ATTACHMENT N

VOLATILE ORGANIC COMPOUND MONITORING PLAN

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ACRONYMS, ABBREVIATIONS, AND UNITS

ARA	additional requested analyte
BS/BSD	blank spike/blank spike duplicate
CFR	Code of Federal Regulations
CH	Contact-handled
CRQL	contract-required quantitation limit
DOE	U.S. Department of Energy
DRVMP	Disposal Room VOC Monitoring Program
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
ft	feet
GC/MS	gas chromatography/mass spectrometry
HI	hazard index
HWDU	Hazardous Waste Disposal Unit
IUR	inhalation unit risk
L	liter
LCS	laboratory control sample
LPEP	Laboratory Performance Evaluation Plan
m	meter
MDL	method detection limit
mm	millimeter
MOC	Management and Operating Contractor
MRL	method reporting limit
mtorr	millitorr
NIST	National Institute of Standards and Technology
NMAC	New Mexico Administrative Code
NMED	New Mexico Environment Department
PASK	passive air sampling kit
ppbv	parts per billion by volume
ppmv	parts per million by volume
QA	quality assurance
QAPjP	Quality Assurance Project Plan
QC	quality control
RfC	reference concentration
RH	remote-handled
RPD	relative percent difference

RVMP	Repository VOC Monitoring Program
SOP	standard operating procedure
TIC	tentatively identified compound
TRU	transuranic
VOC	volatile organic compound
WIPP	Waste Isolation Pilot Plant

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ATTACHMENT N

VOLATILE ORGANIC COMPOUND MONITORING PLAN

N-1 Introduction

This Permit Attachment describes the monitoring plan for volatile organic compound (**VOC**) emissions from mixed waste that may be entrained in the exhaust air from the U.S. Department of Energy (**DOE**) Waste Isolation Pilot Plant (**WIPP**) Underground Hazardous Waste Disposal Units (**HWDUs**) during the disposal phase at the facility. The purpose of VOC monitoring is to ensure compliance with the VOC action levels and limits specified in Permit Part 4. This VOC monitoring plan consists of two programs: (1) the Repository VOC Monitoring Program (**RVMP**), which assesses compliance with the action levels in Permit Part 4, Section 4.6.2.3; and (2) the Disposal Room VOC Monitoring Program (**DRVMP**) (includes ongoing disposal room VOC monitoring), which assesses compliance with the disposal room action levels and limits in Permit Part 4, Tables 4.6.3.2 and 4.4.1. This plan includes the monitoring design, a description of sampling and analysis procedures, quality assurance (**QA**) objectives, and reporting activities.

N-1a Background

The Underground HWDUs are located 2,150 feet (ft) (655 meters [m]) below ground surface, in the WIPP underground. As defined for this Permit, an Underground HWDU is a single excavated panel consisting of seven rooms and two access drifts designated for disposal of contact-handled (**CH**) and remote-handled (**RH**) transuranic (**TRU**) mixed waste. Each room is approximately 300 ft (91 m) long, 33 ft (10 m) wide, and 13 ft (4 m) high. Access drifts connect the rooms and have the same cross section. The Permittees shall dispose of TRU mixed waste in Underground HWDUs designated as Panels 1 through 8.

This plan addresses the following elements:

1. Rationale for the design of the VOC monitoring programs, based on:
    - Possible pathways from WIPP during the active life of the facility
    - Demonstrating compliance with the disposal room limits by monitoring VOCs in underground disposal rooms
    - Demonstrating compliance with the ambient air monitoring action levels by monitoring VOC emissions on the surface
    - VOC sampling operations at WIPP
    - Optimum locations for sampling
2. Descriptions of the specific elements of the VOC monitoring programs, including:
    - The type of monitoring conducted
    - Sampling locations
    - The monitoring interval

- The specific hazardous constituents monitored
- VOC monitoring schedule
- Sampling equipment
- Sampling and analytical techniques
- Data recording/reporting procedures
- Notification and action levels for remedial action

The technical basis for Disposal Room VOC Monitoring is discussed in detail in the Technical Evaluation Report for Room-Based VOC Monitoring (WRES, 2003).

N-1b Objectives of the Volatile Organic Compound Monitoring Plan

The CH and RH TRU mixed waste disposed in the WIPP Underground HWDUs contain VOCs which could be released from WIPP during the disposal phase of the project. This Plan describes how:

- VOCs released from waste panels will be monitored to confirm that the running annual average risk to the non-waste surface worker due to VOCs in the air emissions from the Underground HWDUs do not exceed the action levels identified in Permit Part 4, Section 4.6.2.3. and calculated from measured VOC concentrations using risk factors identified in Table 4.6.2.3. Appropriate remedial action, as specified in Permit Section 4.6.2.4, will be taken if the action levels in Permit Part 4, Section 4.6.2.3 are reached.

- VOCs released from waste containers in disposal rooms will be monitored to confirm that the concentration of VOCs in the air of closed and active rooms in active panels do not exceed the VOC disposal room limits identified in Permit Part 4, Table 4.4.1. Appropriate remedial action, as specified in Permit Part 4, Section 4.6.3.3, will be taken if the original sample results are greater than or equal to the action levels in Permit Part 4, Table 4.6.3.2.

N-2 Target Volatile Organic Compounds

The target VOCs for repository monitoring (Station VOC-C and VOC-D) and disposal room monitoring are presented in Table N-1.

These target VOCs were selected because together they represent approximately 99 percent of the carcinogenic risk due to air emissions of VOCs.

N-3 Monitoring Design

Detailed design features of this plan are presented in this section. This plan uses available sampling and analysis techniques to measure VOC concentrations in air. Subatmospheric sample collection units are used in the Repository and Disposal Room VOC Monitoring Programs. These sample collection units are described in greater detail in Section N-4a(2).

N-3a Sampling Locations

Air samples will be collected at the WIPP facility to quantify airborne VOC concentrations as described in the following sections.

N-3a(1) Sampling Locations for Repository VOC Monitoring

Mine ventilation air, which could potentially be impacted by VOC emissions from the Underground HWDUs identified as Panels 1 through 8, will exit the underground through the Exhaust Shaft. Building 489 has been identified as the location of the maximum non-waste surface worker exposure. Air samples will be collected from Station VOC-C located at the west air intake for Building 489 (Figure N-1) to quantify VOCs in the ambient air. Background VOCs will be measured by sampling from Station VOC-D located at groundwater pad WQSP-4 (Figure N-1). This pad is located approximately one mile southeast (upwind based on the predominant wind direction) of the Exhaust Shaft within the WIPP facility boundary.

N-3a(2) Sampling Locations for Disposal Room VOC Monitoring

For purposes of compliance with Section 310 of Public Law 108-447, the VOC monitoring of airborne VOCs in underground disposal rooms in which waste has been emplaced will be performed as follows:

1. A sample head will be installed inside the disposal room behind the exhaust drift bulkhead and at the inlet side of the disposal room.

2. TRU mixed waste will be emplaced in the active disposal room.

3. When the active disposal room is filled, another sample head will be installed to the inlet of the filled active disposal room. (Figure N-3 and N-4)

4. The exhaust drift bulkhead will be removed and re-installed in the next disposal room so disposal activities may proceed.

5. A ventilation barrier will be installed where the bulkhead was located in the active disposal room's exhaust drift. Another ventilation barrier will be installed in the active disposal room's air inlet drift, thereby closing that active disposal room.

6. Monitoring of VOCs will continue in the now closed disposal room. Monitoring of VOCs will occur in the active disposal room and all closed disposal rooms in which waste has been emplaced until commencement of panel closure activities (i.e., completion of ventilation barriers in Room 1).

This sequence for installing sample locations will proceed in the remaining disposal rooms until the inlet air ventilation barrier is installed in Room 1. An inlet sampler will not be installed in Room 1 because disposal room sampling proceeds to the next panel.

