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Quality Assurance Project Plan for

RE-EVALUATION OF THE RELATIONSHIP BETWEEN COLLOCATED SOIL AND VAPOR SAMPLE VOC CONCENTRATIONS

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by
Lockheed Martin Environmental Services
Las Vegas, Nevada 89119

for
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A. Project Management

1. Project Organization

The project organization and names of responsible individuals are given in Figure 1. The Client Representative, Dr. Brian Schumacher, of the Environmental Protection Agency (EPA) Environmental Sciences Division-Las Vegas (ESD-LV), will be responsible for direction and oversight of all field sampling and analytical laboratory work for this project. This includes review of all applicable quality control procedures and results, and of all documentation of laboratory activities and observations in project notebooks. George Brilis, ESD-LV Quality Assurance (QA) Manager, will ensure that the project planning and the Quality Assurance Project Plan (QAPP) conforms to the quality standards set by the EPA.

The Lockheed Martin (LM) QA Representative will verify that the QAPP is comprehensively developed and implemented.

The LM Task Lead will be responsible for ensuring that:

- the QAPP is implemented,
- the project schedule is followed,
- decisions are made concerning any necessary adjustments or clarifications to procedures during implementation,
- procedural documentation is regularly reviewed,
- deliverables meet the goals of the project,
- communications with the Client Representative are maintained, including reports of any major problems, required modifications to the QAPP, and draft and final written reports.

Both LM and EPA personnel will participate in the field effort. The sampling personnel will be responsible for conducting the field procedures in accordance with this QAPP, implementing the sampling of soil vapor and soil, and recording technical observations and environmental

conditions during field operations as specified in this QAPP.

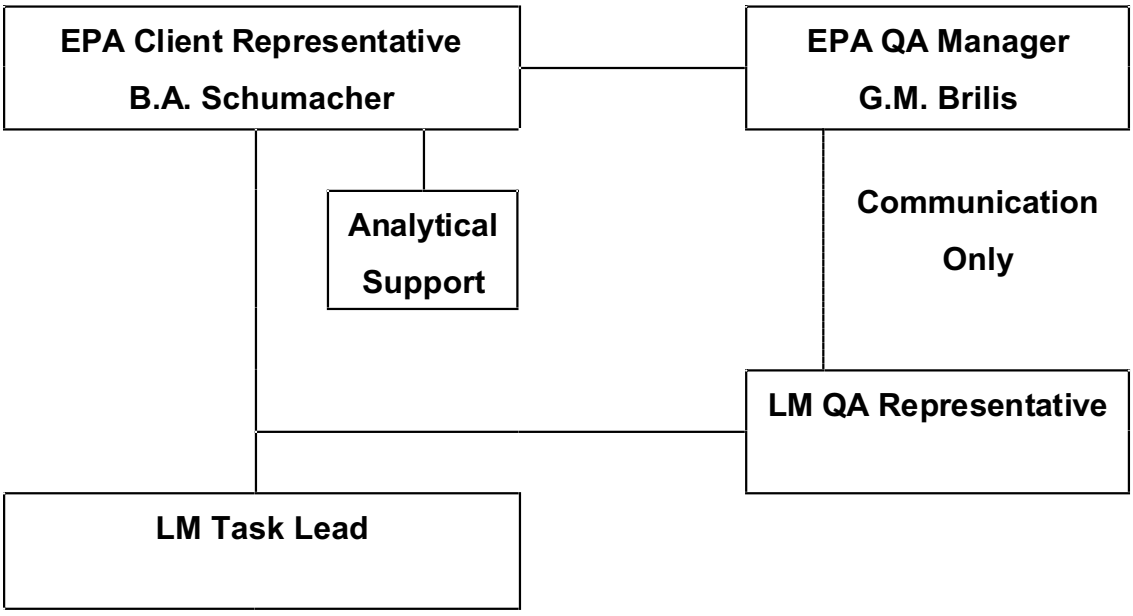


Figure 1. Project Organization Chart

2. Problem Definition

Soil vapor surveys are commonly used as a screening technique to delineate volatile organic compound (VOC) contaminant plumes and provide information for soil sampling plans. Soil sample results are then used to develop and implement monitoring or remediation plans. If a site-specific correlation between collocated soil and vapor sample concentrations could be established it would decrease the time and cost of developing and implementing monitoring and remediation plans. However, the use of inappropriate, imprecise, or biased sampling or analysis methodologies could be a significant deterrent to achieving good field correlations.

Three field studies have evaluated correlations between collocated soil and vapor VOC concentrations and reported no obvious relationship (Minnich et al., 1997; Smith et al., 1990; Sextro, 1996). Soil VOC data were subject to potential bias in the studies of Smith et al. (1990) and Sextro (1996) as a result of the methodologies used for soil sampling and analysis. In the Smith et al. (1990) study, the soil core was homogenized in a glass jar prior to subsampling for analysis. Although no methods were specified, the large study discussed by Sextro (1996) undoubtedly used the analytical procedures accepted at that time which would have involved a laboratory subsampling step. With the promulgation of SW-846 Method 5035, it has become widely recognized that the previously used methods for soil VOC sampling and analysis included steps for transport, transfer, and subsampling that allowed large and unquantified VOC losses (USEPA, 1997). In the third study, Minnich et al. (1997) minimized losses through immediate subsampling of the soil core in field, followed by methanol preservation or headspace analysis on site. Still, the data from two field sites were examined, and neither site showed a correlation between collocated soil and vapor sample VOC concentrations (Minnich et al., 1997).

A recent laboratory study looked at the correlations between soil and vapor VOC concentrations on three different soil types fortified with five VOCs (Hewitt, 1998a). The procedures used in the study eliminated soil sampling transfer steps. Linear partitioning was observed between soil vapor and bulk soil VOC concentrations, although data for each of the three soils were plotted as separate correlations. It was observed that data for soils taken at two depths (e.g., 10-30 cm, > 30 cm) at the same site showed linear partitioning with different slopes.

Hewitt followed the laboratory study with a field study in the near-surface vadose zone at one site (Hewitt, 1998b). The data from this field study demonstrated a good correlation ($r^2 = 0.950$) between soil and vapor trichloroethylene concentrations at a uniform depth. Hewitt (1998b) not only used the best available methods for maintaining the integrity of the soil VOC sample, he also implemented a micro-purge vapor sampling technique. In previous studies the common approach to soil-vapor removal was to purge three dead volumes of the sampling system and then pull a sample, often expelling more than a liter of vapor in the process. The micro-purge

technique minimizes the vapor sample volume allowing Hewitt to achieve a total purge volume of 5 mL at a depth of 1 m. This reduction in sample and purge volume was achieved by a reduction in the internal volume of the sampling equipment, which contained an approximate dead volume of 1.2 mL. Hewitt's micro-purge probe was modeled after a earlier study design in which the probes contained approximate dead volumes of 5 - 30 mL, depending upon the sampling depth (Hughes et al., 1992; Conant et al., 1996).

The transport of vapor through soil should be analogous to the transport of water through soil. A study of unsaturated-zone water sampling methods concluded that significant VOC concentration variations can exist in unsaturated-zone water collected over distances as small as a few centimeters and may, in fact, vary in water collected from the same soil volume but from pores of different sizes (Smith et al., 1992). In a more recent study of unsaturated soil water flow, a distinction is made between flux water and resident water. Flux water is described as the volume of fluid passing through a given cross section in a given time period, while resident water is the fluid contained in a volume of soil at a given instant (Brandi-Dohrn et al., 1996). The flux water exhibits preferential flow patterns that often bypass a large portion of the soil matrix. The solute concentration in these two types of water is not necessarily the same because the water in the two regimes are slow to mix. Collection of the flux and the resident soil water was accomplished through the use of passive, capillary samplers and suction cup samplers, respectively. Passive, capillary samplers maintain a constant head equal to the tension at which the flux water is moving through the soil, while suction cup samplers operate at a much higher tension, but under a falling head. The flux water showed earlier solute breakthrough than the resident water. The velocity at which a soil water is sampled influences which pore sizes are sampled, and we surmise that this also applies to soil vapor sampling.

