

FINAL

# **Technical Evaluation Report for WIPP Room-Based VOC Monitoring**

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## Executive Summary

This document details the proposed plan to monitor for volatile organic compounds (VOCs) in disposal rooms of the open panels and to use active operational controls to protect against possible roof fall events in open rooms where waste emplacement is occurring in the Waste Isolation Pilot Plant (WIPP) underground. Background information involving VOC emissions is discussed in this report. The information includes discussion of the 1996 permit application, New Mexico Environment Department (NMED) risk scenarios, and current methods that WIPP is using to determine compliance with the room-based limits described in the WIPP Hazardous Waste Facility Permit (HWFP). This report also discusses new information on VOCs received from current headspace gas sampling results and disposal-room VOC monitoring. WIPP proposes that by monitoring the active panel and exhaust drift, compliance with the room-based limits can be demonstrated. The proposed methods for determining compliance described in this document will be conducted in the absence of headspace gas sampling, which is the current method for maintaining compliance with the requirements in the HWFP. Discussion points about this proposed monitoring, including methodology and actions to protect worker safety, are noted in the Technical Evaluation Report.

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## Acronym List

ACGIH	American Conference of Governmental Industrial Hygienists
DOE	Department of Energy
EPA	Environmental Protection Agency
ETEC	Energy Technology Engineering Center
FWF	Final Waste Form
HBL	Health-Based Level
HSG	Headspace Gas
HWDU	Hazardous Waste Disposal Unit
HWFP	Hazardous Waste Facility Permit
IDLH	Immediately Dangerous to Life and Health
INEEL	Idaho National Environmental and Engineering Laboratory
LANL	Los Alamos National Laboratory
MDL	Method Detection Limit
NMED	New Mexico Environment Department
NOD	Notice of Deficiency
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PMR	Permit Modification Request
RCRA	Resource Conservation and Recovery Act
RFETS	Rocky Flats Environmental Technology Site
TLV	Threshold Limit Value
TRU	Transuranic
VOC	Volatile Organic Compound
WAP	Waste Analysis Plan
WIPP	Waste Isolation Pilot Plant
WSMS	Washington Safety Management Solutions
WWIS	WIPP Waste Inventory System

## Technical Evaluation Report of WIPP Room-Based VOC Monitoring

### 1.0 Introduction

The WIPP Hazardous Waste Facility Permit (HWFP) establishes room-based limits for target VOCs in the air of rooms in individual disposal panels. This Technical Evaluation Report evaluates an alternative method of demonstrating compliance with the room-based VOC limits.

#### 1.1 What are the Room-Based VOC Concentration Limits?

The room-based VOC limits are in Module IV of the HWFP, and are shown in Table 1 below.

Compound	VOC Room-Based Concentration Limit (ppmv)
Carbon Tetrachloride	9625
Chlorobenzene	13000
Chloroform	9930
1,1-Dichloroethene	5490
1,2-Dichloroethane	2400
Methylene Chloride	100000
1,1,2,2-Tetrachloroethane	2960
Toluene	11000
1,1,1-Trichloroethane	33700

ppmv (parts per million by volume)

**Table 1** Room-Based VOC Concentration Limits  
(from Table IV.D.1 of the HWFP)

The average concentration of target VOCs in the air within an individual disposal room in an active panel must be less than the concentration limits in Table 1 above, even if some containers in the disposal room exceed the room-based concentration limits. The room-based limits were generated as a necessary component of the Resource Conservation and Recovery Act (RCRA) Part B Permit Application, since the waste emplaced in WIPP would be emitting VOCs during the WIPP operational phase. To satisfy the requirement to protect human health, meaning that hazardous constituent concentrations shall not exceed those associated with agency-approved human health-based levels (HBLs), an analysis was performed to determine chronic exposure levels for the public and surface WIPP workers as receptors. Points of compliance were determined, VOC concentrations at the points of compliance calculated for various average VOC level source terms, and a comparison to the HBL at each compliance point to the calculated VOC levels observed.

Data used were from the Idaho National Environmental and Engineering Laboratory (INEEL) 930-drum data set, where weighted-average container headspace VOC levels were projected for 28 VOCs for mixed waste destined for WIPP. VOC levels at the compliance points were determined and found to be well within the HBLs of 1 in  $1 \times 10^6$  for type A and B carcinogens and 1 in  $1 \times 10^5$  for type C carcinogens. Levels were also within the Occupational Safety and Health Administration (OSHA) time-weighted average exposure limits for non-carcinogens.

The greatest health-based risk from VOCs was found to be to a surface worker when the point of compliance was in the downstream flow just outside the exhaust shaft. Maximum average container headspace concentrations were determined and the maximum permissible exposures were calculated in accordance with EPA's public risk policy. The analysis set the maximum VOC levels in a room at EPA-acceptable exposure levels. NMED recalculated the maximum VOC levels that met EPA-acceptable exposure levels. NMED determination reduced the maximum VOC levels in a room for chlorobenzene and toluene to the lower explosive limit and 1,2-dichloroethane and 1,1,1-trichloroethane to the Immediately Dangerous to Life and Health (IDLH), all of which were less than the calculated values to meet EPA-acceptable exposure levels. These maximum average container headspace concentrations determined by NMED are the room-based limits.

## 1.2 Methods of Determining Compliance with the Room-Based VOC Limits

Currently, there are two methods described in the HWFP to demonstrate compliance with the room-based VOC concentration limits. The first method involves measuring and tracking the VOC concentrations in the headspace gas (HSG) of each container of transuranic (TRU) waste destined for WIPP. The second method involves measuring trace amounts of VOCs in the main exhaust drift of the WIPP underground. Each method is described in more detail in Section 2.2 below.

## 1.3 Development of a New Waste Analysis Plan for WIPP

A HWFP modification request (PMR) has been developed proposing a new waste analysis plan (WAP) for WIPP. Among other things, the new WAP PMR proposes to change the current practice of sampling and analyzing the HSG of each container of TRU waste destined for WIPP to determine the concentration of VOCs.

## 1.4 Purpose of this Report

As proposed in the new WAP PMR, container-by-container HSG VOC measurements will no longer be made. In the absence of such container-specific VOC data, WIPP must utilize an alternative method to demonstrate compliance with the room-based VOC limits. This report provides information on an alternative VOC monitoring method to determine compliance with the room-based limits and demonstrates how the alternative method protects human health and the environment.

## 2.0 Background Information

This section provides an overview of how the room-based VOC limits were derived, occupational exposure risks room-based limits were designed to protect against, and describes current methods for determining compliance with the room-based limits.

### 2.1 The 1996 RCRA Permit Application

In 1996 as part of the WIPP RCRA Part B Permit Application and the associated WIPP No-Migration Variance Petition, an assessment of potential environmental and human health impacts associated with waste emplacement was necessary. This assessment was to demonstrate that no hazardous constituents would migrate beyond the boundary of the disposal unit at levels in excess of acceptable agency-approved human health-based standards for the constituents.

Since VOCs in the emplaced waste would become entrained in the mine ventilation air and make their way to the surface, part of the 1996 application required an assessment of the risk associated with VOCs in the waste and a determination of controls on VOC emissions that was protective of the public, environment, and WIPP workers, both at the surface and in the underground. This section details the determination of the risk associated with the VOCs in the waste and the controls implemented to meet emission limits.

#### 2.1.1 Estimate of VOC content of the TRU Waste Inventory (930 Drums)

As part of the RCRA Part B Permit Application in 1996 and the No-Migration Variance Petition, an assessment of the potential VOC release rate from WIPP during the waste emplacement phase was required. The complete details of this assessment are contained in Appendix C2 of the WIPP RCRA Part B Permit Application, DOE/WIPP 91-005. To satisfy this requirement HSG waste characterization data that were available in 1995 were assembled and a profile of the VOCs typically observed was determined. The available data were from INEEL and Rocky Flats Environmental Technology Site (RFETS). They were comprised of a 930-drum data set representing 10 of the 12 waste matrix code groups (now identified as final waste forms).

The 930-drum data set reported 28 VOC HSG concentrations that represented the VOCs associated with the hazardous waste constituents in the waste. The average HSG concentration value for each of the 28 VOCs was determined for each waste matrix code group. A projected full WIPP VOC source term profile was calculated by first determining the weighted average HSG concentrations for 28 VOCs within each waste matrix code group. The weighted averages for a given VOC in each waste matrix code group were then summed to obtain a full WIPP source term for each VOC.

Weighting factors were obtained by determining the fraction of waste in a projected full WIPP that each waste matrix code group represented in the TRU Waste Baseline Inventory Report, Revision 3. Waste matrix code groups and weighting factors used in the calculation of the waste matrix codes contribution to the full WIPP source term are displayed in the Table 2.

