VOC RISKS IN THE PERMIT

In order to evaluate the impacts of redistributing the risk and to demonstrate that the proposed reapportionment does not increase the overall risk to surface workers, it is necessary to understand the risk model that was used to establish the risk limits in the Permit. There are three principle components of the model: the source term, the pathway, and the receptor. These are explained below along with sample calculations using the concentration limits for disposal rooms specified in the Permit.

SOURCE TERM

The source term is characterized by two factors, the chemical and its concentration. The chemicals of interest are the nine volatile organic compounds listed in Module IV of the Permit for the VOC Monitoring System. Six of the compounds are listed by the US Environmental Protection Agency as suspected human carcinogens. Three are non-carcinogens. This distinction is important in determining how the compound affects the receptor. The following compounds are suspected human carcinogens:

- 1,1,2,2-Tetrachloroethane
- 1,1-Dichloroethene
- 1,2-Dichloroethane
- Carbon Tetrachloride
- Chloroform
- Methylene Chloride

The concentration is a variable since it may be different in each container. The common practice is to use an average concentration, as described in the WIPP Permit Application, DOE/WIPP 91-005, Rev. 6, Appendix C2 and D9. The concentrations in the Permit Application were derived from measurements on a population of containers stored at the Idaho National Laboratory. When calculating the risk due to the disposal of specific waste, the concentration is an input to the calculations. However, when calculating the risk-based limits for a facility, such as the WIPP facility, concentration becomes an output in the form of a Permit limit that assures the risk is within acceptable limits.

The source term is expressed in concentration units, usually parts per million by volume (ppmv). Generally, risk calculations use different units of concentration, expressed as the mass of the compound per unit volume. Therefore it is necessary to convert each compound from ppmv to units such as micrograms per cubic meter (µg/m^3). This is done by applying the ideal gas law and converting the volume units. The parameters are the molecular weight ($\boldsymbol{MW_{VOC}}$) of the compound in g/mole, the temperature (***T***) in degrees Kelvin, the pressure (***P***) in kilopascals (kPa), the volume (***V***) in liters (L), and the number of moles of the compound (**n**). Under repository conditions, T= 299 K and P = 101.325 kPa. The Gas Law (***PV = nRT***) can be written as V (L) = n (mol) * [8.31 (kPa L/K mol)*299K]/(101.325 kPa) = n (mol) * 24.45 L/mol.

In order to convert a gas concentration in ppmv to µg/m^3, the first step is to calculate the fraction of each mole of gas that contains the VOC of interest (referred to as the mole fraction, MF_{VOC} in mol/mol). This is done by dividing the concentration by 1,000,000 and expressing it as moles of VOC per mole of gas. Multiplying this by the molecular weight gives the number of grams of VOC per mole of gas; multiplying by 1,000,000 yields the number of µg/ mol of gas; since a mole of gas occupies 24.45 liters at repository conditions, the concentration of VOC can be converted to µg/m^3 by dividing by 24.45 L/mol and multiplying by 1,000 L/m^3. This initial set of calculations is shown in Table 1.

TABLE 1 Conversion of VOC Concentration from ppmv to µg/m^3

		Carbon Tetrachloride	Chlorobenzene	Chloroform	1,1, - Dichloroethylene	1,2-Dichloroethane	Methylene Chloride*	1,1,2,2-Tetrachloroethane*	Toluene	1,1,1-Trichloroethane
Concentration*	ppmv	9,625	13,000	9,930	5,490	2,400	100,000	2,960	11,000	33,700
MF_{VOC}	mol/mol	0.009625	0.013	0.00993	0.00549	0.0024	0.1	0.00296	0.011	0.0337
MW_{VOC}	g/mol	153.84	112.56	119.39	96.95	98.97	84.94	167.86	92.13	133.42
Concentration	µg/m^3	6.06E+07	5.98E+07	4.85E+07	2.18E+07	9.71E+06	3.47E+08	2.03E+07	4.14E+07	1.84E+08

*Concentrations shown are the room based limits in Table IV.F.3.b of the Permit

PATHWAY

The pathway is perhaps the most complex part of the assessment. It must account for VOCs being released from containers into repository areas that are either open to ventilation or closed to ventilation. Once in the air stream, the VOCs are emitted from a stack, and dispersed in the vicinity of the receptors. The emission rates from the containers are variable depending on the type of filter that is used on the container and the concentration gradient across the filter (Filter diffusivity, D_{voc} in mole/s/mole fraction/drum). Default values for an NFT 013 filter were used, although values for other types of filters can be determined by comparing the mobility of VOCs in air to the mobility of Hydrogen in air. Once the waste is disposed, the VOC will exit the drum and be diluted in the repository air stream. Three different air streams are of interest: room ventilation (V_{ROOM}); E-300 ventilation ($V_{E\text{-}300}$) and total ventilation (V_{TOTAL}). These are expressed in cubic feet per minute. A flow in cubic feet per minute is converted to cubic meters per minute by multiplying by 0.0283 cubic meters per cubic foot.