Further investigation is needed on the micro-purge versus macro-purge, and the low-velocity versus high- velocity soil-vapor sampling techniques and their correlation to the soil VOC concentration. These investigations should determine not only the most appropriate sampling technique but also the effect of other parameters (e.g., different soil types, soil sample technique,

sampling depth, different compounds) upon a selected sampling technique.

3. Project Description

The purpose of this study is to provide field data on the correlation between collocated soil and vapor sample VOC concentrations. At least two sites will be sampled, collecting collocated soil and vapor samples at 24 points per site. Three different methods for vapor collection will be compared: 1) active/micro-volume; 2) active/macro-volume; and 3) passive. The active/micro-volume vapor sample will have a total purge volume $\leq$ 50 mL and the active/macro-volume vapor sample will have a total purge volume $\geq$ 1 L. The passive vapor will be collected over 24 hr $\pm$ 2.4 hr. A high- and low-level soil sample will be collected at each sampling point. All samples will be collected at 1 m $\pm$ 0.1 m below ground surface. Soil characterization samples for determining corresponding soil moisture, organic carbon content, and particle size will be taken at each sampling point.

It is expected to take one week to complete the sampling at each site. All samples will be shipped to the EPA ESD-LV laboratory for analyses. Vapor and soil samples will be analyzed by purge-and-trap gas chromatography mass spectrometry (PT/GC/MS) and thermal desorption gas chromatograph mass spectrometry (TD/GC/MS), respectively.

4. Data Quality Objectives

This study will provide data to promote a better understanding of the relationship between soil vapor and soil VOC concentrations. It includes three methods of collecting VOCs in soil vapor and two methods of collecting VOCs in soil, because the best correlation is likely to be when the methods of measuring these parameters utilize analytes from the same source of VOCs. The data are intended to be of interest to regulators and researchers that are concerned with the methods of measuring soil VOCs.

Significant correlations and the differences between the various correlations that can be attributed to the vapor collection methods must be identified. The data will need to be categorized as to the specific soil types or conditions that were present which may have influenced the results. Significance at a 95% confidence level will be reported.

An ancillary question concerning vapor VOC concentration changes during vapor sample removal will also be addressed in this study. Data will be evaluated as to the relationship of soil VOC concentration to individual active vapor sampling periods, mean values, and the sum of the analyte content over all six vapor sampling periods.

4.1 Project Quality Objectives

To meet the project objectives, the data and the interpretation of those data must be reliable. Critical to this experiment are the soil and vapor VOC concentration measurements. Comparability of these results across field sites will depend on the differences between the sites, based on field observations and soil characteristics. Particle size distribution, soil moisture, and organic carbon content will be measured to assist in site comparisons. Data quality objectives (DQOs) are discussed in the following two sections. Quality control samples are discussed in Section 8.

4.2 Instrument Measurement Performance Criteria

4.2.1 Soil and Vapor Sample Analyses

In the laboratory, precision will be established for each analyte of interest as the relative standard deviation (RSD) of the response factor (RF) from each point of a five-point calibration curve. Separate calibration curves will be generated for the soil and vapor sample analyses using PT/GC/MS and TD/GC/MS, respectively. The DQO for calibration curve precision will be to achieve an RSD of $\leq$ 15% for each analyte.

Bias for the soil and vapor samples will be determined by comparing measurements of the mid-point calibration standard with measurements of a second-source-certified standard (from Restek or equivalent). The second-source standard will be analyzed twice for each initial calibration curve. The DQO for bias will be a recovery (%R) of 100% ± 20%.

The instrument detection limit (IDL) is the lowest concentration of an analyte that the measurement system can consistently detect and/or measure in replicate standards. A GC IDL of 10-ng total on-column for each analyte of interest is expected.

4.2.2 Soil Characterization Analyses

The DQOs for soil characterization parameters are shown in Table 1.

Table 1. DQOs for Soil Characterization Parameters

Parameter	Reporting Units	Precision[a]	Bias[b]
gravel[c]	weight %	25.0	25.0
sand[c]	weight %	25.0	25.0
silt plus clay[c]	weight %	25.0	25.0
organic carbon	weight %	25.0	25.0
soil moisture	weight %	25.0	NA

[a] Given as relative percent difference (RPD) between duplicates.

[b] Given as RPD between observed reference datum and "correct" reference value.

[c] Particle size fractions as defined by USDA particle size classification system.

5. Documentation and Records

All soil and vapor VOC concentration data will be generated in electronic and hard copy formats via the instrument-associated software. All data will be transferred to electronic spreadsheets for

analysis and presentation. If the Client Representative directs Lockheed Martin to prepare a QA report, final report, and/or draft article, the Client Representative will provide all required data in electronic and hard copy formats. The records of the study will be maintained by Lockheed Martin for two years after the final report is accepted and then transferred to the EPA for storage. If the Client Representative prepares a QA report, final report, and/or draft article, copies of all records of the study in the custody of Lockheed Martin will be supplied to the EPA.

B. Data Acquisition

6. Experimental Design

This field experiment will be performed at a minimum of two sites. Soil and vapor sample VOC concentrations will be measured at 24 locations on each site. Three methods of vapor sample collection will be compared for achieving a correlation between soil and vapor sample VOC concentrations:

1) active/micro-volume ($\leq$ 50 mL @ 1-m depth);
2) active/macro-volume ($\geq$ 1 L @ 1-m depth);
3) passive (@ 1-m depth)

Data will be analyzed to elicit: a) the correlation between soil VOC concentration and the vapor VOC concentration for three vapor sampling methods; and b) the effect of soil characteristics on the correlation coefficients.

This experiment is designed to study the effects of vapor sampling method parameters on the relationship (or fit) between collocated soil and vapor sample VOC concentrations. A good fit will be a linear fit, that is, the concentration of soil VOCs will be predicted by a slope and intercept derived from a plot of collocated soil versus vapor sample VOC concentrations. The superior method for vapor collection will be that method resulting in the best regression fit. A

multiple regression technique may be applied to determine the degree to which the soil characterization parameters are useful for predicting the linear fit line of different soil types. The limitation of this experiment is collecting a sufficient amount of data to properly evaluate the soil/vapor relationship and the effect of soil characterization parameters on the correlation of collocated soil and vapor VOC concentrations.

6.1 Site Selection

An appropriate site will be one which is contaminated over tens of square meters with one or more of the VOCs listed in Table 2. The compounds in Table 2 are the most frequently detected organic compounds in disposal site ground water (Plumb, 1991). Soil that varies widely in type within a short distance (few meters) or horizontally will be useful for generating a varied data set displaying the effects of soil type. Soil porosity must be capable of conducting soil vapor. Neither clay soils or soils with water content near saturation are appropriate.

The Client Representative will secure access to appropriate field sites. The soils at the field sites should not be so stony as to preclude sampling using a soil-coring device. The soil types should also contain sufficient air pore space to allow collection of soil vapor. The aerial extent of the contaminated soil should be sufficient to provide 24 sampling points.