<b>Waste Matrix Code Group</b>	<b>Weighting Factor</b>
Combustibles	0.353
Filter	0.0148
Graphite	0.0043
Heterogeneous	0.222
Inorganic non-metal	0.0102
Lead/cadmium metal	0.0018
Salt waste	0.000852
Soils	0.00739
Solidified inorganics	0.194
Solidified organics	0.0126
Uncategorized metal	0.171
Unknown	0.00966
<b>TOTAL</b>	<b>1.00</b>

**Table 2** Waste Matrix Codes and Weighing Factors

### 2.1.2 VOCs that Pose Health Risk at WIPP

The assessment performed on the 930-drum set included weighted average HSG concentrations projected for a full WIPP. A determination of the risk to the public and WIPP workers associated with the 28 VOC constituents was made. This assessment was required to satisfy both the WIPP RCRA Part B Permit Application and the No-Migration Variance Petition submitted to EPA. This assessment was completed before the Land Withdrawal Act amendments excluded WIPP waste from the No-Migration provision. The full assessment is contained in Appendix D13 of the WIPP RCRA Part B Permit Application, DOE/WIPP 91-005; the WIPP No-Migration Variance Petition, DOE/CAO-96-2160; and in comments from Steve Zappe, NMED, titled “*NMED Calculations for VOC Concentrations in WIPP Underground HWDUs*”, 11/19/98.

The assessment determined a risk (based on an EPA method risk score) considering type of risk, toxicity, and weighted average VOC concentration for each of 28 VOCs. The scores ranked 28 VOCs as to their risk to health of the public and WIPP workers. From the ranking and a determination of VOCs that represented approximately 99 percent of the risk due to air emissions, target VOCs were selected as indicator VOCs to be monitored for compliance with VOC emission levels. Target VOCs and the room-based limits are shown in Table 1 in Section 1.1 of this report.



### 2.1.3 VOC Exposure Scenarios at WIPP

During the RCRA permit application process, four general VOC exposure scenarios were evaluated by NMED, and environmental performance standards were established. The exposure scenarios and performance standards are summarized in the following table:

VOC Exposure Scenario	Environmental Performance Standards
1) Resident living at WIPP site boundary, <u>chronic</u> exposure to VOCs	<ul style="list-style-type: none"> <li>• For carcinogens, total individual risk less than <math>10^{-6}</math></li> <li>• For non carcinogens, hazard index from exposure less than 1</li> </ul>
2) WIPP non-waste surface worker, <u>chronic</u> exposure to VOCs	<ul style="list-style-type: none"> <li>• For carcinogens, total individual risk less than <math>10^{-5}</math></li> <li>• For non carcinogens, hazard index from exposure less than 1</li> </ul>
3) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in an <u>open</u> room	<ul style="list-style-type: none"> <li>• Concentrations of four VOCs immediately after a roof-fall less than the IDLH concentrations (1,1,1-trichloroethane, 1,2-dichloroethane, carbon tetrachloride, and 1,1,2,2-tetrachloroethane)</li> </ul>
4) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in a <u>closed</u> room	<ul style="list-style-type: none"> <li>• Concentrations of four VOCs immediately after a roof fall less than the IDLH concentrations (1,1,1-trichloroethane, 1,2-dichloroethane, carbon tetrachloride, and 1,1,2,2-tetrachloroethane)</li> <li>• Concentration of two VOCs in disposal room less than the LEL concentration (toluene, and chlorobenzene)</li> </ul>

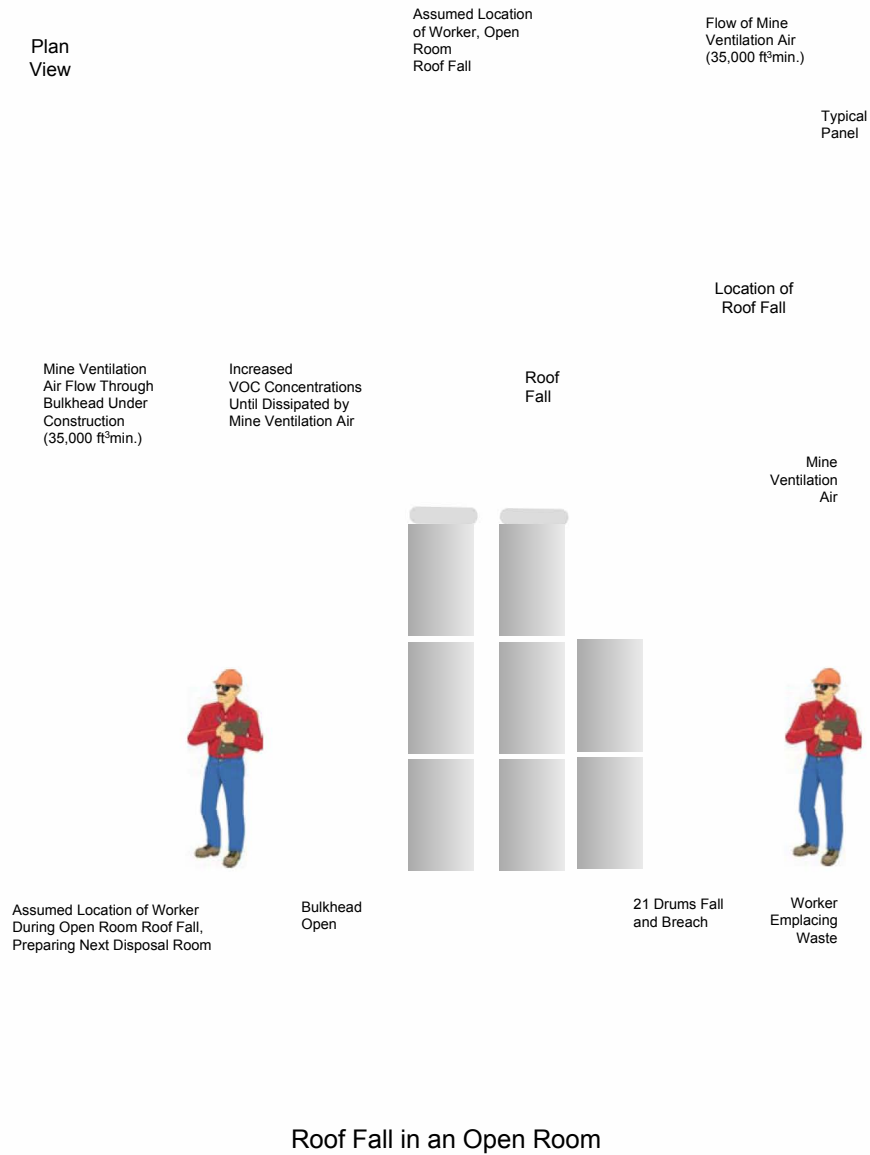
**Table 3 - WIPP VOC Exposure Scenarios Evaluated by NMED**  
*(Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)*

This Technical Evaluation Report considers Scenarios 1 and 2 to represent risks that current and proposed underground monitoring collectively are to be protective of with regard to the public and workers. The report focuses on the two WIPP underground waste worker acute exposure scenarios (Scenarios 3 and 4) and the alternative method of demonstrating compliance with room-based limits in the absence of container-by-container HSG measurements.

### 2.2 Two Scenarios for Acute VOC Exposure to Workers in Disposal Rooms

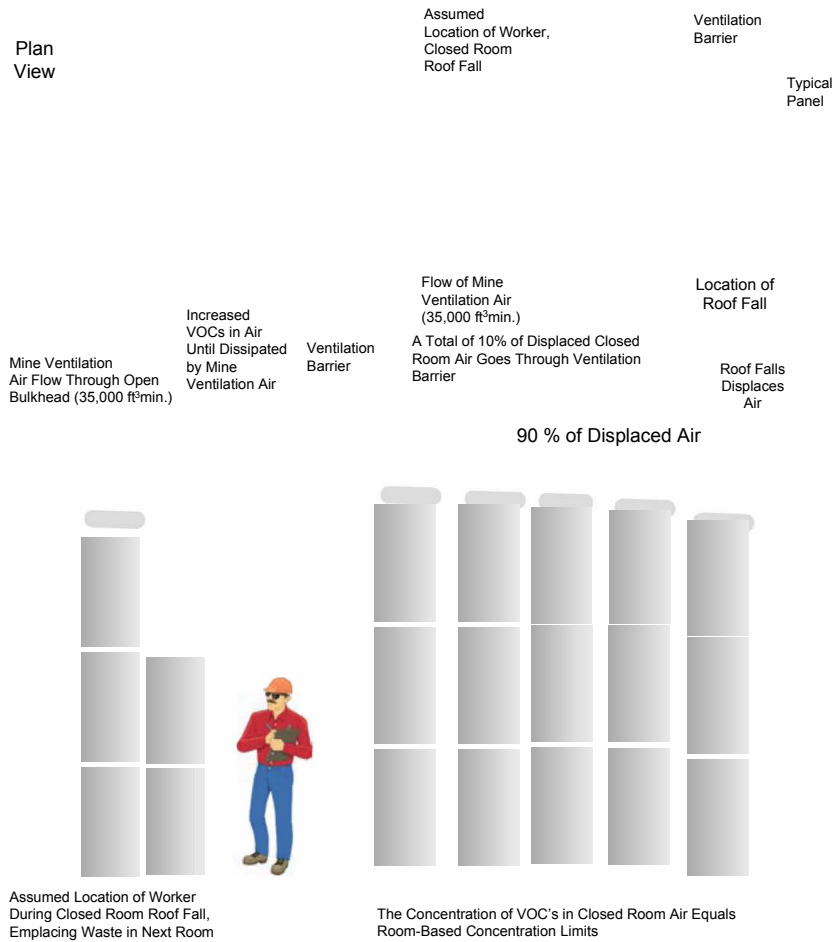
Revision 5.2 of the RCRA Permit Application was submitted to NMED on January 17, 1996. In response, NMED issued a Notice of Deficiency (NOD) and requested the applicants to evaluate two acute VOC exposure scenarios to underground waste workers (Ref #1-*Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999*).

