,y,vocid,ap,ad,xp,xd,pHg,temp,dch2,test)
      real y(9,4),ap(3),ad(3),xp(3),xd(3),temp,pHg,test,dch2
      character*21 vocid(9)
      integer n
      write(2,150)test
150   format('Trial 'f5.2)
      write(2,*)' '
```

```
      write(2,152)
  152 format('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('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('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('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:'
      if(ly.eq.4)then
        write(2,164)
  164   format('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('Compound',15x,'Drum*',3x,'Drum Liner',2x,'Large Bag',
     #  4x,'DH/LB')
        write(2,266)
  266   format('--------',15x,'------',2x,'----------',2x,'---------')
      end if
      do 200 n=1,9
        if(y(n,ly).eq.0)goto 200
        ratio=y(n,ly)/y(n,1)
        if(ly.eq.4)then
          write(2,168)vocid(n),y(n,4),y(n,3),y(n,2),y(n,1),ratio
  168     format(a21,2x,f6.1,4x,f6.1,5x,f6.1,5x,f6.1,7x,f5.3)
        else
          write(2,268)vocid(n),y(n,3),y(n,2),y(n,1),ratio
  268     format(a21,2x,f6.1,4x,f6.1,5x,f6.1,7x,f5.3)
        end if
  200 continue
      write(2,*)' '
      write(2,*)'*  Reference concentration'
      write(2,*)' '
      write(2,170)temp
  170 format('Drum temperature (C):',2x,f4.1)
      write(2,172)pHg
  172 format('Ambient pressure (cm Hg):',2x,f4.1)
      write(2,174)dch2
  174 format('Hydrogen diffusion characteristic across filter(mol/mol fr
     #action/s):',e12.5)
      return
      end
```