Table 2. List of Potential Compounds of Interest

Compound	Site Detection Frequency* (%)
Trichloroethylene (TCE)	27.6
Toluene	27.3
Benzene	25.1
trans-1,2-Dichloroethene**	24.2
Tetrachloroethylene (PCE)	23.2
Ethyl benzene	22.8
1,1-Dichloroethane	22.5
1,1,1-Trichloroethane	21.1
Chloroform	18.9
Chlorobenzene	18.0
1,2-Dichloroethane	17.1
1,1-Dichloroethene	15.7

* adapted from Plumb, 1991.

** cis-1,2-DCE was reported as trans-1,2-DCE in older data sets, Howard et al., 1990.

6.2 Enumeration of Samples

At each site a total of 24 sampling points will be selected. At alternating sampling points a micro-volume, macro-volume, or passive vapor sample will be collected. Soil samples will be collected at each sampling point. If no problems are encountered and six points can be sampled each day, the sampling at each site can be completed in five days. The fifth day will be needed to retrieve the samples from the last two passive sampling points and may be used for collecting active vapor/soil samples on a contingency basis.

Six consecutive active vapor samples will be collected at each active vapor sampling point. Therefore, 96 active vapor samples will be taken at each site. Duplicate passive vapor samples will be taken at each passive vapor sampling point for a total of 16 passive vapor samples at each

site. Two soil samples, one low and one high-level, will be taken at each soil vapor sampling point. Duplicate high- and low-level soil samples will be taken once each day. The sampling point where the duplicate soil samples are taken will alternate each day to a different type of vapor sample point. Therefore, 16 soil samples will be taken for each of the vapor collection methods, with 8 duplicates, for a total of 56 soil samples per site. Soil characterization samples (soil moisture, particle size analysis [PSA], and organic carbon) will be collected at each sampling point. At two sampling points duplicate soil characterization samples will be collected, for a total of 26 soil characterization samples per site.

6.3 Sampling Procedures

6.3.1 Equipment

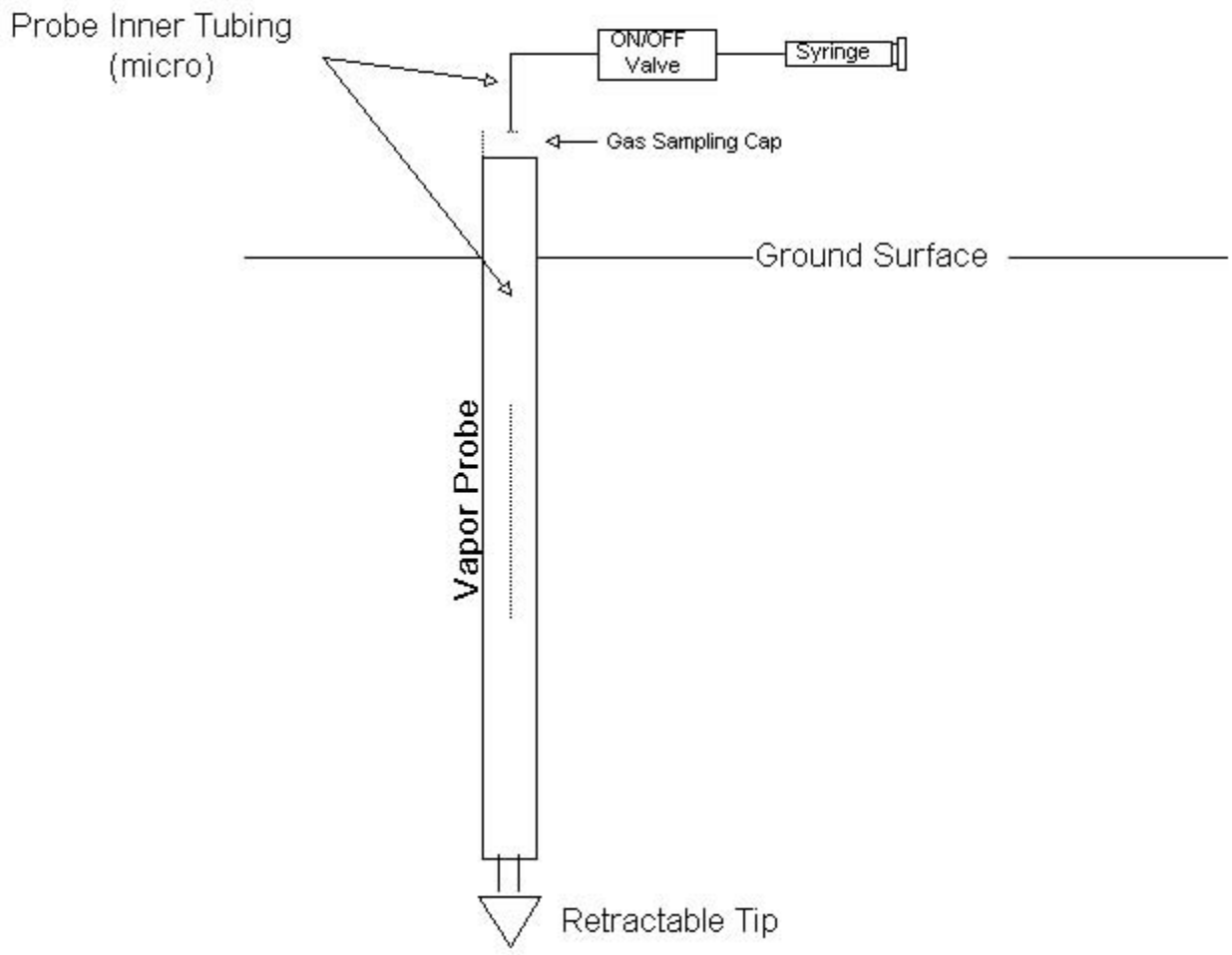
The soil and active vapor sampling will be achieved using hydraulic push equipment, such as the Geoprobe® system. The active vapor sampling system will have a retractable tip with inner tubing connected from the tip to the sampling port tee through hollow probe rods (Figure 2). A syringe will be used for active soil vapor sampling. Once the active soil vapor samples have been collected in the syringe, they will be transferred to TD tubes. Passive vapor samples will be collected directly in TD tubes.

The TD tubes will be stainless steel, 8.9-cm long by 0.64-cm diameter, sealed at each end with brass Swagelok endcaps fitted with Teflon® ferrules (as recommended by the manufacturer for long-term storage). Each tube will contain 180 mg Carbotrap B on the inlet side, followed by 70 mg Carboxen 1000 (Supelco Inc., Bellefonte, PA). The more easily sorbed compounds will be retained near the front of the tube on the weaker sorbent (Carbotrap B) while the low molecular weight, less easily sorbed compounds will be retained on the stronger sorbent (Carboxen 1000).

To collect the micro-volume vapor samples, the basic soil-vapor sampling system (Figure 2) will be modified so that the internal volume of the sampler will be approximately 8 mL at a 1-m sampling depth. This will be accomplished using small-diameter stainless steel tubing (2.00-mm

outer diameter [OD] and 1.19-mm inner diameter [ID]) attached to the retractable soil vapor sampling tip (Figure 2). The end of the stainless steel tubing extending out the top of the probe will be capped during insertion of the probe into the subsurface. The internal volume of the micro-system is calculated as 0.011 cm^2 times the length of the tubing in centimeters, plus 6.4 mL to account for the internal volume of the retractable drive-point assembly used for vapor sampling. For a tubing length of 120 cm, the sampling system internal volume is 8 mL.