The first acute VOC exposure scenario, involving a roof fall in an open room, is shown in Figure 1 below:



**Figure 1 - Acute VOC Exposure Scenario, Roof Fall in an Open Room**  
(Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)

The second acute VOC exposure scenario, involving a roof fall in a closed room, is shown in Figure 2 below:



Roof Fall in Closed Room

**Figure 2 - Acute VOC Exposure Scenario, Roof Fall in a Closed Room**  
(Ref #1-NMED's Direct Testimony Regarding Regulatory Process and Imposed Conditions, 1999)(SIC)

## 2.3 Current Methods of Determining Compliance with Room-Based VOC Limits

In evaluating WIPP's RCRA Permit Application in 1999, NMED determined that environmental performance standards for protection of human health and environment from VOC releases into the air could be satisfied by maintaining the room-based VOC limits. There are two methods specified in the current HWFP for determining compliance with room-based VOC limits.

VOC Exposure Scenario and Corresponding Environmental Performance Standard	Current Method of Determining Compliance
1) Resident living at WIPP site boundary, <u>chronic</u> exposure to VOCs: total carcinogen risk < 10 <sup>-6</sup> , and non-carcinogen exposure hazard index < 1	Confirmatory monitoring of trace amounts of VOCs in the main exhaust drift in the WIPP underground
2) WIPP non-waste surface worker, <u>chronic</u> exposure to VOCs: total carcinogen risk < 10 <sup>-5</sup> , and non-carcinogen exposure hazard index < 1	Confirmatory monitoring of trace amounts of VOCs in the main exhaust drift in the WIPP underground
3) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in an <u>open</u> room: concentrations of VOCs immediately after roof fall < IDLH	Tallying individual waste container HSG VOC measurements in the WIPP Waste Information System
4) WIPP underground waste worker, <u>acute</u> exposure to VOCs from a roof fall in a <u>closed</u> room: concentrations of VOCs in closed room < IDLH and <LEL	Tallying individual waste container HSG VOC measurements in the WIPP Waste Information System

**Table 4** - Current Methods of Determining Compliance with Room-Based VOC Limits

### 2.3.1 Tracking VOC Concentrations in the Headspace Gas of Individual Containers

As provided in the current HWFP, container-by-container HSG VOC measurements are made and the data are entered into the WIPP Waste Information System (WWIS). The WWIS in turn is able to track and tally the average VOC HSG concentrations of containers emplaced within a particular disposal room at WIPP. This method is used to determine compliance with the two specific environmental performance standards and those that protect underground waste workers against acute exposures to VOCs.

### 2.3.2 Confirmatory Monitoring of VOCs

The VOC Confirmatory Monitoring Program is designed to differentiate VOC concentrations attributed to open and closed panels from other potential sources. VOC monitoring confirms compliance with HWFP VOC emission requirements. The only pathway for VOCs during the operational phase is via airborne transport. VOCs released in the underground facility would become entrained in the underground ventilation air and released to the atmosphere through the exhaust shaft. VOC emissions from emplaced waste pass by a monitoring system as they are directed to the exhaust shaft.

Sources of VOC emissions related to WIPP mine operational activities also exist below ground surface. Fuel combustion, painting activities, cleaning solvents, and air conditioners are potential sources of VOCs. Ambient air is monitored in the underground for the target compounds at two locations in the facility to quantify airborne VOC concentrations. VOC concentrations attributable to VOC emissions from open and closed panels containing transuranic mixed waste are measured by placing one VOC monitoring station just downstream from HWDUs at VOC-A and another station upstream from the open panel at VOC-B.

In this configuration, VOC-B measures VOC concentrations attributable to releases from the upstream sources and other background sources of VOCs. VOC-A measures upstream VOC concentrations plus any additional VOC concentrations resulting from releases from the open panel and closed panels. A sample is collected from each monitoring station on designated sample days. For each quantified target VOC, the concentration measured at VOC-B is subtracted from the concentration measured at VOC-A to assess the magnitude of VOC releases from closed and open panels.

Sampling locations were selected based on operational considerations. There are several different potential sources of release for VOCs. These sources include incoming air from above ground, facility support operations, open waste panels, and closed waste panels. In addition, because of the ventilation requirements of the underground facility and atmospheric dispersion characteristics, any VOCs released from HWDUs may be difficult to detect and differentiate from other sources of VOCs at any underground or above ground location further downstream of Panel 1. By measuring VOC concentrations close to the potential source of release (i.e., at Station VOC-A), it is possible to differentiate potential releases from background levels (measured at Station VOC-B).

The field sampling systems are operated in the pressurized mode. In this mode, air is drawn through the inlet and sampling system with a pump and then pumped into an initially evacuated SUMMA passivated canister by the sampler, which regulates the rate and duration of sampling. The passivation process forms a pure chrome-nickel oxide on the interior surfaces of the canisters. By the end of each sampling period, the canisters will be pressurized to about two atmospheres absolute. In the event of shortened sampling periods or other sampling conditions, the final pressure in the canister may be less than two atmospheres absolute.

### **3.0 New Information on VOCs in TRU Waste and Behavior of VOCs in the Repository**

The 1995 VOC study was comprehensive, encompassing nearly 1,000 drums (*Ref #2-Appendix C2*). Since that time a great deal of additional information has been collected because sites increased their characterization efforts to enable shipment to WIPP. The characterization process has included developing compliant acceptable knowledge as well as physically sampling nearly 100 percent of the shipped inventory HSG (the exceptions are those allowed by the WAP, which history shows that they underwent thermal processing which would eliminate the constituents of concern from the headspace. These containers have been statistically sampled according to the WAP requirements).

### 3.1 Headspace Gas Measurements Made since 1996

Three additional data sources were developed after the initial study:

- WWIS data ranging from March 1999 to May 2003
- 2,366-drum from IT Corporation survey of VOCs in drums at RFETS that could impact hydrogen-getters through poisoning by VOCs (*Ref #3-Parameters for Testing Impacts of VOCs as Poisons on Hydrogen Getter Performance*).
- 103 drums of IDC 003 RFETS waste at INEEL analyzed to determine hydrogen and flammable VOC content for shipment of this waste to WIPP (*Ref #4-IDC 003 Organic Setups Study*).

With the limitations of the initial data set, it is reasonable to re-evaluate conclusions reached earlier regarding expected VOC levels in the WIPP repository. LANL performed a new assessment of VOC levels in TRU waste using known, currently available VOC data (*Ref #5-Analysis of VOC Levels in the TRU Waste Inventory*). In 2003 the DOE Complex performed a waste inventory update in support of the WIPP Performance Re-certification Application (*Ref #6-Transuranic Waste Inventory Update Report 2003*). That inventory information provided the basis to project expected VOC contributions by final waste forms (FWFs) from the waste to be contained in a full WIPP repository.

The data from the three sources listed above were combined with data from the original 1995 study with adjustments to remove sources of error. Analytical issues were resolved in a WIPP-compliant manner. Also, the same screening process was applied to the original 1995 data set so that meaningful comparisons could be made. Full details regarding the LANL inventory evaluation appear in the LANL report, *Analysis of VOC Levels in the TRU Waste Inventory*, LA-UR-03-5393.

