

ADVISORY – ACTIVE SOIL GAS INVESTIGATION

Comment period open until April 15, 2010. Submit comments to:

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Disclaimer

This document is a compilation of available information, knowledge, experience, and best practices regarding soil gas sampling for site assessment and remediation. This document does not contain regulatory requirements. In general, this document should be used as a reference. Differences may exist between the recommendations in this document and what is appropriate under site-specific conditions. The recommendations do not represent the positions or opinions of the Agencies. This document does not represent endorsement of practitioners or products mentioned in the document by the participating government agencies.

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LIST OF ACRONYMS

AGSI	Active Soil Gas Investigation
ASAP	As soon as possible
AST	Aboveground Storage Tank
ASTM	American Society of Testing and Materials
BFB	Bromofluorobenzene
Cal/EPA	California Environmental Protection Agency
CHHSLs	California Human Health Screening Levels
COPC	Chemical of Potential Concern
CSM	Conceptual Site Model
1,1-DFE	1,1-Difluoroethane, Freon 152A
DFTPP	Decafluorotriphenylphosphine
DL	Detection Limit
DQO	Data Quality Objective
DTSC	Department of Toxic Substances Control
ECD	Electron Capture Detector
ECL	Environmental Chemistry Laboratory, DTSC
ELAP	Environmental Laboratory Accreditation Program
EPA	Environmental Protection Agency
ETBE	Ethyl tertiary butyl ether
FID	Flame Ionization Detector
Freon 11	Trichlorofluoromethane
Freon 12	Dichlorodifluoromethane
Freon 113	1,1,2-Trichloro-1,2,2-trifluoroethane
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
CRWQCB	California Regional Water Quality Control Board
GEM	Gas Emission Monitor
HECD	Hall electrolytic conductivity detector
IDW	Investigation Derived Waste
ITRC	Interstate Technology & Regulatory Council
LARWQCB	Los Angeles Regional Water Quality Control Board
LCS	Laboratory Control Samples
L-D PE	Low Density Polyethylene
µg/L	Microgram per liter
µg/m ³	Microgram per cubic meter
MS	Mass Spectrometer
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MTBE	Methyl tertiary butyl ether
ND	Non-detect
NELAP	National Environmental Laboratory Accreditation Program
NIST	National Institute of Standard and Technology
OEHHA	Office of Environmental Health Hazard Assessment
PAHs	Polycyclic Aromatic Hydrocarbons

PCE	Tetrachloroethylene, Tetrachloroethene or Polychloroethylene
PE	Performance Evaluation
PEEK	Polyetheretherketone
ppmv	parts per million by volume
ppbv	parts per billion by volume
PID	Photoionization Detector
RL	Reporting Limit
%RPD	Percent Relative Percent Difference
%RSD	Percent Relative Standard Deviation
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
REF	Reference
SAP	Sampling and Analysis Plan
SCAQMD	South Coast Air Quality Management District
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SUMMA®	Passivated Stainless Steel Canister
SVE	Soil Vapor Extraction
SVOCs	Semi-volatile Organic Compounds
SW-846	Solid Waste-846; USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
TAME	Tertiary amyl methyl ether
TBA	Tertiary butyl alcohol
TCD	Thermal-Conductivity Detector
TCE	Trichloroethylene or Trichloroethene
TICs	Tentatively Identified Compounds
TO-15	Toxic Organic-15 Analytical Method (USEPA, Compendium Method TO-15 for the Determination of Toxic Organic Compounds in Ambient Air)
TO-17	Toxic Organic-17 Analytical Method (USEPA, Compendium Method TO-17 for the Determination of Toxic Organic Compounds in Ambient Air)
TPHs	Total Petroleum Hydrocarbons
USEPA	United States Environmental Protection Agency
USTs	Underground Storage Tanks
VOA	Volatile Organic Analysis
VOCs	Volatile Organic Compounds

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1.0 INTRODUCTION

The Advisory – Active Soil Gas Investigation (ASGI or Advisory) provides technically consistent approaches for collecting and analyzing soil gas samples. The Advisory is not a regulation, nor does it impose any requirements or obligations on the regulated community. Rather, it provides a technical framework and reference for addressing soil gas sample collection and analysis. Other technically equivalent procedures may exist, and this Advisory is not intended to exclude alternative approaches or methodologies.

Active soil gas sampling and analysis refers to the methods utilized to collect vapor phase data at sites potentially affected by volatile organic compounds (VOCs), including chlorinated solvents, petroleum hydrocarbons, methane, hydrogen sulfide and semi volatile organic compounds (SVOCs). The data obtained from a soil gas investigation can be used to identify the source and spatial distribution of contamination at a site or to estimate indoor air concentrations for risk assessment purposes.

Collecting and analyzing soil gas samples allows the practitioner to:

- (1) Determine if discharges of contaminants have occurred which may impact indoor-air, outdoor-air and groundwater;
- (2) Determine the spatial patterns and extent of vapor phase soil contamination;
- (3) Establish the distribution of contaminated vapor for effective design of soil vapor extraction (SVE) systems; and
- (4) Determine the effectiveness of remedial action to reduce the threat of contaminated vapors to receptors, including groundwater.

Within the unsaturated vadose zone, contaminants may partition into the following phases:

- (1) Solid phase by adsorbing onto the organic fraction of soil;
- (2) Aqueous phase by dissolving in groundwater;
- (3) Free liquid phase; and/or
- (4) Gaseous phase, by accumulating in the interstitial space of soil particulates as soil gas.

Thus, soil matrix, groundwater, and soil gas sampling and analysis should be performed for site characterization in order to ensure that all potential phases of VOCs are evaluated. Using appropriate methodology, soil gas sampling is practicable and preferred for many geologic materials including fine-grained soil formations. For evaluating the risk associated with vapor intrusion to indoor air, including sub-slab sampling, consult the vapor intrusion guidance (Cal/EPA 2005a or its revisions).

This document supersedes the 2003 Advisory – Active Soil Gas Investigation (Cal/EPA, 2003) and 1997 LARWQCB “Interim Guidance for Active Soil Gas Investigation” (CRWQCB, 1997). Unless otherwise noted in this Advisory, active soil gas investigations should be performed in accordance with this document. Passive soil gas sampling methods are discussed briefly in Appendix A. Sites where sampling methods other than soil gas investigations are necessary should be addressed separately with the regulating agency.

2.0 Project Scope

Study Purpose and Data Quality Objectives: A single soil gas investigation is often undertaken for multiple purposes. Subsequently, each purpose will have significantly different data quality objectives (DQOs), particularly the target contaminant concentrations. Examples of different purposes for performing a soil gas investigation are provided below:

- Transaction audit screening for potential leaks at aboveground storage tanks (AST), underground storage tanks (USTs) or other underground pollution sources
- Monitoring the performance of a SVE system
- Mapping soil vapor plumes to select houses for indoor-air monitoring
- Stand-alone data set for performing a vapor intrusion risk assessment using generic attenuation factors or a mathematical model to estimate indoor-air concentrations from soil gas data
- Designing mitigation measures and performance monitoring

The DQO process is a systematic planning tool based on the scientific method for establishing criteria for data quality and for developing data collection designs. By using the DQO process to plan environmental data collection efforts, the effectiveness, efficiency, and defensibility of decisions can be improved in a resource-effective manner. DQOs should be established before the study is conducted. Example input parameters to the DQOs include the site scenario (such as residential use versus commercial use), action levels for the site, method reporting limits that need to be met, and the appropriate measurement method to be used. The expected output is the most resource-effective design for the study. Information concerning DQOs is provided in USEPA (1994a, b, 2000a).

Technical Reports

The following reports should be completed and submitted for all soil gas investigations:

- Workplan, including a detailed Conceptual Site Model (CSM)
- Sampling and Analysis Plan (SAP) (may be a component of the Workplan)

- A Soil Gas Investigation Report

Workplan

A workplan should be prepared and submitted to the regulating agency for review and approval at least 30 days prior to its proposed implementation schedule. Any variations or deviations from this Advisory should be specified in the workplan. The soil gas workplan may be incorporated as part of a comprehensive site investigation workplan or as a stand-alone document, depending on site-specific circumstances. The workplan should include DQOs and a Conceptual Site Model (CSM) that identifies the contaminant source(s), pathway(s) and potential receptor(s) to aid in the justification for the number, location and frequency of samples.

Development of Conceptual Site Model

A CSM is an integral part of all site investigations. The purpose of a CSM is to provide a conceptual understanding of the potential for exposure to hazardous contaminants at a site based on the sources of contamination, the release mechanisms, the transport media, the exposure pathways, and the potential receptors. The CSM should include a diagrammatic or schematic figure that relates the sources of contamination to receptors and the environment, and should identify all potential sources of contamination, the potentially contaminated media, and exposure pathways. The CSM organizes and communicates information about the site characteristics and provides all interested parties with a conceptual understanding of the potential for exposure to chemicals of potential concern (COPCs) at a site. Additional resources regarding CSMs include: (1) Cal/EPA, 2005; (2) ITRC 2007; (3) Cal/EPA, 1999; (4) USEPA, 1988; (5) USEPA, 1989; and (6) USEPA, 1994a.

The basic components of a CSM are:

- (1) Type of contaminants, including VOCs, currently or previously stored or handled at the site
- (2) Known concentrations of COPCs in media such as soil gas, soil and groundwater
- (3) Identification of the primary and secondary sources of COPCs, including: location, depth, and phase(s) of COPCs
- (4) Primary release mechanism
- (5) Contaminant transport mechanism and pathway(s), including the identification of preferential pathways and vapor entry points
- (6) Exposure media such as surface soil, drinking water, and air
- (7) Potential receptors including human and ecological receptors, inhabitants of residential building(s), inhabitants of commercial buildings, and groundwater

- (8) Vapor distribution and migration
- (9) Unique site features.

The CSM is a dynamic and iterative tool, and is meant to be updated as new information becomes available. Therefore, it should be revised after each stage of the investigation.

To identify sources, potential release mechanism(s) and pathway(s) for vapor migration, collect some or all of the following information:

- soil types
- subsurface geology
- hydrogeology (local and regional) including groundwater flow direction
- subsurface heterogeneity
- groundwater quality data
- regional groundwater flow direction
- well records
- boring logs
- surficial features of the area, such as ground cover and surface water bodies.

A cross-sectional diagram or equivalent depicting a three-dimensional concept of the site may be helpful in demonstrating and understanding site dynamics. Examples of features to include for the three-dimensional conceptual model include the items listed above as well as:

- point of source entry into the vadose zone
- primary and secondary source location and depths
- vertical profiling of lithologic changes down to the first occurrence of groundwater
- location of above ground buildings and receptors relative to the source.

Elements of the Workplan

Provide details of the study design in the Workplan, which include:

- (1) A scaled site map which identifies proposed sampling points, with locations and coordinates of identifiable geographic landmarks, such as street center-line, benchmarks, street intersection, and wells. The site map should also include the known or inferred extent of contamination as well as, pertinent features that represent potential or known areas of concern. Examples of pertinent features include existing or former sumps, trenches, drains, sewer lines, clarifiers, septic systems, piping, and locations of ASTs, USTs, and chemical or waste management units.

- (2) The number and location of initial sampling points in potential source areas and areas with known contamination. The rationale for the number, location and depth of sampling points selected should be provided.
- (3) A clear statement as to whether permanent or temporary vapor wells are to be installed, and the rationale for making that decision.
- (4) A clear statement as to whether a mobile and/or stationary laboratory will be used when samples are collected, and the rationale for making that decision. Note that non-specific portable organic vapor analyzers and/or gas chromatograph (GC)-based handheld detectors should not be used for quantification during a soil gas investigation. As of the date of this document, a laboratory certification program is in progress. Once certification program is available by the California Department of Health Services, laboratories should apply for a certification program as soon as possible.
- (5) A schematic diagram of the well design and a cross-section of the site showing the major lithologic units and zones for vapor monitoring should be included in the workplan (see Figures 1 and 2).
- (6) A clear statement as to how to prevent infiltration of surface runoff with contaminants into the vadose zone, groundwater, and the monitoring points.
- (7) A clear statement as to how unauthorized access to the permanent monitoring points will be prevented, for example, by a locking subsurface utility vault)
- (8) Considerations for sampling frequency pursuant to the DQOs established for each site.
- (9) Procedures for properly installing soil gas sampling points. The workplan should provide sufficient details concerning installation of sampling points based on known site conditions.
- (10) Procedures to properly decommission monitoring vapor wells that are no longer needed. The decommissioning activity should achieve an effective and long-term seal of subsurface geologic materials and prevent cross-contamination in the subsurface.
- (11) A health and safety plan for the project.

2.1 Field Activities

The project proponent should notify the regulating agency 10 working days prior

to implementation of field activities. All necessary permits and utility clearance(s) should be obtained prior to conducting any investigations described in this Advisory.

The regulating agency staff may request raw data for evaluation either in the field or in the office at any time during the investigation. Hard copies of the complete raw laboratory data, including handwritten data and field notes, should be provided to the regulating agency staff upon request. Adjustments or modifications to the sampling program may be required by the regulating agency staff to accommodate changes mandated by evaluation of the data set or unforeseen site conditions. The project proponent should keep the following guidelines in mind during the course of the investigation.

Sampling and Analysis Plan

The SAP should have enough flexibility to allow for modifications to be made as real-time evaluation of analytical test results occurs. Examples of modifications include sample density, location and depth. The decision-making criteria for these adjustments should be included in the SAP. Modifying decisions made in the field should be detailed in the Soil Gas Investigation Report. Field decisions should be made in consultation with the regulating agency.

Re-sampling should occur at any sampling point where anomalous data are obtained. Anomalous data are defined as two to three orders of magnitude difference from surrounding samples. Additional points may be required to resolve the spatial distribution of the contaminants within the interval in question.

Investigation Derived Waste

Manage Investigation Derived Waste (IDW) as hazardous waste until proven otherwise or until specifically approved by the regulating agency as being non-hazardous waste. Handle and dispose of IDW in accordance with federal, state, and local agency requirements.

Field Variations

A proposal for contingencies should be included in the project workplan to expedite the completion of field activities and to avoid potential project delays. An example of a contingency plan would be a decision criterion if low flow conditions are encountered during the proposed soil gas investigation.

The regulating agency should be informed of any problems, unforeseen site conditions, or deviations from the approved workplan. When it becomes necessary to implement modifications to the approved workplan, the regulating agency should be notified and provided an opportunity to review the changes prior to implementation.

Soil Matrix Sampling

Companion soil matrix sampling may be conducted concurrently with a soil gas investigation. Soil matrix sampling should be performed pursuant to USEPA Method 5035 for collection of samples for VOC analysis (Cal/EPA, 2004).

2.2 Soil Gas Investigation Reports:

At the conclusion of the soil gas investigation, submit a Soil Gas Investigation Report (Report) to the regulating agency. The Report should document analytical results, field operations, deviations from the approved workplan, data inconsistencies, and other significant operational details. The Report may either be a stand-alone document in a format recommended by the regulating agency or be included within a site-specific assessment report. Reports should also include a revised CSM based on data obtained from the soil gas investigation. At a minimum, the report should contain the following:

1. Site plan map and vapor well location map at an appropriate scale as specified in the workplan;
2. A map and/or cross-sectional diagram that depict all contamination found during the soil gas investigation. When sufficient data are available, iso-concentration maps should be prepared. Data from previous investigations should be incorporated as appropriate;
3. Design Drawings: As-built diagrams for soil gas wells should be submitted with the soil gas investigation report detailing the well identification and corresponding vapor well depths. A typical vapor well construction diagram may be submitted for vapor wells with common design and installation;
4. Summary tables for analytical data;
5. Legible copies of field and laboratory notes or logs;
6. All analytical results and Quality Assurance/Quality Control (QA/QC) information including tables and explanation of procedures, results, corrective actions and effect on the data. Upon request, all raw data including chromatograms and calibration data should be submitted to the regulating agency;
7. Electronic data deliverables submitted in the format specified by the regulating agency;

8. An assessment of the adequacy of the current CSM and a subsequently revised CSM;
9. Data gaps identified based on revised CSM; and
10. Conclusions and recommendations:

All engineering or geologic work (e.g., logging continuous soil cores, soil description) should be performed or supervised by a California Registered Professional in accordance with the Business and Professions Code, Chapters 7 and 12.5, and the California Code of Regulations, Title 16, Chapters 5 and 29.

2.3 Soil Gas Sampling Location and Sampling Wells/Probes Installation

Lithology

Use site soil or lithologic information to select appropriate locations and depths for soil vapor monitoring wells. If on-site lithologic information is not available prior to conducting the soil gas investigation, at least one (1) continuously cored boring to the proposed greatest depth of the soil gas investigation should be installed at the first sampling location, unless specifically waived or deferred by the regulating agency. Depending on site conditions, additional continuously cored borings may be necessary. If the soil gas data are to be used for human health risk assessment or vapor intrusion assessment, the lithology/geology should be understood and documented in an appropriate level of detail. Geotechnical information required to be collected for vapor intrusion risk assessment purposes can be found in the DTSC Vapor Intrusion Guidance (Cal/EPA, 2005, Appendix H). A statistically sufficient number of geotechnical samples should be collected for vapor intrusion (i.e., Johnson & Ettinger) modeling used for the risk assessment.

Prepare lithologic logs prepared for all borings, soil matrix sampling, and geotechnical sampling. Information gathered from the continuously cored borings may include soil physical parameters, geotechnical data and contaminant data. Use information collected from borings to modify the CSM. Provide all boring logs to the agency.

Sample Spacing

Sample spacing should be in accordance with the study design rationale provided in the workplan, and may be modified based on site-specific conditions

with regulatory agency approval. The sampling locations should include biased sampling locations to optimize detecting and delineating VOCs. Selection of appropriate number, locations and sampling depths are site-specific, and should be based on the CSM and the project DQOs.

Sample Depth

Soil gas sample depths should be chosen to minimize the effects of changes in barometric pressure, temperature, or breakthrough of ambient air from the surface and to ensure that representative samples are collected. Consideration should be given to source location, types of chemicals of concern, and the lithology encountered.

Vapor monitoring wells should be installed at a minimum of two sample depths, at approximately five (5) feet below ground surface (bgs) and 10 to 15 ft bgs. Variation of sample depths and the need for deeper sample locations will be evaluated based on site specific characteristics.

For shallow contaminant sources of less than 10 feet bgs, collect soil gas samples immediately above the source. Samples collected at less than 5 feet bgs may be subject to barometric pressure effects and are more prone to ambient air breakthrough. For deep contaminant sources, collect soil gas samples starting at 10-15 feet bgs.