N-3b Analytes to Be Monitored

The VOCs that have been identified for repository and disposal room VOC monitoring are listed in Table N-1. The analysis will focus on routine detection and quantification of these target analytes in collected samples. As part of the analytical evaluations, the presence of other compounds (i.e., non-target VOCs) will also be monitored. Some non-target VOCs may be included on the laboratory's target analyte list as additional requested analytes (**ARAs**) to gain a better understanding of potential concentrations and associated risk. The analytical laboratory will be directed to calibrate for ARAs, when necessary. The analytical laboratory will also be directed to classify and report other non-target VOCs as tentatively identified compounds (**TICs**)

when tentative identification can be made. The evaluation of TICs in original samples will include those concentrations that are ≥10 percent of the relative internal standard. The evaluation of ARAs only includes concentrations that are greater than or equal to the MRLs listed in Table N-2.

Non-target VOCs classified as ARAs or TICs meet the following criteria: (1) are listed in Appendix VIII of 40 Code of Federal Regulations (**CFR**) Part 261 (incorporated by reference in 20.4.1.200 New Mexico Administrative Code (**NMAC**)), and (2) are detected in 10 percent or more of any original VOC monitoring samples collected over a 12-month timeframe. Non-target VOCs will be added, as applicable, to the analytical laboratory target analyte list for both the repository and disposal room VOC monitoring programs, unless the Permittees can justify their exclusion. Non-target VOCs reported as "unknown" by the analytical laboratory are not evaluated due to indeterminate identifications.

Additional requested analytes and TICs detected in the repository and disposal room VOC monitoring programs will be placed in the WIPP Operating Record and reported to the New Mexico Environment Department (**NMED**) in the Semi-Annual VOC Monitoring Report as specified in Permit Part 4, Section 4.6.2.2. As applicable, the Permittees will also report the justification for exclusion of the ARA or TIC from the target analyte list (e.g., the compound does not contribute to more than one percent of the risk; the compound persists in the background samples at similar concentrations). If new targets are required, the Permittees will submit the appropriate permit modification annually (in October) to update Table 4.6.2.3 to include the new analyte and associated recommended U.S. Environmental Protection Agency (**EPA**) risk values for the inhalation unit risk (**IUR**) and reference concentration (**RfC**). Added compounds will be included in the risk assessment described in Section N-3e(1).

N-3c Sampling and Analysis Methods

The VOC monitoring programs include a comprehensive VOC monitoring program established at the facility; equipment, training, and documentation are already in place.

The sampling methods used for VOC monitoring are based on the concepts contained in the EPA Compendium Method TO-15 (EPA, 1999). The TO-15 sampling concept uses 6-liter passivated stainless-steel canisters to collect integrated air samples at each sample location. This conceptual method will be used as a reference for collecting the samples at WIPP. The samples will be analyzed using gas chromatography/mass spectrometry (**GC/MS**) under an established QA/quality control (**QC**) program. Laboratory analytical procedures have been developed based on the concepts contained in both TO-15 and 8260B. Section N-5 contains additional QA/QC information for this project.

The TO-15 method is an EPA-recognized sampling concept for VOC sampling and speciation. It can be used to provide subatmospheric samples, integrated samples, or grab samples, as well as compound quantitation for a broad range of concentrations. This sampling technique is also viable for use while analyzing the sample using other EPA methods such as 8260B.

For subatmospheric sampling, air is collected in an initially evacuated passivated canister. When the canister is opened to the atmosphere, the differential pressure causes the sample to flow into the canister. Flow rate and duration are regulated with a flow-restrictive inlet and flow controller. The air will pass through a particulate filter to prevent sample and equipment contamination. Passivated sampling equipment components are used to inhibit adsorption of compounds on the surfaces of the equipment. The required Method Reporting Limit (**MRL**) for

the RVMP is 0.2 parts per billion by volume (**ppbv**) in SCAN mode and 0.1 ppbv in SIM mode. Consequently, low concentrations can be measured. The required MRL for DRVMP is 500 ppbv (0.5 parts per million by volume (**ppmv**)) to allow for reliable quantitation. The MRL is a function of instrument performance, sample preparation, sample dilution, and all steps involved in the sample analysis process. The DRVMP will employ sample collection units that will provide a subatmospheric sample within a short duration (less than 1 hour). Passivated sampling lines will be installed in the disposal room as described in Section N-3a(2) and maintained (to the degree possible) after the room is closed, until the panel associated with the room is closed. The independent lines will run from the sample inlet point to a sampling manifold located in an area accessible to sampling personnel.

N-3d Sampling Schedule

The Permittees will perform sampling on the following schedule in accordance with standard operating procedures.

N-3d(1) Sampling Schedule for Repository VOC Monitoring

Routine collection of a 24-hour time-integrated sample will be conducted two times per week. The RVMP sampling will continue until the certified closure of the last Underground HWDU.

N-3d(2) Sampling Schedule for Disposal Room VOC Monitoring

The disposal room sampling in open panels will occur once every two weeks, unless the need to increase the frequency to weekly occurs in accordance with Permit Section 4.6.3.3.

Beginning with Panel 3, disposal room sampling in filled panels will occur monthly until final panel closure unless an explosion-isolation wall is installed. The Permittees will sample VOCs in Room 1 of each filled panel.

N-3e Data Evaluation and Reporting

N-3e(1) Data Evaluation and Reporting for Repository VOC Monitoring

When the Permittees receive laboratory analytical data from an air sampling event, the data will be validated as specified in Section N-5d. After obtaining validated data from an original surface VOC monitoring sample obtained during an air sampling event, the data will be evaluated to determine whether the VOC emissions from the Underground HWDUs exceed the action levels in Permit Part 4, Section 4.6.2.3. The values are calculated in terms of excess cancer risk for compounds believed to be carcinogenic and hazard index (**HI**) for non-carcinogens as follows:

Calculate the carcinogenic risk for the non-waste surface worker (for each target VOC) using the following equation:

$$R_{VOCj} = \frac{Conc_{VOCj} \times EF \times ED \times IUR_{VOCj} \times 1000}{AT} \quad \text{(N-1)}$$

Where:

R_{VOCj} = *Risk due to exposure to target VOC$_j$*

$Conc_{VOC_j}$ = *Concentration target VOC$_j$ at the receptor (mg/m^3), calculated as the concentration at VOC-C (mg/m^3) – the concentration at VOC-D (mg/m^3)*

EF = Exposure frequency (hours/year) = 1,920 hours per year

ED = Exposure duration, years = 10 years

IUR_{VOCj} = *Inhalation unit risk factor from Table 4.6.2.3 (µg/m^3)$^{-1}$*

AT = Averaging time for carcinogens, = 613,200 hours based on 70 years

1,000 = µg/mg

The total carcinogenic risk is then the sum of the risk due to each carcinogenic target VOC:

$$\text{Total Carcinogenic Risk} = \sum_{j=1}^{m} R_{VOC_j} \quad \text{(N-2)}$$

Where:

Total Risk must be less than 10^{-5}

m = the number of carcinogenic target VOCs

The formula for calculating the non-carcinogenic hazard index is similar:

$$HI_{VOC_j} = \frac{Conc_{VOC_j} \times EF \times ED}{AT \times RfC_{VOC_j}} \quad \text{(N-3)}$$

Where:

HI_{VOC_j} = *Hazard Index for exposure to target VOC$_j$*

$Conc_{VOC_j}$ = *Concentration target VOC$_j$ at the receptor (mg/m^3), calculated as the concentration at VOC-C (mg/m^3) – the concentration at VOC-D (mg/m^3)*

EF = Exposure frequency (hours/year) = 1,920 hours per year

ED = Exposure duration, years = 10 years

RfC_{VOC_j} = *Reference concentration from Table 4.6.2.3 (mg/m^3)*

AT = Averaging time for non-carcinogens, = 87,600 hours, based on exposure duration

The total hazard is the sum of the hazard index due to each non-carcinogenic target VOC:

$$\text{Total Hazard Index} = \sum_{j=1}^{m} HI_{VOC_j} \quad \text{(N-4)}$$

Where:

Hazard Index must be less than or equal to 1.0

m = the number of non-carcinogenic target VOCs

The total carcinogenic risk (Equation N-2) and the total HI (Equation N-4) calculated from the surface VOC concentrations for each sampling event will be compared directly to the action levels in Permit Part 4, Section 4.6.2.3. This will establish whether any of the concentrations of VOCs in the emissions from the Underground HWDUs exceeded the risk and HI action levels at the time of the sampling.

