ENVIRONMENTAL EVALUATION GROUP

March 12, 2004

Mr. Steve Zappe
New Mexico Environment Department
Hazardous Waste Bureau
2905 Rodeo Park Drive East
Building 1
Santa Fe, NM 87505

Dear Mr. Zappe:

The US Department of Energy and Washington TRU Solutions (the Permittees) submitted a Class 2 Permit Modification Request (PMR) affecting **Drum Age Criteria (DAC)** to the New Mexico Environment Department (NMED) in January 2004.

Environmental Evaluation Group (EEG) staff members have performed an independent, technical review of this PMR and our comments are enclosed. Please feel free to contact me if you have any questions about our comments.

Sincerely,

Matthew K. Silva
Director

MS:SW:pf
Attachment

cc: Paul Detwiler, DOE/CBFO
     Steven Warren, WTS

040319

EEG Comments on the Class 2 Permit Modification Request submitted in January 2004 concerning Packaging-Specific Drum Age Criteria for New Approved Waste Containers

Summary and Conclusions

The US Department of Energy and Washington TRU Solutions (the Permittees) submitted a Class 2 Permit Modification Request (PMR) affecting Drum Age Criteria (DAC) to the New Mexico Environment Department (NMED) in January 2004. This modification would add package-specific DAC values for direct loaded 85-gallon drums, 100-gallon drums, and ten-drum overpacks (TDOPs). The new DAC values were calculated with the model specified in <u>Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations</u>[1], which was also used to calculate currently permitted DAC values. A similar PMR was submitted in May 2003, but that request was denied by NMED due to significant technical concerns. *It appears that some of those concerns were not addressed in the January 2004 DAC PMR.*

The Environmental Evaluation Group (EEG) used a conceptual model of an idealistic waste package to qualitatively understand the mathematical model used by the Permittees to calculate new DACs. This model was also used to form conclusions regarding the 13 May 2002 Class 3 DAC PMR. Details of the analyses are included. The current evaluation led to the following conclusions:

1. The Permittees have not provided adequate technical calculations, modeling results, or mathematical analyses to fully support the adequacy of the VDRUM model to calculate appropriate DAC values for wastes with multiple compacted drums containing plastic liners. Our conceptual model indicated that the VDRUM model may be sensitive to the volume of plastic liner material in waste containers. (p. 2-9)
2. EEG again found it difficult to determine which parameter values were used to calculate different DAC values. Again we recommend that the Permittees tabulate, in a central document, the values used for each parameter in every DAC scenario and include this in the public record. The Permittees should demonstrate that using reference values for a parameter or calculating that parameter inside VDRUM from other parameters does not affect the DAC result. (p. 9)
3. The question of VOC stratification, due to vapor density differences, inside large waste containers should be technically addressed by the Permittees. Specifically, the Permittees should determine whether or not stratification would affect the DAC time necessary to collect a representative sample. (p. 10-11)

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[1] Document reference number: INEEL/EXT-2000-01207, Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho [BWXT (2000)]

Specific Comments on the Class 2 PMR submitted in January 2004 concerning Packaging-Specific DACs for New Approved Waste Containers

<u>Questions on 55-gallon drums with plastic liners in 100-gallon drums</u>
In Attachment C of the current, January 2004 DAC PMR, the Permittees provided the assumptions and results of the VDRUM modeling effort used to calculate the new DACs. One of the assumptions for the 100-gallon drum was,

> In some cases, 55-gallon drums may be supercompacted and packaged as "pucks" directly into 100-gallon drums. Compacted 55-gallon drums containing rigid drum liners placed inside the 100-gallon drum must meet the appropriate 55-gallon drum DAC value established by the Permit [2] prior to compaction. This ensures that VOC solubility associated with the presence of the 55-gallon rigid drum liner does not impact the calculated DAC for a 100-gallon drum.

This last statement is also the assumption stated verbatim in Attachment C (also results of the VDRUM model) of the May 2003 DAC PMR.

EEG submitted comments[2] on the May 2003 DAC PMR to NMED and the Permittees. Included were the concerns that,

> When the 100-gallon drum is the container being sampled for headspace gas, the sorption of the liner would also potentially affect the gas dispersal from other compacted 55-gallon drums packaged in the 100-gallon drum and there would be a potential need for a correction factor to the 100-gallon drum DAC, not just that of the 55-gallon drum in its pre-compacted state. This might be the case, for example, if the [Volatile Organic Compounds] VOCs in the 55-gallon drum with the liner do not saturate the liner, but that drum is on top of the other compacted drums in the 100-gallon container that have VOC-emitting materials in them, in which case the liner could potentially absorb these VOCs until saturation is reached. The NMED may want to establish whether or not such a possibility would affect achieving steady-state equilibrium prior to approving this PMR.

and

> It was recognized by the Permittees that rigid drum liners in compacted 55-gallon drums would affect the transport of VOCs inside the 100-gallon drum, and it was prudent to allow time for the VOC/liner interactions to come into near equilibrium. However, DAC modeling is based on hypothetical drum systems that are closed except for filter vents. Crushing a drum that has been closed for some DAC period destroys the equilibrium (or near equilibrium) and essentially violates the closed system and basis for the DAC model. ... That is,

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[2] Letter from EEG to NMED with copies to Permittees dated 9 July 2003.

instead of waiting for a DAC then crushing the 55-gallon drum, the drum should be crushed, placed in the 100-gallon drum, then wait for the DAC because the system is closed. NMED should ask the Permittees to recalculate the DAC based strictly on closed system (except for filter vents) dynamics.

The Permittees responded[3] to the EEG comments with the following statements,

In the event that 55-gallon drums of different total VOC concentrations are placed together in a 100-gallon drum, VOC desorbtion from the rigid liners of the high VOC concentration drums may occur concurrent with VOC absorption from the rigid liners of the low VOC concentration drums. In this situation, VOCs would simultaneously be released from and absorbed by liner material. Unlike in a new drum with a rigid liner, VOCs are being released from the liner material into the drum headspace as well as being absorbed. The presence of liner material amidst the compacted 55-gallon drums does not impact the steady-state conditions in the 100 gallon drum.

and

The requirement for 55-gallon drums with rigid liners to meet the higher 55-gallon drum DAC values prior to compaction is conservative compared to the case where the crushed 55-gallon drums may include desorbing liner material. The presence of desorbing liner material would result in the 90% steady-state concentration being achieved more quickly than is represented by the proposed 100-gallon drum DAC values.

Therefore, the Permittees claimed, without supporting calculations or modeling efforts, that either the liners in the crushed 55-gallon drums do not affect the steady-state VOC concentration (and hence the time required to reach that concentration), or they can affect the time it takes to reach steady-state VOC concentration (although they did not take credit for the reduced time). In the Attachment to the letter[4] denying the DAC PMR, NMED stated,

The assumptions made by the Permittees that all compacted drums in a larger container would have the same source concentration (and hence the same rigid poly liner equilibrium concentrations) is not fully supported by information provided by the permittees. ...However, the Permittees' calculations did not account for the additional time needed for the exposed poly liners in the compacted drums to reach equilibrium with each other once they are placed in the larger container.

and

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[3] Letter from CBFO to Stakeholders dated 15 July 2003 with an enclosure titled Response to Public Comments.
[4] Letter to the Permittees from NMED dated 11 September 2003.