When evaluating vapor intrusion, obtain soil gas samples at appropriate depths so that risk to human exposure can be adequately quantified. Empirical studies indicate that shallow soil gas measurements at 5 feet bgs may not be indicative of soil gas concentrations under buildings (Hers et al., 2006; DiGiulio and Cody, 2006). These studies suggest that soil gas samples collected at depth of 10 to 15 feet are a better indicator of vapor intrusion risk than samples collected at 5 feet bgs when the source depth is greater than 15 feet bgs. Numerical modeling also suggests this relationship (Abreu and Johnson, 2005; Abreu et al, 2006). Hence, risk quantified with shallow soil gas measurements (5 feet bgs) using the Johnson and Ettinger (1991) model may yield estimates that are biased low if the soil gas is from a deep source.

For vapor intrusion evaluations, soil gas sample depth is dependent on the depth of the contaminants. Deeper sampling would be needed when evaluating buildings with basements (Abreu et al., 2006).

Vertical Profiling

Vertical profiling is achieved by collecting soil gas samples at varying depths in a single location, or by using closely spaced vapor monitoring wells installed at varying depths. Use vertical profiling in areas where significant contaminant concentrations are identified. The objectives of vertical profiling are to:

- (1) Assess the vertical distribution of contaminants in the vapor phase within the unsaturated zone;
- (2) Identify migration pathways at depth along which contaminants may have migrated from sources; and
- (3) Serve as discrete monitoring points to evaluate the efficiency of a cleanup action.

Vertical profiling depends on DQOs and the CSM. Vertical profiling may or may not be appropriate at any given site. Describe the rationale for vertical profiling in the workplan for regulatory review prior to commencement of field work. Vertical profiling is appropriate for any of the following locations:

- Sites identified with subsurface structures such as USTs, sumps, clarifiers, waste or chemical management units
- Sites with subsurface sources such as oil fields, artificial fill, or buried animal waste
- Sites with heterogeneous lithology
- Sites with contaminated groundwater
- Areas with significantly elevated VOC concentrations detected during previous sampling
- Areas where elevated field instrument readings are encountered from soil matrix cuttings, cores or samples
- In the annular space of groundwater monitoring wells during construction where an assessment of the vertical extent of soil gas contamination is necessary.

All available information such as geologic logs and field instrument readings from soil cuttings or cores should be used to select appropriate depths to collect soil gas samples. Probes should be installed at depths with elevated vapor readings and/or slightly above fine-grained soils. If vertical characterization to groundwater is required, the deepest soil gas sample should be collected near the top of the capillary fringe. Soil gas probes should not be installed within or below the capillary fringe. Where deeper soil gas sampling is necessary and no lithologic change or technical basis is observed, then default sampling depths of 10 to 15 foot intervals may be selected for multi-depth sampling, until either groundwater is encountered or VOCs are not detected. Nested vapor wells may be installed in the annular space of groundwater monitoring wells to serve as a dual-purpose well if both vapor and groundwater monitoring are required.

Sampling Tubing

Small diameter (1/8 to 1/4 inch) sampling tubes made of material, which will not react or interact with site contaminants should be used. Use small-diameter continuous tubing attached from the vapor probe to the ground surface to minimize

purge volume.

1. Clean, dry tubing should be used at all times. If any moisture, water, or an unknown material is present in the probe prior to insertion, decontaminate or replace the tubing.
2. The bottom-end of the tubing should be attached to an appropriate vapor probe tip. The probe tip design should allow for optimum air flow and prevent air flow restriction. Ensure the connection between the tubing and the vapor probe tip is air-tight to prevent leakage.
3. Metal tubes should not be used for collection of hydrogen sulfide samples. Nylaflo[®], polyetheretherketone (PEEK), and Teflon[®] are recommended for use in the soil vapor sampling train. Use of low-density polyethylene (L-D PE) is discouraged due to decreased performance relative to other tubing types in both introduction of background analytes and sample recovery. Reduced recovery of naphthalene was reported when using Nylaflo[®] tubing with small sample sizes (see Appendix B).

Soil Vapor Well Installation

Vapor well installation procedures are described below. The probe tip, probe and probe connectors should all have the same diameter to provide a good seal between the formation and the sampling assembly. Seal all holes and spaces with bentonite slurry to prevent ambient air intrusion.

Installation Methods and Design: Soil vapor wells may be installed using a variety of drilling methods, such as direct push methods, hollow stem auger, or other techniques, as appropriate. Certain types of drilling methods, such as air rotary and rotosonic, are not recommended because they can adversely affect soil gas data during and after drilling. However, for deeper soil gas wells or for drilling in denser/coarser formations, alternate drilling methods (e.g., air rotary and rotosonic methods) may be employed with longer equilibration times prior to sampling. The mud rotary drilling method is not acceptable for soil gas probe emplacement under any circumstances. When additional sampling is not anticipated, properly remove or decommission vapor wells with concurrence from the regulatory agency and in accordance with State and local requirements.

- A. Place the probe tip midway in the sand pack, as shown on Figure 1. The sand pack should be a minimum of one (1) foot thick. Install the sand pack to minimize disruption of airflow to the sampling tip.
- B. Emplace at least one (1) foot of dry granular bentonite on top of each sand pack, as shown on Figure 1. Following the dry bentonite, grout the borehole to the surface with hydrated bentonite. The purpose of the dry granular

bentonite between the sand pack and the hydrated bentonite is to preclude the hydrated bentonite grout from infiltrating the sand pack. Follow a similar procedure for deep well construction with multiple probe depths, in that one foot of dry granular bentonite should be emplaced on top of the sand pack encasing each probe, followed by hydrated bentonite grout. The hydrated bentonite grout should continue until the next sand pack, as shown on Figure 2. A cement/bentonite mixture in accordance with California well construction standards may also be used above the dry bentonite layer to seal the borehole annulus.

- C. A tremie pipe should be used for soil vapor wells deeper than 15 feet, to avoid bridging or segregation during placement of the sand pack and bentonite seal.
- D. The use of a down-hole probe support may be required for vapor wells in excess of 40 feet bgs. The probe support may be constructed from a one-inch diameter bentonite/cement grouted PVC pipe or other solid rod, or equivalent, allowing probes to be positioned at measured intervals prior to installation. The support should be solid or properly sealed to avoid possible cross contamination or ambient air intrusion. Alternative probe support designs with accompanying descriptions may be proposed in the project workplan. Justification should be included in the project workplan if the project proponent chooses not to use probe support for deep vapor wells.

Tubing Protection: Tubing should be protected from damage or clogging from subsurface soil materials by placing the tubing inside a flush-mount casing. For deep vapor wells ensure the probe tip and tubing are properly placed and tubing is not damaged or kinked. Properly mark tubing at the surface to identify the probe location and depth.

Soil Gas Well Completion: Soil gas wells should be properly secured, capped and completed to prevent infiltration of water or ambient air into the subsurface and to prevent accidental damage or vandalism. For surface completions, the following components may be installed:

- a. Gas-tight valve or fitting for capping the sampling tube;
- b. Utility vault or meter box with ventilation holes and lock;
- c. Surface seal; and
- d. Guard posts.

Temporary Soil Vapor Wells: Post-run tubing and drive point methods¹ used to create temporary soil vapor wells are not recommended for soil gas sampling (McAlary, et al, 2009). The tubing used to create temporary soil vapor wells for the post-run method is prone to sealing issues associated with connecting the tubing to the drive point. Additionally, the drive point probes may be deflected by cobbles, which can create gaps between the outer wall of the casing and the geologic materials that are difficult to observe and equally difficult to seal. A hydrated bentonite plug at ground surface does not stop communication along the outer wall of the casing between different depth intervals. Samples collected under these circumstances will draw soil gas primarily from the most permeable layer above the tip of the probe which may introduce a significant bias. Moreover, this condition cannot be identified by any tracer applied at or near ground surface. Temporary soil vapor wells may also yield questionable results in moderate to low permeability soils such as clay and/or silt clay lenses, where the flow of gas through the geologic materials is low. In such case, soil gas will be collected from the path of least resistance at any depth along the drive shaft.

Equilibration Time

Subsurface conditions are disturbed during probe placement. To allow for subsurface conditions to equilibrate and vapor concentrations to stabilize, the following procedures are recommended:

1. For soil vapor wells installed with the direct push method, do not conduct the purge volume test, leak test, and soil gas sampling for at least 30 minutes following vapor probe installation.
2. For soil vapor wells installed with hollow stem or hand auger drilling methods, do not conduct the purge volume test, leak test, and soil gas sampling for at least 48 hours after vapor probe installation.
3. For soil vapor wells installed with the rotosonic or air rotary method, do not conduct the purge volume test, leak test, and soil gas sampling until it can be empirically demonstrated that the subsurface equilibrium time is sufficient for representative sample collection.

Vapor well installation method and equilibration time should be recorded in the field log book or field form.

Decontamination

Decontaminate all reusable equipment to prevent cross contamination.

¹ Drive point methods may be appropriate for certain site conditions or circumstances depending on DQOs. The use of post-run tubing should be discussed with the Agency prior to inclusion in the workplan.

Decontamination may consist of steam cleaning or a three-stage wash and rinse consisting of a wash with a non-phosphate detergent, a rinse with tap water, and a final rinse with distilled water. Collect one equipment blank at the beginning of sampling, and at least one each day after decontamination. Air dry equipment prior to re-use. Use new or unused sample tubing for each probe location. Reuse of tubing is not recommended.

Sub-Slab Investigation Methods

The procedure for collecting sub-slab soil gas samples are the same as for collecting sub-surface soil gas samples except that a slower flow rate and lower vacuum should be utilized. Using a flow rate of less than or equal to 50 milliliters per minute (mL/min) and maintaining a low vacuum of less than 100 inches of water should prevent ambient air breakthrough into samples (McAlary et al., 2009). Methods and procedures for installing sub-slab vapor wells are described in the DTSC Vapor Intrusion Guidance (Cal/EPA, 2005, Page G-1)

2.4 Soil Gas Sampling

Before obtaining soil gas samples, leak and purge volume tests are necessary.

Leak Test

A leak test is used to evaluate whether a good seal was established in the sampling train, ground surface, and probe interface. A leak test should be conducted at every vapor monitoring well each time a soil gas sample is collected because a poor seal may result in soil gas samples that are diluted by ambient air. This may result in an underestimation of actual site contaminant concentrations or, alternatively, introduce external contaminant into samples from ambient air.

Shut-In Test: Prior to purging or sampling soil gas, a shut-in test should be conducted to check for leaks in the above ground fittings. The shut-in test consist of assembling the above-ground apparatus (e.g., valves, lines and fittings downstream from the top of the probe), and evacuating the lines to a measured vacuum of about 100 inches of water column (in-H₂O), then shutting the vacuum in with closed valves on opposite ends of the sampling train. The vacuum gauge connected to the line via "T"-fitting is observed for at least one minute, and if there is any observable loss of vacuum, the fittings are adjusted as needed until the vacuum in the above-ground portion of the sample train does not noticeably dissipate (McAlary et al., 2009).

Leak Check Compounds: Liquid tracer compounds, such as hexane, pentane, and n-propanol, can be used to evaluate the sample integrity. Typically, liquid

tracer compounds are applied to towels or clean rags and placed around all connections in the sampling train in order to evaluate potential leaks of ambient air into the sampling train. The leak check compound selected should not be a suspected site-specific contaminant.

Seal integrity is confirmed by analyzing subsequent soil gas samples for the tracer compound. Alternatively, gaseous tracer compounds, such as helium, isobutene, propane, and butane, can be used along with a shroud or tent over the sampling equipment. Procedures for conducting a quantitative leak test using helium as a tracer compound are described in Appendix C.

Leak check compounds (i.e., liquid tracer compounds) should be included in the method analyte list. The laboratory reports should quantify and annotate all detections of the leak check compound at the reporting limit of the target analytes. If the concentration of the leak check compound is greater than or equal to ten times the reporting limit for the target analyte(s), then corrective action is necessary as discussed below.

If a leak check compound (i.e., liquid tracer compounds) is detected in the sample, the cause of the leak should be determined, evaluated, and corrected through retesting. If a leak is confirmed and the problem cannot be corrected, the ambient air leak may be quantified using a gaseous tracer with a shroud, as described in Appendix C. An ambient air leak up to five (5) percent is acceptable if quantitative tracer testing is performed by shrouding. Otherwise, the soil gas vapor well should be decommissioned if the leak cannot be corrected.

Replacement vapor wells should be installed at least five (5) feet from location where the original vapor well was decommissioned due to a confirmed leak. Include the leak check compound concentrations detected in the soil gas samples in the laboratory report and discussed in the site characterization report.

Note that if sampling is done exclusively from a SUMMA[®] canister at a stationary laboratory and there is a significant leak, it will not be identified until after the sample has been collected and analyzed. Therefore, field screening prior to laboratory confirmation is recommended.

2.5 Purge Volume Test

The purpose of a purge volume test is to ensure stagnant or ambient air is removed from the sampling system and to ensure samples collected are representative of subsurface conditions. The purge volume test should be the first soil gas sampling activity at the selected purge volume test point, and should be located as near as possible to the anticipated or confirmed contaminant source, and in an area where soil gas concentrations are expected to be elevated, based on lithology. The purge volume test is conducted by collecting and analyzing a sample for target compounds after removing one, three, and ten

purge volumes.

The purge volume (also referred to as the “dead space volume”) can be estimated by summation of the following components: (a) the internal volume of tubing used; (b) the void space of the sand pack around the probe tip; and (c) the dry bentonite in the annular space. Sample containers are not included in the purge volume calculation, except when non-evacuated glass bulbs are used. In those instances, the volume occupied by the non-evacuated glass bulbs should be added to the purge volume to account for mixing and dilution of gasses inside the glass bulb. The step purge tests of one (1), three (3), and ten (10) purge volumes should be conducted to determine the purge volume to be applied at all sampling locations. Select the appropriate purge volume based on the highest concentration of the compound(s) of concern detected during the step purge volume test. Optimize the purge volume for the compound(s) of greatest concern. Avoid extensive purging for soil gas samples collected at less than five (5) feet bgs. Conduct the step purge test and purging at the same flow rate and applied vacuum as soil gas samples. If the pump is battery operated, check the batteries before and during operation to insure a proper charge is maintained.

A default of three (3) purge volumes should be extracted prior to sampling in the following cases:

- If VOCs are not detected in any of the step purge tests
- If a SUMMA[®] canister is used for sampling soil gas
- For shallow soil gas samples (collected at less than five feet bgs)

Include the purge test data in the report to support the purge volume selection. The data set should include the purge volume test as well as the flow rate, vacuum exerted on the formation, and duration of each purge step.

Additional Purge Volume Tests

Additional purge volume tests may be necessary when warranted by site-specific situations. For example if widely variable or different site soil types are encountered during continuous coring conducted prior to the soil gas survey, or if the default purge volume of (3) is used and another VOC of concern not detected previously is subsequently detected.

If a new purge volume is selected in areas of similar lithology after additional step purge volume tests are conducted, then ten percent of the previously-completed vapor wells should be re-sampled using the new purge volume. Re-sampling may be necessary for all previously sampled vapor wells depending on site conditions. The soil gas investigation may then be continued with the revised purge volume in the remaining areas.

If a new purge volume is selected in areas of different lithology, then the soil gas investigation may be continued with the revised purge volume in the remaining areas with the same lithology.

2.6 Purge/Sample Flow Rate and Applied Vacuum

Purge/sample flow rates between 100 to 200 mL/min and vacuums less than 100 inches of water for standard small diameter (1/8 to 1/4 inch) tubing should be maintained to minimize partitioning of vapors from pore water to soil gas (i.e., stripping), prevent ambient air from diluting the soil gas samples, and to reduce the variability of purging rates from contractor to contractor. Low flow purge/sample rates and vacuums of less than 100 inches of water increases the likelihood that representative samples will be collected. The purge/sample rate may be modified based on conditions encountered in individual vapor wells. These modified rates should be documented in the soil gas report. A flow rate greater than 200 mL/min may be used in certain cases, such as when larger diameter tubing are used with deeper vapor wells that are greater than 40 feet bgs. However, a vacuum of 100 inches of water or less must be maintained during sampling whenever a higher flow rate is used. Large volume sample containers, such as the 6L-SUMMA[®] canisters should be avoided for shallow samples collected at less than five feet bgs.

Evaluate lithologic conditions adjacent to the vapor well to determine if the purge/sample flow rate is attainable. A vacuum gauge or similar device should be used between the soil gas sample tubing and the soil gas extraction devices, such as a vacuum pump, or SUMMA[®] canister. Gas tight syringes may also be used to qualitatively determine if a high vacuum soil condition is present. If a high vacuum condition due to tight or low permeability soil is present, the sampling technician will have a feeling of suction while the plunger on the syringe is being withdrawn. Conduct soil gas permeability testing at an optimal vacuum to determine the gas permeability of the soil surrounding the probe tip (McAlary, et al., 2009) (See Appendix D).

2.7 Sample Containers

Collect samples in gas-tight containers and handle in a manner that will prevent photo degradation of the target analytes. Sample containers should not compromise the integrity of the samples.

1. If a syringe is used, it should be leak-checked before each use by closing the exit valve and attempting to force ambient air through the needle. The use of gas-tight glass syringes with Teflon[®] seals is preferred. The use of plastic syringes is discouraged because of the interaction between the plastic (or rubber) of syringes and some target analytes.

2. If a SUMMA[®] canister is used, place a flow regulator and vacuum gauge between the vapor well and the SUMMA[®] canister. Perform near surface (e.g., less than five (5) feet bgs) sampling using 1L-SUMMA[®] or smaller containers.
3. If the Tedlar[®] bags or glass bulbs are used, add surrogates within 15 minutes of collection and analyze the samples as soon as possible after collection and within 6 hours after collection (see Appendix B).
4. Sorbent Tube sampling procedures: Details concerning selection of tube and sorbent, conditioning of tube, sampling apparatus, sampling rates, preparation of sample collection, set flow rates, and other sampling procedures are provided in the Compendium Method TO-17 (USEPA, 1999).
5. Specific recommendations for methane and hydrogen sulfide sample containers are specified in Section 3.9
6. Alternate Sample Containers (see Appendices B) are also available for sampling soil gas. Add surrogates in samples collected in glass containers within 15 minutes and analyze the samples within 6 hours of collection. MiniCans, smaller and lighter versions of the passivated SUMMA[®] canisters, can be used with the same limitations as the regular SUMMA[®] canisters. The use of alternate size or type of container should seek prior approval by the agency.

Sample Handling for All Sample Containers and Sorbent Tubes:

Soil gas samples should be analyzed as soon as possible after sampling. Ideally, samples are collected and analyzed immediately by a mobile laboratory; however, if samples need to be shipped to a fixed laboratory, then follow special handling procedures.