#### 3.1.1 Fewer VOCs in TRU Waste Inventory than Originally Estimated

Using the much larger population of HSG samplings, a new weighted average VOC source term for 28 VOCs was determined. VOC concentration measurements decreased significantly with respect to previously projected values. The principal VOCs contributing to the new source term were reduced in number from four in the 1995 data to two in the new data set. These dominant VOCs, 1,1,1-trichloroethane and carbon tetrachloride, showed decreases in weighted-average concentrations to about one-third and one-half of the 1995 values, respectively. All VOCs decreased to less than half of their 1995 values, with methylene chloride decreasing to only 2 percent of the 1995 projection. The full results are reported in the LANL report, *Analysis of VOC Levels in the TRU Waste Inventory*, LA-UR-03-5393.

#### 3.1.2 Small Amount of TRU Waste Inventory Contributes Most of VOCs

According to the LANL waste inventory evaluation, one FWF contributes most of the VOC source term (the 1995 study showed three FWFs had significant contributions). The FWF responsible for the overwhelming majority of the source term is solidified organics. All VOC gas concentration data for this FWF were obtained from TRU waste that originated from RFETS. While this is a limitation, it represents a bounding case because solidified organics from DOE

Hanford and LANL are not expected to contain higher concentrations of VOCs.<sup>1</sup> According to projections based on the 2003 Inventory Update, the majority of solidified organics resides at only four sites. The sites are RFETS, INEEL, LANL, and Hanford (ETEC and LLNL have only about 13 m<sup>3</sup> total). The solidified organic FWF represents approximately 1 percent of total inventory with the fraction originating from RFETS and INEEL accounting for about one-third of the total.

### 3.1.3 1996 RCRA Permit Appendices Were Conservative and Are Not Challenged by This Report

As reported in Section 2.1, a 1996 assessment was made of potential environmental and human health impacts of VOCs associated with waste emplacement. This was done in support of the WIPP RCRA Part B Permit Application and the No-Migration Variance Petition. The assessment was to show that even at very high VOC concentrations, exposure levels at the surface for two chronic exposure scenarios were well within acceptable levels for no migration of hazardous contaminants. By limiting average VOC levels to room-based limits, a conservative approach was adopted to keep WIPP VOC emissions below acceptable exposure levels.

Verification that WIPP remained in compliance was accomplished by environmental monitoring in the E300 exhaust drift at S1300, a point downstream of all the panels. The assessment was based on VOC data available at the time (a 930-drum set at INEEL). The data set included HSG data for all but two of the waste matrix code groups although the drum count in any group was generally less than 100 drums. VOC averages by waste matrix code group in this data set clearly showed there were very few cases where room-based limits for a VOC could have been exceeded. In risk assessments made using this VOC data, a number of conservative assumptions were made on the movement of VOCs from the drum headspace to the room air. Because of the small number of data points in a waste matrix code group, a conservative approach was taken to ensure that room-based limits would not be exceeded.

The data set for a 2003 assessment of VOCs in DOE waste includes approximately 45,000 drums representing about 5 percent of the full WIPP volume. All but the soils waste matrix code group is included in this assessment. The results represent at least 2,000 data points in each waste matrix code group except solidified organics. The data also demonstrate that average VOC levels have declined significantly for all waste matrix code groups except solidified organics.

The VOC with average concentrations exceeding room-based limit in any waste matrix code group was carbon tetrachloride and that was only for solidified organics, which makes up, at most, about 1 percent of the total waste destined for WIPP and less than one-half of the solidified organics waste matrix code group or about 3,000 drums contain high levels of carbon tetrachloride. With the currently available data, the conservative approach taken in 1996 is not required since there does not appear to be sufficient inventory of high-VOC concentration waste to fill a room. (*Ref #9-Statistical Analysis of VOC Levels in the TRU Waste Inventory*).

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<sup>1</sup> The solidified organics from INEEL and RFETS came from a process known as Oil and Solvent Immobilization System (OASIS). In the OASIS process, a mixture of approximately 25 vol. percent cutting oil and 25 vol. percent solvents (mostly carbon tetrachloride and 1,1,1-trichloroethane) was mixed with 50 vol. percent gypsum cement. This represents close to the theoretical limit of solvents that can be immobilized without giving rise to free liquids. Other methods such as the use of clay absorbents or vermiculite typically are used to immobilize <25 vol. percent of solvents.

### 3.2 Experimental Disposal-Room Monitoring in Panel 1

In 2001, a task team began meeting to determine how to eliminate HSG sampling from the HWFP while maintaining compliance with environmental performance standards in the HWFP. The group decided that collecting samples inside the disposal-room environments might provide empirical data of value for a future permit modification process.

The current VOC monitoring system was tested to determine if the system could detect releases of VOCs from the panel area. This test involved the release of a known gas in Panel 1 while collecting ambient air samples at VOC-A and VOC-B. The results indicated that VOC concentrations emitted from open and closed panels could be detected by the system in place (*Ref #10-VOC Test Release Report*).

An additional test was performed by the Carlsbad Environmental Monitoring and Research Center to determine if the long lengths of tubing necessary to perform this sampling would pose problems with analysis of samples collected through the tubing. The test indicated that the long lengths of tubing caused no significant impact to sample quality (*Ref #11-Silicosteel Tubing Evaluation*).

#### 3.2.1 Apparatus and Methods

Sampling for VOCs in disposal-room environments began on August 29, 2001, in Room 7 of Panel 1. The sampling method and procedures were adopted from the established Confirmatory VOC Monitoring Program. As ventilation barriers were installed, siliconized stainless steel tubing was installed at the exhaust side of the room. A manifold consisting of the siliconized stainless steel tubing was designed and constructed to create three sample inlet points. Each of these sample points collected air samples in the disposal room at different elevations to account for settling of different target compounds.

The sample line was then connected to a sampling unit further down the exhaust drift. The sampling unit was eventually installed at the same location that housed VOC-A. Dual particulate filters were installed close to the point at which the tubing connected to the sampling unit to prevent salt and other particulates from entering the system. Figure 4 shows the sample locations during the disposal-room sampling of Panel 1.

Additional sampling locations were operated during the life of Panel 1. These included an inlet location in Room 4, inlet and exhaust locations in Room 3, and an exhaust location in Room 2. The inlet side sample locations in Panel 1 did not include a manifold setup at the sample inlet point. All other aspects of the setup were the same as in Room 7. The components of the disposal-room monitoring system were the same as those used in the Confirmatory VOC Monitoring Program, described in Section 2.3.2 of this report.

#### 3.2.2 Results of VOC Measurements in Disposal Rooms

Disposal-room monitoring conducted in Panel 1 started in August 2001 and lasted through February 2003. EPA method TO-14 was used in the analysis of disposal-room samples. This is the same method as is used in confirmatory monitoring. Results were validated by VOC monitoring personnel using existing procedures. Data from monitored rooms indicated that over time VOC concentrations in disposal rooms do build up to higher levels than are measured at



VOC-A. The highest concentration measured in Panel 1 was in Room 7 for 1,1,1-trichloroethane at a concentration of 450 parts per billion by volume (ppbv), very low considering the room-based limit for this compound is 33,700 ppmv.

### 3.2.3 Rank-Order Correlation of Disposal-Room VOCs to HSG Data

Over time the concentrations began to rise in each room. Data collected in Panel 1 was compared to WWIS data on a room-by-room basis. A statistical analysis was performed on these data to decide if a correlation of the disposal-room data and the WWIS data existed. The Washington Safety Management Solutions (WSMS) analysis produced the following information:

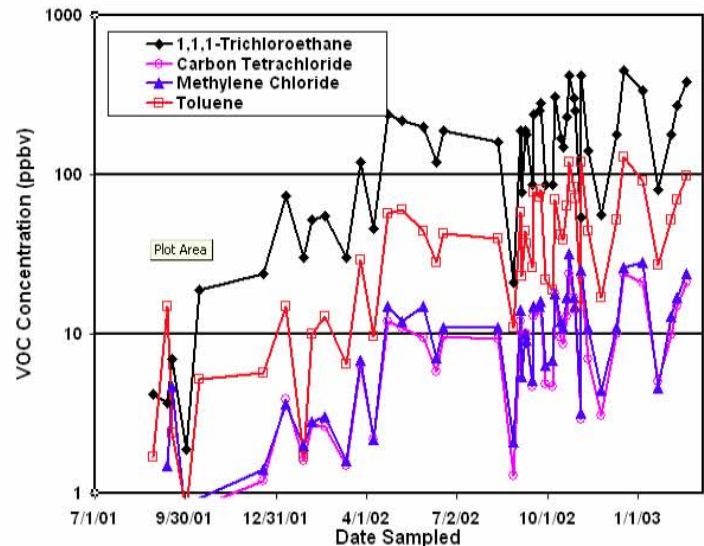
*“Logic suggests that the VOC representing the most volume (in liters) placed in a room should be measured at the highest concentration in the air, with the next highest volume VOC being measured at lower concentrations in the air, and so on as VOC concentrations decrease. In Room 7, the four highest volumes of VOCs have the following rank order:*