The Permittees did not fully support the adequacy of the VDRUM model to calculate appropriate DAC values for wastes with multiple VOC sources or sources that do not have constant VOC concentrations, as would be encountered in the compacted drum wastes. ... However, NMED questions whether this simplifying assumption is appropriate because the assumption of equivalent VOC [Head Space Gas] HSG concentrations within each compacted drum is not well supported, and therefore these compacted drums and their exposed poly liners would not be in equilibrium with each other when placed together in a container. The Permittees did not adequately account for the likelihood that poly liners with higher equilibrium concentrations would act as additional and non-constant VOC sources until a new equilibrium concentrations is reached within all the compacted rum ply liners. Based on the stated working assumptions of the VDRUM model, it is unclear if the VDRUM model can adequately support scenarios where there are multiple VOC sources with different and non-constant VOC concentrations DOE should consider these issues, and determine whether the VDRUM software is adequate for determining the DACs when multiple sources or sources with non-constant concentrations may be present.

EEG concurs with the NMED assessment, i.e. the Permittees did not demonstrate that containers with multiple VOC sources/liners, regardless of how long they sat before they were combined, could be adequately modeled using VDRUM. Additional modeling, calculations, or clarifying information to address the NMED concerns of the May 2003 DAC PMR were not present in the January 2004 DAC PMR, although it did state that,

This PMR incorporates responses to applicable stakeholder and New Mexico Environment Department (**NMED**) comments on the previous Class 2 PMR ... submitted on May 13, 2003 and is a resubmittal of the May 13, 2003 PMR. ... Many of the stakeholder and NMED comments focused on one particular use of 100-gallon drums to package super compacted 55-gallon drums. ...These comments requested technical information related to super compacted waste and suggested the need to perform additional DAC modeling for this waste. The CBFO has fully addressed these comments in a companion document entitled Response to Stakeholder and NMED Comments on the May 13, 2003 DAC Submittal. [underline added] The reason this information is a companion document is to emphasize that while the question and concerns expressed by stakeholders and the NMED regarding the super compaction process are valid, this PMR is only focused on simply establishing DAC values for specific packaging configurations using the accepted methodology.

However, a draft titled Response to Stakeholder and NMED Comments on the May 13, 2003 Permit Modification Request Entitled "Packaging-Specific Drum Age Criteria for

New Approved Waste Containers" was provided to EEG by the permittees on 6 March 2004. These responses to the NMED concerns were very similar to the responses made to EEG, e.g. the draft stated:

> The assumption in the model that all supercompacted drums in the larger container would have a constant source concentration is considered by CBFO to be conservative for the following reason: When multiple supercompacted drums are placed into a single 100-gallon drum, the potential exists for one supercompacted rigid drum liner to be saturated with VOCs while the others are not (e.g., 55-gallon drums containing waste with little or no VOCs). It is assumed that supercompaction of the waste reduces the resistance to diffusion across the 55-gallon drum and drum liner, resulting in a significant decrease in the VOC concentration surrounding the breached liner. Under this scenario, the VOC concentration in the 100-gallon drum is determined by the VOC concentration surrounding the supercompacted 55-gallon drum saturated liner. In this scenario, the saturated liner will desorb VOCs and the unsaturated liners will adsorb VOCs with the net result being that the 100-gallon drum concentration will remain nearly the same or may decrease. The DAC value is calculated as the time for the initial distribution to occur. Any sampling after this time will meet or exceed the 90% steady-state values. Therefore, the presence of the crushed 55-gallon drum liners will not negatively impact the calculated DAC for the 100-gallon drum.

and

> When multiple supercompacted drums are placed into a single 100-gallon drum, the potential exists for one supercompacted breached and crushed rigid drum liner to be saturated with VOCs while the others are not (e.g., supercompacted 55-gallon drums containing waste with little or no VOCs). When the 100-gallon container is closed, the saturated liner will desorb VOCs at a rate equal to or greater than the other liners will absorb VOCs. The net result is bounded by the case of a waste 55-gallon drum containing a liner assumed to be saturated before supercompaction.

Again, no calculations, modeling results, or mathematical analyses were provided by the Permittees in the draft to support the proposed capability of the VDRUM model. The additional, draft, 'companion' comments provided no further clarification on the capability of the model to accurately reflect the proposed drum configurations. Also, the lack of availability of an essential, referenced document during the majority of the public comment period, and then to issue a draft that did not respond to earlier public comments as suggested in the proposed title, may not have given some reviewers adequate time or reasons to respond to the current PMR.

In order to understand the possible behavior of the model under the assumptions and modifications used by the Permittees, EEG re-visited the conceptual model that was used in comments made on the 13 May 2002 Class 3 DAC PMR[5]. Figure 1 in that document (See Attachment A) was revised to reflect the concept of placing a compacted drum/liner with a source of VOCs into a 100-gallon drum with other compacted drum/liners with no VOCs.

Figure A. Diagram of a conceptual 100-gallon waste drum with inner lid and two
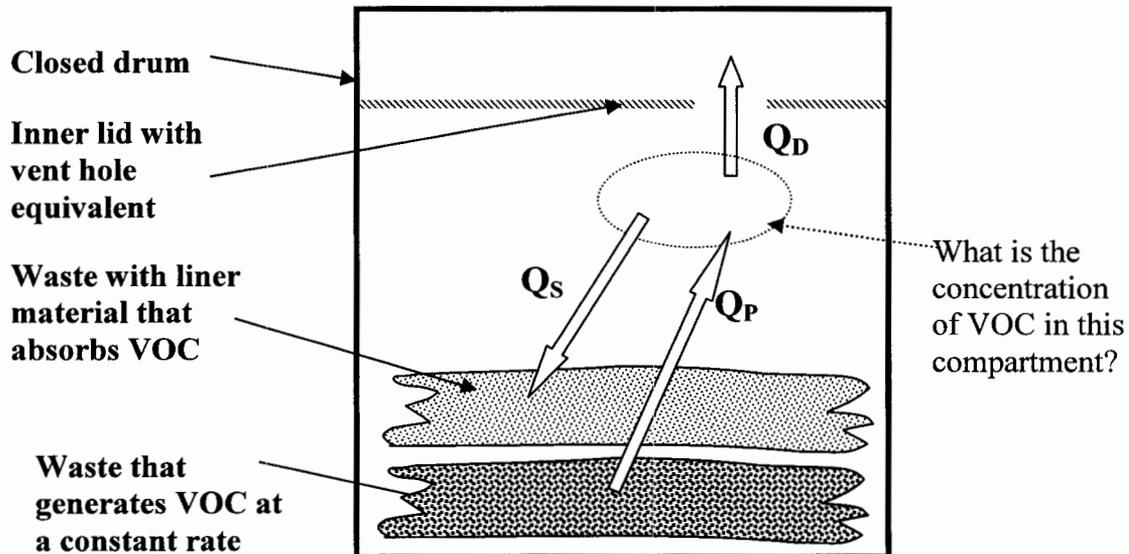
compacted 55-gallons drums with plastic liners. One drum had a source of VOC, the other did not.