Figure 2. Active Soil-Vapor Sampling System



The macro-volume soil-vapor sampling system will consist of the basic sampling apparatus described above, with no inner tubing (Figure 2). The end of the probe extending above the surface of the ground will be capped during insertion of the probe. The drive cap will be

removed from the sampling system and replaced with a gas sampling cap. One end of a section of Teflon® tubing (0.79 cm ID x 0.95 cm OD x 20 cm length) will be attached to the gas sampling cap (Figure 2). The other end of the Teflon® tubing will be attached to a on/off valve. The opposite end of the on/off valve contains a septum port through which a syringe is inserted to collect a sample. The internal volume of the macro-system is calculated as 1.99 cm^2 times the length of the probe rod in centimeters, plus 6.4 mL to account for the internal volume of the retractable drive-point, vapor sampling assembly. For a probe length of 100 cm and 20 cm of Teflon® tubing, the internal volume of the sampling system is 250 mL. The passive vapor sampling system consists of a pair of TD tubes with defusion caps attached to both ends, suspended on a wire from a metal rod. The metal rod will be inserted in the hole created during soil sampling (Figure 3).

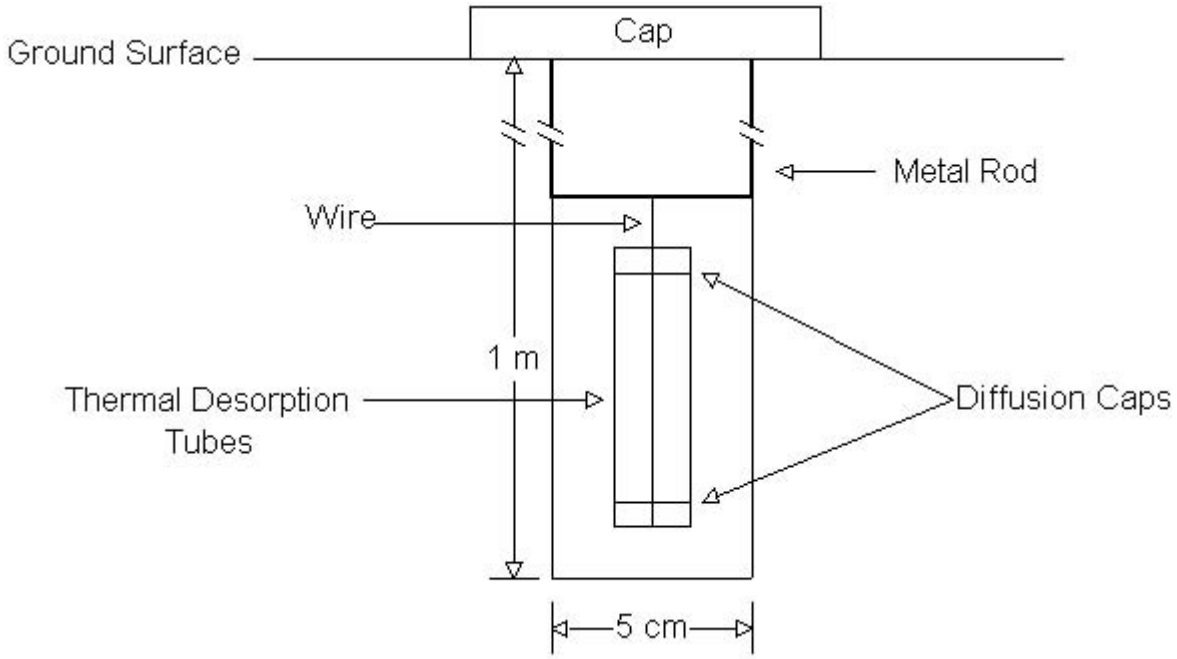


Figure 3. Passive Soil Vapor Sampling System

A cap will be used to seal the opening of the sampling hole. The tubes will be suspended within 5 cm of the bottom of the hole, i.e., approximately 1 m below ground surface (bgs).

Soil sampling will be achieved using the Geoprobe® Macro-Core® sampler in the closed-piston

configuration. The soil sampling system will use a 2" x 24" soil corer with a polyethylene terephthalate (PET) liner. A new liner will be used for each sample point.

Equipment Decontamination - Prior to initiation of sampling or reuse of sampling equipment, the probe and coring equipment will be decontaminated using the following procedure:

Components of the hydraulic push system will be washed with an Alconox and water solution, and rinsed with deionized (DI) water. Each piece of equipment will be rinsed with methanol and air dried. The internal probe tubing or probe, retractable tip, and Teflon® tubing will be replaced at each sampling point. The on/off valve will be rinsed between sampling points by pumping ambient air through the valve.

Decontamination/cleaning of TD tubes is described in Section 7.1.1. Soil sample vials will be purchased precleaned and will not be reused.

6.3.2 Vapor Sampling - Active

Once the desired sampling depth (1 m) is reached, the sampler will be raised approximately 2.5 cm to create a sampling void. The internal tubing will then be connected to one port of an on/off valve (Figure 2). The other port of the on/off valve will be a septum port through which a syringe is introduced to collect a sample. After collection, each sample is transferred to a TD tube using the transfer apparatus (Figure 4).

A pump will be used to maintain a flow of 50 mL/min of filtered ambient air through the transfer apparatus. The on/off valve on TD tube 1 is opened and the first vapor sample is injected into the septum port immediately in front of the tube. The air flow through the tube is maintained for a minimum of 15 min before the valve is closed. This process will be repeated five more times, transferring the second sample to TD tube 2 and so on, to collect a total of six samples at each sampling point. The tube numbers for all active vapor samples collected will be recorded and other sampling point information documented on the Vapor Sample Field Forms as described in

Section 6.3.5. The air temperature and barometric pressure will be taken and recorded in the field notebook during the collection of the third TD tube of each set.

The first three samples taken at each sampling point represent the vapor volume that would be purged prior to collection of a routine sample. This volume is routinely purged to remove air which was contained in the probe system prior to and during the insertion process. These samples

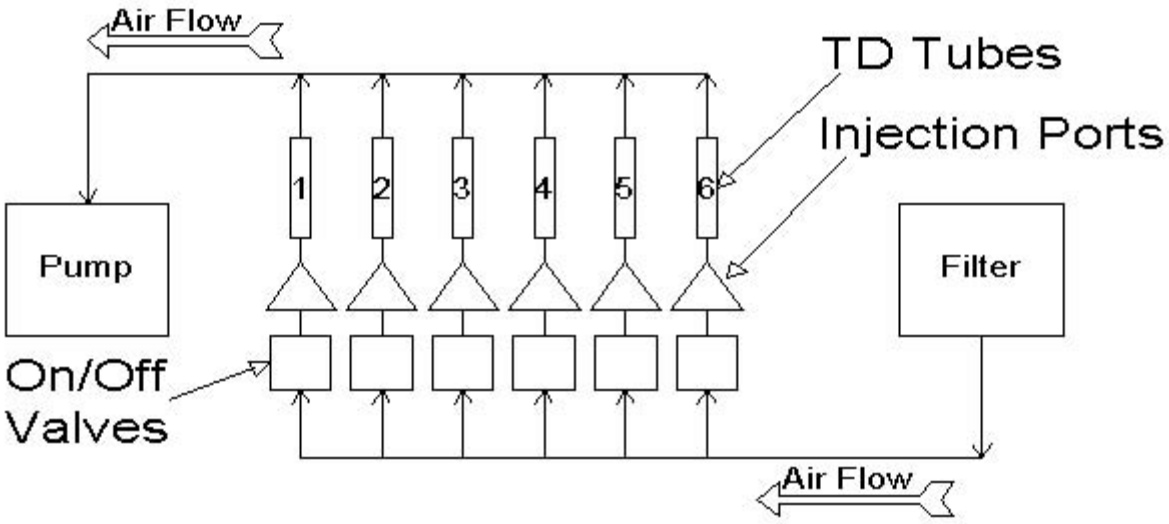


Figure 4. Vapor Sample Transfer Apparatus

are being collected to investigate the need to purge three probe-system volumes prior to collection of routine samples. The second set of three samples are the routine samples and will be treated as triplicate soil-vapor samples for each sample location unless data show otherwise.