As specified in Permit Part 4, the Permittees shall notify the Secretary in writing, within seven calendar days of obtaining validated analytical results, whenever the risk or HI exceeds the action levels specified in Permit Part 4, Section 4.6.2.3.

The surface VOC concentrations for each target VOC that is calculated for each sampling event will then be averaged with the surface VOC concentrations calculated for the air sampling events conducted during the previous 12 months. This will be considered the running annual average concentration for each target VOC. The running annual average risk and HI will be compared to action levels specified in Permit Part 4, Section 4.6.2.3. When a VOC is added to the target analyte list, the running annual average concentration will be calculated using all available data.

As specified in Permit Part 4, the Permittees shall notify the Secretary in writing, within seven calendar days of obtaining validated analytical results, whenever the running annual average risk or HI (calculated after each sampling event) exceeds the action levels specified in Permit Part 4, Section 4.6.2.3.

The Permittees will maintain a database with the VOC air sampling data and the results will be reported to the Secretary as specified in Permit Part 4.

N-3e(2) Data Evaluation and Reporting for Disposal Room VOC Monitoring

When the Permittees receive laboratory analytical data from an air sampling event, the data will be validated as specified in Section N-5d. The validated data will be evaluated to determine whether the VOC concentrations in the air of any closed room, the active open room, or the immediately adjacent closed room exceeded the Action Levels for DRVMP specified in Permit Part 4, Table 4.6.3.2.

The Permittees shall notify the Secretary in writing, within seven calendar days of obtaining validated analytical results, whenever the concentration of any VOC specified in Permit Part 4, Table 4.4.1 exceeds the action levels specified in Permit Part 4, Table 4.6.3.2.

The Permittees shall submit to the Secretary the Semi-Annual VOC Monitoring Report specified in Permit Section 4.6.2.2 that also includes results from disposal room VOC monitoring.

N-4 Sampling and Analysis Procedures

This section describes the equipment and procedures that will be implemented during sample collection and analysis activities for VOCs at WIPP.

N-4a Sampling Equipment

The sampling equipment that will be used includes: 6-liter (L) stainless-steel passivated canisters, passive air sampling kits (**PASKs**), subatmospheric sampling assemblies, passivated stainless-steel tubing, and one or more in-line filters. A discussion of each of these items is presented below.

N-4a(1) Sample Canisters

Six-liter, stainless-steel canisters with passivated interior surfaces will be used to collect and store all ambient air and disposal room samples for VOC analyses collected as part of the monitoring processes. These canisters will be cleaned and certified (batch certification acceptable for disposal room monitoring) prior to their use, in a manner similar to that described by Compendium Method TO-15. The canisters will be certified clean to below the required reporting limits for the VOC analytical method for the target VOCs. The vacuum of certified clean canisters will be verified as adequate upon initiation of a sample cycle as described in standard operating procedures (**SOPs**). The sample canisters are initially evacuated at the analytical laboratory to <0.05 mm Hg (50 mtorr).

N-4a(2) Sample Collection Units

The sample collection unit for surface VOC samples is a commercially available PASK comprised of components that regulate the rate and duration of air flow into a sample canister. It can be operated either manually, using canister valves, or unattended, using a programmable timer.

The sample collection unit for disposal room VOC monitoring is a subatmospheric sampling assembly that regulates the rate and duration of air flow into a sample canister. The subatmospheric sampling assembly also allows for purging of sample lines to ensure that a representative sample is collected.

Sample collection units will use passivated components for the sample flow path. When sample canisters installed on sample collection units are opened to the atmosphere, the differential pressure causes the sample to flow into the canister at a regulated rate. By the end of each sampling period, the canisters will be near atmospheric pressure. Detailed instructions on sample collection will be given in SOPs. A conceptual diagram of the VOC sample collection units are provided in Figure N-2.

N-4a(3) Sample Tubing

The tubing used as a sample path is comprised of passivated stainless-steel to prevent the inner walls from absorbing sample constituents and/or contaminants when they are pulled from the sample point to the sample collection unit.

N-4b Sample Collection

Sample collection for VOCs at the WIPP facility will be conducted in accordance with written SOPs that are kept on file at the facility. These SOPs will specify the steps necessary to ensure the collection of samples that are of acceptable quality to meet the applicable data quality objectives in Section N-5.

Repository VOC samples will be 24 -hour time-integrated samples for each sampling event. Alternative sampling durations may be defined for assessment purposes and to meet the data quality objectives. The selection of sampling days will be specified in SOPs and will be alternated from week-to-week in order to avoid potential bias created by plant operations.

Sample flow for the PASK will be set using an in-line mass flow controller. The flow controllers are initially factory-calibrated and specify a typical accuracy of better than 10 percent full scale. Additionally, each air flow controller is calibrated at a manufacturer-specified frequency using a National Institute of Standards and Technology (**NIST**) primary flow standard.

To verify the matrix similarity and assess field sampling precision, field duplicate samples will be collected (two canisters filled simultaneously) for each VOC monitoring program at an overall frequency of at least 5 percent (see Section N-5a).

Prior to collecting the active open disposal room and closed room samples, the sample lines are purged to ensure that the air collected is not air that has been stagnant in the tubing. This is important in regard to the disposal room sample because of the long lengths of tubing associated with these samples.

N-4c Sample Management

Field sampling data sheets will be used to document the sampler conditions under which each sample is collected. These data sheets have been developed specifically for VOC monitoring at the WIPP facility. The individuals assigned to collect the specific samples will be required to fill in all of the appropriate sample data and to maintain this record in sample logbooks. The program team leader will review these forms for each sampling event.

All sample containers will be marked with identification at the time of collection of the sample. A Request-for-Analysis Form will be completed to identify the sample canister number(s), sample type and type of analysis requested.

All samples will be maintained, and shipped if necessary, at ambient temperatures. Collected samples will be transported in appropriate containers. Prior to leaving the underground for analysis, sample containers may undergo radiological screening, which will ensure that contaminated samples or equipment will not be transported to the surface. Samples will not be accepted by the receiving laboratory personnel unless they are properly labeled and sealed to ensure a tamper-free shipment.

An important component of the sampling program is a demonstration that collected samples were obtained from the locations stated and that they reached the laboratory without alteration. To satisfy this requirement, evidence of collection, shipment, laboratory receipt, and custody will be documented with a completed Chain-of-Custody Form. Chain-of-custody procedures will be followed closely, and additional requirements imposed by the laboratory for sample analysis will be included as necessary.

Individuals collecting samples will be responsible for the initiation of custody procedures. The chain of custody will include documentation as to the canister certification, location of sampling event, time, date, and the name of the individual handling the samples. Deviations from procedure will be considered variances. Variances must be preapproved by the program manager and recorded in the project files. Unintentional deviations, sampler malfunctions, and other problems are nonconformances. Nonconformances must be documented and recorded in

the project files. All field logbooks/data sheets must be incorporated into WIPP's records management program.