For this conceptual model, a compacted drum inside a 100-gallon drum with no liner emits a VOC at a constant rate, but the VOC then permeate through a barrier at rate Q_p (mol s^{-1}). Another compacted drum containing rigid liner material acts as a sink for the VOC that are absorbed at rate Q_s. VOC may also leave the headspace through the filter vent (modeled as a hole of appropriate size) in the inner lid at rate Q_D.

All the equations from the previous work (Appendix A), which were based on the original VDRUM model by Connolly et al., apply in this case, but the model parameters will be modified in an attempt to simulate the assumptions made by the Permittees. The following table lists the parameters values used for this conceptual exercise. Note that this modeling effort, as with the previous work (Appendix A), was done to for a qualitative (vs. quantitative) understanding of the model performance. Actual values are used for methanol where possible to generate more realistic VOC concentration curves.

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[5] Letter dated 27 June 2002 to Steve Zappe containing an analysis titled Evaluation of DAC Mathematical Model.

Table A. List of parameters and values used in the modeling exercise. The source of the parameter values are listed in the notes.

| Parameter	Value	Notes
ρ	13.5×10^{-9} cm^2 s^{-1} cm-Hg^{-1}	Permeability coefficient thru plastic, (1)
A_P	0 cm^2	Bag diffusion cross section area, set to zero to simulate no inner bag (1)
P	76 cm-Hg	Pressure in drum (1)
X_P	0 cm	Thickness of plastic bags, set to zero to simulate no inner bag (1)
C_v	4.46×10^{-6} mol cm^3	Initial gas concentration used to calculate mole fraction difference (2)
V_o	40,000 cm^3	Drum headspace volume below inner lid (1)
D	0.152 cm^2 s^{-1}	VOC diffusivity in air for methanol (1)
A_D	150 cm^2	Cross sectional area of hole in inner lid, sized to represent flow through a filter vent (1)
X_D	1.4 cm	Diffusional path length across hole in inner lid (1)
V_D	40,000	Drum headspace volume, same as V_o since sample is taken inside inner lid (1)
$\acute{\eta}$	2.4×10^{-7} s^{-1}	Mass transfer coefficient (2)
φ	4.46×10^{-5}	Gas concentration constant at STP (2)
V_P	$3,550 - 14,200$ cm^3 (The Permittees used 0.64 cm^3)	Volume of rigid plastic liner, in this the Permittees set the liner thickness to 5×10^{-5} cm to simulate no liner
H	0.027 cm^{-3} voc cm^3 poly cm-Hg	Henry's constant (2)
s	0.042 cm^3 voc cm-^{3} poly cm-Hg^{-1}	Average VOC solubility in drum liner plastic (2)

(1) Input file 'T7000074', p. A-18, January 2004 DAC PMR
(2) Appendix A

It should be noted that the modeling exercise conducted for this paper was not intended to recreate any particular value of a DAC. It was done to ascertain, in a general way, how the mathematical model used to derive DACs would behave when certain input parameters were changed as proposed by the Permittees.

The question of whether or not additional compacted drums containing liner material and no VOC sources may be addressed in this model by allowing the V_P parameter (volume of rigid plastic liner material) to change. A rigid liner from a 55-gallon drum contains approximately 3,550 cm^3 of plastic. If one to four liners are crushed and placed into the 100-gallon drum, then V_P would vary discretely from 3,550 – 14,200 cm^3. The modeling results are shown in Figure B.

Figure B. Conceptual model output with all parameters in Table A held constant except for V_P, the volume of rigid liner plastic, which was allowed to vary discretely from 3,550 – 14,200 cm^3. The X-axis is time and the Y-axis is VOC concentration, but the units are arbitrary since this conceptual model was not intended to produce DAC values. The purpose of the model is to compare output results when input parameters are varied.
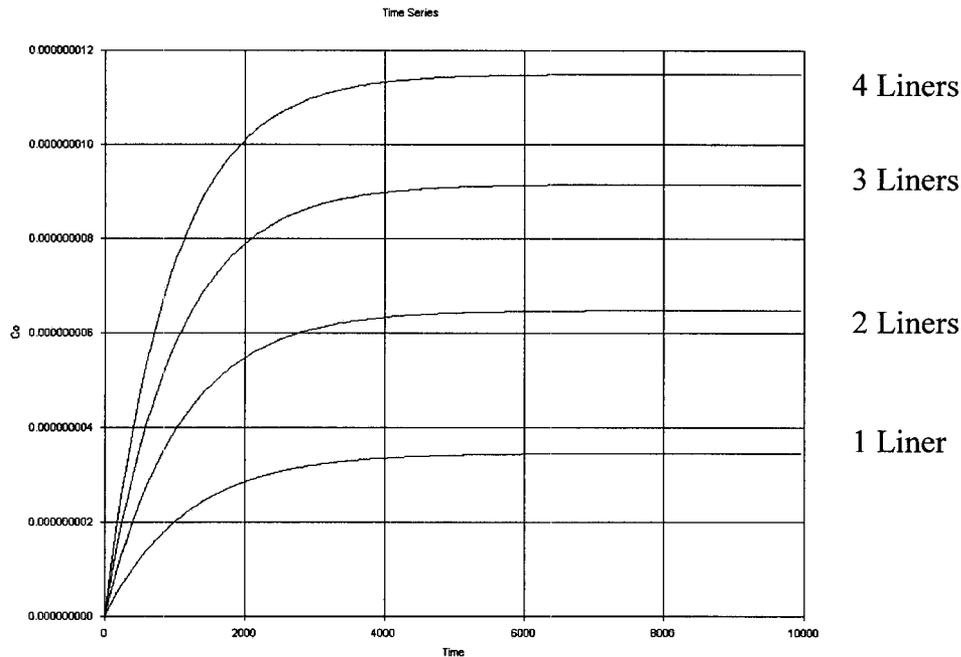
It appears that the model may be sensitive[6] to the amount of plastic rigid liner material that is in a 100-gallon drum. Although the actual DAC may not vary significantly based on the amount of liner material present in the container, the point is that the actual VDRUM model should be examined for such a possible sensitivity. The Permittees' comments to EEG and to NMED did not consider the volume of plastic, container material when they discussed the hypothetical movement of VOC inside a 100-gallon drum. However, in describing the equations used to create the VDRUM model, Connolly et al. (equation A-4, p. A-2, referenced in Appendix A) state that the rate of VOC accumulation, in part, is a function of how soluble the VOC is in the plastic and the total volume of plastic, V_P. Whether or not the plastic is breached, crushed, or placed in bags is not considered in the VDRUM model.