Active/Micro - A 10-mL syringe will be used to collect an 8-mL sample. The sample will be transferred to a TD tube using the transfer apparatus (Figure 4).

Active/Macro - A 250-mL syringe will be used to achieve a sample volume of 250 mL. A 10-mL syringe will then be used to collect an 8-mL subsample from the 250-mL sample. The 8-mL subsample will be transferred to a TD tube using the transfer apparatus (Figure 4).

6.3.3 Vapor Sampling - Passive

The pairs of TD tubes will be left in the soil, 1 m bgs (Figure 3), for 24 hrs and then retrieved. The tube numbers for all passive vapor samples collected will be recorded and other sampling point information documented on the Vapor Sample Field Forms as described in Section 6.3.5.

6.3.4 Soil Sampling

Soils will be collected for both the low- and high-concentration VOC analytical techniques described in SW-846 Method 5035, in conjunction with SW-846 Method 8260 (USEPA, 1997). Prior to sampling, vials for both the low- and high-level sample collection and analysis will be prepared and weighed as per Section 7.2.1.

Low-Level Soil VOC Sampling - Following the removal of the vapor probe from the sampling location, the soil-coring device will be inserted into the sampling point to the depth where the vapor sample was collected (1 m). The soil-coring device will be advanced approximately 10 cm beyond the soil-vapor sampling depth, quickly removed from the sampling hole, and the PET liner will be removed from the corer. The portion of the liner containing the soil sample will be cut in half cross-wise, and a truncated 20-mL syringe will be used to remove (approximately) a 5-g subsample of the soil contained in the upper half of the liner (Figure 5). The soil subsample will be quickly transferred to a vial prepared for low-level analysis (as described in Section 7.2.1). The threads of the vial will be quickly cleaned and the vial sealed with the screw cap and septum seal.

High-Level Soil VOC Sampling - The truncated syringe will next be used to remove (approximately) a second 5-g subsample of the soil contained in the upper half of the liner. The soil subsample will be quickly transferred to a vial prepared for high-level analysis. The vial threads will then be quickly cleaned, and the vial sealed. Both low- and high-level soil VOC

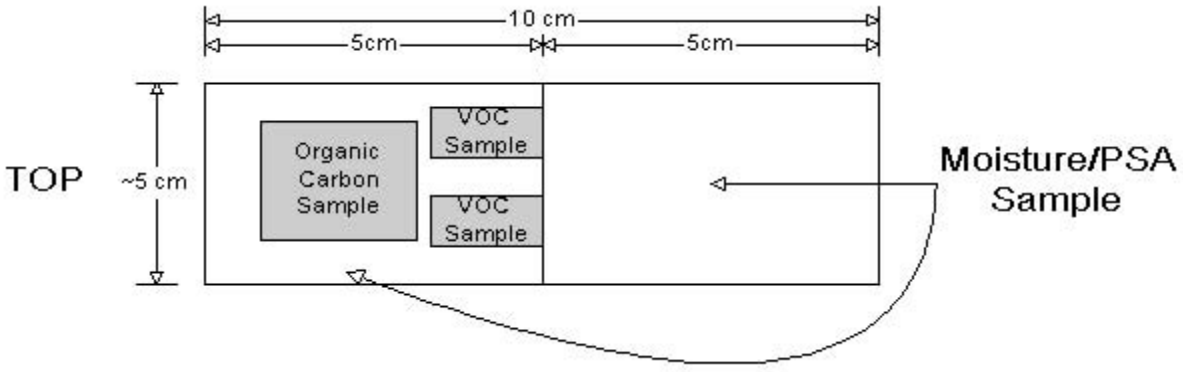


Figure 5. Sampling the Soil Core

samples will be weighed to the nearest 0.01g, the weight recorded on the Soil Sample Tracking Form (Figure 6), and the sample labels completed.

Soil Characterization Sampling - After all VOC samples have been collected from the sample core, the remaining soil in the sample core will be collected for soil characterization. The truncated syringe will be used to remove (approximately) a 10-g subsample of the remaining soil contained in the upper half of the liner. That soil subsample will be transferred to a ziplock bag for organic carbon analysis. A portion of the soil remaining in both halves of the PET liner will be transferred to a pre-weighed soil moisture tin and the reweighed tin sealed with electrical tape. The tins will be weighed to the nearest 0.1g, the weight recorded on the Soil Sample Tracking Form (Figure 6), and the sample labels completed. The sample information will also be entered into a field logbook. Because the soil contained in the soil moisture tin will also be used to determine PSA, minimum sample size of 150 g is required.

Site:		Date:		Balance CAL:		Samplers:			
Sample ID	Sample Time	Prepared Vial Weight (g)		Prepared Vial + Soil Weight(g)	Weight(g) after Shipping	Soil Moisture			
		Lab	Field			Tin No.	Weight (g)		
							Empty	Wet	Dry

Page ___ of ___

Figure 6. Soil Sample Tracking Form

6.3.5 Sample Tracking

Samples will be labeled according to site, sampling point, type of sample, and sequence or replicate number, if applicable. Sites will be given a number. Sampling points will be numbered 01 to 24. The types of samples will be indicated as follows: active/micro-volume soil vapor, I; active/macro-volume soil vapor, A; passive soil vapor, P; soil-low level, L; soil-methanol extract, H; soil moisture, M; soil particle size, PSA; soil organic carbon, O. Sequential active vapor samples will receive numerical designations from 1-6. Passive vapor duplicate samples will receive a 1 or 2. An example of a sample ID is, "202I3". This would mean site 2, sampling point 2, active/micro-volume soil-vapor sample, sequence sample 3.

QC samples will be labeled according to the site, sampling point (if applicable), sample type, analysis type, and sequence or replicate number (duplicates = D). Travel spikes and blanks are not associated with a sampling point and these QC samples will be numbered sequentially. The types of QC samples will be indicated as follows: field blank, FB; travel blank, TB; travel spike, TS. The type of analysis will be indicated as defined above. An example of a QC sample ID is, "201HFB1". This would mean site 2, sampling point 1, soil-methanol extract, field blank, sample 1.

In addition to entering the sample ID and other pertinent information on the Soil Sample Tracking Form, this material will be recorded in field logbooks along with any additional information on the site, soil conditions and characteristics, as well as problems encountered during sampling, handling, or shipment.

6.3.6 Sample Storage and Shipping

TD Tubes - Once the samples are collected, the TD tubes will be removed from the applicable sampling apparatus, capped, placed in labeled zip-closure plastic bags, and held on ice in the field. The TD tubes will be shipped chilled, and stored refrigerated (4 ^{o}C) in the laboratory prior to analysis.

Soil Samples - All soil samples will be placed on ice in the field and shipped chilled to the laboratory. A separate container will be used for storing and shipping the methanol-preserved (i.e., high-level) samples. Upon receipt at the laboratory, the low-level soil VOC samples will require freezing (-12 °C) and the high-level soil VOC samples will be stored refrigerated (4 °C) prior to analysis. Soil characterization samples for organic carbon will be air-dried upon receipt at the laboratory; moisture samples will be oven dried at 105 °C prior to weighing and PSA.