Samples collected in syringes should never be transported; however, samples collected in sorbent tubes and SUMMA[®] canisters may be shipped for analysis at a fixed laboratory. The precautions noted below should be followed.

Sample handling procedures cited in the analytical methods being used should be followed; however, since those methods are not designed for soil gas, additional safeguards should be implemented to maintain the integrity of the soil gas samples.

Syringes and Glass Bulbs:

1. Do not expose samples to light. Keep syringes and glass bulbs in a cool dark location at all times. Cover or wrap samples with foil and place into an insulated container (cooler but without ice) until the samples are analyzed.

Samples collected in syringes and glass bulbs should be analyzed as soon as possible after collection.

2. Do not subject samples to extreme in temperatures. Heat can cause compound degradation and leakage from the syringe or glass bulb. Cold can cause moisture condensation which can affect the recovery of target analytes. If condensation is observed, the sample should be discarded and a new sample should be collected.

Sorbent tubes:

1. Samples tubes should be recapped with metal, Swagelok[®]-type caps and combined PTFE ferrules, rewrapped in aluminum foil (if appropriate) and replaced in the storage container immediately after sampling.
2. Samples collected on tubes should be stored at less than or equal to 4°C and analyzed as soon as possible within 30 days after collection. For certain labile compounds, analysis should be done within one week (USEPA, 1999; Compendium Method TO-17, Section 10.10).
3. Samples collected on tubes containing multiple sorbent beds should be analyzed as soon as possible after collection unless it can be verified that storage will not affect the recovery of analytes (USEPA, 1999; Compendium Method TO-17, Section 10.10).

Tedlar[®] Bags:

If there is an absolute necessity to transport samples in Tedlar[®] bags, the following should be noted:

1. Do not expose soil gas samples in Tedlar[®] bags to light and extreme temperatures. Photodegradation of target analytes is possible with light exposure. Heat can cause expansion of the bag and possibly result in leakage. Cold can cause condensation of the sample.
2. Do not subject soil gas samples in Tedlar[®] bags to changes in ambient pressure. Changes in ambient pressure can adversely affect the integrity of the bags. Increases in pressure may collapse the bag and decreases in pressure may expand the bag. These changes in pressures coupled with possible flaws in the bag may cause sample loss due to leakage. Ambient pressure can change during the transport of samples. Samples traveling from the mountain area (lower pressure) to the lower desert area (such as Death Valley with higher pressure) can be subjected to significant pressure changes that may affect sample integrity. Alternate sample containers should be selected when pressure changes are anticipated.

2.8 Sample Container Cleanliness and Decontamination

1. New containers should be shown to be free of contaminants by providing data from either the supplier or the analytical laboratory.
2. After each use, reusable sample containers should be decontaminated as follows:
 - A. Glass syringes or bulbs should be disassembled and baked at 240° C for a minimum of 15 minutes or at 120° C for a minimum of 30 minutes, or be decontaminated by an equivalent method. If a syringe is re-used, it should be blank tested, and tested for adsorptive losses via spike testing. Blank testing frequency (or certification frequency) of syringes should also be included in the workplan.
 - B. SUMMA[®] canisters should be properly decontaminated as specified in US EPA Method TO-15, and/or should be certified according to project DQOs, either be batch or individually certified.
 - C. Tedlar[®] bags may be reused if data are provided to show the bags are free of contaminants.
 - D. Equipment blanks should be analyzed to verify and evaluate the effectiveness of decontamination procedures for recycled or reused containers. At a minimum, one equipment blank should be run per 20 sample containers cleaned, or at least one per day.

2.9 Sample Collection

1. **Vacuum Pump:** When a vacuum pump is used, collect samples on the intake side to prevent potential contamination from the pump. Use a lung box when collecting samples using Tedlar[®] bag (see Appendix C, Figure C-1). Record vacuum readings and corresponding flow rates on field data sheets for each sample. If the pump is battery operated, the batteries should be checked before and during operation to insure a proper charge is maintained.
- 2.. **Soil Gas Sampling in Low-Permeability Soil:** Soil gas sampling from low permeability material (i.e., silt and clay-rich soils) is feasible and high quality data can be produced with: (1) good annular seals; (2) careful monitoring of flow and vacuum during purging and sample collection; and (3) using tracer gas (i.e., helium) for leak-testing. If the soil gas permeability is too low to allow sustainable purging at appreciable flow rates without applying excessive vacuum, follow the protocols as described in Appendix D. An “appreciable flow rate” is defined as flow of 100 mL/min or greater, and an “excessive vacuum” is defined as any vacuum greater than about 100 inches of water

column. A low-flow or low-permeability probe is defined as a condition where the minimum flow rate (100 mL/min) could not be sustained at the maximum applied vacuum level (100 inches water). See Appendix D for sampling protocols for low-permeability soils.

- 3. Soil Gas Sample Collection using Sorbents for Method TO-17:** Soil gas sampling for analysis by Method TO-17 is described in Appendix E and F. Low permeability materials may result in a lower flow rate. Use of vacuum gage is recommended between the sorbent and extraction device. Permeability testing of soil is recommended to determine the optimal flow rate at a vacuum of less than 100-inches of water (McAlary et al, 2009). TO-17 is currently recommended only for naphthalene analysis; however, TO-17 may also be used for other volatile constituents depending on the DQOs for the project. The regulatory agency should be notified and concurrence is required prior to implementation of sorbent/TO-17 for other volatile constituents other than naphthalene.

3.0 Field Conditions

Field conditions, such as rainfall, irrigation, fine-grained sediments, or drilling conditions may affect the ability to collect soil gas samples.

- 1. Rainfall and Barometric Pressure (see Appendix G):** Rainfall decreases the air-filled porosity of the shallow soil, thereby limiting diffusion transport of volatile contaminants and potentially biasing soil gas sampling results. Hence, do not conduct soil gas sampling during or within five days of a significant rain event (1/2 inch or greater). Stop irrigation or watering of soil at least five days prior to the soil gas sampling event. Likewise, areas subject to soil gas sampling should be free of standing or ponded water for at least five days prior to sampling. Do not perform soil gas sampling in swales or depressions where large volumes of water can potentially accumulate.

Barometric pressure fluctuations associated with the passage of frontal systems can introduce atmospheric air into the shallow vadose zone. Therefore, soil gas sampling should be delayed until frontal systems have passed the area. Alternatively, soil gas sampling times and depths may be chosen to minimize the effects of changes in barometric pressure.

- 2. Wet Conditions:** If no-flow or low-flow conditions are caused by wet soils due to a rain event or irrigation or water is drawn into a probe, cease the soil gas sampling. Low or no-flow condition corresponds to cases where the minimum flow rate of 100 mL/min cannot be sustained at the maximum applied vacuum of 100 inches of water (McAlary et al., 2009). If the low-flow condition is due to wet conditions or shallow groundwater, then passive samplers may be deployed to detect VOCs.

- 3. Fine Grained Soil:** If low-flow or no-flow conditions are caused by fine-grained soil, clay, soil with vacuum readings that exceed approximately 136 inches of water or 10 inches of mercury are encountered at a sampling point, a new vapor well should be installed in a coarser lithology at a different depth or lateral location. The following should be considered if low flow conditions persist:
- evaluate site lithologic logs
 - collect new continuous soil core samples
 - use alternate low flow sampling methods (see Appendix D)
 - re-evaluate the need for the sampling location
 - use passive soil gas methods as described in Appendix A
 - collect and evaluate soil matrix VOCs sample using 5035/8260 (Cal/EPA, 2004)
4. If moisture or unknown material is observed in the glass bulb or syringe, cease soil gas sampling until the cause of the problem is determined and corrected.
5. If refusal occurs during drilling, soil gas samples should be collected as follows:
- A. For sample depths less than five feet, collect a soil gas sample following the precautions for shallow soil gas sampling (i.e., Section 2.3, Sample Depth & Sub-Slab Investigation Methods; Section 2.5, Purge Volume Test; and Section 2.6, Purge/Sample Flow Rate and Applied Vacuum).
 - B. For sample depths greater than five feet, collect a soil gas sample at the depth of refusal.
 - C. Install a replacement vapor well at least five (5) feet laterally from the original vapor well decommissioned due to refusal. If refusal still occurs after three tries, use alternate vapor well installation methods.

3.1 Chain of Custody Records

A chain-of-custody form should be completed reconstructing how and under what circumstances samples were collected, and include any problems encountered during sample collection. U.S. EPA provides a complete description of chain-of-custody and records management (USEPA, 1998, 1998a). The chain-of-custody procedure is intended to prevent misidentification of the samples, tampering with the samples during shipping and storage, allow easy identification of any tampering, and allow for easy tracking of sample possession. Samples should always be stored in a secure area. To avoid water damage of the chain-of-

custody forms during transport, the forms should be placed into a water-tight sealable bag and placed on top of the sample container.

3.2 Analysis of Soil Gas Samples

Details concerning the analytical methods, quality assurance/quality control (QA/QC), reporting, and laboratory certification are described in Appendix F and H.

Target Compounds:

Target compounds are commonly-found VOCs which should be considered during initial site investigation.

Organic Common Target Compound List

Halogenated

1. Bromochloromethane
2. Bromodichloromethane
3. Bromomethane
4. Carbon tetrachloride
5. Chloroethane
6. Chloroform
7. 1,1-Dichloroethane
8. 1,2-Dichloroethane
9. 1,1-Dichloroethylene
10. cis-1,2-Dichloroethylene
11. trans-1,2-Dichloroethylene
12. Dichlorodifluoromethane (Freon 12)
13. Dichloromethane(methylene chloride)
14. Tetrachloroethylene (PCE)
15. 1,1,1,2-Tetrachloroethane
16. 1,1,2,2-Tetrachloroethane
17. 1,1,1-Trichloroethane
18. 1,1,2-Trichloroethane
19. Trichloroethylene (TCE)
20. Trichlorofluoromethane (Freon 11)
21. 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
22. Vinyl chloride

Aromatics and Oxygenates

23. Benzene
24. n-Butylbenzene
25. sec-Butylbenzene
26. tert-Butylbenzene
27. 1,4-Dichlorobenzene
28. Di-isopropyl ether (DIPE)
29. Ethylbenzene
30. Ethyl tertiary butyl ether (ETBE)
31. Isopropylbenzene
32. p-Isopropyltoluene
33. Methyl tertiary butyl ether (MTBE)
34. Naphthalene
35. n-Propylbenzene
36. Tertiary amyl methyl ether (TAME)
37. Tertiary butyl alcohol (TBA)
38. Toluene
39. 1,2,4-Trichlorobenzene
40. 1,2,4-Trimehtylbenzene
41. 1,3,5-Trimethylbenzene
42. Xylenes

Others

43. Acetone
44. Carbon disulfide
45. 2-Hexanone
46. Styrene
47. Methyl ethyl ketone
48. Methyl isobutyl ketone
49. Ethylene dibromide

Include or exclude additional analytes based on site history and DQOs. A vapor-intrusion specific list can be found in the Vapor Intrusion Guidance (Cal/EPA 2005a).

3.3 Reporting Limits for Target Compounds

Consideration and determination of appropriate reporting limits (RLs) should be based on the DQOs of the investigation.

1. During the workplan development, the target concentrations should be identified for the site specific compounds of potential concern and select appropriate analytical methods to achieve the RLs at or below the target levels. The RLs for the tracer compound and analytes should be adjusted accordingly. If the soil gas data are to be used to support risk assessment

activities, a RL that is health protective is appropriate for the initial screening when evaluating all targeted VOCs.

2. For results with a high RL due to dilution, the laboratory should provide a written explanation. Re-sampling and analyses may be required at the appropriate RL for specific compounds. A higher RL as a result of sample dilution is acceptable only for the compound(s) whose concentration in an undiluted sample exceeds the upper level of an initial calibration range. Non-detected (ND) results for all target compounds shall be reported at the lowest dilution(s) or no dilution.

3.4 Quality Assurance/Quality Control (QA/QC)

The analytical laboratory should comply with the project Quality Assurance Project Plan (QAPP), EPA Methods, and the criteria included in this Advisory. The analytical data should be consistent with the DQOs established for the project. Refer Appendix F for recommendations on analytical requirements.

The regulating agency staff may inspect the field and/or laboratory QA/QC procedures. Copies of the QA/QC plan and laboratory calibration data should be presented to the regulating agency field staff upon request.

Document all calibration and QA/QC standards which should be traceable to a source. Continuing calibration and QC standards, such as matrix spikes, should be from a second source or a different lot from the same supplier. Vapor phase standards are preferred.

At a minimum, the following criteria should be included in EPA Methods:

- initial calibration
- daily calibration/continuing calibration
- laboratory control spike
- internal standards
- surrogates
- method blank
- field blank

All surrogate recovery data should comply with the laboratory derived control limits. For data evaluation purposes, surrogate recovery limits should be ± 25 percent. Recovery levels are dependent on sample introduction technique and are compound specific. If this limit is not selected, provide an explanation justifying the limit used. See Appendix F for surrogate introduction techniques.

Field QC samples should be collected, stored, transported and analyzed in a manner consistent with site samples. The following QC samples should be

collected to support the sampling activity:

1. **Sample Blanks:**

- A. **Method Blanks:** Method blanks should be used to verify the effectiveness of decontamination procedures and to detect any possible interference from ambient air.
- B. **Trip Blanks for Off-site Shipments:** Trip Blanks are not necessary for SUMMA[®] canister samples.
- C. **Soil Vapor well materials:** An assembled soil gas probe, tip and tubing should be blank tested prior to installation at a frequency of 1 installation per new batch of tubing used.
- D. **Equipment Blanks:** Equipment blanks should be collected from decontaminated equipment before reuse at a frequency specified in the workplan. At a minimum, one equipment blank should be run per 20 sample containers cleaned, or at least one per day.

2. **Duplicate or Replicate Samples:** Two samples must be collected simultaneously for duplicate samples. Samples collected sequentially are replicate samples. At least one (1) duplicate or replicate sample should be collected and analyzed per 20 samples or per batch, whichever is more often. Duplicate (or replicate) samples should be collected from contaminated areas at a frequency depending on the project DQOs. The frequency of duplicates (or replicate) per laboratory per day used by the mobile laboratory should be specified. There are other types of replicate samples, which may be valuable: (1) spatial replicate (i.e., sample collected at a similar depth a few feet from the investigative sample), and (2) temporal replicates (i.e., sample collected at the end of field activities from same depth and locations as the first sample).

- A. Duplicate (or replicate) samples should be collected in separate sample containers, at the same location and depth.
- B. Replicate samples can be collected immediately after the original sample or a duplicate sample can be collected simultaneously by use of a splitter (T) at the point of collection to divide the sample stream into two separate sample containers.

3. **Laboratory Control Samples and Dilution Procedure Duplicates:**

Laboratory Control Samples (LCS) should be done in accordance with the discussion provided in Appendix F.

4. **Split Samples:** The regulating agency staff may request that split samples be collected and analyzed by a separate laboratory.

3.5 Laboratory Certification:

The California Department of Health Services, Environmental Laboratory Accreditation Program (ELAP) currently requires certification for soil gas analytical laboratories. Laboratories utilizing EPA Methods 8260B, 8021B, 8015B, TO-15 and TO-17 for analyses of soil gas samples should obtain ELAP certifications for such EPA analytical methods accordingly. The regulating agencies or DTSC's Environmental Chemistry Laboratory (ECL) staff may inspect the laboratory. Further recommendations concerning laboratory certification are provided in Appendix F.

3.6 Holding Time:

All soil gas samples, with the exception of hydrogen sulfide samples, should be analyzed within 5 minutes of sample collection by an on-site mobile laboratory. Hydrogen sulfide samples should be analyzed as specified in Section 3.9 (2.B). Under the following conditions, holding times may be extended and analyses performed off-site:

1. Soil gas samples collected in glass bulbs with surrogates added within 15 minutes of collection may be analyzed within 6 hours after collection;
2. Soil gas samples collected in glass-lined or silicon coated SUMMA[®] canisters may be analyzed within 14 days from collection (see Appendix B); and
3. Methane samples may be analyzed as specified in Section 3.9.

3.7 Analytical Methods:

There are no approved U.S. Environmental Protection Agency (USEPA) methods specifically designed to analyze VOCs in soil gas samples. Consequently, modified versions of existing EPA methods were adopted to analyze VOCs in soil gas samples.

There are numerous modifications of EPA methods being used for VOC analysis in soil gas in California. Each modification has its advantages and disadvantages. For general purposes, Table 1 below summarizes the preferred EPA methods and their modifications for soil gas analysis. These modifications are preferred because they provide the most reliable and defensible data based on generally accepted DQOs.

Soil gas analysis for VOCs should be performed in accordance with the protocols noted in the respective USEPA method(s) concomitantly with the specific requirements for soil gas samples outlined in Table 1. Parameters not listed should be followed as stated in the original USEPA method.

For a more detailed discussion on the various types of modifications and other applications, consult Appendix F.