EEG disagrees with the Permittees' statement (p. 6 of the March 2004 draft 'companion' document) that, "The net result is bounded by the case of a waste 55-gallon drum containing a liner assumed to be saturated before supercompaction." Fig. B indicates that the equilibrium time, or DAC, may vary with the amount of liner material in the 100-gallon drum. If the Permittees do not assume that the 55-gallon drum liner is already saturated, then it becomes another liner that will absorb VOC and the DAC could actually be longer. The bounding case of a pre-saturated liner is also not supported

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[6] EEG did not analyze the sensitivity of the drum liner volume in the previous work (Appendix A) because it was considered a constant at that time.

because there does not appear to be a provision in the PMR to ensure that the time period between compacting a 55-gallon drum that has waited some DAC and packaging it in a 100-gallon drum with other drum liners won't be excessively long. In other words, to meet the assumption of a saturated liner, the 55-gallon drum containing VOC should not have the opportunity to desorb VOC from the liner into the air, rather than into another liner or the headspace of the 100-gallon drum.

EEG, therefore, based on a crude analysis of the sensitivity of the DAC calculational model, maintains that the Permittees have not supported their assumptions of the adequacy of the VDRUM model to simulate VOC transport inside the 100-gallon drum under certain conditions. EEG believes that the Permittees could simulate various waste packaging scenarios using the VDRUM input files, vary VDRUM parameters that may affect the scenarios, run and re-run the actual VDRUM code, and report the results of such experiments to clarify and support their assumptions in a more technical manner.

EEG continues to urge that future DAC PMRs contain tabulated parameter values for the VDRUM model (see Table A) to clarify which parameters were changed between assumptions and why they were changed. For example, input files 'T7000074' (p. A-18 of the January 2004 DAC PMR) and 'T7037074' (p. A-9) list the methanol diffusivity in air as 0.152 cm^2 s^{-1} and 0 cm^2 s^{-1}, respectively; and the VOC mass transfer coefficients as 6.5 x 10-5 s^{-1} and 0 s^{-1}, respectively; with all other VOC specific parameters being the same for methanol between the two files. Such parameter switching was evident for other VOCs in the input files, but the reasons for them appear to be undocumented[7]. Since these are VOC specific and constant parameters, the NMED may want to request that the Permittees demonstrate that changing the parameters has no effect on the reported DAC results.

Questions on VOC headspace concentrations considering vapor densities

A question was posed at the 19 February 2004 public meeting in Santa Fe, NM on the DAC and other PMRs that concerned the possible settling of VOC vapors in the bottom of containers such that a sample taken in the headspace at the top of the container may not accurately reflect the concentration of VOC in the container. All the VOC listed as analytes of interest in the WIPP Hazardous Waste Facility Permit (HWFP Table B-3) have vapor densities (defined in various references in Appendix B of this paper) greater than air (Table B), so the vapors from them may settle in the bottom of waste containers.

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[7] After discussions with the K. Liekhus on 10 March 2004, EEG understands that D (VOC diffusivity in air parameter) may be calculated from other VOC parameters, but the reasons why it is listed in one case and calculated in another case remain unclear.

Table B. Vapor Densities of the Volatile Organic Compounds listed in Table B-3 of the WIPP hazardous waste facility permit. All the compounds have vapor densities greater than air (>1.0).

Compound	Molecular Formula	Vapor Density Value
Benzene	C_6H_6	2.71
Bromoform	$CHBr_2$	6.00
Carbon tetrachloride	CCl_4	5.32*
Chlorobenzene	C_6H_5Cl	3.91
Chloroform	$CHCl_3$	4.11
1,1-Dichloroethane	$C_2H_2Cl_2$	3.37
1,2-Dichloroethane	$C_2H_2Cl_2$	3.37
1,1-Dichloroethylene	C_2HCl_2	3.33
(cis)-1,2-Dichlorethylene	C_2HCl_2	3.33
(trans)-1,2-Dichlorothylene	C_2HCl_2	3.33
Ethyl Benzene	$C_6H_5C_2H_5$	3.69
Ethyl ether	$(C_2H_5)_2O$	2.57
Formaldehyde	HCHO	1.04
Hydrazine	N_2H_4	1.11
Methylene chloride	CH_2Cl_2	2.95
1,1,2,2-Terachloroethane	$C_2H_2Cl_4$	5.83
Tetrachloroethylene	C_2Cl_4	5.76
Toluene	$C_6H_5CH_2$	3.16
1,1,1,-Trichloroethane	$C_2H_3Cl_3$	4.63
Trichloroethylene	$C_2 H Cl_3$	4.53*
1,1,2-Trichloro-1,2,2-trifluorethane	$C_2 Cl_3 F_3$	6.4*
Xylenes	$C_6H_4(CH_3)_2$	3.69
Acetone	CH_2COCH_3	1.98
Butanol	$C_4H_{11}OH$	2.64
Methanol	CH_2OH	1.08
Methyl ethyl ketone	$CH_3COC_2H_5$	2.50
Methyl isobutyl ketone	$C_6H_{12}O$	3.48

(*Reference: Properties of Common Refrigerants, p. E-34, CRC Handbook of Chemistry and Physics, 67th Ed.)

It seems possible, therefore, that the greatest concentrations of most VOCs could be at the bottom of the containers. If a concentration gradient exists the problem of collecting a representative gas sample in the headspace would be worse for taller containers such as the TDOP. This concern was not addressed during the formulation of the VDRUM model perhaps because empirical testing was done on 'cut-down' 55-gallon drums (See Connolly et al. referenced in Appendix A), or sludge drums where heavy vapors had no room to settle at the bottom.

The Permittees addresses this concern in a draft document titled Stratification Scenario that was e-mailed to EEG on 6 March 2004. It reads:

> A scenario which proposes that molecules in a system naturally separate into unique and orderly stratifications occupied by different compounds as a result of density differences is in direct contradiction to the second law of thermodynamics.
>
> The mixing of two materials is enhanced by several factors including,
>
> 1. Low interfacial tension that inhibits the formation of interfaces
> 2. Similar densities that prevent separation by stratification induced by gravity and centrifugal fields
> 3. Low viscosities that promote fluidity and the penetration of one fluid element into another.
>
> Materials that fulfill the above requirements mix almost spontaneously (e.g. gas mixing, alcohol-water mixing).
>
> The density differences between air and air containing VOCs is negligible and there is no basis to expect stratification of gas phases that contain VOCs.
>
> Mixing is a natural and irreversible process. Stratification or any separation process that concentrates a compound requires a mechanical process to reverse the mixing process. Since no such process is present in the waste drums, there is no basis to expect compound stratification in the waste or packaging container.

The first statement by the Permittees does not seem to apply in this case. Although EEG does not deny that entropy is increasing, it cannot deny that stratification based on density is possible. For example, a real-world example of stratification may be seen in every garage with a gas water heater. Safety codes require that they be lifted well above the floor level to prevent the ignition of VOC vapors (gasoline, etc.) that tend to stratify in air and collect near the floor.

EEG does not agree that the densities of air and some VOCs are similar. Many of the compounds listed in Table B have densities 300 – 600 % greater than air. Furthermore, EEG does not understand the concept that VOC vapor properties are based on mixtures of VOC and air. The VDRUM model uses parameter values such as solubility, permeation, and mass transfer based on the VOC, not on a dilution of vapor and air. If the Permittees wish to claim that "The density differences between air and air containing VOCs is negligible…," then they should provide air/VOC concentrations that bound their assumption.