N-4d Maintenance of Sample Collection Units

Periodic maintenance for sample collection units and associated equipment will be performed as needed. This maintenance may include cleaning, replacement of damaged or malfunctioning parts, and leak testing. Additionally, complete spare sample collection units will be maintained on-site to minimize downtime because of equipment malfunction.

N-4e Analytical Procedures

Analytical procedures used in the analysis of VOC samples from canisters are based on concepts contained in Compendium Method TO-15 (EPA, 1999) and in SW-846 Method 8260B (EPA, 1996).

Analysis of samples will be performed by a certified laboratory. Methods will be specified in procurement documents and will be selected to be consistent with Compendium Method TO-15 (EPA, 1999) or EPA recommended procedures in SW-846 (EPA, 1996). Additional detail on analytical techniques and methods will be given in laboratory SOPs.

The Permittees will establish the criteria for laboratory selection, including the stipulation that the laboratory follow the procedures specified in the appropriate Air Compendium or SW-846 method and that the laboratory follow EPA protocols. The selected laboratory shall demonstrate, through laboratory SOPs, that it will follow appropriate EPA SW-846 requirements and the requirements specified by the EPA Air Compendium protocols. The laboratory shall also provide documentation to the Permittees describing the sensitivity of laboratory instrumentation. This documentation will be retained in the facility operating record and will be available for review upon request by NMED.

The SOPs for the laboratory currently under contract will be maintained in the operating record by the Permittees. The Permittees will provide NMED with an initial set of applicable laboratory SOPs for information purposes, and provide NMED with any updated SOPs on an annual basis by January 31.

Data validation will be performed by the Permittees. Copies of the data validation report will be kept on file in the operating record for review upon request by NMED.

N-5 Quality Assurance

The QA activities for the VOC monitoring programs will be conducted in accordance with the documents: *EPA Guidance for Quality Assurance Project Plans QA/G-5* (EPA, 2002) and the *EPA Requirements for Preparing Quality Assurance Project Plans, QA/R-5* (EPA, 2001). The QA criteria for the VOC monitoring programs are listed in Table N-2. This section addresses the methods to be used to evaluate the components of the measurement system and how this evaluation will be used to assess data quality. The QA limits for the sampling procedures and laboratory analysis shall be in accordance with the limits set forth in the specific EPA Method referenced in standard operating procedures employed by either the Permittees or the laboratory. The Permittees standard operating procedures will be in the facility Operating Record and available for review by NMED at anytime. The laboratory standard operating

procedures will also be in the facility Operating Record and will be supplied to the NMED as indicated in Section N-4e.

N-5a Quality Assurance Objectives for the Measurement of Precision, Accuracy, Sensitivity, and Completeness

QA objectives for this plan will be defined in terms of the following data quality parameters.

Precision. For the duration of this program, precision will be defined and evaluated by the RPD values calculated between field duplicate samples and between laboratory duplicate samples.

$$RPD = \left(\frac{(A - B)}{(A + B)/2} \right) * 100 \qquad \text{(N-5)}$$

where: A = Original sample result

B = Duplicate sample result

Accuracy. Analytical accuracy will be defined and evaluated through the use of analytical standards. Because recovery standards cannot reliably be added to the sampling stream, overall system accuracy will be based on analytical instrument performance evaluation criteria. These criteria will include performance verification for instrument calibrations, laboratory control samples, sample surrogate recoveries (when required by method or laboratory SOPs), and sample internal standard areas. Use of the appropriate criteria as determined by the analytical method performed, will constitute the verification of accuracy for target analyte quantitation (i.e., quantitative accuracy). Evaluation of standard ion abundance criteria for BFB will be used to evaluate the accuracy of the analytical system in the identification of targeted analytes, as well as the evaluation of unknown contaminants (i.e., qualitative accuracy).

Sensitivity. Sensitivity will be defined by the required MRLs for the program. Attainment of required MRLs will be verified by the performance of statistical method detection limit (**MDL**) studies in accordance with 40 *Code of Federal Regulations* §136. The MDL represents the minimum concentration that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. An MDL study will be performed by the program analytical laboratory prior to sampling and analysis, and annually thereafter.

Completeness. Completeness will be defined as the percentage of the ratio of the number of valid sample results received (i.e., those which meet data quality objectives) versus the total number of samples collected. Completeness may be affected, for example, by sample loss or destruction during shipping, by laboratory sample handling errors, or by rejection of analytical data during data validation.

N-5a(1) Evaluation of Laboratory Precision

Laboratory sample duplicates and blank spike/blank spike duplicates (**BS/BSD**) will be used to evaluate laboratory precision. QA objectives for laboratory precision are listed in Table N-2, and are based on precision criteria proposed by the EPA for canister sampling programs (EPA, 1991). These values will be appropriate for the evaluation of samples with little or no matrix effects. Because of the potentially high level of salt-type aerosols in the WIPP underground environment, the analytical precision achieved for WIPP samples may vary with respect to the

EPA criteria. RPDs for BS/BSD analyses will be tracked through the use of control charts. RPDs obtained for laboratory sample duplicates will be compared to those obtained for BS/BSDs to ascertain any sample matrix effects on analytical precision. BS/BSDs and laboratory sample duplicates will be analyzed at a frequency of 10 percent, or one per analytical lot, whichever is more frequent.

N-5a(2) Evaluation of Field Precision

Field duplicate samples will be collected at a frequency of at least 5 percent for the RVMP and at least 5 percent for the DRVMP. The data quality objective for field precision is 35 percent for each set of field duplicate samples.

N-5a(3) Evaluation of Laboratory Accuracy

Quantitative analytical accuracy will be evaluated through performance criteria on the basis of (1) relative response factors generated during instrument calibration, (2) analysis of laboratory control samples (**LCS**), and (3) recovery of internal standard compounds. The criteria for the initial calibration (5-point calibration) is $\leq$ 30 percent relative standard deviation for target analytes. After the successful completion of the 5-point calibration, it is sufficient to analyze only a midpoint standard for every 24 hours of operation. The midpoint standard will pass a 30 percent difference acceptance criterion for each target compound before sample analysis may begin.

A blank spike or LCS is an internal QC sample generated by the analytical laboratory by spiking a standard air matrix (humid zero air) with a known amount of a certified reference gas. The reference gas will contain the target VOCs at known concentrations. Percent recoveries for the target VOCs will be calculated for each LCS relative to the reference concentrations. Objectives for percent recovery are listed in Table N-2, and are based on accuracy criteria proposed by the EPA for canister sampling programs (EPA, 1991). LCSs will be analyzed at a frequency of 10 percent, or one per analytical lot, whichever is more frequent.

Internal standards will be introduced into each sample analyzed, and will be monitored as a verification of stable instrument performance. In the absence of any unusual interferences, areas should not change by more than 40 percent over a 24-hour period. Deviations larger than 40 percent are an indication of a potential instrument malfunction. If an internal standard area in a given sample changes by more than 40 percent, the sample will be reanalyzed. If the 40 percent criterion is not achieved during the reanalysis, the instrument will undergo a performance check and the midpoint standard will be reanalyzed to verify proper operation. Response and recovery of internal standards will also be compared between samples, LCSs, and calibration standards to identify any matrix effects on analytical accuracy.

N-5a(4) Evaluation of Sensitivity

The presence of aerosol salts in underground locations may affect the MDL of the samples collected in those areas. The sample inlet of these sample collection units will be protected sufficiently from the underground environment to minimize salt aerosol interference. Up to two filters, inert to VOCs, will be installed in the sample flow path to minimize particulate interference.

The MDL for each of the target VOCs will be evaluated by the analytical laboratories before sampling begins. The initial and annual MDL evaluation will be performed in accordance with 40

Code of Federal Regulations §136, and with EPA/530-SW-90-021, as revised and retitled, "Quality Assurance and Quality Control" (Chapter 1 of SW-846) (1996).