1. 1,1,1-Trichloroethane
2. Toluene
3. Methylene Chloride
4. Carbon Tetrachloride

*“Air monitoring measurements would be expected to show that, over time, 1,1,1-trichloroethane concentrations exceed those for toluene, which exceed those for methylene chloride, which exceed those for carbon tetrachloride. This also implies that we expect the nature of the rank order to be non-random. Figure 4 is a graph showing concentrations of all four VOCs listed above over time. The graph shows that 1,1,1-trichloroethane concentrations are consistently above those for toluene, which are above those for methylene chloride, and so forth.*

*“Rank-order correlation assumes that the results of experiments are random events. Examples of experiments could be the measurements of VOCs in the air. If, for example, we measure four VOCs in underground room air and their ranks are random, then there is a 25 percent chance (1 in 4) that any particular VOC will emerge as the highest concentration for a set of four measurements. The chance that a given VOC will rank as the number one constituent in air twice in a row is 1 in 16, with the likelihood of three or more “#1” rankings decreasing the more times we run the experiment, i.e. sample the air.*

*“The probability that the VOCs will exhibit the same ABCD rank order in the drums as in the air simply by chance is 1 in 24. Obviously, a 1 in 24 chance is possible, occurring about four times out of every 100 sampling events, on average. The probability of this ranking occurring*



**Figure 3**  
Room 7/WWIS Time Series Plot (Ref #12-Draft Rank Order Correlation in Underground Air at the WIPP)

*consecutively two or more times decreases rapidly as the experiment is performed over and over.*

*“Figure 4 shows that VOC concentrations have been checked in Room 7 almost 50 times between 8/29/01, and 2/19/03, with 44 of these events measuring all four VOCs of interest. For convenience, we can call 1,1,1-trichloroethane “A,” toluene “B,” methylene chloride “C,” and carbon tetrachloride “D.” Of the measurements shown in Figure 4, 39 exhibit the ABCD ordered ranking in the air monitoring samples, which matches exactly the rank order ABCD in the drum HSG measurements.*

*“The probability of observing the ABCD order 39 times out of 44 sampling events is virtually zero. As a perspective, you are about a million times more likely to die in a tornado than to have this consistently ordered VOC result by chance. From this evidence, we conclude that the rank order of VOCs is not a random event; rather, it is a function of the most abundant VOCs that are contained in the drums in a particular underground room.” (Ref #12-Draft Rank Order Correlation in Underground Air at the WIPP)*

#### **4.0 Proposed Method for Determining Compliance: Closed-Room Roof Fall**

WIPP is proposing a system to monitor VOC concentrations inside disposal rooms. This sampling will provide an accurate evaluation of accumulated VOCs that have the potential to be pushed past ventilation barriers in the event of a roof fall. The monitoring system will allow for a real measure of worker protection and ensure that room-based limits are not exceeded.

For purposes of compliance with the disposal room performance standards of Section 311 of Public Law 108-137, the VOC monitoring of airborne VOCs in underground disposal rooms in which waste has been emplaced will be performed as follows:

- A sample head will be installed inside the active disposal room behind the exhaust drift bulkhead in the active disposal room.
- TRU mixed waste will be emplaced in the active disposal room
- When the room is filled, another sample head will be installed in the inlet of the filled active disposal room.
- The exhaust drift bulkhead will be removed and re-installed in the next room so disposal activities may proceed.
- A ventilation barrier will be installed where the bulkhead was located in the rooms exhaust drift. Another ventilation barrier will be installed in the room’s air inlet drift, thereby closing that disposal room
- Monitoring of VOCs will continue in the now closed disposal room. Monitoring of VOCs will occur only in the active disposal room and closed room immediately adjacent to the active open room
- This sequence will proceed in the remaining disposal rooms until panel closure activities are initiated. Panel closure is initiated when the inlet air ventilation barrier is installed in room one.

#### **4.1 Closed-Room Exposure Scenario**

The closed-room exposure scenario depicted in NMED's testimony shows that the workers downstream from the exhaust of open panels have the potential to be exposed to high levels of VOCs in the event of a roof fall in the adjacent closed room. The scenario assumes that 10 percent of VOC concentrations in the affected closed room are pushed past the ventilation barrier into the air stream. It also assumes that workers are in the exhaust at the time of the fall.

#### 4.2 Disposal-Room VOC Monitoring

The proposed VOC monitoring allows for the quantification of the VOC concentrations in disposal rooms of the remaining HWDUs in the underground. The monitoring will in essence take the place of HSG sampling at-generator sites. HSG sampling is currently performed, in part, as a conservative control on the VOC release to the surface and to ensure that workers will not be subject to an acute VOC exposure in the event of a roof fall in a closed room adjacent to an open room.

The monitoring approach offers an actual air composition analysis, to address the real hazard in the fall scenario depicted in NMED testimony regarding regulatory process and imposed conditions. HSG analysis indicates what is contained in drums and not what is actually likely to be pushed out of the ventilation barrier during a roof fall. In the event that VOC concentrations reach a hazardous point, mitigating actions will be taken. These levels and actions are discussed in the following sections. Sampling locations for disposal-room monitoring are demonstrated in Figure 5.

##### 4.2.1 Apparatus and Methods

Disposal room sampling consists of the same instrumentation that is currently used for the confirmatory VOC monitoring program described in Section 2.3.2 of this report. Sampling will be conducted in all rooms in which waste has been emplaced until initiation of panel closure activities. VOC sampling will begin at the outlet side of each disposal room behind the bulkhead, downstream of the waste, as waste is initially emplaced in each room. When disposal operations in each room are completed, ventilation barriers will be installed at the upstream end of the room, and VOC sampling will begin behind the ventilation barrier for that room, except in Room 1, because there is no adjacent open disposal room. Since disposal operation completion in Room 1 is coincident with initiation of panel closure activities (i.e., installation of ventilation barriers in the panel access crossdrifts), no inlet monitoring in Room 1 will be initiated.

##### 4.2.2 Frequency of Sampling

Frequency for disposal-room sampling would be once every two weeks. For Panel 1, disposal-room samples were initially collected twice each week. After reviewing data from these samples, bi-weekly sampling per sampling location was deemed sufficient. Data do not indicate the disposal-room environment was changing quickly enough to warrant more frequent sampling, Figure 3 shows this gradual rise. In the event that higher concentrations of VOCs were detected, more frequent sampling could be implemented.

#### 4.3 Action Levels

One action level exists for the disposal-room monitoring system. Table 6 shows the action level of 95 percent of room-based limits specified in the HWFP. It was determined that 95 percent of the room-based limits would be sufficient at which to begin remedial action by evaluating the gradual rise of VOC concentrations in Room 7, Panel 1. The gradual concentration rise in Room 7, Panel 1 along with the relatively short time frame to complete remediation provides confidence in the action level. Remedial action is detailed in Section 4.4 of this report.

<b>Compound</b>	<b>Action Level in ppmv</b>
Carbon tetrachloride	9,145
Chlorobenzene	12,350
Chloroform	9,433
1,1-Dichloroethene	5,215
1,2-Dichloroethane	2,280
Methylene Chloride	95,000
1,1,2,2-Tetrachloroethane	2,812
Toluene	10,450
1,1,1-Trichloroethane	32,015

**Table 6** Disposal-Room Action Level

#### 4.4 Actions to Mitigate Risk From High-VOC Conditions

Upon receipt of analytical results indicating one or more compounds have exceeded half the action level, sampling frequency would increase to determine how fast the concentrations are rising. In the event VOC concentrations inside the disposal room reach the action level, measures would be taken to mitigate hazards. If the condition rises to the 95 percent action

level, another sample would be taken to confirm such a condition. If the second sample confirms the 95 percent limit, the current active room would be abandoned and two ventilation barriers of the type shown in Figure 7 would be installed. This action scenario is shown in Figure 6. A typical (single layer) ventilation barrier is shown in Figure 7.

#### 5.0 Proposed Method of Determining Compliance – Open-Room Roof Fall

In the event of a roof fall in accordance with conditions outlined in HRM 98-04(P) New Mexico Environment Department's Direct Testimony Regarding Regulatory Process and Imposed Conditions, NMED is concerned about formation of an Immediately Dangerous to Life and Health (IDLH) atmosphere in the hypothetical event of a roof fall in an active room. This scenario "assumes that an underground waste worker who is upwind of the waste stack will be exposed to the VOCs from 21 drums which, in response to a roof fall, will fall from the top row and breach." NMED considers that such an event may create an IDLH concentration of VOCs in the breathing zone of a worker in the active room. As explained in NMED's testimony, the location of such an occurrence is at the emplacement face of the open room.