In order to quantify how much of the source term becomes available for exposure at the receptor, it is first necessary to determine the rate at which the VOC diffuses out of the drum (ADE_{VOC} in moles/year/drum). This can be calculated as the product of the mole fraction of the VOC in the drum times the diffusion rate for that VOC, converted from

seconds to years (31,536,000 seconds per year). By multiplying this by the number of drums in an open room, the emission rate from an open room (***AORE***$_{VOC}$) can be calculated in moles/room/year. The number of containers is assumed in the original calculation is 81,000 drums per panel with these being evenly distributed over the 7 rooms of a waste panel.

The greatest emission rate will occur when 9 of the panels are filled and closed; six rooms in the remaining panel are filled and ventilation barriers are in place, and the last room is filled but still ventilated. Each case has a separate emission rate. For closed areas, the emission from behind the closures is driven by gas generation and creep closure. This is derived in the Permit Application and is set at 0.5 moles of gas per drum per year (***GR*** in moles per drum per year). Diffusion does not have a role in this calculation. The closed areas are assumed to be at the average concentration of the VOC in the headspace of the containers in the room, therefore, the emission rate for any VOC (***ACRE***$_{VOC}$ in moles/room/year) is simply the product of the ***MF***$_{VOC}$ times the number of drums times ***GR***. The rate for a closed panel is 7 times this number while the rate for an open panel (***AOPE***$_{VOC}$ in moles/room/year) consisting of 6 filled rooms with ventilation barriers and one filled room without a barrier is 6 times ***ACRE***$_{VOC}$ plus ***AORE***$_{VOC}$ in moles/room/year.

The next part of the pathway is the ventilation system to the Exhaust Shaft. Calculation involves assuming the continual release of VOC into the active ventilation system. The amount released can be calculated as a concentration at the Exhaust Shaft individually from each closed panel (***SCPE***$_{VOC}$ in µg/m^3) and one open panel with ventilation barriers in six rooms (***SXPE***$_{VOC}$ in µg/m^3). In each case, the concentration in µg/m^3 can be calculated as the product of the release rate times the number of containers involved times the mole fraction times the molecular weight divided by the ventilation flow rate and converted to micrograms and cubic meters.

The final step is to consider the portion of the pathway between the Exhaust Shaft and the receptor. The VOCs will disperse in the ambient atmosphere, resulting in a concentration at the receptor depending on the air dispersion factors. It is assumed here that the air dispersion factor (***ADF***) is 0.0123 based on the modeling in the Permit Application.

Table 2 shows these calculations and the resulting concentration at the receptor on the surface (***R***$_{conc}$ in ppmv and µg/m^3).

RECEPTOR

The final component is the receptor. In the Permit Application, the DOE considered four receptors. Three are on the surface and include: full time resident at the WIPP site boundary; ranch hand working within the WIPP site boundary but outside the exclusion area for a significant part of each work year; the surface worker that spends 10 years working in the Training Building which is the closest continuously occupied building to the exhaust point. The fourth receptor is a worker in the underground in the vicinity of

the waste.

TABLE 2 Pathway Parameters for the WIPP Miscellaneous Unit

		Carbon Tetrachloride	Chlorobenzene	Chloroform	1,1, - Dichloroethylene	1,2-Dichloroethane	Methylene Chloride*	1,1,2,2-Tetrachloroethane*	Toluene	1,1,1-Trichloroethane
D_{voc}	mol/s/mol fraction/ drum	1.21E-06	1.16E-06	1.34E-06	1.40E-06	1.32E-06	1.47E-06	1.21E-06	1.19E-06	1.21E-06
V_{ROOM}	ft^3/min	35,000	35,000	35,000	35,000	35,000	35,000	35,000	35,000	35,000
V_{E-300}	ft^3/min	130,000	130,000	130,000	130,000	130,000	130,000	130,000	130,000	130,000
V_{TOTAL}	ft^3/min	260,000	260,000	260,000	260,000	260,000	260,000	260,000	260,000	260,000
ADE_{VOC}	mole/drum/year	3.67E-01	4.76E-01	4.20E-01	2.42E-01	9.99E-02	4.64E+00	1.13E-01	4.13E-01	1.29E+00
Containers	drums/panel	81,000	81,000	81,000	81,000	81,000	81,000	81,000	81,000	81,000
$AORE_{VOC}$	moles/room/year	4.25E+03	5.50E+03	4.86E+03	2.80E+03	1.16E+03	5.36E+04	1.31E+03	4.78E+03	1.49E+04
GR	moles/drum/year	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$ACRE_{VOC}$	moles/room/year	55.69	75.21	57.45	31.76	13.89	578.57	17.13	63.64	194.98
$AOPE_{VOC}$	moles/room/year	4,584.03	5,954.23	5,200.37	2,995.33	1,239.37	5,7114.16	1,409.74	5,158.62	16,050.07
$SCPE_{VOC}$	$\mu g/m^3$	15.51	15.32	12.42	5.57	2.49	88.95	5.20	10.61	47.09
$SXPE_{VOC}$	$\mu g/m^3$	182.35	173.30	160.54	75.09	31.72	1254.41	61.19	122.89	553.71
ADF		0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
R_{CONC}	$\mu g/m^3$	3.96	3.83	3.35	1.54	0.67	25.28	1.33	2.69	12.02
R_{CONC}	ppmv	6.29E-04	8.31E-04	6.86E-04	3.89E-04	1.64E-04	7.28E-03	1.94E-04	7.13E-04	2.20E-03