N-5a(5) Completeness

The expected completeness for this program is greater than or equal to 95 percent. Data completeness will be tracked monthly.

N-5b Sample Handling and Custody Procedures

Sample packaging, shipping, and custody procedures are addressed in Section N-4c.

N-5c Calibration Procedures and Frequency

Calibration procedures and frequencies for analytical instrumentation are listed in Section N-4e.

N-5d Data Reduction, Validation, and Reporting

Field sampling data sheets will contain documentation of all pertinent data for the sampling and will at a minimum include the following; sample identification, sample location, sample collection date, initial vacuum, ending vacuum, collection start and collection stop time, flow rate and ambient temperature.

Data validation procedures will include at a minimum, a check of all field data sheets for completeness and correctness. Sample custody and analysis records will be reviewed by the analytical laboratory QA officer and the analytical laboratory supervisor at a frequency of at least 10 percent.

Electronic Data Deliverables (**EDDs**) are provided by the laboratory prior to receipt of hard copy data packages. EDDs will be evaluated within five calendar days of receipt to determine if VOC concentrations are at or above action levels in Permit Part 4, Section 4.6.3.2 for disposal room VOC monitoring data, or the action levels specified in Permit Part 4, Section 4.6.2.3 for repository monitoring data. If the EDD indicates that VOC concentrations are at or above these action levels or concentrations, the hard copy data package will be validated within five calendar days as opposed to the 14 calendar day time frame.

Data will be reported as specified in Section N-3(e) and Permit Part 4.

Acceptable data for this VOC monitoring plan will meet stated precision and accuracy criteria. The QA objectives for precision, accuracy, and completeness as shown in Table N-2 can be achieved when established methods of analyses are used as proposed in this plan and standard sample matrices are being assessed.

N-5e Performance and System Audits

The Permittees will evaluate whether the monitoring systems and analytical methods are functioning properly through performance and system audits. The assessment period will be determined by the Permittees. System audits will initially address start-up functions for each phase of the project. These audits will consist of on-site evaluation of materials and equipment, review of certifications for canisters and measurement and test equipment, review of laboratory qualification and operation and, at the request of the QA officer, an on-site audit of the

laboratory facilities. The function of the system audit is to verify that the requirements in this plan have been met prior to initiating the program. System audits will be performed at or shortly after the initiation of the VOC monitoring programs and on an annual basis thereafter.

Performance audits will be accomplished as necessary through the evaluation of analytical QC data by performing periodic site audits throughout the duration of the project, and through the introduction of third-party audit cylinders (laboratory blinds) into the analytical sampling stream. Performance audits will also include a surveillance/review of data associated with canister certifications and measurement and test equipment, a project-specific technical audit of field operations, and a laboratory performance audit. Field logs, logbooks, and data sheets, as applicable will be reviewed during data validation. Blind-audit canisters will be introduced once during the sampling period. Details concerning scheduling, personnel, and data quality evaluation are addressed in the QAPjP.

By May 1, 2016 the Permittees shall develop and implement a RVMP Laboratory Performance Evaluation Plan (**LPEP**) that has been reviewed and approved by the Secretary prior to use, for Repository VOC ambient monitoring. In addition to the timely submittal of validated data packages under this LPEP to the Secretary, the results shall also be reported annually in the October Semi- Annual VOC Monitoring Report. The second contract laboratory performing the performance evaluation to be used for comparison to the primary contract laboratory shall use the required MRLs as required in Table N-2, which are defined to be equivalent to the CRQLs. Any contract laboratory involved in this program shall have a site specific quality assurance project plan and an associated QA/QC program that are acceptable and aligned with EPA guidance. The LPEP shall, at a minimum, include the following sections:

1. Table of Contents
2. Introduction
3. Background
4. Scope/Objectives: this section shall include comparative testing of subatmospheric sampling containers, the field background canisters, and a test of the cleanliness of the canister less than the SIM mode MRL in Table N-2.
5. Laboratory Specific SOPs
6. Sampling Methodologies
7. Analytical Methodologies
8. Quality Assurance Requirements
9. Schedules
10. Reporting: data packages shall contain all applicable sections found in the document "*Statement-of-Work for the Analysis of Air Toxics from Superfund Sites*" (EPA 1990), Exhibit B, Section 2, "*Reporting Requirements and Order of Data Deliverables"* and as approved by the Secretary.

As an alternative to the LPEP, the Permittees will notify the Secretary of their intention to require the contract laboratory to participate in proficiency testing. The Permittees will then, within 90 days, submit to the NMED for approval, a proposal for proficiency testing. If the Permittees are unable to develop a proficiency testing plan that is acceptable to the NMED, then the Permittees will prepare and submit the LPEP. The proposal for proficiency testing will include the following, as applicable:

- Specific analytical method(s)
- Schedule for proficiency testing implementation

- Provision for the periodic reporting of proficiency testing results and corrective actions, if any

Results of proficiency testing will be reported in the Semi-Annual VOC Monitoring Report as specified in Permit Part 4, Section 4.6.2.2.

N-5f Preventive Maintenance

Maintenance of sample collection units is described briefly in Section N-4d Maintenance of analytical equipment will be addressed in the analytical laboratory SOP.

N-5g Corrective Actions

If the required completeness of valid data (95 percent) is not maintained, corrective action may be required. Corrective action for field sampling activities may include recertification and cleaning of sample collection units, reanalysis of samples, additional training of personnel, modification to field and laboratory procedures, and recalibration of measurement and test equipment.

Laboratory corrective actions may be required to maintain data quality. The laboratory continuing calibration criteria indicate the relative response factor for the midpoint standard will be less than 30 percent different from the mean relative response factor for the initial calibration. Differences greater than 30 percent will require recalibration of the instrument before samples can be analyzed. If the internal standard areas in a sample change by more than 40 percent, the sample will be reanalyzed. If the 40 percent criterion is not achieved during the reanalysis, the instrument will undergo a performance check and the midpoint standard will be reanalyzed to verify proper operation. Deviations larger than 40 percent may indicate instrument malfunction.

The laboratory results for samples, duplicate analyses, LCSs, and blanks should routinely be within the QC limits. If results exceed control limits, the reason for the nonconformances and appropriate corrective action must be identified and implemented.

N-5h Records Management

The VOC Monitoring Programs will require administration of record files (both laboratory and field data collection files). The records control systems will provide adequate control and retention for program-related information. Records administration, including QA records, will be conducted in accordance with applicable DOE, MOC, and WIPP requirements.

Unless otherwise specified, VOC monitoring plan records will be retained as lifetime records. Temporary and permanent storage of QA records will occur in facilities that prevent damage from temperature, fire, moisture, pressure, excessive light, and electromagnetic fields. Access to stored VOC Monitoring Program QA Records will be controlled and documented to prevent unauthorized use or alteration of completed records.

Revisions to completed records (i.e., as a result of audits or data validation procedures) may be made only with the approval of the responsible program manager and in accordance with applicable QA procedures. Records of project activities will be maintained at the WIPP site. Documentation will be available for inspection by internal and external auditors.

N-6 Sampling and Analysis Procedures for Disposal Room VOC Monitoring in Filled Panels

Disposal room VOC samples in filled panels will be collected using the subatmospheric pressure grab sampling technique described in Compendium Method TO-15 (EPA, 1999). This method uses an evacuated passivated canister (or equivalent) that is under vacuum (0.05 mm Hg) to draw the air sample from the sample lines into the canister. The sample lines will be purged prior to sampling to ensure that a representative sample is collected. The passivation of tubing and canisters used for VOC sampling effectively seals the inner walls and prevents compounds from being retained on the surfaces of the equipment. By the end of each sampling period, the canisters will be near atmospheric pressure.