Table 1: Preferred Analytical Methods and Modifications*

Method/ Parameter	GC/MS Methods			GC Methods		COMMENTS
	Modified USEPA 8260	Modified USEPA TO- 15	Modified USEPA TO-17	Modified USEPA 8015	Modified USEPA 8021	
Applicability/Analytes	Most VOCs; <i>confirmation sampling for Naphthalene should be performed by USEPA TO-17.</i>	Most VOCs; <i>confirmation sampling for Naphthalene should be performed by USEPA TO-17.</i>	Most VOCs where approximate concentrations are predetermined by another method.	Limited number of VOCs; gasoline/TPH	Most VOCs; <i>confirmation sampling for Naphthalene should be performed by USEPA TO-17</i>	See Appendix F of this guidance for discussion.
Sample Introduction Technique	Modified Purge-and-trap (USEPA 5030)	Samples collected in passivated canisters; VOCs are concentrated on sorbent trap	Samples pulled through sorbent pack; thermally desorbed into GC.	Modified Purge-and-trap (USEPA 5030)	Modified Purge-and-trap (USEPA 5030)	See Appendix F of this guidance for discussion.
Sample Size	Purge-and-trap: 5 to 250 mL (cc) (See Appendix F for discussion)	To be determined by sample delivery technique and sample concentration.	To be determined by a combination of factors: sorbent selected, tube length, humidity, temperature; typically 1 to 4 liters. "Safe Sample Volume"	Purge-and-trap: 5 to 250 mL (cc) (See Appendix F for discussion)	Purge-and-trap: 5 to 250 mL (cc) (See Appendix F for discussion)	See Appendix F of this guidance for discussion. Dilution may be needed if high level sample is suspected.
Method Validation ⁽¹⁾	As per Section 8.4 of USEPA 8000B	As per Section 8.4 of USEPA 8000B	As per Section 8.4 of USEPA 8000B	As per Section 8.4 of USEPA 8000B	As per Section 8.4 of USEPA 8000B	
Initial Calibration	Minimum of 5 levels, lowest at Reporting level. Use method acceptance criteria.	Minimum of 5 levels, lowest at Reporting level. Use method acceptance criteria.	Minimum of 5 levels, lowest at Reporting level. Use method acceptance criteria. Preloaded certified standard tubes may be used for calibration.	Minimum of 5 levels, lowest at Reporting level. Use method acceptance criteria.	Minimum of 5 levels, lowest at Reporting level. Use method acceptance criteria.	Vapor-phase standards are preferred. Liquid standards may be used for USEPA Methods 8260, 8015, 8021 and TO-17 provided calibration curve is

Method/ Parameter	GC/MS Methods			GC Methods		COMMENTS
	Modified USEPA 8260	Modified USEPA TO- 15	Modified USEPA TO-17	Modified USEPA 8015	Modified USEPA 8021	
						validated. See Appendix F of this guidance.
Continuing Calibration	Mid-level calibration standard run every 12 hours. Use method acceptance criteria.	Mid-level calibration standard run every 12 hours. Use method acceptance criteria.	Mid-level calibration standard every 10 sample batch (Section 12 of USEPA TO-17)	Mid-level calibration standard run every 12 hours. Use method acceptance criteria.	Mid-level calibration standard run every 12 hours. Use method acceptance criteria.	
Calibration Validation	At minimum, vapor-phase validation check standard ⁽²⁾ analyzed and evaluated for each new calibration curve (% Difference ≤ 20%).	Not Applicable.	No vapor-phase standard validation needed for liquid standards.	At minimum, vapor-phase validation check standard ⁽²⁾ analyzed and evaluated for each new calibration curve (% Difference ≤ 20%).	At minimum, vapor-phase validation check standard ⁽²⁾ analyzed and evaluated for each new calibration curve (% Difference ≤ 20%).	Validation not needed if calibration curve is prepared with vapor-phase standards.
End of Run Calibration Check	Mid-level calibration standard run for each 20 sample batch or at end of run, whichever is more often.	Mid-level calibration standard run for each 20 sample batch or at end of run, whichever is more often.	Mid-level calibration standard run for each 20 sample batch or at end of run, whichever is more often.	Mid-level calibration standard run for each 20 sample batch or at end of run, whichever is more often.	Mid-level calibration standard run for each 20 sample batch or at end of run, whichever is more often.	
Surrogates	As per Section 5.9 of USEPA 8260.	Optional.	Optional.	To be determined by lab. ⁽³⁾	As per Section 5.10 of USEPA 8021.	Recovery acceptance limits to be determined by lab. Default=70-130%.
Internal Standards	As per Section 5.10 of USEPA 8260.	As per Section 9.2.2.3 of USEPA TO-15.	As per Sections 6.12.2 and 9.4 of USEPA TO-17.	To be determined by lab. ⁽³⁾	As per Section 5.9 of USEPA 8021.	
Accuracy/Precision Matrix Spike/Matrix Spike Duplicate	See Appendix F of this guidance.	Optional	Optional	See Appendix F of this guidance.	See Appendix F of this guidance.	See Appendix F of this guidance for discussion. Recovery acceptance limits to be determined by lab. Default=70-130%. %RPD=25%.

Method/ Parameter	GC/MS Methods			GC Methods		COMMENTS
	Modified USEPA 8260	Modified USEPA TO- 15	Modified USEPA TO-17	Modified USEPA 8015	Modified USEPA 8021	
Duplicates	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	See Appendix F of this guidance for discussion. %RPD=25%.
Replicates	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	One per 20 samples or batch, whichever is more often.	See Appendix F of this guidance for discussion. %RPD=25%.
Laboratory Control Samples (LCS)	Optional	Not Required	Not Required.	Optional	Optional	See Appendix F of this guidance for discussion.
Method Detection Limit/Reporting Limit	See Appendix F of this guidance.	See Appendix F of this guidance.	See Appendix F of this guidance.	See Appendix F of this guidance.	See Appendix F of this guidance.	See Appendix F of this guidance for discussion.
Reporting Limit Verification	One per batch of samples. ⁽⁴⁾	One per batch of samples. ⁽⁴⁾	One per batch of samples. ⁽⁴⁾	One per batch of samples. ⁽⁴⁾	One per batch of samples. ⁽⁴⁾	See Appendix F of this guidance for discussion.
Method Blanks	Method blank using <i>humidified lab grade ultra pure air</i> as sample and per Section 8.4.1 of USEPA 8260.	As per Section 10.7 of USEPA TO-15.	As per Section 10.7.1 of USEPA TO-17.	Method blank using <i>humidified lab grade ultra pure air</i> as sample and per Section 9.5 of USEPA 8015C.	Method blank using <i>humidified lab grade ultra pure air</i> as sample and per Section 8.4 of USEPA 8021.	
Container Blank	One sample container per 20 samples or per batch, whichever is more often.	One sample container per 20 samples or per batch, whichever is more often.	One sorbent tube blank per 20 samples or per batch, whichever is more often.	One sample container per 20 samples or per batch, whichever is more often.	One sample container per 20 samples or per batch, whichever is more often.	Monitor other components (i.e., fittings/valves) of sampling system if needed.
Holding Time	Analyze ASAP. Samples collected in passivated canisters can be held up to 14 days. Tedlar® bag use is discouraged.	Analyze ASAP. Up to 14 days for samples in passivated canisters. Tedlar® bag use is discouraged.	Analyze ASAP. Up to 30 days refrigerated. Exceptions as noted in Section 10.10 of USEPA TO-17.	Analyze ASAP. Samples collected in passivated canisters can be held up to 14 days. Tedlar® bag use is discouraged.	Analyze ASAP. Samples collected in passivated canisters can be held up to 14 days. Tedlar® bag use is discouraged.	

Method/ Parameter	GC/MS Methods			GC Methods		COMMENTS
	Modified USEPA 8260	Modified USEPA TO- 15	Modified USEPA TO-17	Modified USEPA 8015	Modified USEPA 8021	
Other Requirements	Tuning: 50 ng Bromofluorobenzene (BFB) initially and every 12 hours. Meet acceptance criteria as per Table 4 of USEPA 8260.	1. Tuning: 50 ng BFB initially and every 24 hours. Meet acceptance criteria as per Table 3 of USEPA TO-15. 2. Must meet equipment specifications in Section 7.2 of USEPA TO-15 to report results as modified TO-15.	1. Analytical protocol as per USEPA TO-15. 2. Condition freshly packed (new) sorbent tubes. 3. Collect and analyze "Distributed Volume Pairs" for uncharacterized sites. 4. Determine/validate "Safe Sampling Volume" (SSV) if needed as per Sections 10.8 and 13.1.2 of USEPA TO-17; analyze as per USEPA TO-15 and Section 11.2 of USEPA TO-17. 5. Analytical precision test as per Section 11.3.2.2 of USEPA TO-17. 6. Performance criteria as per Section 14 of USEPA TO-17.	Use only for routine monitoring at well-characterized sites. Other than TPH,, identification of new compounds must be confirmed either by second column or different detector, and then 10% of those samples must be confirmed with a GC/MS method.	Use only for routine monitoring at well-characterized sites. Identification of new compounds must be confirmed either by second column or different detector, and then 10% of those samples must be confirmed with a GC/MS method.	

* Adapted from "Guide to Environmental Analytical Methods" 5th Edition, Edited by Roy-Keith Smith, Ph.D., Genium Publishing Corp., 2003.

(1) Initial, one-time, demonstration of ability to generate acceptable accuracy and precision. Procedure may need to be repeated if changes in instrument, methodology or personnel occur. USEPA Method 8000B (Determinative Chromatographic Separations), Revision 2, December 1996 (SW-846 Manual).

(2) Mid-level NIST (National Institute of Standard and Technology) traceable (where available or equivalent) vapor-phase standard.

(3) No internal standards and surrogates were suggested by the method. The compounds are to be selected by the analyst (lab) and they must be similar in analytical behavior to the compounds of interest. The analyst needs to demonstrate the internal standards are not affected by method or matrix interferences.

(4) There is no limit on the number of samples per batch for Reporting Limit Verification. Once per day is sufficient

3.8 Soil Gas Sample Analysis:

1. **VOC Samples:** All VOC samples should be analyzed using only a Gas Chromatograph/Mass Spectrometer (GC/MS) method (e.g., EPA Method 8260B, used for analysis of soil gas samples, EPA Method TO-15, TO-17 or equivalent), except at well-characterized sites (e.g., VOCs are known to be present and confirmed based on previous GC/MS analyses). A non-GC/MS method (e.g., EPA Method 8021B, used for analysis of soil gas samples) may be used only for routine monitoring of VOC contamination at well-characterized sites. Sample introduction methods (i.e., TO-15, TO-17, TO-13A, and modified GC methods such as EPA Methods 8015 and 8021) and their advantages and disadvantages are further discussed in Appendix F. Detailed discussion is provided in Appendix E for specifics concerning soil gas containing naphthalene.

If during routine monitoring, new VOC(s) were detected by a non-GC/MS method, then at least 10 percent of the samples with each newly identified VOCs should be confirmed by a GC/MS method. Thereafter, routine monitoring can resume with the non-GC/MS method, including the new analyte(s).

2. **VOCs:** Identify all quantifiable VOCs and report all results

Include the estimated results of all Tentatively Identified Compounds [TICs] detected in the report. If TICs are identified, contact the regulating agency to determine whether additional action is required (e.g., running additional standards to quantify TICs) and whether the use of these estimated data for risk evaluation is appropriate.

3. **Leak Check Compounds:** All results should be reported as specified in Section 2.4
4. **Specific Compounds:** Based on the site history and conditions, analyses for specific compounds may be required by the regulating agency staff.

Examples include:

- A. In areas where USTs or fuel pipelines are identified, soil gas samples should be analyzed for oxygenated compounds [e.g., methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), di-isopropyl ether (DIPE), tertiary amyl methyl ether (TAME), tertiary butyl alcohol (TBA), and ethanol];
- B. At oilfield sites where semi-VOCs or total petroleum hydrocarbons (TPHs)

are detected in the soil gas samples, fixed and biogenic gas (oxygen, carbon dioxide, and methane) data should be obtained using a Thermal-Conductivity Detector (TCD) or a hand-held instrument;

- C. At petroleum contaminated sites (including oilfields), concentrated animal facilities and operations, wetlands, landfills or other sites where the presence of methane and/or hydrogen sulfide is suspected, soil gas samples should be analyzed for methane and/or hydrogen sulfide;
 - D. At sites where use of chlorinated solvents with 1,4-dioxane is suspected or known to exist, soil gas samples should be analyzed for 1,4-dioxane at a reporting limit which is health protective.
5. **Auto samplers:** Auto samplers for Method 5030/8260B are not recommended; and therefore, this technique should not be used because transfer of sample from a soil gas collection vessel such as syringes to another secondary container (e.g., VOA-vials) may result in sample loss (See Appendix F). Furthermore, auto samplers are not capable of handling variable volumes of soil gas sample, especially larger sample volumes, to adjust for the desired RLs for the site-specific compounds of potential concern.

3.9 Methane and Hydrogen Sulfide Sampling Programs:

If the presence of methane and/or hydrogen sulfide is suspected, they should also be included in the analytical plan.

1. **Methane Sampling Program:** Methane samples may be analyzed by a GC using modified EPA Method 8015B, EPA Method TO-3, EPA 3C, or by Land Tech Gas Analyzer GA-90, Gas Emissions Monitor GEM-500, GEM-2000 or other appropriate hand-held instruments.
 - A. **Reporting Limit:** The RL for methane analysis should not exceed 500 parts per million by volume (ppmv).
 - B. **Methane Sample Containers:** In addition to the gas-tight sample containers previously specified in Section 2.7, Tedlar[®] bags may be used for collection of methane samples with a holding time of no more than 24 hours.
 - C. **Methane Screening Level:** When methane is detected at 1,000 ppmv or more, additional sampling and/or further investigation is recommended to identify the source(s).
 - D. **Fixed and Biogenic Gases:** At sites where methane is investigated and

detected at a level of 5,000 ppmv or more, obtain fixed and biogenic gas (e.g., oxygen, carbon dioxide, methane, and ethylene) data by using a Thermal-Conductivity Detector (TCD) or a hand-held instrument. The RL for oxygen and carbon dioxide should be one percent or less.

- E. **Pressure Reading:** Record pressure readings of each sampling tube system in the field logs and report along with the methane concentration to determine if the area is pressurized
 - F. **Special GC Requirements:** The GC method requires calibration curves for analytes such as methane since it is not a normal target analyte for such an analytical method.
 - G. **Special Hand-Held Instruments Requirements:** Hand-held instruments should be calibrated in accordance with the manufacture's instructions. When a hand-held instrument is used to analyze methane samples, confirm at least 10 percent of all positive methane samples (e.g., more than 5,000 ppmv), rounded to the nearest whole number, by another hand-held instrument (different unit or brand) or by a GC method.
2. **Hydrogen Sulfide Sampling Program:** Hydrogen sulfide may be analyzed by a GC using the South Coast Air Quality Management District (SCAQMD) Method 307-91 or EPA Method 16, or by an appropriate hand-held instrument (e.g., LTX-310 calibrated for hydrogen sulfide, Jerome 631-X or Drager™ tubes).
- A. **Reporting Limit:** The RL should be equal to or less than 0.5 ppmv or be sensitive enough to allow for a modeled ambient air concentration (at least one microgram per cubic meter) at the soil surface.
 - B. **Holding Time:** Hydrogen sulfide samples should be extracted directly into a hand-held analyzer within 30 minutes of collection to minimize the risk of losing the hydrogen sulfide due to reaction with active surfaces. If a hand-held instrument is not used, hydrogen sulfide samples should be analyzed as below:
 - a. Within 30 minutes of collection, using the GC procedures; or
 - b. Within 24 hours of collection, if a surrogate is added to the samples or 100 percent duplicate samples are collected.
 - C. **Sample Containers:** The following sample containers are recommended for hydrogen sulfide:
 - a. Minimum one (1) liter black Tedlar® bag fitted with polypropylene

valves or the equivalent;

- b. 100-mL gas-tight syringe fitted with an inert valve and wrapped in aluminum foil;
- c. Gas-tight glass bulb wrapped in aluminum foil; or
- d. Glass-lined or silicon coated SUMMA[®] canister.

D. Precautions

- a. Hydrogen sulfide is extremely unstable in the presence of oxygen and moisture; therefore, avoid contact of hydrogen sulfide samples with oxygen and moisture.
- b. Due to the high reactivity of hydrogen sulfide gas, avoid contact of hydrogen sulfide samples with metallic or other non-passive surfaces during sample collection, storage, and analysis.
- c. Care must be taken so that GC components do not react with the sample. Typically glass-lined injection ports and Teflon[®] tube packed columns are used to avoid loss of hydrogen sulfide due to reaction with active surfaces.

4.0 Analytical Result Reporting:

Consult Appendix H for reporting format and parameters.

4.1 REFERENCES:

Abreu, L.D.V., P.C. Johnson. 2005. "Effect of Vapor Source – Building Separation and Building Construction on Soil Vapor Intrusion as Studied with a Three-Dimensional Numerical Model", Environmental Science and Technology, v. 39, no. 12, p. 4550-4561.

Abreu, L., P.C. Johnson, T. McAlary. 2006. "3D Model Simulations and Implications to Near Building Sampling", AEHS Vapor Intrusion Work Shop, San Diego, March 16, 2006.

ASTM, 1993: American Society for Testing and Materials, "Standard Guide for Soil Gas Monitoring in the Vadose Zone, ASTM Standard D 5314-92," January 1993; Reapproved 2001; website <http://www.astm.org>

API, 2005: American Petroleum Institute, "Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Site", Publication #4741. Washington, D.C.: API.

Cal/EPA, 1999: California Environmental Protection Agency, Department of Toxic Substance Control, Preliminary Endangerment Assessment Guidance Manual, January 1994 (Second Printing, June 1999).

Cal/EPA, 2003: California Environmental Protection Agency, Advisory – Active Soil Gas Investigations, Department of Toxic Substances Control & California Regional Water Quality Control Board, Los Angeles Region.
http://www.dtsc.ca.gov/LawsRegsPolicies/Policies/SiteCleanup/upload/SMBR_A DV_activesoilgasinvst.pdf

Cal/EPA, 2004: California Environmental Protection Agency, Department of Toxic Substances Control (DTSC), "Guidance Document for the Implementation of United States Environmental Protection Agency Method 5035: Methodologies for Collection, Preservation, Storage, and Preparation of Soils to be Analyzed for Volatile Organic Compounds", November 2004.
http://www.dtsc.ca.gov/SiteCleanup/upload/HWMP_Guidance_Method-5035.pdf

Cal/EPA, 2005: California Environmental Protection Agency, Department of Toxic Substance Control, State of California Vapor Intrusion Guidance Document – Final Interim. Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air, Interim Final, December 15, 2004 (Revised February 7, 2005), and references therein.

CRWQCB, 1997: California Regional Water Quality Control Board, Los Angeles Region, "Interim Guidance for Active Soil Gas Investigation," February 25, 1997

CRWQCB, 2000: California Regional Water Quality Control Board, Los Angeles Region, "General Laboratory Testing Requirements for Petroleum Hydrocarbon Impacted Sites," June 22, 2000

DiGiulio, D.; R. Cody. 2006. "Evaluation of the "Unconstrained Version" of the J&E Model and Comparison of Soil-Gas and Sub-Slab Air Concentrations at the Raymark Superfund Site", AEHS Vapor Intrusion Work Shop, San Diego, March 16, 2006.

Hers, I., H. Dawson, R. Truesdale. 2006. "Testing Exterior Tier 3 Screening with Site Data", AEHS Vapor Intrusion Work Shop, San Diego, March 16, 2006.

ITRC, 2007: ITRC (Interstate Technology & Regulatory Council), "Vapor Intrusion Pathway: A Practical Guideline, VI-1, Washington D.C.: Interstate Technology & Regulatory Council, Vapor Intrusion Team. www.itrcweb.org ; Appendix D, Section D.4.7, Leak Tests; January, 2007

Johnson, P.C., R.A. Ettinger. 1991. "Heuristic Model for Predicting the Intrusion of Contaminant Vapors into Buildings", Environmental Science and Technology, v. 25, n. 8, p. 1445 – 1452.

McAlary, T.A. P. Nicholson, H. Groenevelt, D. Bertrand, 2009. "A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low Permeability) Soils", Ground Water Monitoring & Remediation, 29, No. 1, p 144-152.