For surface exposures, the receptor at the Training Building is considered the individual that is exposed to the greatest risk. This receptor is characterized by both exposure factors and risk factors. Exposure factors include the amount of time that the individual spends in an area where he is exposed. In the risk calculation, this is referred to as the exposure duration (***ED***) in years. For this individual, 10 years is assumed. Related to this is the exposure frequency (***EF***), which is taken to be 8 hours per day, 5 days per week, and 48 weeks per year or 1,920 hours. The final factor is the Averaging Time (***AT***) which represents the time period over which the exposure is averaged. By convention, 70 years is used for carcinogens and the exposure duration (***ED***) is used for non carcinogens.

The biological effect of the compound on the receptor is characterized by the Unit Risk Factor (***URF***) which is defined as the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to a carcinogenic VOC at a concentration of 1 $\mu g/m^3$ in air. The interpretation of unit risk would be as follows: if unit risk = 2×10^{-6} per $\mu g/m^3$, 2 excess cancer cases (upper bound estimate) are expected to develop per 1,000,000 people if exposed daily for a lifetime to 1 µg of the chemical per m^3 of air.

For non carcinogens, the reference concentration (***RfC***) is used to relate dose to health effect. The reference concentration is defined as the concentration of a chemical in air that is very unlikely to have adverse effects if inhaled continuously over a lifetime.

The underground worker is modeled as a waste handler that experiences a plume of contaminated air resulting from a roof fall in the adjacent filled room. In this case, the volume of air displaced is equal to one tenth of the headspace volume in the room, with one half of the amount exiting from each end of the room. Factors of concern are the concentration that the worker is exposed to and the duration of the exposure. The concentration in the closed room is assumed to be the average concentration in the headspace of the drums. A volume of this air equal to 5 percent of the room void volume (taken to be 5 percent of 1.5 feet times 300 feet times 33 feet or 743 ft^3) is "puffed" into a ventilation stream that is flowing at 35,000 ft^3/min. The duration is calculated as the ratio of the volume expelled from the room to the ventilation flow rate. The duration and concentration allow the calculation of time weighted averages for comparison to industrial health standards. Table 3 contains the exposure factors needed to calculate risk for the Surface and Underground receptors at the WIPP facility.

TABLE 3 Surface Worker and Underground Worker Exposure Factors

		Carbon Tetrachloride	Chlorobenzene	Chloroform	1,1, - Dichloroethylene	1,2-Dichloroethane	Methylene Chloride*	1,1,2,2-Tetrachloroethane*	Toluene	1,1,1-Trichloroethane
EF	hours/year	1,920	1,920	1,920	1,920	1,920	1,920	1,920	1,920	1,920
ED	years	10	10	10	10	10	10	10	10	10
AT	hours	613,200	87,600	613,200	613,200	613,200	613,200	613,200	87,600	87,600
URF	$m^3/\mu g$	1.5E-05		2.3E-05	5.0E-05	2.6E-05	4.7E-07	5.8E-05		
RfC	mg/m^3		2.0E-02						4.0E-01	7.0E-01
Room headspace	ft	2	2	2	2	2	2	2	2	2
Room width	ft	33	33	33	33	33	33	33	33	33
Room length	ft	300	300	300	300	300	300	300	300	300
Volume displaced	10 percent	1,485	1,485	1,485	1,485	1,485	1,485	1,485	1,485	1,485
Volume expelled	1/2 displaced	743	743	743	743	743	743	743	743	743
Exposure duration	minutes	2.1E-02	2.1E-02	2.1E-02	2.1E-02	2.1E-02	2.1E-02	2.1E-02	2.1E-02	2.1E-02

RISK

Risk for carcinogens can be calculated using the formula ***Risk =*** R_{CONC}****URF*EF*ED/AT*** and the Hazard Index for non carcinogens is ***Hazard Index =*** $(R_{CONC}$****EF*ED)/(AT*RfC)***. The NMED established environmental performance standards for the WIPP in accordance with the requirements of 40 CFR 264, Subpart X, Miscellaneous Units. The environmental performance standards require that the carcinogenic risk be limited to a

total risk of 1 in 100,000 and that the non-carcinogenic risk have a total hazard index of less than 1. Risk to workers is calculated as the 8 hour time weighted average and the maximum one minute exposure. These are required to be within established worker protection standards for the facility. Table 4 includes the risks calculated for the set of conditions in Tables 1 through 3.