##### 5.1.1 Active Operational Controls – Emplacement Face

WIPP procedures and Mine Safety and Health Administration (MSHA) regulations require that ground conditions be examined or inspected at the start of every shift, and as conditions warrant, to ensure that the workplace is safe. Should an unsafe condition be found, work is stopped, Underground Services is notified, and personnel are not allowed to work in the area until any hazards are mitigated.

The toppling and breach of 21 or more waste containers at the emplacement face is a self-evident event to personnel in the active room. Per current WIPP procedure, the event triggers evacuation of all personnel from the emplacement face. Current ALARA procedures require personnel to remain away from the emplacement face when not otherwise required by job tasks, thus ensuring that workers will be capable of providing an alarm should drums topple. In such an event, the Central Monitoring Room (CMR) would be notified and the CMR Operator would issue an evacuation alarm for all areas downwind of the active room (the exhaust drift).

##### 5.2 Active Operational Controls – Exhaust Drift Access

For the protection of the worker, personnel are not allowed access to the exhaust drift without approval from Underground Services. The ground at the emplacement face is examined for safety prior to entry of personnel into the exhaust drift. Should an unsafe condition be found, work is stopped, Underground Services is notified, and personnel are not allowed to work in the area until any hazards are mitigated.

### 5.3 Mitigation of High-VOC Conditions if a Roof Fall Occurs

In the event of a roof fall and subsequent VOC release in the active room, the action is to evacuate that room and the exhaust drift pending evaluation of the event. As explained in NMED's testimony, the VOCs resulting from a roof fall in an open room would be quickly dissipated by ventilation. In the unlikely event of a roof fall, in accordance with WIPP procedures, workers would not be allowed to return to such an area until it was deemed safe.

## 6.0 Conclusions Regarding Proposed New Methods of Determining Compliance

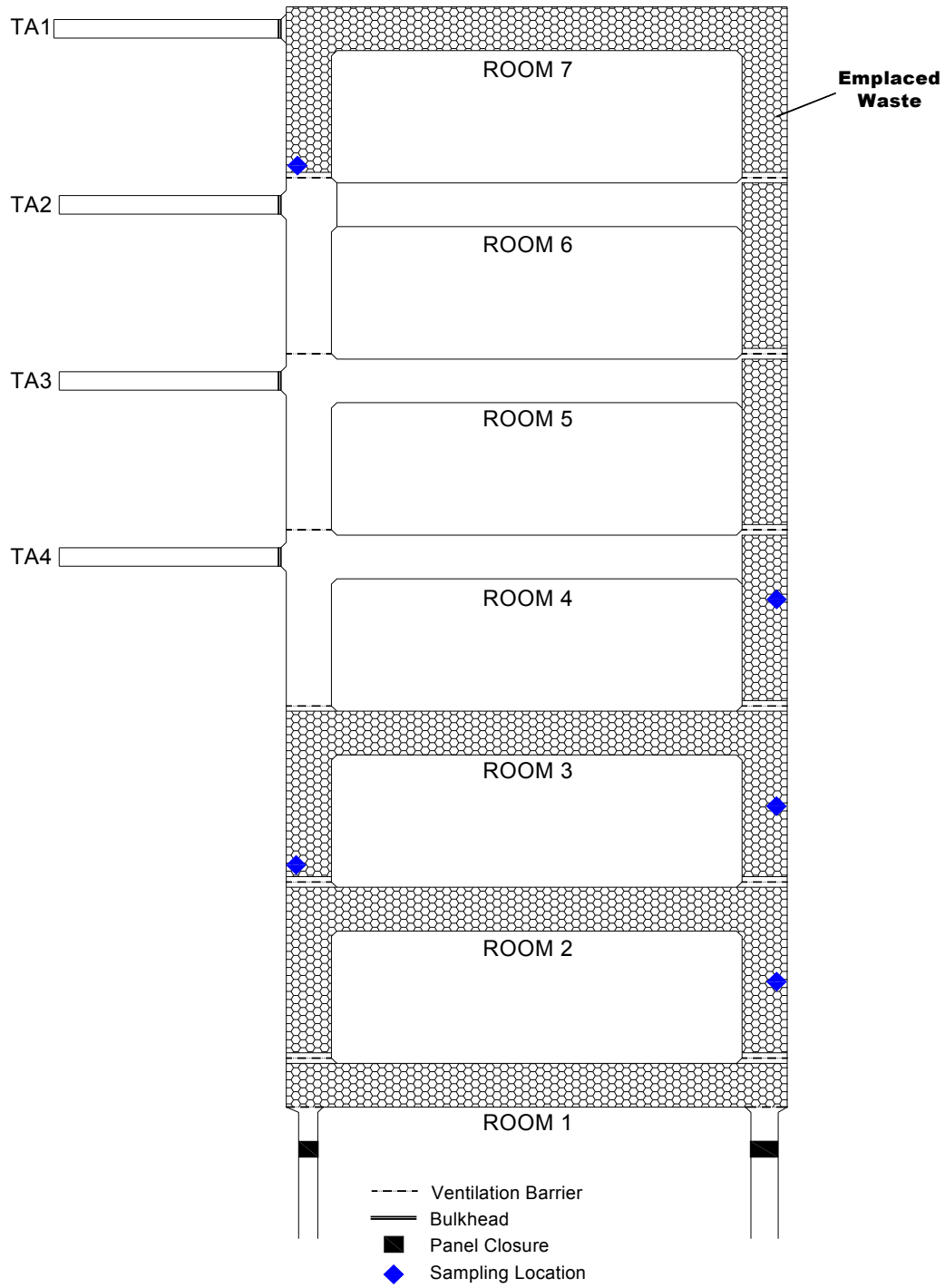
The methods proposed to address VOC emissions in the open panel offer a safe, more effective process for determining compliance with HWFP room-based limits. In addition, worker safety will be enhanced by the use of active operational controls to protect against a roof fall in an active room.

### 6.1 Effectiveness

The above strategy addresses worker exposure as the result of an event within either a disposal room or the active room. In case of an event of sufficient magnitude to generate significant VOC concentrations, the methods described herein provide an effective process to ensure that workers are alerted to evacuate in a timely manner.

### 6.2 Technical Validity

Sampling methods used for monitoring disposal rooms will be approved and accepted laboratory and industrial standards. The sampling of these locations will provide reliable information on the concentration of VOCs in disposal rooms.