6.4 Design Rationale and Assumptions

Each soil and site is expected to have somewhat different factors controlling the release of VOC vapors. The concentration of the VOCs in the soil is predicted to affect the concentration of the vapors released, but no direct proportionality across sites or compounds is anticipated. This study is designed to examine and compare the different quantities of vapor released among soils and sites. The proportion of soil VOCs released as vapor from each soil will be inferred, for micro- versus macro-volume sampling. The release rates may be related to soil moisture content and, if so, would vary at a specific site over time.

The basic assumption underlying this project is that data from a large number of sampling points and soil types will provide enough information to demonstrate correlations between the soil parameters and the soil and vapor VOC concentrations. The specific compounds and concentrations of the VOCs at each site are expected to vary independent of the soil characteristics. Specific correlations may be difficult to formulate without an extended data set. To guard against premature conclusions using a limited data set, correlation coefficients ≤ 0.85 or statistical significance at $p \leq 0.05$ will be required in formal hypothesis testing.

7. Analytical Methods

7.1 Soil Vapor Samples

The handling, preparation, and analysis of TD tubes with vapor samples will be performed as described in the CMB standard operating procedure (SOP) #320, *Analysis of Volatile Organics in Soil Vapor using Thermal Desorption/ Gas Chromatography/ Mass Spectrometry*.

7.1.1 Preparation of TD Tubes

New, preconditioned TD tubes will be precleaned by heating to 370 ºC for 30 minutes while passing 100 mL/min of ultrapure helium (He) gas through them. (If new and unconditioned, precleaning will require 2 hours per tube.) The tube endcaps and diffusion caps will be cleaned by baking at 150 ºC for 90 minutes. The TD tubes will be assembled (finger tight) after cleaning, and stored refrigerated (4 ºC) in plastic, zip-closure bags. Subsequent use of the TD tubes will not require additional conditioning unless the previous use indicated high levels of contaminants.

Following the conditioning, internal standards (IS) will be spiked on every TD tube using a commercially available Method TO-14 (US EPA, 1997b) internal standard/tuning mix: bromochloromethane, 4-bromofluorobenzene, chlorobenzene-d5, and 1,4-difluorobenzene (Restek, Belefonte, PA). Each TD tube will be connected to a tank of ultrapure nitrogen (N_2) gas through a Swagelok® tee containing a septum-port sidearm. The N_2 gas will flow through the inlet end of the TD tube at 50 mL/min, and 1.22 mL of a 1 ppmv mix of the IS compounds will be injected into the stream of N_2, supplying 50 pmole of each compound (see Appendix II). The gas flow will be maintained for fifteen minutes following the injection of the IS standard. Once spiked, the tube will be sealed with endcaps, returned to the plastic bag, and stored at 4 ºC.

Travel Spikes (TS) will also be prepared using the procedure described above. To prepare these QC samples, 100 pmoles of the calibration standard gas mixture (245 uL of each of the 10 ppmv standards) will also be spiked into the TD tube (in addition to the ISs). Prior to the start of the experiment the laboratory will analyze 5 tubes spiked with TS and IS compounds to demonstrate reproducibility of the spiking procedure.

TD tubes will be spiked no more than 7 days before field use. Freshly spiked tubes will be shipped from the laboratory to the field site via overnight express as needed during extended sampling events.

7.1.2 Analysis of TD Tubes

Analysis will closely follow the TD/GC/MS method reported by Pankow et al. (1998). In that study, 79 analytes were spiked on TD tubes packed with Carbotrap B and Carboxen 1000. The recovery of analytes (listed in Table 2) were within 10% of the initial value after 27 days of storage on the TD tubes. It is assumed that the holding time of 27 days can be achieved by adhering to the procedures of Pankow et al.

Prior to desorption and analysis, the TD autosampler (Perkin-Elmer ATD 400) will test each TD tube for leaks within the sample desorption system. TD tubes that fail the test will be automatically resealed by the autosampler and replaced in the sample carousel. The following day, the analyst will inspect these TD tubes, correct any obvious problems, and return the tube to the carousel for analysis.

The autosampler will prepurge each TD tube prior to analysis to remove water (N_2 gas at 50 mL/min for 8 min at ambient temperature). Each tube will then be desorbed at 360 ºC for 15 minutes using 60 mL/min flow of ultrapure He. The "air-toxics trap" at -10 ºC will be used as an intermediate focus prior to transfer to the GC/MS. A one-third split-to-vent may be necessary to reduce the amount of water on the column. The focusing trap will be desorbed at a 40 ºC/s ramp to 370 ºC and held for 3 min with a flow of He at 4 mL/min. The flow will be directed at 32 psi onto the GC column at 45 ºC through heated (200 ºC), deactivated silica tubing.

A 60-m capillary GC column (DB-VRX, 0.25 mm id, 1.4 µm film thickness, or equivalent) will be used. The GC oven temperature program will be: Initial hold for 10 min at 45 ºC; 12 ºC/min to 190 ºC; hold for 2 min; 6 ºC/min to 240 ºC; hold for 2 min. The GC/MS transfer line (210 ºC) should end within 1 mm of the MS source.

7.2 Soil VOC Samples

The handling, preparation, and analysis of soil samples will be performed as generally described in CMB SOP #310, *Analysis of Volatile Organics in Soil using Purge-and-Trap/ Gas Chromatography/ Mass Spectrometry*.

7.2.1 Preparation of Vials

Vials to be used for soil samples will be precleaned, 40-mL glass vials with Teflon®-lined, septum-sealed screw tops; commonly known as VOA vials. The vials will be prepared for low- and high-level sample collection as specified in Method 5035 and will be weighed before transport to the field. The prepared vial weights and preservative method will be recorded on the Soil Sample Tracking Form (Figure 6) and in the field notebook.

Alternatively, VOA vials may be shipped directly to the field by the manufacturer. The vials may be ordered pre-filled with methanol and all are labeled with vial or vial + methanol weights.

7.2.2 Analysis of Soil Samples

All soil samples will be analyzed for VOCs by PT/GC/MS. The samples will be analyzed by SW-846 Method 5035, modified as described below, in conjunction with SW-846 Method 8260. Since methanol is not included as a matrix to be analyzed by SW-846 Method 5035, a modification to the method will be made as follows:

> A 100-µL subsample of each high-level soil sample methanol extract will be analyzed as a low-level soil. The subsample will be transferred to a 40-mL vial. Water (10-mL) containing the internal standards (ISs) and surrogates will be added to the vial by the automated purge-and-trap instrument. Smaller aliquots of the methanol extract will be analyzed if necessary to bring the instrument response within the calibration curve.

Method 8260 modifications include a reduced list of compounds of interest, no system performance check compounds, no laboratory matrix spike/matrix spike duplicate samples, and QC sample analyses and acceptance criteria as listed in Table 3.

7.3 Soil Characterization Samples

7.3.1 Organic Carbon

Samples will be air dried within a day of receipt at the laboratory. Total carbon will be measured on the soil sample after testing for inorganic carbon. If inorganic carbon is present, HCl will produce effervescence, and the samples will be pretreated with dilute H_2SO_4 for removal of carbonate. Total carbon (or remaining organic carbon) will be measured gravimetrically as sorbed CO_2 after combustion. Procedures will follow the method for high-temperature induction furnace described in Section 29-2.2.4 of Nelson and Sommers (1982).