EEG is not recommending that vapor mixing is necessary in order to collect a representative sample in the headspace. However, we are concerned that the subject of vapor stratification has not been considered in headspace gas sampling or in DAC calculations. NMED may wish to further explore this topic as it relates to sampling in waste containers and in the disposal rooms.

Attachment A

Evaluation of DAC Mathematical Model

Introduction

Each container shipped for disposal at the WIPP must be sampled for VOC, but VOC migrate from the waste to the sampling site inside the containers at rates that depend on a number of factors. Therefore, the DAC is a prescriptive waiting period to ensure that enough time has elapsed between packaging the waste and sampling for VOC so that the measured VOC adequately characterizes the total VOC in the containers. DACs are calculated from chemical vapor transport theory and equations.

The current Hazardous Waste Facility Permit (HWFP) requires DACs of 142 and 225 days (d) depending on the type of waste/packaging. The US Department of Energy and Westinghouse TRU Solutions LLC, the permittees, have proposed new DACs as short as 4 d based on new calculations of VOC migration in various waste packaging configurations. The permittees have cited three reports by Connolly et. al. (1998), Liekhus et. al. (1999), and Liekhus et. al. (2000) that describes the original calculations of the 142 d and 225 d DACs and the changes proposed for new DACs.

This paper describes an effort to qualitatively (vs. quantitatively) understand the mathematical model used to calculate the DACs and to form a conclusion as to whether the newly calculated DACs may be adequate to ensure that VOC sample results reflect the total VOC quantity in the containers and ultimately, if the new DACs provide the same level of safety for New Mexico citizens as the current DACs. Comments will also be offered concerning the adequate documentation of mathematical input parameters, output presentations, and confirmation of the facts of the waste/packaging before selecting a DAC.

Method

A conceptual model of an idealistic waste package was used to visualize VOC transport and to build a simple mathematical model to describe it. Figure 1 is a diagram of closed waste drum with a plastic drum liner (and vent hole) with waste contained in a single, sealed plastic bag. The permittees have proposed both more and less complex scenarios and calculated DACs for them. All the equations used in this analysis were from the original study on calculating DACs (Connolly 1998) because the permittees stated that the subsequent new DACs were based on these equations. Using a simple arrangement for this evaluation helps in the understanding of the model behavior more than in the actual results produced.

The VOC accumulation in the drum liner compartment was modeled for simplicity. VOCs enter this compartment by permeation through the plastic bag at rate Q_P and leave the compartment by diffusion through the vent hole, rate Q_D, and absorbing into the plastic liner at rate Q_S. The original study conservatively (and appropriately) assumes that the waste continues to generate VOCs at a constant rate.

Figure 1. Shown is a diagram of a conceptual waste container. The compartment of interest for this analysis is the void within the drum liner. Also shown are the VOC transport vectors.
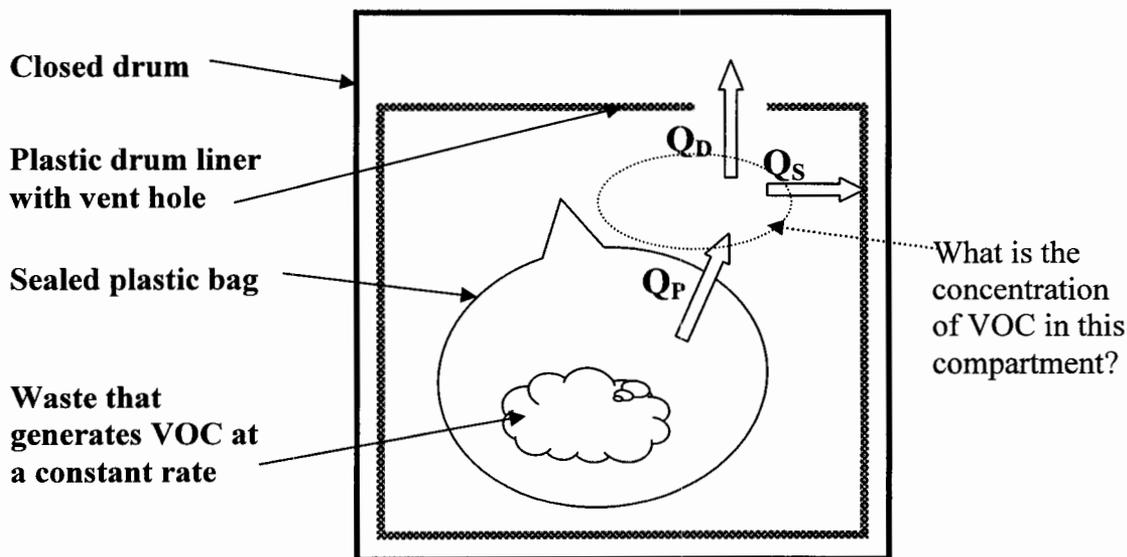
The change in the VOC concentration, or overall rate at which VOCs enter the compartment (Q, in the units of moles per second, mol s^{-1}) is simply the sum of the individual rates:

$$Q = Q_P - Q_D - Q_S$$

where Q_D and Q_S are negative because VOCs are leaving the compartment. The concentration (C, in units of moles per cubic centimeter, mol cm^{-3}) in the compartment at some time (t) may be expressed as:

$$C = \frac{Q \cdot t}{V}$$

where V (cm^3) is the volume of the compartment of interest. However, the rates are time dependent, that is, the rates change with time. It is important, therefore, to find when the rate of change of the concentration is zero (at steady state) because the VOC concentration will be same anywhere in the system, i.e., it will be the same at the sampling location as it is next to the waste. To find the change in concentration with a change in time, one must differentiate the concentration equation, or:

$$dC = \frac{Q}{V} dt \xrightarrow{\text{or}} \frac{dC}{dt} = \frac{Q}{V}$$

Usually in a complex, dynamic system of material flow between compartments, several differential equations will be solved simultaneously. For this paper, the single differential equation was solved numerically using a fourth –order Runge-Kutta method (Kirchner 2002) to generate time series graphs of the concentration (Figure 2).

The primary purpose of this experiment was to observe how the concentration varies with changes in the parameters that describe the waste or waste packaging. For example, the thickness of the plastic bag surrounding the waste is represented by the "X_P" term in the permeation rate (Q_P) equation. Changing individual parameters to observe the model output is known as a sensitivity analysis, i.e., which parameter causes the greatest change in the results or to which parameters is the model most sensitive. This was accomplished using a software program designed to estimate the uncertainties in model output given the uncertainty in parameters (Kirchner 2002). For each test, all the parameters were held constant except for one that was allowed to vary over a specified range. The results of the sensitivity analysis are shown in Figures 2 and 3.

The equations for these rates and the parameters are described in Connolly et. al (1998) and are repeated below for completeness and comment. A full dimensional analysis was also performed to ensure that the units of each parameter were valid for the DAC model.