The analytical procedures for disposal room VOC monitoring in filled panels are the same as specified in Section N-4e.

N-7 References

40 CFR Part 136, "*Guidelines Establishing Test Procedures for the Analysis of Pollutants*."

Section 310 of Public Law 108-447 of the *Consolidated Appropriations Act of 2005.*

U.S. Environmental Protection Agency, 1991. Contract Laboratory Program, *Volatile Organics Analysis of Ambient Air in Canisters (Draft)*, EPA540/R-94-085, December 1991, Washington, D.C.

U.S. Environmental Protection Agency. 1996. SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Third Edition. Office of Solid Waste and Emergency Response, Washington, D.C.

U.S. Environmental Protection Agency. 1999 *Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) In Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry(GC/MS)*, EPA 625/R-96/010b. Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH, January 1999.

U.S. Environmental Protection Agency. 2001. *EPA Requirements for Quality Assurance Project Plans, QA/R-5*, EPA 240/B-01/003, March 2001, Washington, D.C.

U.S. Environmental Protection Agency. 2002. *Guidance for Quality Assurance Project Plans*, QA/G-5*,* EPA 240/R-02/009, December 2002, Washington, D.C.

Washington Regulatory and Environmental Services, 2003. *Technical Evaluation Report for WIPP Room-Based VOC Monitoring*.

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TABLES

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Table N-1
Target Analytes and Methods for Repository VOC (Station VOC-C and VOC-D)
Monitoring and Disposal VOC Room Monitoring

Target Analyte	EPA Standard Analytical Method
Carbon tetrachloride	EPA TO-15[a] EPA 8260B[b]
Chlorobenzene	
Chloroform	
1,1-Dichloroethylene	
1,2-Dichloroethane	
Methylene chloride	
1,1,2,2 -Tetrachloroethane	
Toluene	
1,1,1- Trichloroethane	
Trichloroethylene	

[a] U.S. Environmental Protection Agency, 1999, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air- Second Edition, http://www.epa.gov/ttn/amtic/airtox.html

[b] U.S. Environmental Protection Agency, SW-846 Test Methods for Evaluation Solid Wastes, Chemical and Physical Methods, http://www.epa.gov/epaoswer/hazwaste/test/main.html

Table N-2
Quality Assurance Objectives for Accuracy, Precision, Sensitivity, and Completeness

Target Analyte	Accuracy (Percent Recovery)	Precision (RPD) Laboratory	Precision (RPD) Field	Required Repository Surface Monitoring MRL for SCAN Mode (ppbv)	Required Repository Surface Monitoring MRL for SIM Mode (ppbv)	Required Disposal Room MRL (ppbv)	Complete-ness (Percent)
Carbon tetrachloride	60 to 140	25	35	0.2	0.1	500	95
Chlorobenzene	60 to 140	25	35	0.2	0.1	500	95
Chloroform	60 to 140	25	35	0.2	0.1	500	95
1,1-Dichloroethylene	60 to 140	25	35	0.2	0.1	500	95
1,2-Dichloroethane	60 to 140	25	35	0.2	0.1	500	95
Methylene chloride	60 to 140	25	35	0.2	0.1	500	95
1,1,2,2-Tetrachloroethane	60 to 140	25	35	0.2	0.1	500	95
Toluene	60 to 140	25	35	0.2	0.1	500	95
1,1,1-Trichloroethane	60 to 140	25	35	0.2	0.1	500	95
Trichloroethylene	60 to 140	25	35	0.2	0.1	500	95

MRL maximum method reporting limit for undiluted samples
RPD relative percent difference

FIGURES

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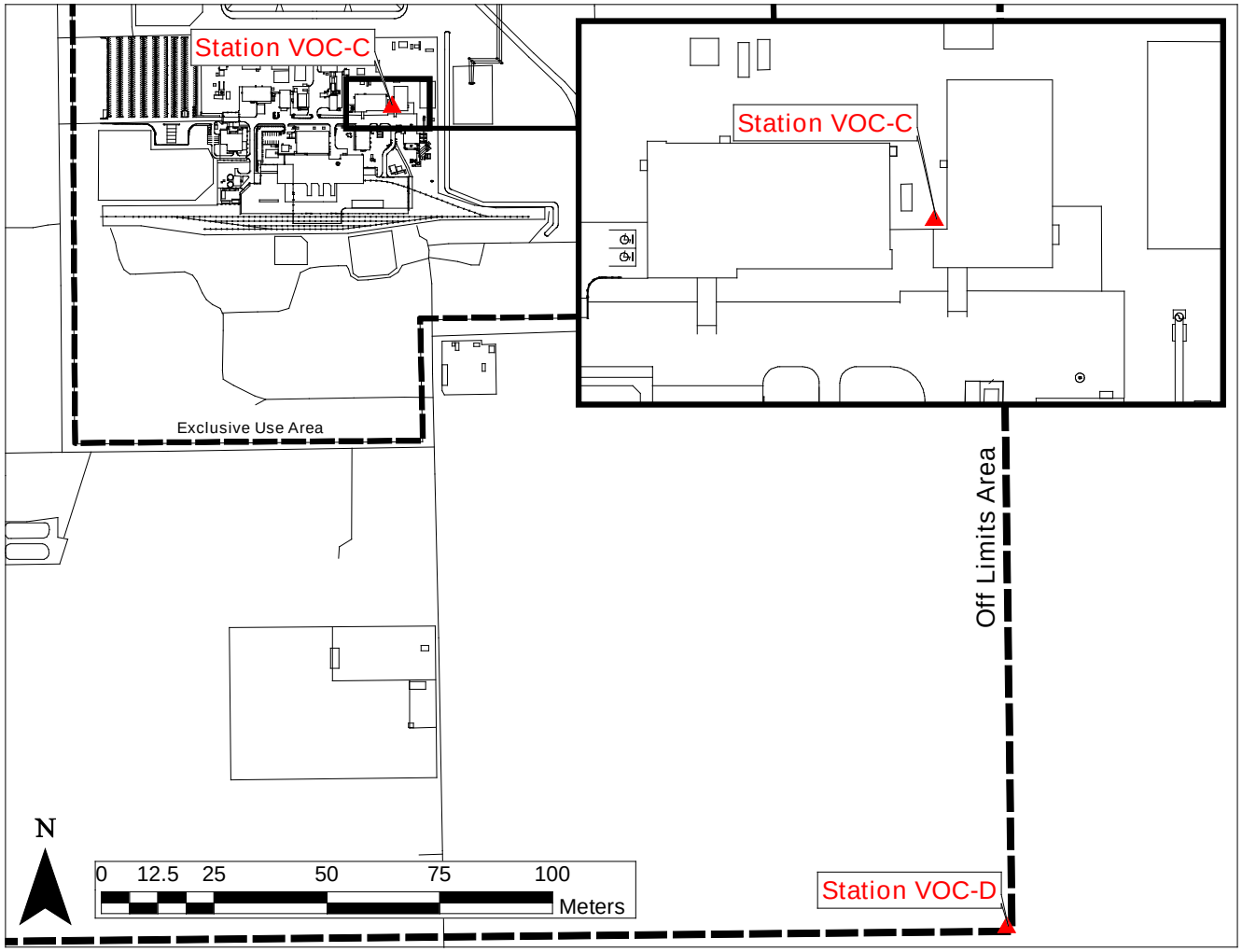
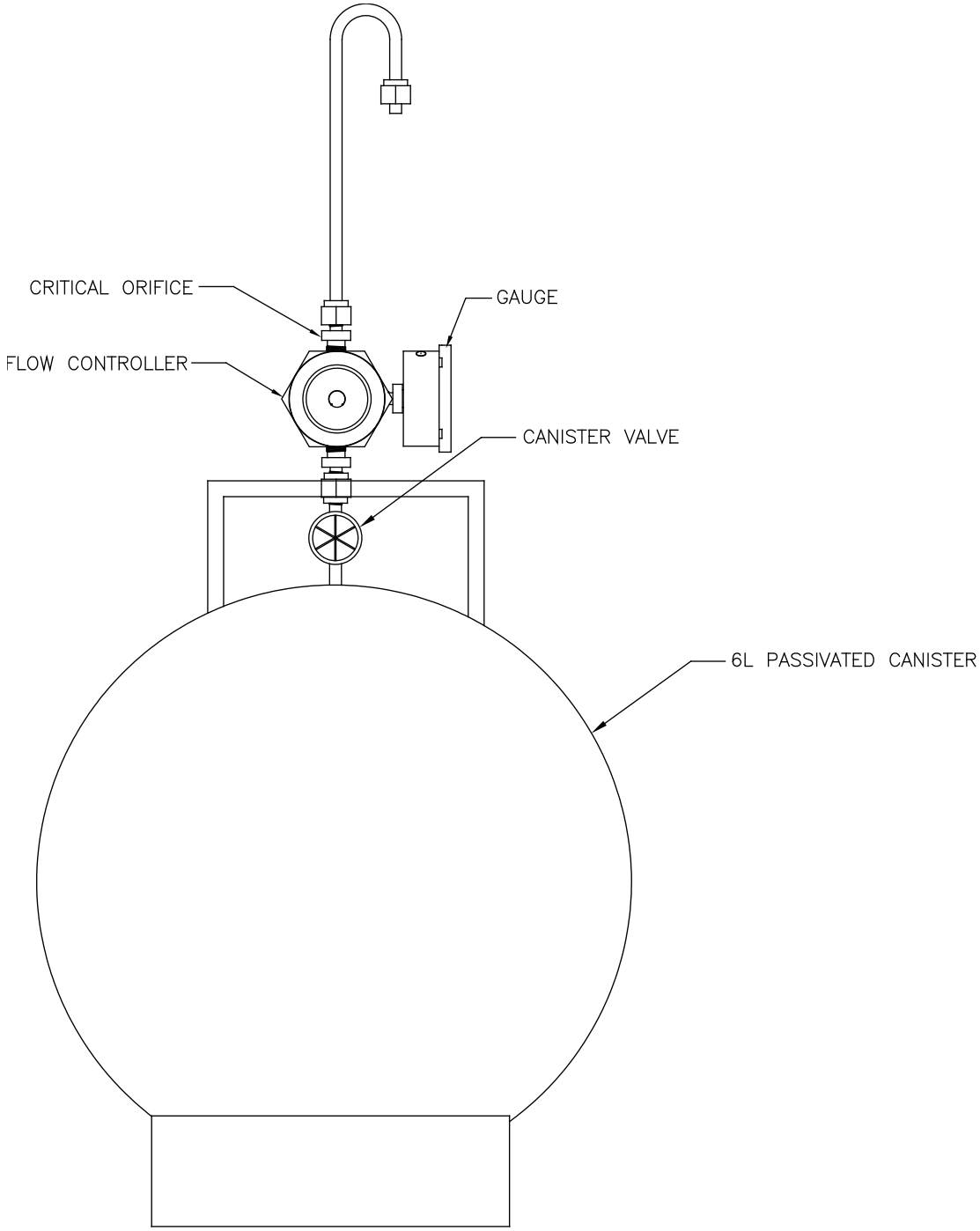