Nicholson, P. D. Bertrand. T. McAlary, 2007. "Soil Gas Sampling in Low-Permeability Soils"; Vapor Intrusion: Learning from the Challenges, Air & Waste Management Association's Proceedings, pp 299, September, 2007, Providence, RI

USEPA, 1988: United States Environmental Protection Agency, "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA, Interim Final", Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, October 1988; EPA/540/G-89/004.

USEPA, 1989: United States Environmental Protection Agency, Risk Assessment "Guidance for Superfund, Volume I, Human Health Evaluation Manual (Part A), Interim Final", Office of Emergency and Remedial Response, December 1989; EPA/540/1-89/00

USEPA, 1994a: United States Environmental Protection Agency, "Guidance for the Data Quality Objective Process II (EPA QA/G-4), Office of Research and Development. Document No. EPA/600R-96/055", September 1994.

USEPA, 1994b: United States Environmental Protection Agency, "U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data

Review, EPA 540/R-94/012,” February 1994; website
<http://www.epa.gov/region09/qa/superfundclp.html>

USEPA, 1994c: United States Environmental Protection Agency, “SUMMA[®] Canister Cleaning Procedures, SOP #1703, Rev. #: 0.0,” 09/01/94; website
http://www.ert.org/respns_resrcs/sops.asp

USEPA, 1996: United States Environmental Protection Agency. “Soil Gas Sampling, SOP#: 2042, Revision #: 0.0,” June 1, 1996; website
http://www.ert.org/respns_resrcs/sops.asp

USEPA, 1998: United States Environmental Protection Agency. “*Test Methods for Evaluating Solid Waste, SW 846*”, Office of Solid Waste and Emergency Response., November 1986, (Update III Revision 5, dated September, 1998).

USEPA, 1998a: United States Environmental Protection Agency. “Guidance for Quality Assurance Project Plans (QA/G-5), EPA/600/R-98/018”, Office of Research and Development, February 1998.

USEPA, 1999: United States Environmental Protection Agency. “Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes; Compendium Method TO-17. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition”. Center for Environmental Research Information, Office of Research and Development; Cincinnati, Ohio. January 1999.
[<http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf>]

USEPA, 2000a: United States Environmental Protection Agency, “Data Quality Objectives Process for Hazardous Waste Site Investigations, EPA/600/R-00/007”, January 2000 and references therein; website
<http://www.epa.gov/QUALITY/qs-docs/g4hw-final.pdf>

USEPA, 2000b: United States Environmental Protection Agency, “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW-846, Third Edition,” November 1986, as amended by Updates I (Jul. 1992), II (Sep. 1994), IIA (August 1993), IIB (Jan. 1995), III (Dec. 1996), IIIA (Apr. 1998), IVA (Jan. 1998) and IVB (Nov. 2000); website <http://www.epa.gov/SW-846/main.html>

USEPA, 2003: United States Environmental Protection Agency. Analysis of Volatile Organic Compound (VOCs) in Air Collected in Specially Prepared Canisters or Tedlar[®] Bags. U.S EPA Region 9 Laboratory, Richmond, California. Standard Operating Procedure # 310.
<http://www.prescott.edu/users/jherring/downloads/JATAP%20QAPP%20Files/Appendix%20M1%20EPA%20R9%20SOP%20310.pdf>

Figures – Soil Gas Vapor Well Emplacement Methods

Figure 1 – Permanent/Semi-permanent Gas Vapor well Construction Diagram

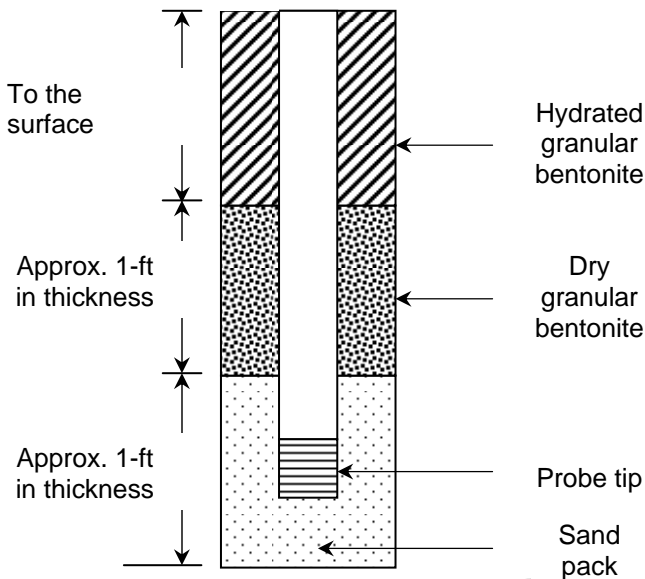


Figure 2 – Multi-depth Gas Vapor well Construction Diagram

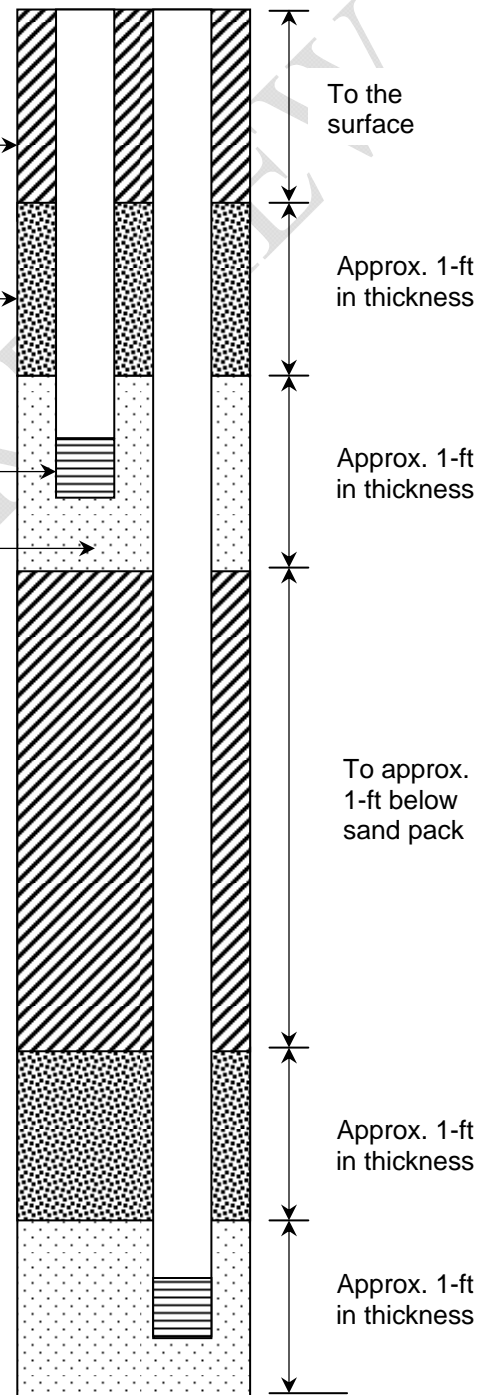
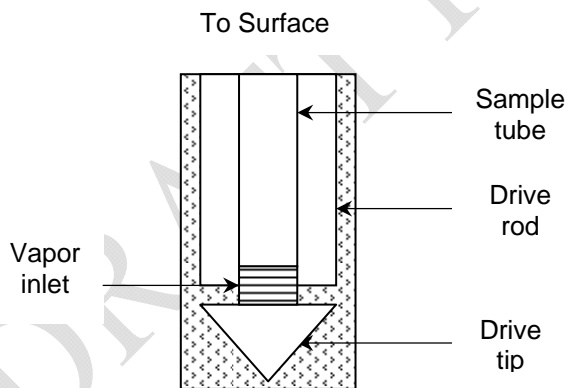


Figure 3- Temporary Gas



APPENDIX A

PASSIVE SOIL GAS METHOD

Both passive and active soil gas sampling and analyses may need to be performed to provide multiple lines of evidence to evaluate vapor intrusion exposure to organic vapors. Passive soil gas sampling is a qualitative method, which consists of the burial of an adsorbent material into the subsurface soil with subsequent retrieval and measurement of organic vapors passively amassed onto the absorbent material. Unlike active soil gas sampling, which consists of the physical withdrawal of the soil gas from the subsurface, with passive sampling, there is no forced movement of soil gas into the sampling vessel. Instead, as the vapors migrate, the sorbent acts as a sink for the volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) found in soil gas.

Passive soil gas methods measure a mass (e.g. micrograms) of contaminant that has diffused onto an adsorbent media. Unlike active soil gas methods which yield concentration data (e.g., ug/m^3 or ug/L) that can directly be compared to risk-based screening levels or used in predictive models, passive soil gas methods do not generate contaminant concentration data. While there are published methods and procedures to generate concentration data from a passive sorbent-based sampler in ambient air, there are no published studies demonstrating the applicability of this method to soil gas. This is because the gas-phase diffusivity in the vadose zone is unknown for the calculation of a concentration from the adsorbed mass. There are a limited number of field studies that attempt to calibrate the mass of contaminant collected by passive method to actual soil gas concentrations and for derivation of a method for this conversion. For this reason, passive soil gas sampling and analysis is presently not considered to be applicable as a stand-alone method for determination of vapor intrusion risk.

Although passive soil gas methods do not provide contaminant concentration data for use in predictive modeling and therefore is considered to be a qualitative tool, this method does have applications in plume characterization and vapor intrusion assessments. Potential uses and advantages of this method are as follows:

- Locate contaminant hot spots for later sampling and plume characterization: Passive soil gas can be a viable, cost-effective and simple screening tool to determine areas of contamination. The location of sources and subsurface plumes can be mapped, particularly edges of plumes to determine whether contamination is near existing or future buildings.
- Locate preferential pathways: Passive methods offer a quick and inexpensive means to find vapor migration pathways into and around buildings and other sub-surface structures such as sewer and utility corridors. Other preferential pathways for migration such as geological features including potential spatial variability in the lithology can be identified by use of the passive sampling technique.

- Evaluate whether a release has transpired: One of the circumstances where passive methods are effective in collecting soil gas samples are in areas with low permeability and high moisture setting (i.e., soil in areas with shallow groundwater due to high water table) where active soil gas samples are more difficult to obtain. When the depth to groundwater is shallow (i.e., within 5 ft bgs), the capillary fringe may prevent sample collection by conventional active methods due to moisture preventing soil gas flow into the probe. Passive soil gas methods can be used to determine whether or not volatile compounds have contaminated the soil of current or historic industrial operations along coastal areas with a high water table or to determine whether or not naphthalene is present in soil gas. Sampling for naphthalene by active methods may be difficult due to absorption or plating of naphthalene onto the tubing and collecting vessels.
- Additional advantages over active soil gas methods:
 1. Passive soil gas methods give a time-integrated measurement, and therefore, reduce the uncertainty due to temporal variations.
 2. Passive soil gas methods are frequently capable of detecting and reporting compounds present at very low levels not detected by active methods.
 3. Simplicity of installation and retrieval: Unlike the active sampling method which involves withdrawal of the soil gas (forced extraction) from the subsurface, there is no forced movement of soil gas into the sampling vessel with passive methods. Therefore, the seal integrity of the vapor probe does not need to be ensured as in the case of the active method.

Provide Additional Line of Evidence for Vapor Intrusion: Attribution of chemicals in indoor air to vapor intrusion can be a complex and difficult task. Therefore, it is important to use multiple lines of evidence to reach decisions based on professional judgment. In this regard, alternative sampling methods, in addition to the active soil gas sampling procedures may be employed especially in certain circumstances as described above. All available data from the multiple lines of evidence collected during the investigation (active and passive) should be used in determining whether vapor intrusion is occurring and whether there are potential public health concerns.

Attempts should be made to collect active soil gas data from specific locations after the presence and composition of subsurface chemical constituents in the vadose zone has been established by the passive method. Active soil gas sample collection from areas with tighter lithology or in areas with shallow groundwater may need to be collected using a vacuum of less than 100-inches of water column at a rate less than or equal to 100 mL/min using canisters to provide a more representative sample (McAlary et al, 2009).

Deployment depths, deployment durations and analytical procedures will depend on the manufacturer's recommended procedures. Some samplers currently available can be installed at any depth, and at the same sampling density as the active method. For typical soil gas sampling installation, a slam bar or electric rotary hammer-drill is used to auger a ¾ to 1-inch diameter hole to depth of three or more feet below grade. For site assessment applications, the suggested exposure time for soil gas sampling is 10 to 14 days. Analytical instrumentation consists of gas chromatographs and mass selective detectors (e.g., EPA Methods TO17/8260/8270 GC/MS), as well as automated thermal desorption units. Sample preparation prior to analysis can be very simple and may involve cutting the tip off the bottom of the sampler and transferring an exposed sorber to a thermal desorption tube. The replicate samples, if collected, are retained for approximately two weeks after initial analysis. When parallel studies were performed comparing active and passive methods, the passive method was able to detect the same VOCs, which were below the limit of detection of the active method and detect additional VOCs or SVOCs not detected by the active method (Environmental Technology Report, 1998a and 1998b). Performance testing results of the more commonly used passive sampler types are described in the following references: (1) Environmental Technology Report, 1998a; (2) Environmental Technology Report, 1998b; and (3) Plantz, G.M., 2007.

References:

Cal/EPA, 2005: California Environmental Protection Agency, Department of Toxic Substance Control, State of California Vapor Intrusion Guidance Document – Final Interim. Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air, Interim Final, Department of Toxic Substances Control, December 15, 2004 (Revised February 7, 2005), Page 10.

CRC, 2008: Chemical Rubber Company, BESURE Passive Soil Gas Sampler in "Field Sampling Methods for Remedial Investigations", CRC Press, New York, Byrnes, M.E. p. 120

Environmental Technology Verification Report, 1998a: Passive Soil Gas Sampling, W.L. Gore & Associates, Inc., GORE-SORBER® Screening Survey; Prepared by Tetra Tech, San Diego, CA; Prepared for U.S. Environmental Protection Agency (EPA) Superfund Innovation Technology Evaluation Program, Contract No. 68-C5-0037; EPA/600/R-98/095, August, 1998. Website: <http://www.epa.gov/ORD/SITE/reports/600r98095/600r98095.pdf>

Environmental Technology Verification Report, 1998b: Soil Gas Sampling Technology Quadrel Services Inc., EMFLUX Soil Gas System; Prepared by Tetra Tech, San Diego, CA; Prepared for U.S. Environmental Protection Agency (EPA) Superfund Innovation Technology Evaluation Program, Contract No. 68-C5-0037; EPA/600/R-98/095, August, 1998. Website: <http://www.epa.gov/ORD/SITE/reports/600r98096/600r98096.pdf>

GORE™ SURVEY Environmental Site Assessment, Focusing Your Remediation Efforts, Soil Gas Sampling – Description of Service, W.L. Gore & Associates, Inc., 100 Chesapeake Blvd, Elkton, MD.; www.gore.com/surveys.

Hodny, J.W., J.E. Whetzel and H.S. Anderson. 2007, Vapor Intrusion Investigations and Passive Sampling; Air & Waste Management Associations Proceedings, Vapor Intrusion: Learning from the Challenges; September, 2007; Page 311-322.

Hodny, J.W., J.E. Whetzel and H.S. Anderson. 2006. Cobb, D. M.; The Use of Passive Samplers in Vapor Intrusion Investigations; AWMA Specialty Conference – Vapor Intrusion, Los Angeles, CA, September 13-15, 2006.

ITRC, 2007: Interstate Technical and Regulatory Council, "Vapor Intrusion Pathway: A Practical Guideline, VI-1, Washington D.C.: Interstate Technology & Regulatory Council, Vapor Intrusion Team, www.itrcweb.org ; Pages 5-6; Appendix D, Pages D-16 to D-17; Appendix E, Pages E-2 and E-3; January, 2007.

McAlary, T.A., P. Nicholson, H. Groenevelt, D. Bertrand. 2009. A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low-Permeability) Soils, Ground Water Monitoring & Remediation, 29, no. 1, Winter 2009, Pages 144-152.

Plantz, G.M. 2007. "Collection of Soil Gas on Adsorbents & Passive Samplers", USEPA Soil Gas Sample Collection & Analysis Workshop, San Diego, CA, March 21-22, 2007, http://iavi.rti.org/attachments/WorkshopsAndConferences/06_Plantz_Adsorbitive_media.pdf

USEPA, 2008: U.S. Environmental Protection Agency, Beacon PSG Sampler in "Brownfields Technology Primer: Vapor Intrusion Consideration for Redevelopment", EPA 542-R-08-001, March 2008, p. 15.

APPENDIX B

CANISTER HOLDING TIME, USE OF TEDLAR[®] BAGS, AND TUBING TYPES

Holding Times for SUMMA[®]s

Soil gas samples collected in SUMMA[®] canisters may be analyzed with 14 days from collection (see Section 3.6).

Justification

The Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, states that storage times of up to 30 days have been demonstrated. The EPA Method TO-15 summary document refers to holding times as technical and contract. The technical holding time is stated as 14 days from collection and 10 days from the receipt at laboratory (USEPA, 1999). It is unclear whether total holding time can be interpreted as 24 days.

Several studies have been conducted to demonstrate stability of VOCs in SUMMA[®] canisters. A study conducted by Sin et al (2001) indicated stability of 143 VOCs up to 4 months assuming consistent environmental conditions. However, eight VOCs showed significant loss beginning at approximately 25 days. The average loss was less than 15 percent during the entire study period of four months. Brymer et al (1996) demonstrated that certain VOCs (mercaptans, dimethyl acetal and bis-[chloromomethyl] ether) are not suitable for collecting samples in a SUMMA[®] canister at lower concentrations. The study indicates that storage pressure and humidity in a canister are also important factors that determine recoveries. Oliver and Pliel (1985) also showed stability of 15 VOCs for 7 and 30 days storage and periods. Of all of these compounds tested, none showed significant loss or gain in concentration during the test period. The study stated that holding period between collection and analysis should be minimized to improve recovery of VOC mixtures. Bontempo (2004) tested 44 VOCs on days 0, 7, 15, and 33 and indicated that analysis by TO-15 at parts per trillion by volume should be performed within 14 days to minimize high or low biased data. Kelly and Holdren (1995) concluded that most volatile organics show sufficient stability during storage in a SUMMA[®] canister. US EPA Region 9 SOP 310 specifies a holding time of 30 days, which is based on studies referenced in Method TO-15 that indicate stable storage of up to 30 days for most VOCs (USEPA, 2003).

Use of Tedlar[®] Bags

While the use of Tedlar[®] bags is discouraged, samples collected using Tedlar[®] bags should be analyzed as soon as possible, and within six hours of sample collection (see Section 2.7).