7.3.2 Soil Moisture

Samples will be placed in preweighed moisture tins and sealed with electrical tape in the field. At the laboratory, the electrical tape and lid will be removed from the labeled tins and the tins weighed to 0.001 g. The tins will be placed in an oven at 105° C for at least 24 hours. Oven-dried soil samples will be allowed to cool and reweighed to 0.001g. All data will be recorded on the Soil Sample Tracking Form (Figure 6).

7.3.3 Soil Particle Size

Sand, gravel, and cobble fractions will be recovered by sieving the oven-dried soils used to determine the soil moisture content. The target sample size will be 150 g. Sieved samples will be pretreated with glacial acetic acid to destroy the carbonate. Organic matter will be oxidized with peroxide. Particle size analysis of the fines will be by hydrometer as specified in Gee and Bauder (1986). Percentages of silt and clay will be determined from the hydrometer readings, temperature, and Stokes Law, following CMB SOP #220, *Hydrometer Method and Particle-Size Analysis.*

8. Quality Control

Table 3 summarizes the QA/QC samples, acceptance criteria, and corrective actions for the VOC samples. A general discussion of the specific QC components for VOC analysis by TD/GC/MS

and PT/GC/MS is presented in sections 8.1 through 8.3. The specific QC samples for organic carbon and PSA are discussed in sections 8.4 and 8.5, respectively.

8.1 VOC Precision

Precision represents the reproducibility of measurements under a given set of conditions and provides an estimate of random error (Taylor, 1987). Method precision will be monitored by: (1) examining the consistency of analyte response factors over the range of the calibration curve, (2) analyzing on-going calibration check (OCC) standards, and (3) analyzing sample duplicates. In conjunction with the initial calibration curve, precision will be established for each analyte as the RSD of the response factors (RFs) from each point of a five-point calibration curve. The RF of a standard is defined as:

$$RF = (A_S \times C_{IS}) \div (A_{IS} \times C_S)$$

where A_S and A_{IS} are the area of standard and its associated internal standard, respectively. C_S and C_{IS} are the nominal concentration of the standard and its associated internal standard, respectively. The RSD is given as:

$$RSD = (SD_{x-1} / \text{mean}) \times 100$$

where SD_{n-1} is the standard deviation of the replicate measurements.

Table 3. VOC QA/QC Samples, Frequency, and Acceptance Criteria

QC Sample	Purpose	Frequency	Acceptance Criteria	Corrective Action
Bromofluoro-benzene (BFB)	Analytical bias	Beginning of each 24-hour analytical period	Ion abundance ratio, Appendix I	Reanalyze, perform instrument maintenance
Initial Calibration (IC)	Precision	Prior to sample analysis, and if OCC fails	%RSD of each RF≤ 15%	Perform instrument maintenance, reanalyze

QC Check Standard (QCCS)	Analytical bias	Duplicates per system each time a new IC is analyzed	%R = 100 ± 20%	Reanalyze; obtain new lot or vendor QCCS
Instrument Detection Limit	Detection limit	Prior to sample analysis	IS area counts within criteria	Perform instrument maintenance, reanalyze
On-going Calibration Check (OCC)	Precision, calibration drift	Beginning and end of each 12-hour analytical period	%D from IC ≤ 15%	Reanalyze, perform instrument maintenance
Sample Duplicate	Precision	TD/GC/MS: every passive sample. PT/GC/MS: 1 out of 3 soil samples	Other associated samples within criteria	Flag data
Field Blank	Contamination	TD - One per active sample point Soil - One per day	Below analyte IDL or sample values ≥5x Instrument Blank	Flag data
Instrument Blank	Detection limit, contamination	Beginning and end of each 12 hour analytical period	Below analyte IDL or sample values ≥5x Instrument Blank	Reanalyze, perform instrument maintenance, flag data
Travel Blank	Contamination, detection limit	One per sample shipment	Below analyte IDL	Flag data
Travel Spike	Shipping and handling bias	3 per site, per analysis method	Analyte %R = 100 ± 25%	Flag data
Internal Standard (IS) Area Counts	Analytical bias	Each sample, blank, and standard	%D = -50% to +100%	Reanalyze if blank or standard, flag data
Surrogate Recovery *	Analytical bias	Each sample, blank, and standard	%R = 100 ± 25%	Reanalyze if blank or standard, flag data

* PT/GC/MS samples only

The %D from the initial calibration response will be calculated as follows:

$$\%D = ([R1 - R2] / R1) \times 100$$

where "R1" is the initial calibration peak area count and "R2" is the subsequent or daily peak area count.

The precision of sample duplicates will be calculated as the relative percent difference (RPD):

$$RPD = \frac{(C1 - C2) \times 100\%}{(C1 + C2) / 2}$$

where C1 = the larger of the two observed values and C2 = smaller of the two observed values.

8.2 VOC Bias

Bias in the samples and analytical system will be monitored by: (1) checking the tune of the mass spectrometer every 24 hours with bromofluorobenzene (BFB), (2) comparing the data generated in the initial calibration curve with concentrations of the analytes measured in a second-source QC Check Standard, (3) analysis of travel spike samples, (4) area counts of the IS compounds added to every TD tube or 40-mL VOA vial, and (5) surrogate compound recoveries (PT/GC/MS only).

Percent recovery (%R) of the QC check standard and travel spikes will be calculated as follows:

$$\%R = 100 (S/C_{sa})$$

where S is the measured concentration and C_{sa} is the nominal concentration of a given analyte in the standard or travel spike sample.

8.3 VOC Instrument Detection Limits and Contamination

The laboratory-derived instrument detection limit (IDL) will be established following the procedure of USEPA (1992). The IDL is defined as follows:

$$IDL = 3.14*sd$$

where *sd* is the standard deviation (n-1 degrees of freedom) for the analytical results from seven replicate low-level standards and 3.14 is the Student's t-value for a one-sided 99% confidence level. IDLs will be reported in pmoles on-column for TD/GC/MS and ng on-column for PT/GC/MS.

Field blanks are used to monitor the exposure of samples to external contamination during the sampling process. At each sampling point the vapor sampling system to be used will be assembled and three internal volumes of ambient air will be drawn through the sampling system and collected into a clean TD tube. The TD tube will be labeled as a vapor sampling system blank and the information transferred to the field notebook. The TD tube will be capped, placed in a plastic bag, and shipped, stored on ice at 4 °C.

One soil field blank will be taken at one sampling point each day. Prior to the transfer step of the soil sampling procedure at the selected sampling point, the caps will be removed from the prepared high-level sample vials to be used for the blanks, and the vials placed in close proximity to the sampling activity. When the soil sample collection at that point is completed, the field blank vials will be sealed. The field blank labels will be completed and the information transferred to the Soil Sample Tracking Form (Figure 5) and the field notebook. The field blank vials will be shipped and stored at 4° C. If contamination is detected in the field blank, data from samples with measured contaminant concentration $\leq$ 5 x field blank contaminant concentration will be flagged.

Travel blanks are used to monitor the exposure of samples to contamination during shipping and storage. A sealed, prepared TD tube will included in each cooler containing sample TD tubes during shipping to and from the field, and during storage of the sample containers. The same TD

travel blank will be used for active and passive vapor samples. A vial containing methanol will be included in each cooler and used as a travel blank for low- and high-level PT/GC/MS samples. If contamination is detected in a travel blank, all data associated with that blank will be flagged.

Instrument blanks monitor any potential contamination during analysis. Instrument blanks will be included at the beginning and end of each 12-hour analytical period, or at the beginning and end of any run less than 12 hours. If contamination (any compounds of interest at a concentration above the IDL) is detected in an instrument blank at the beginning of a run, no samples will be analyzed until the problem has been identified and corrected. Data from the second half of the run will be flagged if contamination is discovered in a blank at the end of a run. If sample concentrations associated with the faulty blank are $\geq$ 5X the blank contamination, the data will be considered acceptable for use in data analysis steps.