The rate of VOC **permeation** through the plastic bag, Q_P, is described as:

$$Q_P = \frac{\phi \rho A_p P}{X_P} y_P$$

where

- ϕ ("psi") gas concentration constant at standard temperature and pressure (STP) = 4.46×10^{-5} (mol cm^{-3})
- ρ ("rho") VOC permeability coefficient which is different for each chemical compound, allowed to vary between 1×10^{-8} and 10×10^{-8} (cm^3 cm cm^{-2} s^{-1} cm-Hg^{-1}) for this experiment, although Connolly et. al. (1998) reported permeability values between $0.15 \times 10^{-8} - 23 \times 10^{-8}$ (cm^3 cm cm^{-2} s^{-1} cm-Hg^{-1}).
- A_P permeable surface area of plastic bag, 6,000 cm^2 was chosen as a nominal value
- P gas pressure inside container, constrained to be at STP throughout the container (76.0 cm-Hg) in this model

Figure 2. Crude Sensitivity Analysis on DAC Model
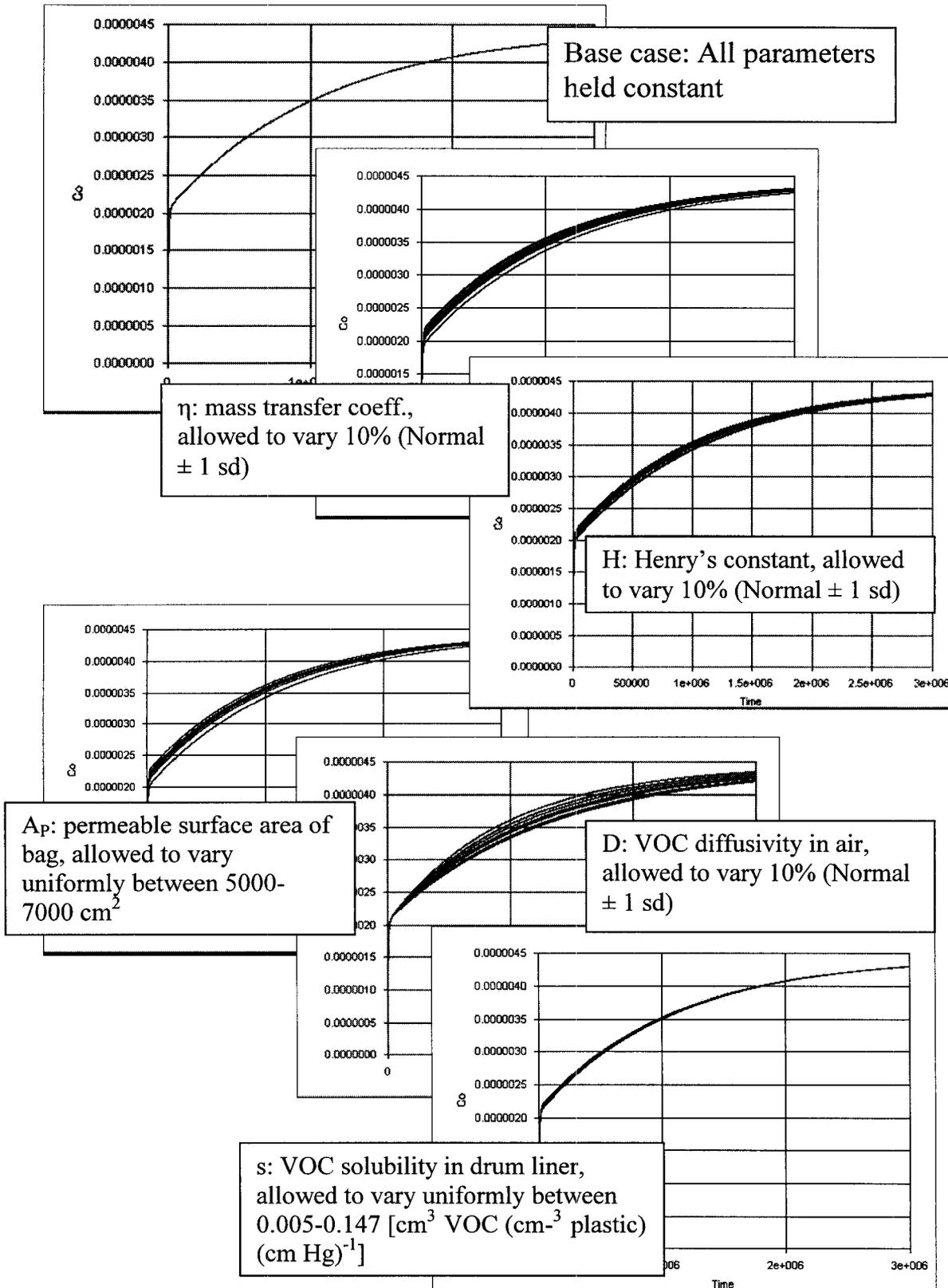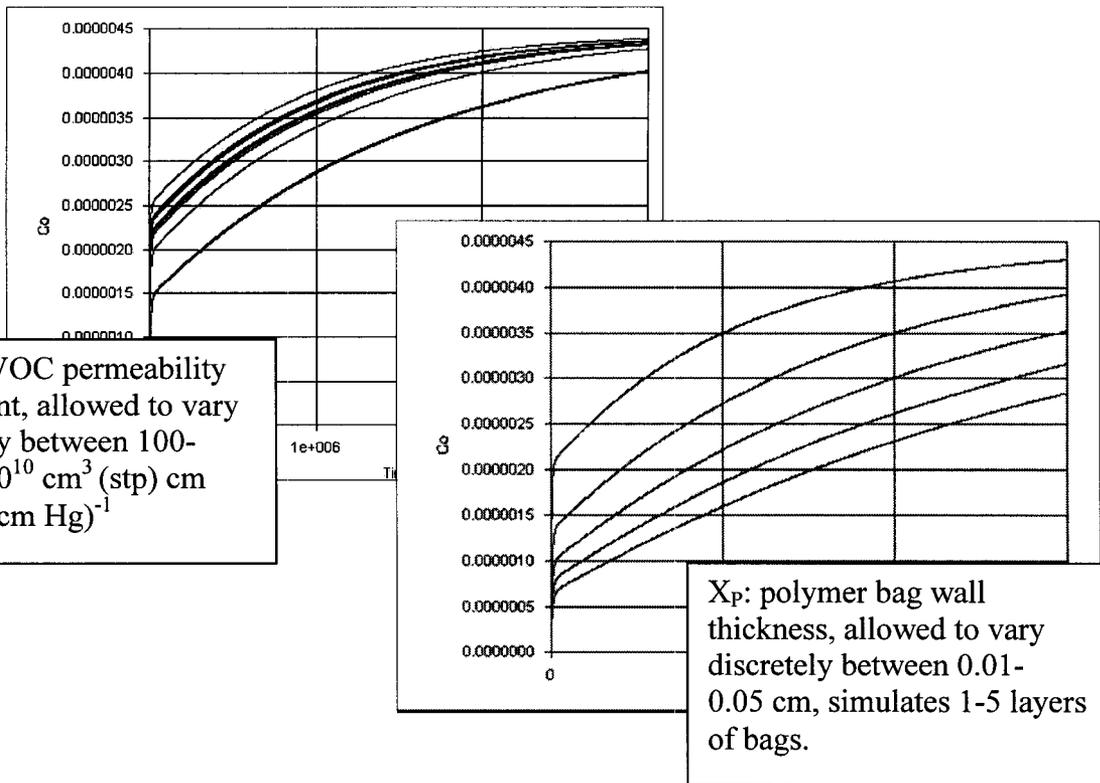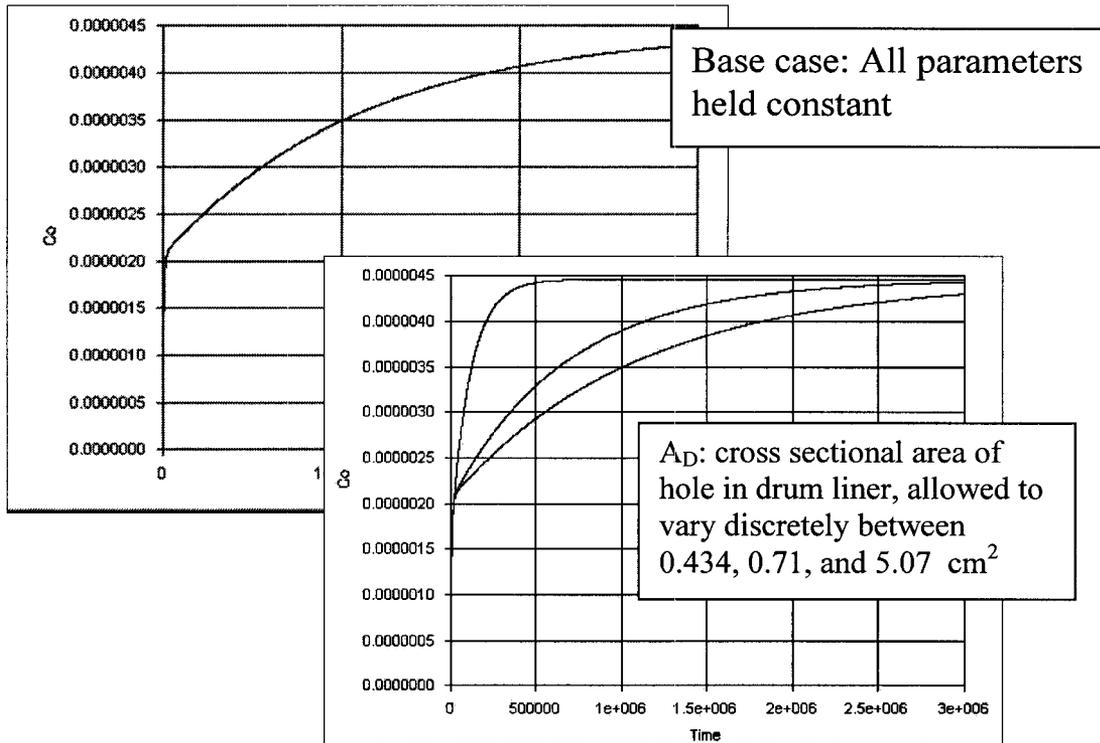**Parameters having little effect on model output.**