**Figure 4**  
Panel 1 Disposal-Room Sampling Locations

### Typical Disposal Panel

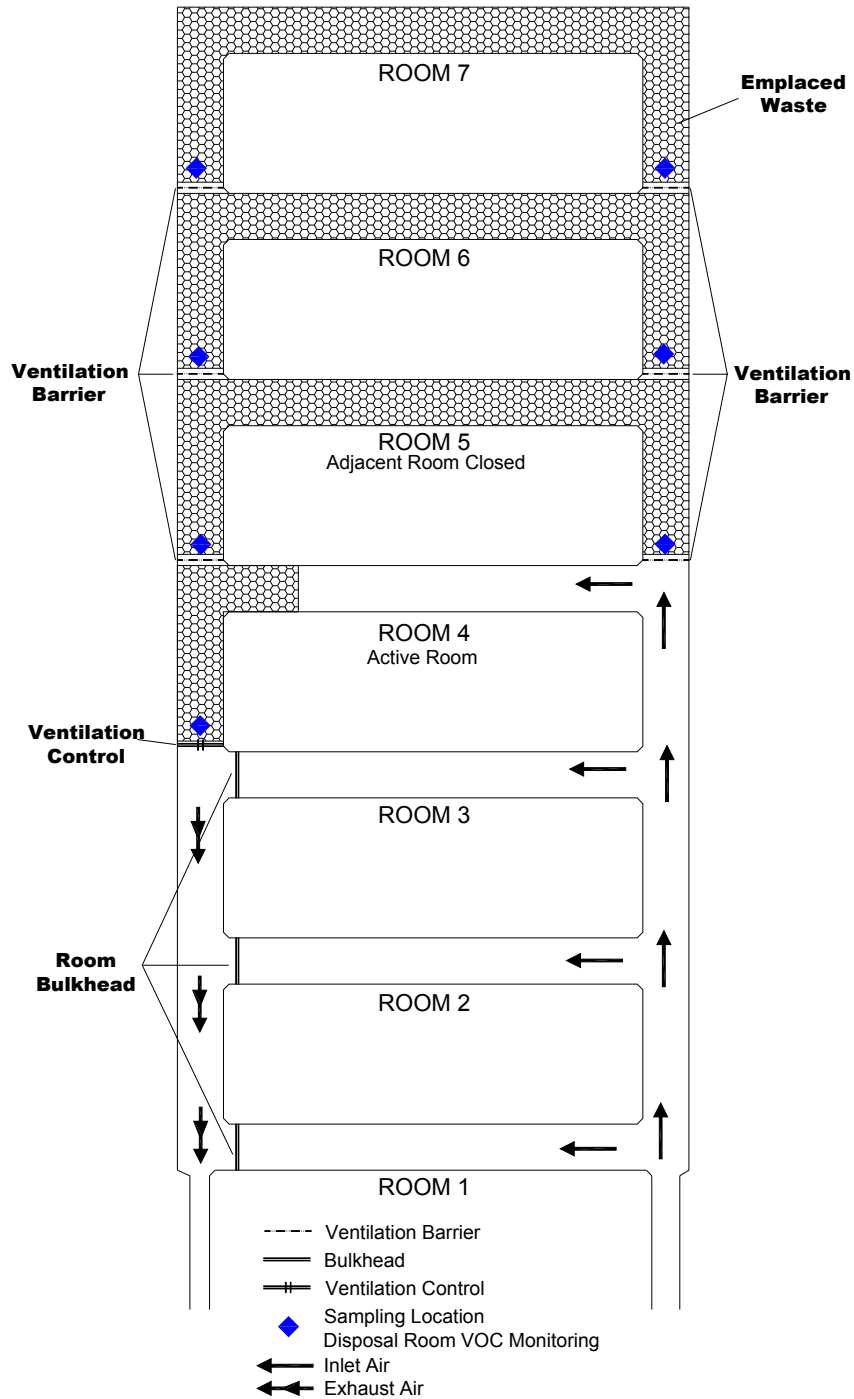
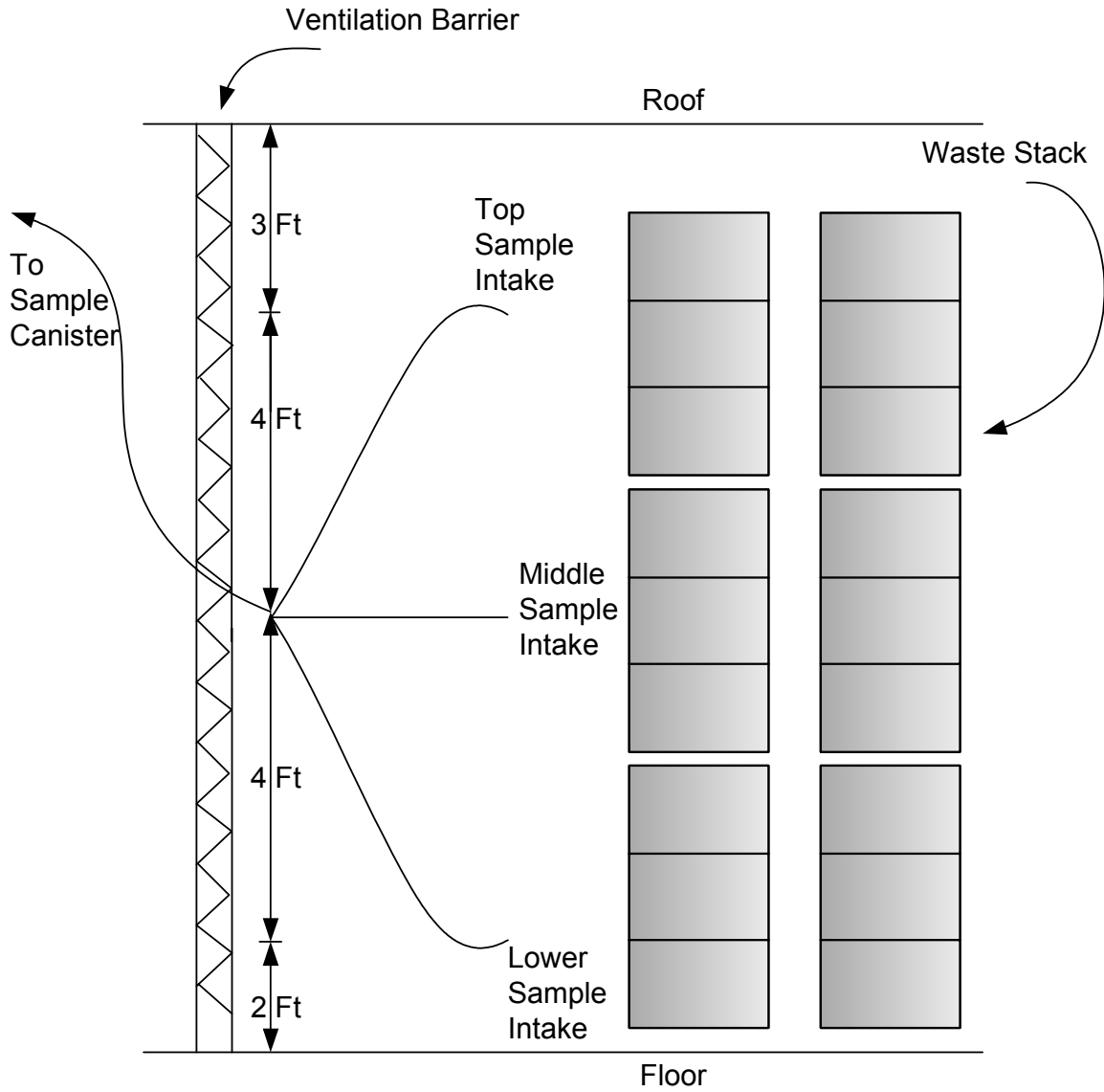