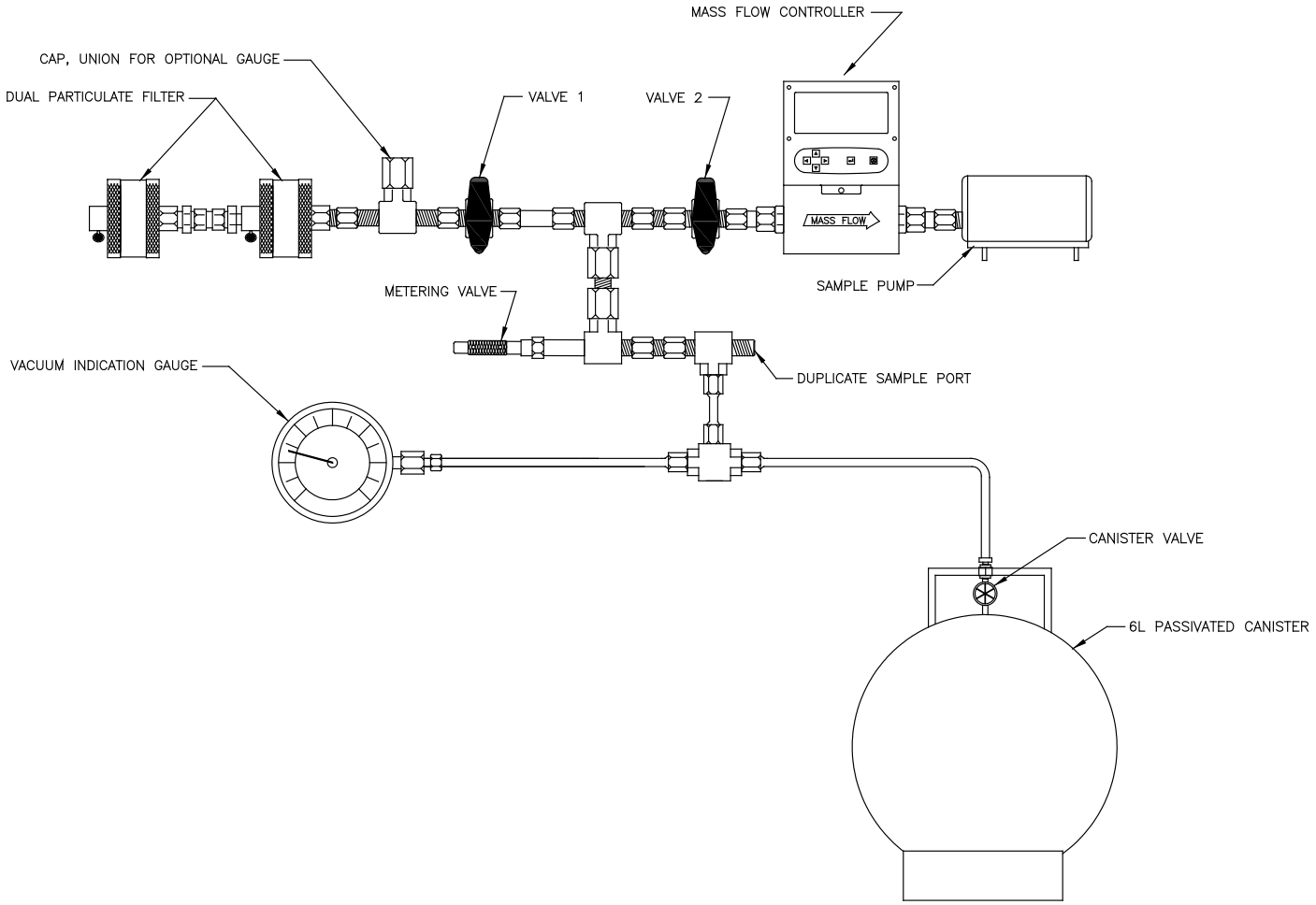
(see Figure D-1 and Figure D-1a for a detailed map and legend of the suface buildings)

Figure N-1
Repository VOC Monitoring Locations



TYPICAL PASSIVE AIR SAMPLING KIT WITH CANISTER

Figure N-2
VOC Monitoring System Design



TYPICAL SUBATMOSPHERIC SAMPLING ASSEMBLY WITH CANISTER

Figure N-2
VOC Monitoring System Design (continued)