Figure 3. Crude Sensitivity Analysis on DAC Model – continued
Parameters having significant effect on model output.

Base case: All parameters held constant

A_D: cross sectional area of hole in drum liner, allowed to vary discretely between 0.434, 0.71, and 5.07 cm^2

Rho, ρ: VOC permeability coefficient, allowed to vary uniformly between 100-1000 x 10^{10} cm^3 (stp) cm cm^2 s^{-12} (cm Hg)$^{-1}$

X_P: polymer bag wall thickness, allowed to vary discretely between 0.01-0.05 cm, simulates 1-5 layers of bags.

X_P thickness of plastic bag in cm, 0.01 cm was chosen as the nominal value in this test. Note, Connolly et. al. (1998) varied this value to simulate the number of layers of plastic bags that a VOC would have to permeate to get to the head space of a drum

y_P VOC mole fraction difference across plastic bag. The mole fraction difference, y_P, is essentially the difference in concentrations, or quantities of VOCs, on either side of the plastic bag. If C_i and C_o are the VOC concentrations inside and outside the bag, respectively, another way to write y_P is:

$$y_P = \frac{C_i}{\phi} - \frac{C_o}{\phi} = \frac{1}{\phi}\left(C_i - C_o\right)$$

and the permeability equation reduces to:

$$Q_P = \frac{\rho A_P P}{X_P}\left(C_i - C_o\right)$$

Please note that Co is the concentration or compartment of interest in this current work. The rate of **diffusion** through the hole in the drum liner lid is expressed by Q_D (mol s^{-1}):

$$Q_D = \frac{CDA_D}{X_D} y_D$$

where

C   concentration of gas (mol cm^{-3}). Connolly et. al. (1998) did not describe this concentration well. It was assumed to be equal to φ for the current test.

D   coefficient describing the VOC diffusivity in air, a nominal value of 0.152 cm^2 s^{-1} was used

A_D cross sectional area of the hole in the drum liner lid (cm^2), set at 0.4, 0.79, and 5.0 cm^2, corresponding to 0.3, 0.375, and 1.0 inch diameter holes respectively

X_D diffusional path length across drum liner lid, set at a nominal value of 1.2 cm

y_D VOC mole fraction difference across drum liner lid. Using the same technique as the permeation equation, the diffusion equation may be reduced to:

$$Q_D = \frac{DA_D}{X_D}\left(C_o - C_D\right)$$

where C_D is the VOC concentration in the drum head space. The final rate equation is to describe how fast VOCs absorb into the plastic drum liner material, or the **solubility** rate, Q_s (mol s^{-1}) of the VOCs:

$$Q_s = \eta \phi V_p P [s_\infty - s]$$

where

η   mass transfer coefficient (s^{-1}). Connolly et. al. (1998) derived this coefficient experimentally, but did not list a table of the researched values. A nominal value of 2.4 x 10^{-7} s^{-1} was selected for this test from the given FORTRAN code examples.