Justification

USEPA (2003) notes that samples collected in Tedlar[®] bags must be analyzed within 72 hours, otherwise the compounds sampled may escape or become altered. The Method TO-15 summary document refers to holding times for Tedlar[®] bags and outlines the holding times as technical and contract. The technical holding time is stated as 72 hours from collection and 36 hours from the receipt at laboratory (USEPA 2003). Studies conducted by Wang, Raihala, and John (1996) examined the issue of VOC losses. The paper cites numerous studies to quantify sample loss. One study noted a 21 percent loss of toluene within 12 hours, with an additional 4 percent loss during the next 12 hours. Similarly, a 15 percent loss of toluene was noted in the first 12 hours while additional 2.9 percent was lost in next 12 hours. Other VOCs showed similar losses. The study clearly indicated that there were significant losses in the commercial Tedlar[®] bags. The losses are generally shown to be associated with hose valve assemblies supplied with the commercial bags. Commercial Tedlar[®] bags and the hose valves replaced with septa and homemade Tedlar[®] bags with Teflon valves both showed much lower losses than the commercial Tedlar[®] bags.

Use of Tubing Types

Nyloflow[®], polyetheretherketone (PEEK), and Teflon[®] are recommended for use in the soil vapor sampling train. Use of low-density polyethylene (L-D PE) is discouraged due to decreased performance relative to other tubing types in both introduction of background analytes and sample recovery. Reduced recovery of naphthalene has been observed when using Nyloflow[®] tubing with small sample sizes (see Sample Tube, Section 2.3 of main text).

Justification

There is very little information available in the literature regarding the effects on various tubing types on sample quality. Hayes et al (2006) evaluated four different tubing types, Nyloflow[®], PEEK, Teflon[®], and L-D PE for contribution to background (off-gassing of VOCs inherent in the tubing structure) and for reactivity (decreased recovery) using zero-air drawn from a 6 L SUMMA[®] canister.

Some off-gassing of toluene, and to a lesser extent benzene, propylbenzene, and methanol were noted with the Nyloflow[®] tubing, though the reported concentrations were less than typical risk-based screening levels. There was low initial recovery of 1,2,4-trimethylbenzene and naphthalene (22 and 12 percent, respectively). Recovery increased with subsequent aliquots, suggesting that the humidified air deactivated reactive binding sites or they became saturated with the increasing sample size. These data suggest the sample loss of 1,2,4-trimethylbenzene and naphthalene would not likely be significant with a 6 L sample. Nicholson et al (2007) noted low recovery of aromatic and cyclic aliphatic hydrocarbons in a 24-hr absorption study of Nyloflow[®] tubing. PEEK tubing exhibited less background contribution than Nyloflow[®], and overall

VOC recovery was also acceptable. Teflon[®] tubing showed very good performance in terms of both background contribution and sample recovery, even at very low initial VOC concentrations. The only detection of significance for Teflon[®] tubing was the non-target compound 1,1-difluoroethane with an average concentration of 5.0 ppbv (0.0135 µg/L) in 67% of the test run samples. Its presence is likely due to the structure of the tubing itself, as Teflon is a fluorinated ethylene polymer.

L-D PE exhibited the lowest overall performance, displaying very poor recovery for a wide number of target analytes (Hayes, 2006). Recovery decreased with decreasing vapor pressure. Unexpectedly high concentrations of certain heavier hydrocarbons were observed in the samples, contributing to artificially high recoveries for some analytes due to co-elution.

The following table summarizes the results of several studies:

Table E-1: Tubing Type Study Results

Tubing Type	Study		
	Ouellette (2005)	Hayes et al. (2006)	Nicholson et al. (2007)
Polyethylene	Sorption of hexane and pentane	Sorption of numerous compounds	N/A
Tygon	Sorption of hexane and pentane	N/A	N/A
Nylaflow [®]	Acceptable	Sorption of naphthalene	Sorption of aromatics
Teflon [®]	Acceptable	Acceptable	N/A
Vinyl	Sorption of hexane and pentane	N/A	N/A
PEEK	N/A	Acceptable	N/A

References:

Bontempo, W., N. Shafer, D. Page, and L. Freeman. 2004. Evaluation of SUMMA[®] Polished Canisters, Silonite, and Silcosteel Treated Canisters for Collection and Storage of Volatile Organics at the Parts per Trillion Levels. Paper #72.

Brymer, D.A., Ogle, L.D., C.J. Jones, and D. L. Lewis. 1996. Viability of Using SUMMA[®] Polished Canisters for the Collection And Storage of Parts per Billion by Volume Level Volatile Organics. Environmental Science and Technology. Vol. 30, No. 1.

Hayes, H., N. Khan, and D. Benton. 2006. Impact of Sampling Media on Soil Gas

Measurements. In Proceedings; Air and Waste Management Association's Vapor Intrusion Symposium: The Next Great Environmental Challenge – An Update. September 13 – 15, 2006, Los Angeles, CA. Pages 69 – 83.

Kelly, T.J., and M. W. Holdren. 1995. Applicability of Canisters for Sample Storage in Determination of Hazardous Air Pollutants. Atmospheric Environment Vol. 29, No. 19.

Nicholson, P., D. Bertrand, and T. McClary. 2007. Soil Gas Sampling in Low-Permeability Soils. In Proceedings; Air and Waste Management Association's Vapor Intrusion; Learning for the Challenges. September 26 – 28, 2007, Providence, RI Pages 299 – 310.

Oliver, K.D., and J. D. Pleil. 1986. Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in SUMMA[®] Polished Canisters. 1986. Atmospheric Environment: Vol. 20. No. 7.

Ouellette, G. 2004. Soil Vapor Sampling and Analysis – Lessons Learned. Presented at the Department of Energy / Petroleum Environmental Research Forum Soil Vapor Workshop. Brea, California; January 27 – 29, 2004.

Sin, D.W., Y. Wong, W. Sham, and D. Wang. 2001. Development of an analytical technique and stability evaluation of 143 C₃-C₁₂ volatile organic compounds in SUMMA[®] canisters by gas chromatography-mass spectrometry. Royal Society of Chemistry 126, 310-321 DOI:10.1039/b008746g

USEPA, 1999: United States Environmental Protection Agency. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, 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).

USEPA, 2003. United States Environmental Protection Agency. Analysis of Volatile Organic Compound (VOCs) in Air Collected in Specially Prepared Canisters or Tedlar[®] Bags. U.S EPA Region 9 Laboratory, Richmond, California. Standard Operating Procedure # 310.
<http://www.prescott.edu/users/jherring/downloads/JATAP%20QAPP%20Files/Appendix%20M1%20EPA%20R9%20SOP%20310.pdf>

Wang, Y., S. Raihala, A.P. Jackman, R. St. John. 1996. Use of Tedlar[®] bags in VOC testing and storage: evidence of significant VOC losses. Environmental Science & Technology, 30: 3115-3117

APPENDIX C

QUANTITATIVE LEAK TESTING USING SHROUD AND HELIUM

To ensure valid soil gas samples are collected with no breakthrough of air down the probe or through leaks in the sampling train, a tracer compound may be applied at the base of the probe and near all connections in the sampling train. Seal integrity is then confirmed by analyzing collected soil gas samples for the tracer. Gaseous compounds such as helium and sulfur hexafluoride (SF_6) using shrouds or liquid compounds such as pentane, propanol, or Freons applied to substrates such as towels are commonly used. Gaseous tracers such as helium are considered to be more difficult to use, especially to cover leakage in the sampling train. However, helium offers a nice advantage in that leakage can be quantified and is readily measured on site with a field meter or by a stationary laboratory after the soil gas sample is collected. Volatile liquid tracers offer logistical simplicity but are more qualitative.

Volatile leak check compounds (e.g., Freons) are acceptable for use; however, if a leak test compound is detected in soil vapor samples, the reported contaminant concentration(s) should be considered biased low due to ambient air dilution.

Additionally, a small contribution from leak-test compound can necessitate the need for sample dilutions prior to analysis, and the resulting reporting limits may no longer meet the project DQO. In most instances, if the gas probes are properly grouted, air leakage at the ground surface and probe interface should not occur. Contingency planning is recommended in the event that breakthrough occurs and liquid tracer compounds are detected in vapor samples. If a leak is detected, a replacement probe can be installed at least 5-feet from the original location, if the problem cannot be corrected. However, probe relocation may not always be feasible due to underground utilities clearance and access restriction. Under these circumstances the shrouding method that utilizes a tracer gas such as helium should be used. The advantage of helium is that it does not interfere with analytical instrumentations; therefore, the reporting limits of chemical constituents in question are not compromised by helium.

An example standard operating procedure (SOP) provided by the courtesy of Geosyntec Consultant is described below with a description and diagram of a shroud setup using helium as a tracer gas. A portable hand held mass spectrometer for helium is used as a leak detection device, which can be rented on a daily basis for a reasonable cost.

Helium Tracer Testing:

Helium can be used to assess the potential for leaks in the sample train and probe annulus by positioning an enclosure or "shroud" over the probe and sampling train, filling it with a measured amount of helium, and measuring the concentration of helium in samples subsequently drawn from the probe.

One of the benefits of this method is that it is reasonably quantitative. The

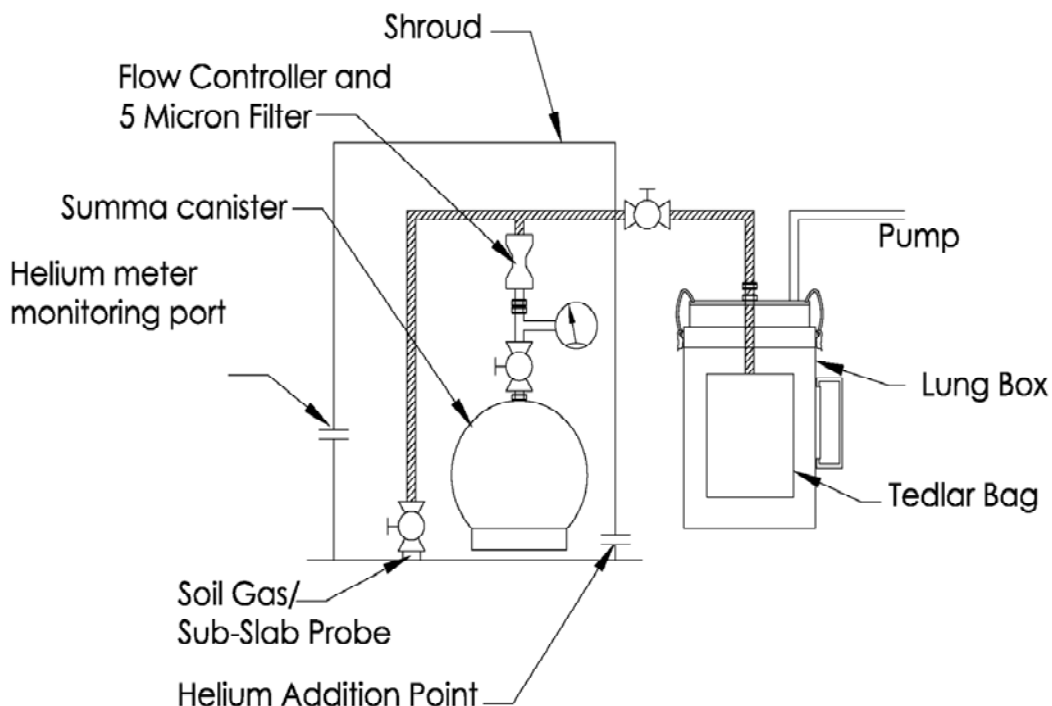
concentration of helium in the sample divided by the concentration of helium in the shroud provides a measure of the proportion of the sample attributable to leakage. Small leaks may be acceptable, as long as the magnitude of the leak is small compared to other unavoidable sources of bias and variability in sampling and analytical data. Laboratories typically assign a relative percent difference of +/- 25% for duplicate samples, so a leak that comprises less than 5% of the sample is relatively insignificant.

An example sample train for the use of helium as a tracer is shown on **Figure C-1**. Helium is released into the shroud and a hand-held helium detector is used to monitor and maintain a reasonably steady concentration of helium within the shroud. The helium concentration in the shroud should be at least 10 % or two orders of magnitude higher than the reporting limit of the laboratory helium analysis or field meter used to analyze the sample, which will provide sufficient resolution against reporting limits. The concentration in the shroud will decay over time after the initial helium dose, depending on the irregularity of the ground surface, wind speed, etc., so the concentration in the shroud should be monitored and adjusted as needed to maintain a reasonable steady state. The monitored helium concentrations in the shroud should be recorded.

Helium screening can be performed in the field by drawing soil gas into a Tedlar[®] bag via a lung-box and screening the contents of the Tedlar[®] bag with a helium meter. This can be performed in combination with other field screening for gases such as oxygen, carbon dioxide or methane. This method will identify leaks in real-time, which will allow corrections to fittings or seals to be made prior to collection of a sample for laboratory analysis. A detail description of a similar Tedlar[®] bag/lung box setup is also described in SW 846 Method 0040 (USEPA, 1996).

Helium screening can also be performed using a laboratory analysis of the contents of a SUMMA[®] canister collected under the shroud. This analysis may provide additional confidence because the helium concentration is measured for the identical parcel of gas for which VOC concentrations are measured. For this option, conduct purging and field screening, then close the valve between the SUMMA[®] canister and the lung-box (see Figure B-1), and open the valve on the SUMMA[®] canister, refresh the helium supply within the shroud and monitor/sustain it during the sample collection interval. The helium concentration is measured in the canister in the analytical laboratory by modified EPA Method TO-3 following analysis of VOCs by EPA Method TO-15. Note that if helium screening is done exclusively from a canister at a stationary laboratory and there is a significant leak, it will not be identified until after the sample has been collected and analyzed. Therefore, field screening prior to laboratory confirmation is recommended. It should be noted when using this method that a helium concentration indicating >5% leakage should be clearly noted and discussed in the data validation process.

Figure C-1: Example Apparatus for Field Screening and Sampling using Helium Tracer



References:

McAlary, T.A., P. Nicholson, H. Groenebelt, D. Bertrand. 2009. A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low-Permeability) Soils, *Ground Water Monitoring & Remediation*, 29, no. 1, pp.144.

USEPA, 1996: United States Environmental Protection Agency, EPA Publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods 0040, Sampling of Principle Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags; National Technical Information Services, U.S. Department of Commerce, Springfield, VA, December, 1996; Section 4.1.2, Figure 1 (<http://www.epa.gov/epaoswer/hazwaste/test/pdfs/004.pdf>)

APPENDIX D

SOIL GAS SAMPLING IN LOW-PERMEABILITY SOIL (EXAMPLE)

Soil-Gas Probe Design and Construction: The following is an example of the probe construction and design, which may be used for collection of soil gas from a low-permeability soil. Alternative designs may be acceptable; however any probe in low permeability material should meet the following conditions:

1. Probes installed in a cored borehole (e.g., Geoprobe® Dual Tube 3.25-inch diameter core barrel system (DT325), or similar);
2. Probes constructed of clean inert materials (i.e., Teflon, PEEK, nylon);
3. Probes having a sand filter pack around the probe tip with a pore volume of about 1L,
4. Probes having an annular seal of well-hydrated bentonite and
5. Probes having a ball valve with compression fitting (e.g., Swagelok™), or Teflon®-taped threaded fittings on the top.

If lithology with low permeability is anticipated, a continuous core should be collected and visual inspection of the core should be performed to assess the moisture profile and the probe screen should be installed at a depth above the capillary fringe. Laboratory analysis of the grain size distribution (sieves and hydrometer) and moisture content in selected samples from the soil core is also recommended.

Soil Vapor Well Emplacement Method: In this example, a screened tip (e.g., Geoprobe® 6-inch permanent implant screen with conical stainless steel tip) is used attached via compression fittings to the ¼-inch tubing. As a precaution, the implant screens are soaked in isopropyl alcohol and oven-dried to remove any cutting oils. An equipment blank sample (i.e., blank air sample) is collected from a fully assembled probe prior to subsurface installation to identify any target analytes that may be attributable to contaminant from the equipment.

The well design described below is a modification of the design in main text. In this example, filter sand is installed in the bottom of the borehole before the probe is inserted, then sand is added to surround and extend above the screen. The total volume of sand should be sufficient to provide a pore volume of at least 1L, assuming 40% porosity. For a 3.25-inch diameter borehole, this corresponds to a filter sand interval of about 18 inches. Above the filter sand, 3 to 6 inches of dry granular bentonite is placed to trap any liquid that might separate from the overlying bentonite slurry or the water used to seal the borehole annulus. The bentonite seal should preferably be mixed as slurry. The actual volume of slurry added to the borehole should be verified to be equal to the calculated volume of the annular space between the probe tubing and borehole wall. Alternatively, the seal may be placed using alternating lifts of water and granular bentonite, provided that a tamping rod is used to facilitate mixing of the two components in-situ. A bolt-down flush-mounted casing or a well box should be installed as a ground surface completion.

When practical, the probes may be left for several days or more between installation and the initial sampling event to facilitate re-equilibration. Otherwise, the probes should be developed by removing a volume of soil gas equal to the dead-volume of the tubing plus the pore volume of the sand pack as soon as feasible after installation. This should be performed using the purging and field screening protocols described below.

Shut-in-Test: Prior to soil-gas permeability testing, purging or sampling, a shut-in test should be conducted to check for leaks in the above ground fittings (see: Page 22).

Soil-Gas Permeability Testing: Prior to sampling, a soil-gas permeability test should be conducted on all soil-gas probes by measuring the flow rate and corresponding vacuum. A vacuum gauge should be connected as near as practically possible to the ball valve on top of the probe using a “T”-fitting. A pump and flow-meter can then be used to withdraw soil gas at a measured rate (See Figure D-1). When practical, flow and vacuum measurements should be made at more than one flow rate (e.g., 50,100, 200 and 500 mL/min) to assess the consistency of the flow/vacuum ratio. These data can be used to calculate the gas permeability of the soils surrounding the probe tip using the method described by Johnson et al. (1990). During this pneumatic test, the applied vacuum should not exceed 100-inches of water column to minimize the risk of drawing water up the probe or upsetting the partitioning of vapors from pore water to soil gas (API 2005).