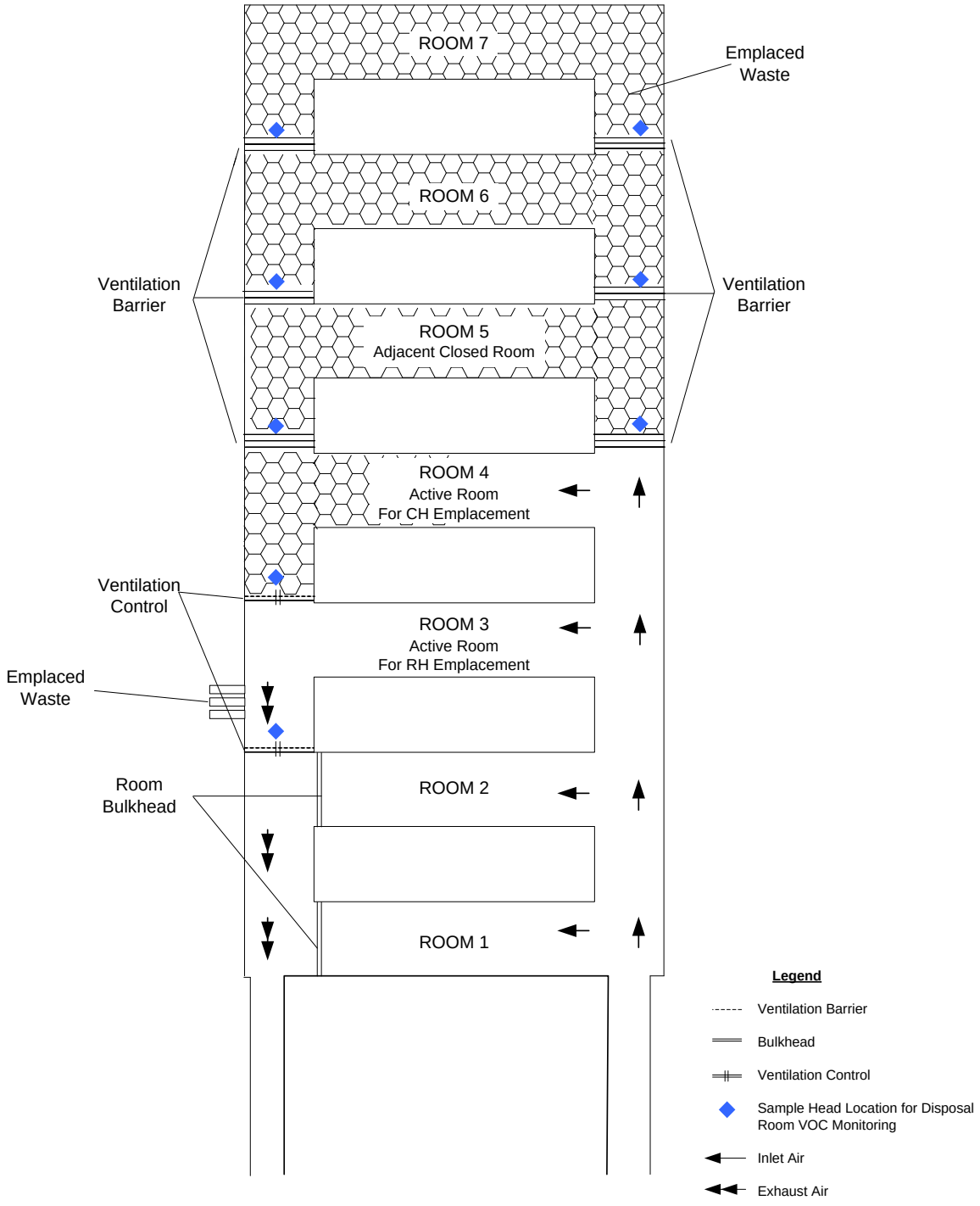


Figure N-3
Typical Disposal Room VOC Monitoring Locations

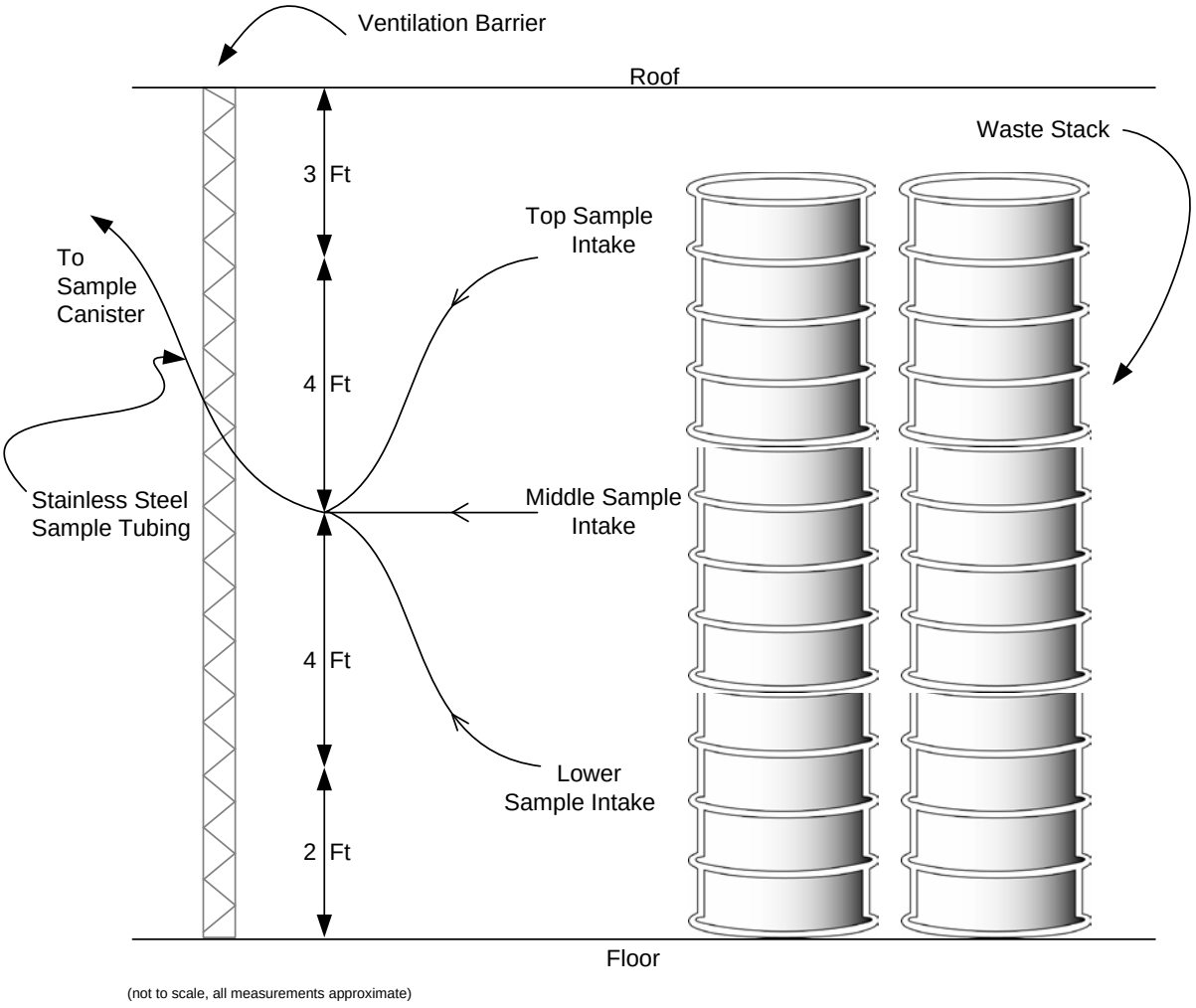


Figure N-4
Disposal Room Sample Head Arrangement

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