φ   ("psi") gas concentration constant at standard temperature and pressure (STP) = 4.46 x 10^{-5} (mol cm^{-3})

V_p volume of plastic in the drum liner, taken to be the product of the given drum liner surface area (15,500 cm^2) and its given thickness (0.229 cm), or constant at 3,550 cm^3

P   gas pressure inside container, constrained to be at STP throughout the container (76.0 cm-Hg) in this model

s   average VOC solubility in drum liner plastic with the units [cm^3 (VOC at STP] [cm^{-3} polymer] [cm-Hg]$^{-1}$. The nominal value of 0.01 [cm^3 (VOC at STP] [cm^{-3} polymer] [cm-Hg]$^{-1}$was derived from the equilibrium concentration values listed by Connolly et. al. (1998) in Appendix D. Note that the values in the appendix had to be transformed (by dividing by P) because the units listed were not what was required by the equation.

s_∞ VOC equilibrium solubility in drum liner plastic with the units [cm^3 (VOC at STP] [cm^{-3} polymer] [cm-Hg]$^{-1}$. This value was estimated by:

$$s_\infty = \frac{y_v}{H}$$

where y_v is the volume average VOC mole fraction in the gas near the plastic drum liner and H is the VOC Henry's constant for the liner. The value of 0.027 [cm-^{3} (VOC at STP] [cm^3 polymer] [cm-Hg] was used in this trial because it was used as an example value in the FORTRAN code. Even with some concern about Henry's constant for toluene and cyclohexane, values for this constant were not listed in Connolly et. al. (1998). It is important to note that y_v is a mole fraction and not a mole fraction difference as used in the previous equations. If it were rewritten as C_o/ϕ (the fraction of VOC in the entire gas inside the liner), then the **solubility** equation may be written:

$$Q_s = \eta \phi V_p P \left[\frac{\left(\dfrac{C_o}{\phi}\right)}{H} - s \right]$$

The final differential equation used in this evaluation of the DAC model is:

$$\frac{dC}{dt} = \frac{Q}{V} = \frac{Q_P}{V_o} - \frac{Q_D - Q_s}{V_D}$$

where V_o is the void volume inside the drum liner and V_D is the void volume in the drum headspace, fixed at 40,000 cm^3 and 28,000 cm^3 respectively (Connolly 1998).

The differential equation was solved by the uncertainty software (Kirchner 2002) and the concentration results were plotted (Figs. 2 and 3). Then selected parameters were given a range of values over which they may vary and the model was re-run ten times using the range of values. Each result was plotted with the others to compare the effect of varying the parameter.

Discussion

It should be strenuously noted that the modeling exercise conducted for this paper was not intended to recreate any particular value of a DAC. It was done to ascertain, in a general way, how the mathematical model used to derive DACs would behave when certain input parameters were changed as proposed by the permittees. The model presented by Connolly et. al. (1998) appears to represent the theoretical kinetics of gas movement well. That is, given nominal values of input parameters, the output time/concentration curves seem reasonable, at least on a visual, qualitative basis.

It appears clear, based on Figure 3, that the diameter of the hole in the drum liner lid (A_D) and the thickness (or number) of plastic bags containing the waste (X_P) have a pronounced impact on how fast the VOC will reach equilibrium concentration. This confirms the permittees' claims that package configurations where these values are optimized will result in shorter DACs. One may conclude, also from Figure 3, that the permeability coefficient (ρ or rho) might significantly affect the DACs as well. This suggests that the time to reach equilibrium concentration throughout the drum is VOC dependent and not strictly packaging dependent as suggested by Liekhus et. al. (2000).

The sensitivity of the DAC to these three parameters requires that the measurements or other methods used to determine the values of the parameters be checked very carefully. On the other hand, using the most conservative known values may be necessary. Acceptable Knowledge programs will be crucial to ensuring that the correct DAC has been selected.

The abbreviated modeling exercise described in this paper did not fully investigate all the DAC claims by the permittees. The experiment also did not examine the possible effects of correlating parameters, i.e., varying two or more parameters at the same time. It does, however, demonstrate a modern method that may be used to display the results of concentration calculations graphically so that any reader may see that equilibrium in the system is being reached near the DAC time. The old adage is still valid that a graphic is worth a thousand words. It would be to the permittees' advantage to graphically represent each DAC scenario so that the public would understand that there were solutions to the differential equations that resulted in DACs.

One of the most difficult tasks of this simple modeling exercise was the compilation of correct parameter values. These values were found scattered between

appendices and documents and may have had different units in each. One example of this was the permeability coefficient (ρ). One can only imagine how easy it would be to confuse parameter values in a more complex scenario using more differential equations and more variables. It is highly recommended, therefore, that the permittees tabulate, in a central document, the values used for each parameter in every DAC scenario. Such a document of clearly described parameter values would be important for the public record.

References

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Kirchner, T.B.. Uncertainty Calculator, Windows 95/98/NT version [software]. ModelWright Software, 1307 S. Country Club Circle, Carlsbad, NM 88220. 2002.

Liekhus, K.J., Djordjevic, S.M., Devarakonda, M., Connolly, M.J.. Determination of transuranic waste container drum age criteria and prediction factors based on packaging configurations. Idaho National Engineering and Environmental Laboratory, Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho 83415. INEEL/EXT-99-01010. November 1999.

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Appendix B. Various citations from world wide web sites defining vapor density.

1. Reference: http://www.ehs.cornell.edu/lrs/chp/16b.MSDS.Howto.htm

Vapor Density: This figure tells whether the vapor is lighter or heavier than air. The density of air is 1.0. A density greater than 1.0 indicates a heavier vapor, a density less than 1.0 indicates a lighter vapor. Vapors heavier than air (gasoline vapor for instance) can flow along just above the ground and can collect in depressions where they may pose a fire and explosion hazard.

2. Reference: http://www.lungusa.org/occupational/read.html

Vapor Density. The weight of vapor or gas compared with an equal volume of air. Air has been assigned a value of one. Vapors that are heavier than air, such as gasoline or hydrogen sulfide, have a vapor density greater than one and accumulate in low places, along floors, in sewers, tank bottoms, manholes and elevator shafts where they may create fire or health hazards.

3. Reference: http://www.trconsultinggroup.com/safety/oct2001.html

Chemicals that have a vapor density greater than one will be found in the bottom of storage containers and will tend to migrate downhill and accumulate in low lying areas. Chemicals that have a vapor density which is the same or less than the vapor density of air will disperse readily into the surrounding environment.

4. Reference: http://www.aps.anl.gov/xfd/tech/safetyenvelopes/safetyguide6_2.htm

1. The vapor density of a flammable material is the density (mass to volume ratio) of the corresponding vapor relative to air under specific temperature and pressure conditions. Flammable vapors with densities greater than unity (and thus "heavier" than air) are potentially lethal because they will accumulate at floor level and flow, with remarkable ease, in much the same manner that a liquid would. The obvious threat is that these mobile vapors may eventually reach an ignition source, such as an electrical outlet.

5. Reference:
http://www.stanford.edu/dept/EHS/prod/aboutus/documents/safetyman/guidetomatsafety.html

Vapor Density at Bp (Air = 1): A comparison between the weight of the substance's vapor and that of air. Will the vapor rise or sink?

6. Reference: http://server.firehouse.com/training/hazmat/studies/1995/05_liquids.html

Another physical characteristic that affects the travel of vapor is vapor density. Vapor density is the relative weight of the vapor compared to the weight of air. Air is given a hypothetical weight value of 1.0. So if the vapor of a material has a density greater than 1.0 it is considered to be heavier than air so the vapor will lay low to the ground or collect in confined spaces and basements. This can cause problems because many ignition

sources in basements, such as hot water heater pilot lights, are low to the floor. If the vapor density is less than 1.0 the vapor is considered to be lighter than air so it will go up and travel farther away from the spill.