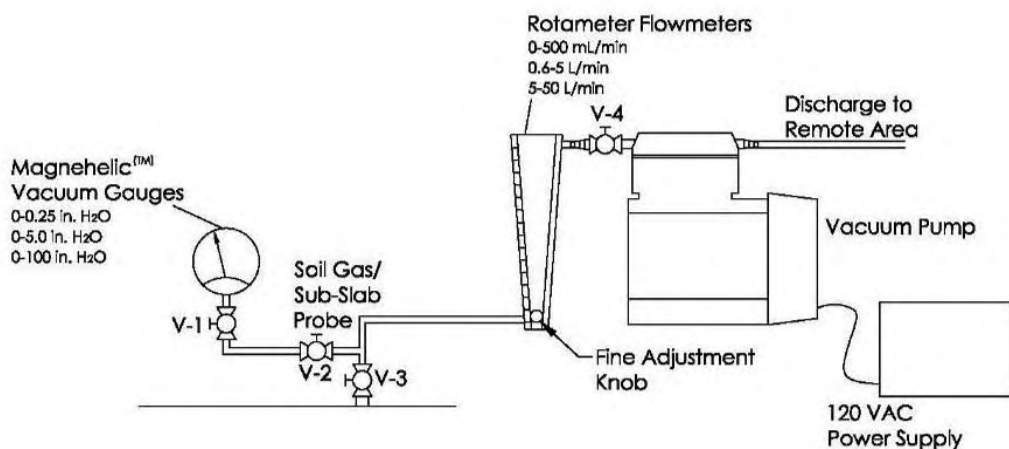


Figure D-1: An example of soil-gas permeability testing equipment (McAlary et al., 2009).

If a probe cannot sustain a flow rate of 100 mL/min for more than three minutes with an applied vacuum less than 100 inches of water, the low-flow probe screening and sampling procedure should be used.

Low-Flow Probe Screening and Sampling: A modified purging and sampling procedure should be used for low-flow probes. If the pore volume of the sand pack plus the dead volume of the tubing up to the surface is about 1L, then approximately 0.3L of soil gas can be extracted under an applied vacuum of about 100 inches water, even if there is no significant influx of gas from the surrounding soil. This yield is essentially the volume of gas removed from the pore space of the filter pack and tubing in response to applying a vacuum of 100 inches of water, according to the Ideal Gas Law. At a flow rate of 100 mL/min, this will take about three minutes, after which, the flow may diminish to a negligible amount.

If a flow of about 100 mL/min is not sustainable, then purging should be suspended when the vacuum reaches about 100 inches of water by closing the ball valve on top of the probe. Over time, as soil gas flows into the sand pack, the vacuum will gradually dissipate. The rate of vacuum dissipation can be monitored using a vacuum gauge with either continuous or intermittent measurements. Each application of this technique yields an aliquot of 0.3 L of soil gas over a period of a few minutes, followed by a period of time over which the vacuum dissipates. This length of time will depend on the gas permeability of the soils surrounding the sand pack. The sampling crew may proceed with other activities while waiting for vacuum to dissipate.

If the probe will be sampled within the first few days after installation, the volume of gas purged prior to sample collection should include at a minimum the volume of atmospheric air entrained during probe installation, which will be approximately equal to the pore volume of the sand-pack plus the dead-volume of the tubing. The volume of sample collected after this should be sufficient for field screening and laboratory analysis. Depending on the field screening instruments and laboratory methods, several aliquots of soil gas samples may be required for each low-flow probe.

Helium Tracer Leak Testing: On-site leak testing with helium can be performed using an apparatus similar to the one shown in Appendix C (Figure C-1) or see McAlary et al. (2009; Figure 5). If the flow controller to SUMMA[®] canister is calibrated to 100 mL/min, an aliquot of 0.3 L of soil gas can be collected in three minutes into the Tedlar[®] bag inside the lung box. In this example, the contents of the Tedlar[®] bag is then screened using a portable helium meter (e.g., MGD-2002[™]) to assess whether there are any unacceptable leaks in real-time. If the helium concentration in the Tedlar[®] bag is less than about 0.05% (if initial helium concentration is 10%), the sample consists of >95% soil gas, which is considered acceptable.

An alternative method using laboratory analysis of helium is also acceptable as described in Appendix C. In this example, a SUMMA[®] canister is connected to the probe through a dedicated flow controller calibrated to 100 mL/min. The probe valve is opened, and the canister and probe is quickly covered with a shroud, which is filled with at least 10% helium for about 3 minutes, after which the canister and the probe valve are both closed, the canister is disconnected and stored and the probe vacuum is allowed to dissipate, typically overnight. This process is repeated until the volume of sample is sufficient to meet analytical requirements. Typically, laboratories request a

residual vacuum in the SUMMA[®] canister of less than 10 inches Hg, which corresponded to a sample volume of about 0.6 L in a 1-L SUMMA[®] canister (i.e., two aliquots of sample would be required). For a low-flow probe the volume of soil gas extracted from the formation is known from the permeability testing and from the volume expected to be collected based on the Ideal Gas Law (i.e., 0.33 L, excluding the dead volume of above ground tubing). Therefore, sample collection into canisters that do not exceed the maximum applied vacuum (100 inches of water) can be collected if the sample collection time (3 minutes) is not exceeded with a calibrated flow of 100 mL/min.

Additional Testing Prior to Soil Gas Sampling: Passive soil gas survey can be performed to determine whether active soil gas samples are required at specific location(s) or throughout the site with low-permeability soil. The passive soil gas sampling method is described in Appendix A. Other guidance documents recommend passive sampling method in low-permeability soil for site characterization purpose (USEPA 2008, Page 13).

The trademarks and brand names mentioned in this appendix is not an endorsement of a specific product but is provided as an example to the reader as a reference to what instrument or material was successfully used in the past. Other products, which meet the similar standards and quality as the above mention products may be acceptable.

References:

API, 2005: American Petroleum Institute. Collecting and interpreting soil-gas samples from the vadose zone: A practical strategy for assessing the subsurface vapor-to-indoor air migration pathway at petroleum hydrocarbon sites. Publication # 4741. Washington, D.C.: API.

Johnson, P.C., M.W. Kemblowski, and J.D. Colthart. 1990. Quantitative Analysis for the Cleanup of Hydrocarbon-Contaminated Soils by In-situ Soil Venting. *Ground Water*, 28(3):413-429.

McAlary, T.A., P. Nicholson, H. Groenevelt, D. Bertrand. 2009. "A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low-Permeability) Soils", *Ground Water Monitoring & Remediation*, 29, No. 1, Winter 2009, pp. 144.

USEPA, 2008: United State Environmental Protection Agency, Brownfields Technology Primer Vapor Intrusion Considerations for Development. EPA 542-R-08-001.
<http://www.brownfieldstsc.org>

APPENDIX E

NAPHTHALENE SOIL GAS COLLECTION

Soil gas sampling for naphthalene is more complex than traditional soil gas investigation procedures. The appropriate sample collection approach for naphthalene is USEPA Method TO-17, requires the use of sorbent tubes (USEPA, 1999). Soil gas investigators should select an appropriate sorbent material pursuant to the physical properties of the subsurface contaminant along with the appropriate applied vacuum, sampling flow rate, and sampling volume. Soil gas workplans should describe how the field investigation will meet all the requirements within this advisory as well as those noted in Method TO-17.

Both passive and active soil gas samples may need to be collected in order to provide multiple lines of evidence to evaluate vapor intrusion exposure to naphthalene. Quantification of the contaminant source term is critical for risk-based decision making. Repetitive soil gas sampling from permanent points may be warranted as soil gas grab samples approach risk-based concentrations. Long-term monitoring may be needed, in a fashion similar to groundwater, to ascertain representative subsurface concentrations and to document contaminant plume stability.

Sampling System Materials

Sorbent/Method TO-17 is recommended for confirmation sampling and analysis for naphthalene in soil gas at probe locations where this chemical was previously detected by another soil gas method such as EPA Methods 5030/8260B or TO-15 or in the soil matrix samples. Naphthalene analysis by EPA Method TO-15 presents several challenges, such as contaminant carryover and variability in recovery (Hayes et al., 2005). EPA Method TO-15 defines target analytes as having a vapor pressure greater than 0.1 mm Hg at 25 °C at 1 atmosphere, and is suitable for organic compounds with carbon content ranging from C3 to C10. However, naphthalene with vapor pressure of 0.087 mm Hg falls just below this threshold for TO-15. USEPA Method TO-17 allows greater flexibility in targeting lower vapor pressure compounds, and hydrophobic sorbents, such as Tenax TA or GR which traps organic compounds ranging from C7 to C20 have been demonstrated to perform well when sampling heavier molecular weight VOCs (or SVOCs) such as naphthalene (Fortune, A. et al, 2008). Data from samples collected in sorbent and analyzed using TO-17 for naphthalene are reliable, provided that the requisite volume of soil gas passes through the sorbent tube. A maximum applied vacuum of 100 inches of water or less with an appropriate flow rate (e.g., ≤ 50 mL/min) derived from the soil gas permeability testing (McAlary, T. et al, 2009) should allow the sampler to collect the requisite soil gas volume.

Some stationary laboratories are capable of obtaining data of acceptable quality using SUMMA[®]/EPA Method TO-15. If EPA Method TO-15 is used for sampling and analysis

of naphthalene, then performance testing for naphthalene recovery and carryover from each laboratory should be conducted. Acceptable recovery of naphthalene should be demonstrated by EPA Method TO-15 from a gas standard at a concentration of 32 ug/m³ or less prepared in a passivated canister of the same make and approximate age as those used for sampling. A blank sample should be processed and analyzed to check for any carry over after the naphthalene gas standard is analyzed and after the highest naphthalene standard analyzed for the calibration curve is processed. Any subsequent carryover concentration of naphthalene from the blank sample, which is greater than the method detection limit (MDL), should be substantially lower than the reporting limit (RL) to assure that the following analyses are not compromised.

Naphthalene may also condense onto the surface of canisters; therefore, storage stability tests for the prepared naphthalene vapor standards should be performed for the duration of expected holding time. A calibration curve, which takes into account any expected carry over or condensation, should be used for quantification. Furthermore, naphthalene readily sorbs onto traditional soil gas sampling tubing such as polyethylene and nylaflow (Hayes et al., 2006; Ouellette, 2004). Thus, the entire sampling system should be composed of Teflon, Polyetheretherketones (PEEK) or other tubing types with demonstrated inertness for naphthalene and with acceptable background criteria. Using proper materials in the sampling system will ensure that soil gas samples are representative of subsurface conditions.

Future recommendation for the naphthalene sample collection method may ultimately depend on the capability of the stationary laboratory performing the analyses. As an example, some laboratories are now equipped with updated Thermal Desorption (TD) units capable of sample reruns as well as dilutions for EPA Method TO-17. The improved TD unit overcomes the perceived limitation of sorbent method being a “one-shot deal” without repeat analysis and reduces concern for the potential mass spectrometer overload (Hayes, H. et al, 2007). A new innovation for EPA Method TO-15 analysis includes design to allow recovery of C2 to C25 compounds with extremely low carryover (<0.1%); therefore, extending EPA Method TO-15 analysis to include a similar compound range as the Tenax/TO-17. The low carryover within the system alleviates the potential for reported naphthalene concentrations to be biased low due to losses within the internal hardware.

Sample Collection Method for Naphthalene

Soil gas samples for analysis by EPA Method TO-17 should be collected with sampling tubes packed with an appropriate sorbent material. For naphthalene, the sorbent material is usually Tenax (e.g., Tenax TA or GR). The analytical laboratory conducting the analysis typically supplies the sorbent tubes used for sampling. As an example, two 3.5-inch Tenax GR traps in series (i.e., front to back) with 200 mg sorbent in each column can be used to monitor breakthrough. Sampling should be based on both flow rate and applied vacuum to address the gas permeability of the soil. Nested semi-permanent or permanent probes should be used for soil gas sampling, with hydrated bentonite seals throughout the annulus with compression fittings. For a probe location

where soil permeability is not an issue, a vacuum of less than 100-inches of water should be applied in conjunction with a flow rate of less than or equal to 100 mL/min (e.g., 50 mL/min for 30 min to collect a 1.5 L sample). Since naphthalene contamination from industrial activities, such as those from manufactured gas plants, is frequently encountered at shallow depths (e.g. 5 ft bgs or less), quantitative tracer testing using helium is recommended to monitor potential ambient air breakthrough. An example sampling setup using Tenax GR for naphthalene can be found in the reference provided below by Hayes et al., 2008. A field duplicate should be collected and a trip blank should be used. When sample collection is complete, the sorbent tube is sealed with dedicated fittings or non-sorbing, non-reactive caps, and the tubes are shipped to the laboratory in a cooler chilled to <4°C. Standard chain-of-custody protocols should be followed. Holding times for most EPA Method TO-17 samples is 30 days.

Items to consider when soil gas sampling and analyses pursuant to Sorbent/Method TO-17 are as follows:

- Practitioner's Unfamiliarity. The practitioner's unfamiliarity with sampling using a vacuum pump due to the recommendation of many guidance documents for use of fixed flow rate (generally 100 or 200 mL/min) rather than the applied vacuum for collection of soil gas samples. The applied vacuum, which is the more important component of soil gas permeability, is frequently overlooked in collecting soil gas samples.
- Perceived Limitations with Sorbent Tubes. Other concerns and perceived limitations with use of the sorbent tube include: (1) lack of repeat analysis for samples collected in sorbent; (2) breakthrough of target analytes during sampling; and (3) potential mass spectrometer overload from high VOCs concentrations. By practice, the trapped VOCs/SVOCs constituents are desorbed completely from the sorbent into the mass spectrometer; therefore, the potential for instrument overload is still possible even with use of the updated TD instrumentation. Unlike the ambient air and indoor air samples where the concentrations of VOCs and SVOCs are in the lower, more predictable range, soil gas concentrations can be variable and are potentially much greater than 1000-fold above the ambient air concentration. Therefore, if the soil gas constituent concentrations from probes are not pre-screened using another active (or passive) method prior to sorbent sampling, there is a potential for analytical instrumentation overload. In this regard, sorbent/EPA Method TO-17 as a "stand alone" method for naphthalene deserves caution. The reporting limit of handheld photo-ionization detectors (PID) are in the range of parts per million (ppmv) and is too elevated for screening chemical constituents for vapor intrusion purposes (except if a more sensitive PID such as ppbRAE™ is used).
- Breakthrough Volumes. The sampling volume should be calculated by taking two-thirds of the estimated breakthrough volume. If breakthrough volumes cannot be determined, sorbent tubes should be arranged in series (as described above) and all tubes should be submitted to the laboratory for analysis.

- Pump Placement. The sorbent tube should be upstream of the sampling pump.
- Sample Collection Flow Rate. The flow rate for sample collection should not vary by more than ten percent.
- Sorbent Tube Orientation. For thermal desorption methods, the sorbent tube must be oriented in the appropriate direction during sample collection, which is usually annotated on the tube by the sorbent manufacturer or laboratory.
- Field Documentation. Field data sheets should be completed in the field and submitted to the analytical laboratory. The sheets should contain the sampling flow rates and sampling volumes required to quantify contaminant concentrations. These field data sheets should be included within the characterization report.
- Leak Check Compounds. Quantitative leak test compound such as helium can be used as described in Appendix C. Leak test compounds, such as helium offer a nice advantage over qualitative leak test compounds (e.g. Freons and alcohols), in that leakage can be quantified and are readily measured on site with a field meter or by a stationary laboratory after the soil gas sample is collected. Qualitative leak test compounds are usually smaller than C7 and are not retained by Tenax. However, if qualitative leak test compounds are used, the probes will need to be prescreened for leaks using EPA Methods 5030/8260 prior to Tenax sorbent sampling. If leak test compounds with carbon range of C7 or greater are used, an elevated concentration absorbed onto the sorbent tube may elevate the RL or even overload the mass spectrometer after desorption. A shut-in test of the above ground apparatus (i.e., fittings, sorbent tube(s) and lines) downstream from the probe should be performed prior to sampling (McAlary, T. et al, 2009).
- Tube Composition. Sorbent tubes composed of metal should be used due to potential photochemical reactions. However, if only glass sampling tubes are available, the tubes should be wrapped entirely in aluminum foil during and after sample collection.
- Duplicate Samples. Duplicate sorbent tube samples should be collected at a pre-determined frequency, usually at a rate of ten percent of the number of samples.
- Trip Blanks. Each shipping cooler should contain a trip blank. The trip blank should be a sealed sorbent tube filled with the same sorbent as the sampling tubes pursuant to the field procedures.

REFERENCES

Fortune, A., L. Gendron, M. Taday. 2008. Comparison of Naphthalene Ambient Air Sampling & Analysis Methods at Former Manufacturing Gas Plant (MGP) Remediation

Sites. In MGP USA: Third International Symposium and Exhibition on the Redevelopment of Manufactured Gas Plant Sites, September 23-25, Mystic, CT.
<http://www.caslab.com/News/Naphthalene-Air-Sampling.pdf>

Hayes, H., D. Benton, S. Grewal, and N. Khan. 2007. Evaluation of Sorbent Methodology for Petroleum-Impacted Site Investigations. In Proceedings; Air and Waste Management Association's Symposium: Vapor Intrusion: Learning from the Challenges. September 26 – 28, 2007, Providence, RI
http://www.airtoxics.com/literature/papers/AWMA_VI_2007.pdf

Hayes, H., D. Benton, S. Grewal, and N. Khan. 2005. A Comparison between EPA Compendium Method TO-15 and EPA Method 8260B for VOC Determination in Soil Gas. In Proceedings; Air and Waste Management Association's Symposium: Air Quality Measurement Methods and Technology. April 19 – 21, 2005, San Francisco, CA.

Hayes, H., N. Khan, and D. Benton. 2006. Impact of Sampling Media on Soil Gas Measurements. In Proceedings; Air and Waste Management Association's Vapor Intrusion Symposium: The Next Great Environmental Challenge – An Update. September 13 – 15, 2006, Los Angeles, CA. Pages 69 – 83.

Hayes, H., Mahfood, J., Shamory, B. 2008. Comparison of EPA Compendium Methods TO-15 and TO-17 for the Measurement of Naphthalene in Soil Gas. In Engineer's Society of Western Pennsylvania Proceeding. April, 2008;
<http://www.eswp.com/brownfields/program.htm#TS4>

McAlary, T. A., P. Nicholson, H. Groenevelt, and D. Bertrand. 2009. A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low Permeability) Soils. Ground Water Monitoring & Remediation. Volume 29, No. 1. Pages 144-152.

Ouellette, G. 2004. Soil Vapor Sampling and Analysis – Lessons Learned. Presented at the Department of Energy / Petroleum Environmental Research Forum Soil Vapor Workshop. Brea, California; January 27 – 29, 2004.

USEPA, 1999: United States Environmental Protection Agency. Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes; Compendium Method TO-17. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Center for Environmental Research Information, Office of Research and Development; Cincinnati, Ohio. January 1999.
[<http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf>]

APPENDIX F

SOIL GAS ANALYTICAL METHOD REVIEW

F-1 SOIL GAS ANALYSIS METHODS

There are no approved U.S. Environmental Protection Agency (USEPA) methods specifically designed to analyze for Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) in soil gas samples. Consequently, modified versions of existing EPA methods are used to analyze soil gas samples.