Figure 5  
Disposal Room Monitoring

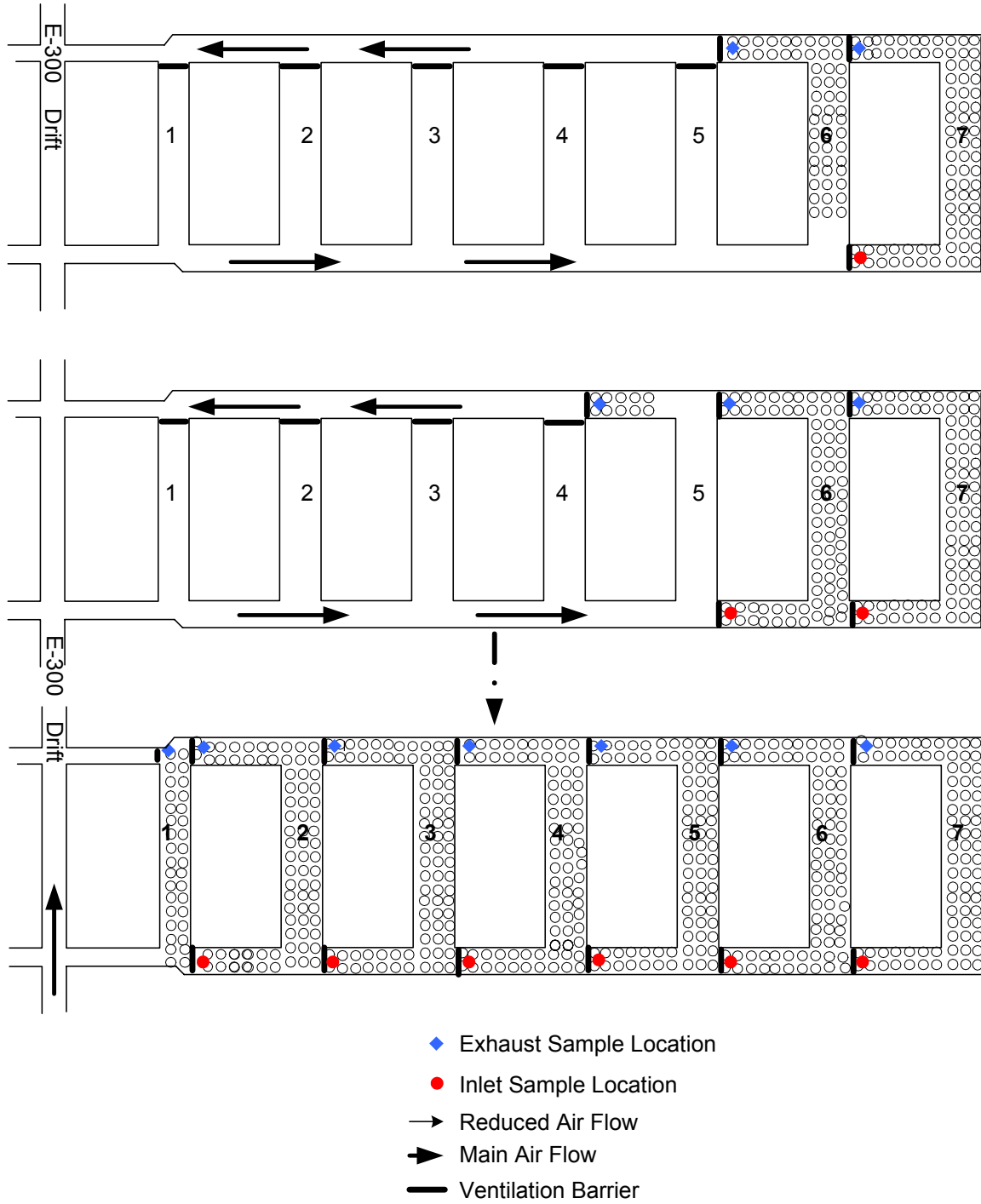




**Figure 5a**  
**Upstream/Downstream Sampling Head Location**

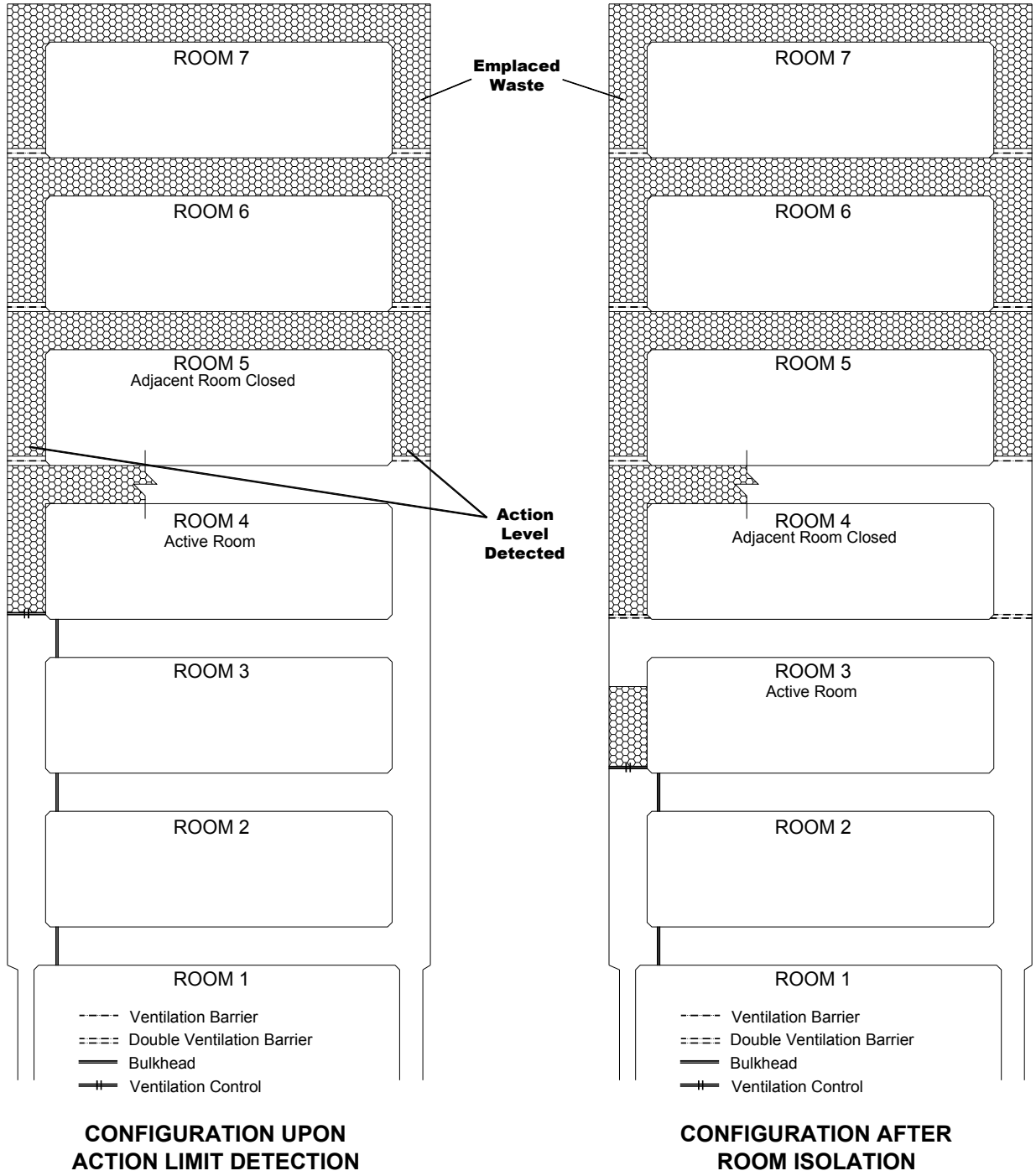
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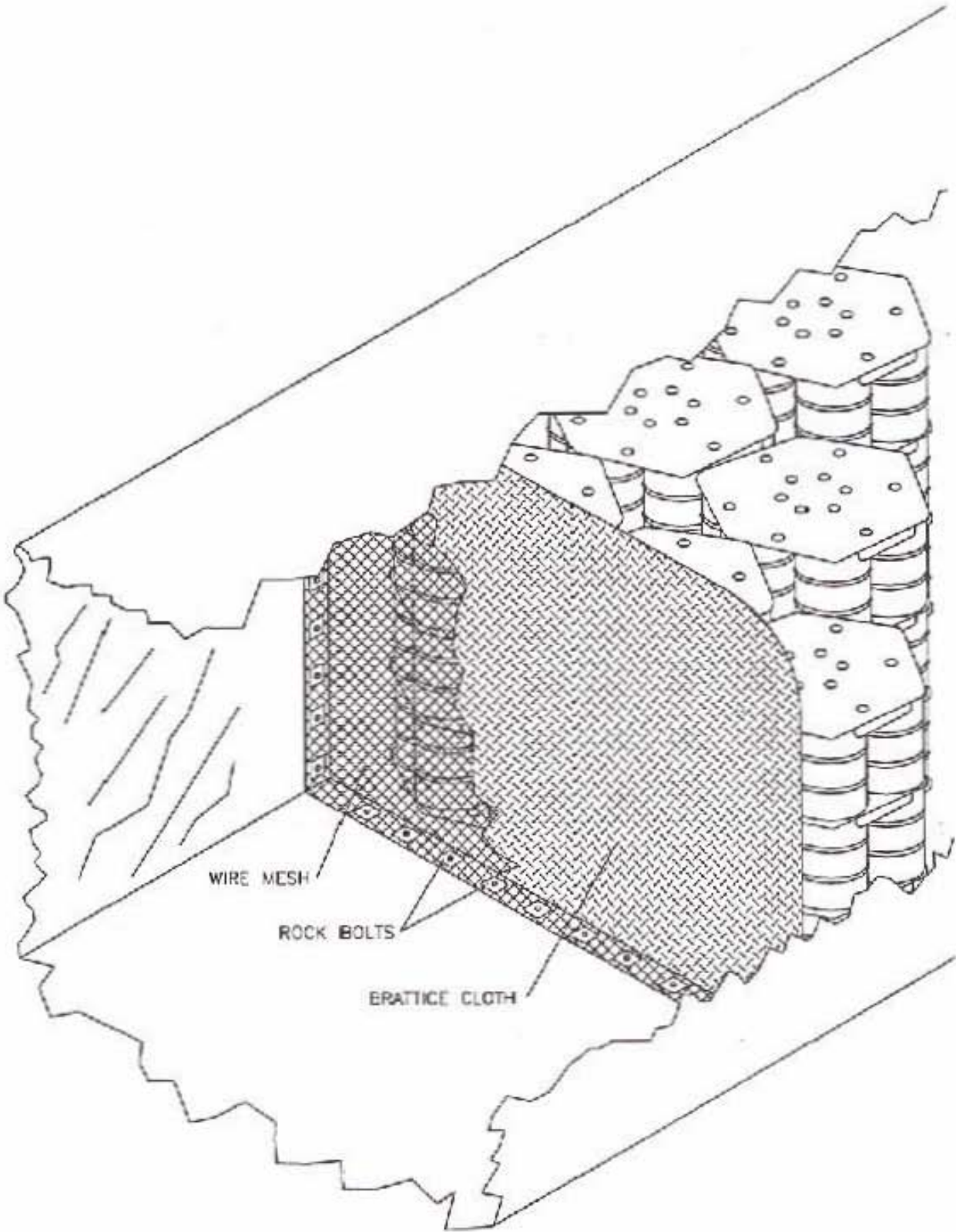
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**Figure 5 b**  
**Exhaust/Inlet**  
**Sampling Point Locations Sequence**  
**As Disposal Room Fills**

**Figure 6**  
Actions for Disposal-Room VOC Exceedence  
**CLOSED ROOM ISOLATION**





**Figure 7**  
Typical Ventilation Barrier

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