8.4 Organic Carbon QC Samples

Method precision will be monitored by analyzing sample triplicates for each soil. The procedure will include at least one soil standard in every set of 10 samples as a check for bias. The soil standard will have been analyzed by an independent source or method. The standard soil will undergo the same pretreatment(s) as the samples. Each soil sample will be visually inspected after combustion for the burn characteristics and will be rerun if combustion was not complete.

8.5 Particle Size Analysis QC Samples

Method precision will be monitored by analyzing three replicates of a laboratory soil standard. One soil standard is to be included in every batch of 12 samples as a check for bias. The silt and sand content of the standard will be compared with the on-going laboratory mean result for these parameters. Duplicate analysis of one sample will be included in each batch, randomly selected from the soil provided. QC results will be reported with the sample data.

9. Instrument Calibration and Frequency

9.1 Thermal Desorption

A five-point calibration curve at nominal concentrations of 50, 100, 200, 300, and 500 pmoles on-column will be established for the site-specific analytes of interest. Pure component gas-phase standards (from Scott Speciality Gases or equivalent) at a nominal concentration of 10 ppmv will be acquired. This means that the gas has 1 µmole of each compound of interest for every mole of gas. A mole of gas occupies 24.5-L at 1 atmosphere pressure and 25 °C. Therefore, a mmole occupies 24.5 mL and a µmole occupies 24.5 µL. A 24.5 µL aliquot of the 10 ppmv gas standard contains 10 pmole of the compounds of interest. The tubes will be spiked with 0.12 , 0.245 , 0.490, 0.735, and 1.225 mL of the 10 ppmv gas to achieve 50, 100, 200, 300, and 500 pmoles of compounds of interest, respectively. (See Appendix II).

TD tubes will be spiked with calibration standards in the same manner used for adding IS compounds to each tube (Section 7.1.1). A Swagelok® tee containing a septum-port sidearm will be inserted in the flow path between the TD tube and a tank of ultrapure N_2 gas. The N_2 gas will be set to flow through the inlet end of the TD tube at 50 mL/min and the IS and calibration compounds will be injected into the stream of N_2. Fifteen minutes of N_2 flow per tube will be allotted to insure complete transfer of the calibration and IS compounds onto the TD tubes. A mid-point calibration check tube (OCC) will be analyzed at the beginning of each sample set and every 12 hours thereafter, or at the beginning and end of each run less than 12 hours. These standards will be prepared no more than 4 days prior to use.

9.2 Purge-and-Trap

A five-point calibration curve consisting of standards at the nominal concentrations of 10, 50, 250, 500, and 1000 ng total on-column will be prepared for each analyte of interest at the sites. A new calibration curve is warranted if fresh OCC standards do not meet the acceptance criteria (Table 3).

9.3 Organic Carbon

The high-temperature induction furnace procedure will include at least one soil standard in every set of ten samples. The soil standards will have been analyzed by an independent source or method.

9.4 Particle Size Analysis

A laboratory soil standard will be included in every batch of 12 samples as a QC check. The silt and sand content of the standard will be compared with the on-going laboratory mean result for these parameters.

9.5 Soil Moisture

When in use, the balance will be calibrated daily against a set of "S" class standard weights. The calibration checks will be recorded with sample weights.

10. Data Management

The EPA Client Representative will be responsible for the management of all laboratory-generated data. If the Client Representative tasks LM to prepare a final report, the client will provide a copy of all soil vapor, soil VOC, and soil characterization data. Lockheed Martin will assume data management responsibility while analyzing the data and writing the report. If the Client Representative prepares the final report, LM will transfer data management responsibilities to the Client Representative. The task of data management for this study includes: (1) generating unique data labels, (2) tracking QC data with sample data, (3) tracking sample dilutions and replicates, (4) creating spreadsheet macros to transfer the electronic data from one software environment to another, minimizing errors that can accumulate from transferring large amounts of data, and (5) maintaining electronic backup of data.

C. Assessment/Oversight

11. Assessment and Response Actions

Problems that arise beyond any anticipated in this QAPP may be caused by uncontrolled laboratory or field factors such as spurious contamination, instrument problems, unanticipated data analysis problems, or field weather conditions. Corrective actions for non-routine problems generally require an assessment of the problem with respect to project objectives, time, and cost considerations. LM management and the Client Representative will be notified of any problems encountered during project implementation and will be directly involved if corrective actions require additional resources. The Client Representative will be consulted if there are any modifications to, or significant deviations from this QAPP.

12. Reports to Management

The Task Lead will be responsible for monthly progress reports to the Client Representative. Separate written communications will be forwarded to the Client Representative regarding any modifications to this QAPP. If the Client Representative requests a draft report, it will include a project summary, a description of the methods, results, and a discussion of the results. Appendices will include: (1) a copy of all raw data, and (2) a QA/QC report which outlines the results of QA/QC procedures and discusses these results with respect to the initial QA objectives.

D. Data Validation and Usability

13. Data Review, Validation, and Verification Requirements

Data will be considered valid for a characterization parameter if all applicable QC data are within method or QAPP-specified windows. Any data generated with the corresponding calibration samples outside of the expected range will be flagged and discussed in the QA/QC report.

Justification for the inclusion or exclusion of qualified data in the data analysis steps will be based in context with the entire data set.

14. Reconciliation of Data Quality Objectives

A Data Quality Assessment (DQA) process will be used for reconciliation of DQOs. This process is designed to determine how well the data satisfy their intended use. This process will consist of the following steps:

(1) A review of all data will be conducted to assess the quality with respect to the QC parameters. Soil VOC concentrations by the low-level and high-level methods will be compared. Either a mean value, or the data set generated using one of the methods will be selected.

(2) Once the data have been verified to be of acceptable quality, plots of collocated soil versus vapor concentrations will be generated for each vapor collection method, by site. The active vapor sampling methods give a minimum of five ways to compare the data utilizing the six sequential samples at each sample point: sum; mean; mode of all six samples; value of fourth sample; mean value of samples 4, 5, and 6. The trend of vapor concentration versus sequential sample number will be plotted first. This plot can then be used for selection or justification of the above-mentioned methods for determining which data to include in the correlation.

(3) Appropriate procedures for summarizing and analyzing the data will be identified from the preliminary review. All assumptions for any statistical procedures deemed appropriate will be identified and verified as acceptable. Conclusions will be stated in terms of trends and statistically significant correlations.

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Appendix I

Ion Abundance Ratio Criteria

Mass (m/z)	Relative Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mas 95
95	Base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	less than 2 percent of mass 174
174*	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

*All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

Appendix II

Calculations for Using 1 ppmv and 10 ppmv Gas Standards

One mole of gas occupies 24.5 L at 25 ºC and 1 atm pressure. Therefore, 24.5 mL contains 1 mmole of gas. A gas standard, to supply 1 ppmv, would contain 1 nmole of analyte in 1 mmole of gas. Standards will be prepared as follows:

Volume of gas standard	Quantity of VOC supplied: 10 ppmv standard	1 ppmv standard
24.5 µL (0.0245 mL)	= 10 pmoles VOC	= 1 pmole VOC
122.5 µL	= 50 pmole	= 5 pmole
245 µL	= 100 pmole	= 10 pmole
490 µL	= 200 pmole	= 20 pmole
735 µL	= 300 pmole	= 30 pmole
1.22 mL	= 500 pmole	= 50 pmole