TABLE 4 Risk Calculations for the WIPP Facility

		Carbon Tetrachloride	Chlorobenzene	Chloroform	1,1, - Dichloroethylene	1,2-Dichloroethane	Methylene Chloride*	1,1,2,2-Tetrachloroethane*	Toluene	1,1,1-Trichloroethane
Risk Carcinogenic (Surface worker)		1.9E-06		2.4E-06	2.4E-06	5.4E-07	3.7E-07	2.4E-06		
Risk Non carcinogenic (Surface worker)			4.2E-02						1.5E-03	3.8E-03
8 hour TWA (Underground worker)	ppmv	4.3E-01	5.7E-01	4.4E-01	2.4E-01	1.1E-01	4.4E+00	1.3E-01	4.9E-01	1.5E+00
1 minute concentration (Underground worker)	ppmv	2.0E+02	2.7E+02	2.1E+02	1.1E+02	5.0E+01	2.1E+03	6.1E+01	2.3E+02	7.0E+02

MISCELLANEOUS UNIT LIMITS

The final step is to derive performance limits that can become enforceable conditions of the permit. Several possibilities can be considered. To protect the surface worker, the R_{CONC} values can be used. However, measuring these very low concentrations (fractions of a ppb) may be difficult in the ambient air. To compensate for this, the limits are projected back along the pathway. C_{ES} represents the concentration without the effects of dispersion. Quantifying C_{ES} would require a measurement within the Exhaust Shaft. $C_{E\text{-}300}$ represents a point at the bottom of the Exhaust Shaft but after the ventilation air flows past the filled panels. In this case, a dilution factor equivalent to the ratio of the E-300 flow and the total repository flow is used to scale the concentrations from those in the Exhaust Shaft. This location is used since the limits are in the hundreds of parts per billion which is well within current measurement technology.

In setting the repository environmental performance limits for the surface worker, the NMED selected a risk level of one excess cancer death in 100,000 for carcinogens and a Health Index of 1 or less for non carcinogens. The NMED further specified that the risk should be assessed as cumulative risk. When NMED performed their risk assessment, they apportioned a total risk of 1.0 E-05 equally between the six carcinogenic VOCs. They then back-calculated an initial set of VOC limits as room-based concentrations. Subsequently, NMED adjusted some of the values to accommodate the roof-fall exposure scenario by reducing some limits and adjusting others to their lower explosive limit. Limits are expressed as concentrations of concern in parts per billion by volume for the surface worker as measured in the E-300 drift..

For the underground worker, the limits are determined based on the concentration that

creates the National Institute for Occupational Safety and Health (NIOSH) immediately dangerous to life and health (IDLH) exposure or the concentration that exceeds the lower explosive limit (LEL) for the compound. Limits are expressed as concentrations of concern in parts per million by volume for the underground worker as measured in the entries of active rooms or the filled room adjacent to an active room.

Table 5 lists the repository environmental performance limits established by the Permit.

TABLE 5 Environmental Performance Limits Established in the WIPP Facility Permit

		Carbon Tetrachloride	Chlorobenzene	Chloroform	1,1, - Dichloroethylene	1,2-Dichloroethane	Methylene Chloride*	1,1,2,2-Tetrachloroethane*	Toluene	1,1,1-Trichloroethane
Concentration of Concern E-300	$\mu g/m^3$	1,050	1,015	890	410	175	6,700	350	710	3,200
Concentration of Concern E-300	ppbv	165	225	185	100	45	1,930	50	190	590
Associated Risk Limit Carcinogenic		1.9E-06		2.4E-06	2.4E-06	5.4E-07	3.7E-07	2.4E-06		
Associated Risk Limit Non carcinogenic			4.2E-02						1.5E-03	3.8E-03
Concentration of Concern Active Panel	ppmv	9,625	13,000	9,930	5,490	2,400	100,000	2,960	11,000	33,700
Associated Risk Limit	ppmv	200	1,000	500	ND	50	2,300	100	500	700
Carcinogenic Risk Distribution for E-300 limits	%	18.58		24.09	24.10	5.41	3.72	24.10		
Non carcinogenic Risk Distribution for E-300 limits	%		88.90						3.12	7.98