There are two basic classes of methods being employed in California for soil gas analysis: 1) Gas Chromatography (GC) with single specific detectors such as Flame Ionization Detector (FID), Electron Capture Detector (ECD), Photoionization Detector (PID) or a series of these detectors and 2) Gas Chromatography with Mass Spectrometer (GC/MS). The GC/MS technique is preferred because of its ability to confirm the identification of compounds.

The modifications made to accommodate soil gas sample include the sample introduction technique and the calibration standards. With the number of variations of sample introduction and calibration techniques available, it is important for consultants, regulators and other stakeholders to evaluate the technique(s) being employed before work begins on a site. All of the modifications have both advantages and disadvantages with some working better for certain compounds than others. Project Data Quality Objectives (DQOs) should be the deciding factor on which technique is the best to use for each phase of work on a particular site. If possible, the parties involved should perform preliminary performance tests (i.e., trial runs) using a selected number of techniques and determine the best method to use on the site.

The analytical methods mentioned in this appendix are those commonly used for soil gas testing. Readers of this Advisory should not be limited by the methods discussed in this appendix or elsewhere in this document. Other methods can also be modified for soil gas testing, especially the ambient air methods (EPA TO compendium series). Whatever methods are being employed for soil gas testing, they should be validated before field use. Validation involves demonstrating that the method is applicable and appropriate for the analysis of the target analytes at the desired data quality objectives (detection levels, precision, accuracy, etc.).

F-2 HISTORICAL AND LATEST VERSIONS OF ANALYTICAL METHODS

Multiple versions of USEPA methods exist and are still in use. Letter suffixes to a method such as "A", "B", etc. are used to identify the revision status of the method. The first version of a method (revision "0" [zero]) does not have a letter suffix.

While most revisions of a method can be used, there are some revisions or methods are declared “obsolete” by the USEPA. Laboratories should not use any revisions or methods that are considered “obsolete”. For the current status of USEPA methods, refer to the “Status Tables for SW-846, Third Edition” via the link:

<http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/methstat.pdf>

For the purpose of this Advisory, suffixes will not be used when referencing methods.

Method revisions are published for a number of reasons. The addition of more analytes, updating instrumentation, and clarifications of requirements/recommendations are some of the reasons. Most revisions do not involve substantial changes to methods. Laboratories are advised to use the latest revisions of the methods. In certain cases, older revisions of methods may be used for historical or consistency reasons. Nevertheless, the parties involved in a project should review the particular revision of a method and confirm that the method version will serve the intended purpose. If laboratories wish to use a new revision of a method, they should carefully review and compare their existing method with the new revision to verify that there are no significant changes that can affect data quality and/or the data quality objectives of their clients.

Laboratories should clearly indicate the exact revision of the method used in their laboratory reports to their clients.

Table F-1 delineates the various versions of USEPA methods referenced in this advisory modified for soil gas testing:

Table F-1: USEPA Soil Gas Testing Methods

EPA METHOD	DESCRIPTION	REVISIONS (DATE)	COMMENTS
8015	Nonhalogenated Organics by Gas Chromatography	“0” (September 1986) “A” (July 1992) “B” (December 1996) “C” (February 2007) “D” (June 2003)	Revision “D” is the latest revision in spite of the later date for revision “C”. Revision “C” was introduced in 2000 as a “draft” update but not finalized until 2007.
8021	Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors	“0” (July 1992) “A” (September 1994) “B” (December 1996)	Replaced methods 8010 & 8020
8260	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)	“0” (July 1992) “A” (September 1994) “B” (December 1996) “C” (August 2006)	
TO-13A	Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)	“First Edition” (TO-13) (March 1989) “Second Edition” (January 1999)	“...Edition” refers to the “Compendium of Methods for the Determination of Toxic Organic Compound in Ambient Air” and not the revision of the method.

EPA METHOD	DESCRIPTION	REVISIONS (DATE)	COMMENTS
TO-15	Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)	"Second Edition" (January 1999)	Method TO-15 was a new method added to the "Second Edition" of the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" It is a spin-off of Method TO-14A.
TO-17	Volatile Organic Compounds (VOCs) in Ambient Air Using Active Sampling Onto Sorbent Tubes	"Second Edition" (January 1999)	Method TO-17 was a new method added to the "Second Edition" of the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" It is an update of Methods TO-1 and TO-2 from the first compendium (1989).

F-3 MODIFIED GC/MS METHODS

A. EPA Method 8260

EPA Method 8260 (*Volatile Organic Compounds by Gas Chromatography /Mass Spectrometry (GC/MS)*) is designed to determine VOCs in a variety of solid and liquid matrices (SW-846, 1996). There are two basic technical modifications made to this analytical method for soil gas sampling. In the first technique, a volume of soil gas sample is injected into the sparge vessel (sparger) containing water and then VOCs are purged out of the sparger with helium gas onto a sorbent trap. VOCs in the sorbent trap are thermally desorbed into the GC column for separation and analysis. This is equivalent to EPA Method 5030 (*Purge-and-Trap for Aqueous Samples*). In the second technique, a small volume of the soil gas sample is directly injected into the GC.

Laboratories employing a modification of EPA Method 8260 to analyze soil gas samples should adhere to all the basic analytical requirements of the original method including purge time, calibration and Quality Assurance/Quality Control (QA/QC). Modifications for soil gas samples are outlined in the following sections.

Either EPA 8260B or 8260C is acceptable. 8260C is an updated version of 8260B. Because the California certification program (ELAP) does not currently certify labs to do 8260C, labs are certified for 8260B only.

1. Sample Introduction

The original EPA Method 8260 outlines five specific methods for sample

introduction (i.e., direct injection, purge-and-trap, vacuum distillation, automated static headspace and cartridge desorption), none of which were designed for soil gas. For soil gas samples, modifications of the introduction step are needed. Based on surveys conducted by DTSC of fixed and mobile laboratories that analyze soil gas samples, there are two basic techniques that are currently being employed for soil gas analysis using Method 8260B/C: purge-and-trap and direct injection. Each sample introduction technique has its own advantages and disadvantages. The advantages and disadvantages of each sample introduction technique are summarized in Table 2.

Table F-2: Advantages and Disadvantages of Sample Introduction Techniques

Sample Introduction Technique	Advantages	Disadvantages	Comments
A volume of soil gas sample is injected (forced) into a purge-and-trap sparger containing water. Analytes are purged out of sparger into the sorbent trap using Helium gas. Analytes in the trap are thermally desorbed into the GC column for separation.	<ul style="list-style-type: none"> • Larger volumes of soil gas sample may be forced into water to achieve lower reporting limits with limitations. • Surrogates, internal standards and spikes are added into the sparger before sample introduction and purging. • Soil gas volumes can be changed by using a smaller syringe or concentrated soil gas samples can be diluted in glass bulb before injecting into sparger. 	<ul style="list-style-type: none"> • Analytes are forced into a water matrix and purged out into trap before entering into GC column. Loss of target analytes possible. • Depending on the type of sample container/vessel in which the sample is collected, sample may need to be transferred before injection into sparger – potential sample loss in transfer process. • Low recovery of polar/water soluble compounds. • Calibration curve not matrix-matched if liquid standards are used. 	<ul style="list-style-type: none"> • Not recommended for polar/water soluble compounds. • Surrogates (liquid-phased) are used but introduced separately into sparger. Does not actually provide true QA/QC info. on soil gas. • Ideal for higher concentration samples. • Not recommended for low level (low concentration) samples. • Recommended for screening of oxygenates & chlorinated compounds due to poor purging efficiency.
Direct Injection of soil gas sample into GC column for separation.	<ul style="list-style-type: none"> • Technique is quick with limited sample handling. • Holding time not an issue, provided samples are injected immediately after collection. • No transfer of analytes from one phase to another (i.e., gas to liquid to gas). • Can handle high level (concentrated) samples. 	<ul style="list-style-type: none"> • Limited sample size; threshold limit on how much sample can be injected into GC column. • Lower reporting limits may not be possible and data may not meet the DQOs for risk assessment purposes. • Calibration not matrix-matched. 	<ul style="list-style-type: none"> • Recommended for screening purposes (qualitative data) and routine monitoring of limited number of known compounds. • Calibration standards prepared by expansion of liquid standards in vials/bulb may not be amenable to all compounds.

2. Calibration

- a. One of the limitations of using EPA Method 8260B for soil gas analysis is the calibration technique. The current practice in most laboratories is to use liquid-phase standards to prepare the calibration curve. For logistical and economic reasons, soil gas calibration curves are prepared with liquid-phase standards. The use of liquid-phase standards may create biases which are undetermined. The chemical dynamics (vapor pressure, solubility, etc.) of each compound is different. The “behavior” of a

compound may be different in a liquid-phase standard than in a vapor-phase standard, especially when it is subjected to being forced into an aqueous phase (in the sparger) and forced out into a gaseous phase again (during the purge). Therefore, the calibration curve should be matrix-matched. Analytical laboratories should use vapor-phase standards to calibrate their instruments when employing EPA Method 8260B/C for soil gas analysis. Gas-phase (or vapor-phase) standards used for ambient air testing are readily available and can be used for soil gas analyses.

- b. A modification using a liquid-phase standard for calibration that attempts to matrix-match the standard to soil gas samples is also being used. The technique entails injecting the liquid standard into an empty VOA vial through the septum or into glass bulbs and allowing the standard to vaporize and equilibrate before taking an aliquot of the vapor and injecting it into the gas chromatograph. This is essentially a headspace technique. This modification attempts to matrix-match the calibration standards to the soil gas samples, but this technique may not be amenable to all VOCs since it is dependent on the vapor pressures of the target analytes and how well they will vaporize in the vial or bulb. The few laboratories that use this technique are analyzing a limited number of analytes. Laboratories using this approach should standardize their procedures (i.e., temperature range, time for equilibration, etc.) in preparing the calibration standards. Furthermore, laboratories using this technique should validate and verify the accuracy of their vaporized standards by comparing their calibration with vapor-phase standards (see next section).

3. Calibration Validation

If liquid-phase standards are used for calibration with EPA Method 8260B/C for soil gas samples, then the analytical laboratory should validate their calibration curve for soil gas analysis. Validation is done by analyzing a mid-level NIST (National Institute of Standard and Technology) traceable (where available or equivalent) vapor-phase standard (vapor-phase validation check standard) on a routine basis. At a minimum, the vapor-phase validation check standard should be analyzed and evaluated every time a calibration curve is generated. Routinely, a vapor-phase check standard should be analyzed with each analytical batch to verify the validity of the liquid calibration curve. In addition, the vapor-phase validation check standard should include all the target analytes in the calibration curve. The percent difference of the validation check standard should be 20% or less in order to assume that the liquid-phase standard calibration curve is valid for soil gas samples. Soil gas sample results can still be reported for those compounds where the percent difference of the validation standard check is greater than 20% provided that the results are clearly flagged to indicate that the results are biased because the calibration standards were not matrix-matched and

validation is outside the 20% acceptance limit. This validation procedure is strongly recommended regardless of the sample introduction technique being used. This validation is not only technically sound, it will enhance the defensibility of the data.

For laboratories that calibrate their analytical system with liquid standards expanded in vials or glass bulbs (headspace technique), validation of the calibration curve should be conducted by injecting an aliquot of a vapor-phase standard (NIST traceable or equivalent) at a volume equal in concentration (this needs to be calculated based on the volume of the vaporized standard injected and the concentration of the standard, etc.) to the mid-point of the calibration curve to validate and to verify the accuracy of their standard preparation technique. The frequency of the validation, percent differences of validation check and reportable data should be the same as for liquid standards.

If vapor-phase standards are used to prepare the calibration curve with EPA Method 8260B, the validation mentioned above is not necessary. However, analytical laboratories should verify the accuracy of their vapor-phase standards periodically by comparing them to a secondary standard either from another source or to a different lot of standards from the same supplier.

4. Sample Size

The amount of sample to be analyzed is determined by the sample introduction technique in conjunction with the data quality objective of the project. If lower reporting limits are desired, then a larger volume of sample needs to be injected. If the direct injection technique is employed, this would be limited since only a very small volume can be injected onto the GC. With the sparger technique, a larger volume can be accommodated. Five (5) to 250 milliliters (mL) of soil gas sample are the typical volumes used, and some laboratories have used up to 500 mL of sample. When a larger volume of sample is used, the sample is introduced into the sparger in aliquots.

When an aliquot of soil gas sample is injected into a sparger filled with water, the gas sample actually spends a very short time in the water. During the injection of the sample, the gas is forced through the water directly into the trap. The contact time with the water is minimal. However, the more water soluble compounds (e.g., ketones, MTBE) will preferentially stay in the water phase until purged out.

As part of the validation process, laboratories should validate their injection technique by injecting aliquots of vapor-phase standards into the sparger and evaluate the recovery levels. Recommended recovery range is 70-130% for most compounds.

5. Purge Time

EPA Method 8260B specifies a purge time of 11 minutes. Laboratories should not deviate from this specification as the method has been optimized for the recovery of all target analytes. If modifications are needed, they should be documented and validated. Validation should be performed with vapor-phased standards.

6. Autosamplers

The utility of using an autosampler with modified EPA Method 8260B/C is questionable. This practice is not recommended since there will likely be sample loss during the sample transfer as well as possible leakage from the vials during the sample run. In addition, the vials may sit in the autosampler for an extended period of time.

7. Screening

Laboratories should screen samples (e.g., with GC/FID), where possible, before analysis to avoid saturation of the mass spectrometer. This will also provide information on the proper dilution(s) needed for quantification.

8. Data Review

Soil gas data generated with EPA Method 8260B should be reviewed in detail to ensure that all QA/QC parameters are within specified control limits before they are to be used for risk assessments/management or other critical decision making purposes.

9. Applicability

Modified Method 8260B works well for soil gas samples with high concentrations of VOC (i.e., $> 0.1 \mu\text{g/L}$ or $100 \mu\text{g/m}^3$) and for most compounds. However, this method may not be ideal for more polar/water soluble compounds and soil gas samples with lower concentrations of VOC (i.e., $< 0.1 \mu\text{g/L}$ or $100 \mu\text{g/m}^3$). Samples with constituent concentrations lower than $0.1 \mu\text{g/L}$ and/or with polar/water soluble compounds should be confirmed by Method TO-15.

10. Other Modifications

Any other modifications not mentioned in this guidance should be reviewed by all parties involved prior to being put to use for a project. The standard operating procedures (SOP) for the sample preparation and analysis should

be provided by the laboratory. The laboratory using the modification must validate the procedures before implementation. The validation data and report should be made available for review by all affected parties. If needed, the Department of Toxic Substances Control's (DTSC) Environmental Chemistry Laboratory (ECL) should be consulted on modifications.

B. EPA Method TO-15

EPA 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)*) is traditionally used to analyze for VOCs in ambient air samples (USEPA, 1999). Samples are collected into specially prepared stainless steel canisters. VOCs in a known volume of sample are concentrated onto a solid sorbent trap, and refocused on a second trap before being thermally desorbed onto the GC column for separation.

There are two techniques for introducing whole air samples by TO-15 from the canister into the gas chromatograph: (1) multisorbent pack method; and (2) a concentrator where the VOCs are condensed on a reduced temperature surface (i.e., cold trap). For the multisorbent pack method, there are different types of solid sorbent trap available depending on the compounds of interest. Traps with different type of sorbent packing have different retentive properties which can be used to selectively concentrate analytes of interest.

Laboratories employing EPA Method TO-15 to analyze soil gas samples should adhere to all the basic requirements of the method including calibration and QA/QC protocols. Method TO-15 is best suited for soil gas analysis since it is designed for gas samples. However, there are other modifications referred to as TO-15, which are described in Table 3. The advantages and disadvantages of these modifications are summarized below. Note that some of the modifications are not in technical compliance with the method.

Table F-3: Advantages and Disadvantages of Modifications

Modification	Advantages	Disadvantages	Comments
Samples collected in Tedlar® bags.	<ul style="list-style-type: none"> • Lower Cost. • Easily transported. • Selected compounds have been shown to be stable⁽¹⁾. 	<ul style="list-style-type: none"> • Significant background (off-gas). • Adsorption of some compounds. • Bags do not conform to TO-15 protocol. • Limited holding time (24-36 hours for most compounds). 	<ul style="list-style-type: none"> • Not recommended. • Technically not TO-15
Samples injected into instrument by filling injection loop with syringe.	<ul style="list-style-type: none"> • Good for highly concentrated samples. 	<ul style="list-style-type: none"> • Limited volume can be analyzed (0.5 – 5 cc). • Not suited for low concentration samples. 	Not recommended. Sample collection technique does not comply with TO 15 ⁽²⁾
Use of portable GC/MS system (e.g., Hapsite®)	<ul style="list-style-type: none"> • Ideal for field screening. 	<ul style="list-style-type: none"> • May not be able to handle the various types of sampling media. Samples have to be transferred for analysis (e.g., Canister to syringe or Tedlar® bag). 	<ul style="list-style-type: none"> • Considered to be an "automated" gas chromatograph under Section 1.6 of method.

¹ Hartmam, 2006

² DTSC Environmental Chemistry Laboratory (ECL) should be consulted

1. Quality Assurance/Quality Control (QA/QC)

The QA/QC requirements for Method TO-15 are different than that of EPA Method 8260B/C. The calibration curve and tuning need to be checked every 24 hours for Method TO-15 compared to every 12 hours for Method 8260B/C.

There are no requirements to verify the calibration curve with a second-source standard, to analyze matrix spike/matrix spike duplicate samples (MS/MSD), laboratory control samples (LCS) or use surrogates for Method TO-15.

Consultants, regulators and other parties involved with using Method TO-15 for soil gas analysis may include additional QA/QC requirements not required by Method TO-15 to their testing protocol. Discretion should be used in deciding whether additional QA/QC will provide any additional data validation information.

2. Autosamplers

Samples in passivated stainless steel canisters (i.e., SUMMA[®]s) can be analyzed with an autosampler if the canisters are directly connected to the autosampler without any further sample transfer. Additional blank samples should be included in the sample sequence to evaluate possible carryover of highly contaminated samples.

3. Canisters certification

Canisters used with EPA Method TO-15 must be certified clean with the same data acquisition mode as the sample analysis. See Discussion on Scan vs. SIM mode.

4. Shipping of soil gas samples, especially in pressurized containers, by air should be avoided. There are Federal restrictions on shipping pressurized containers by air. Check with the shipper first if there is a need to ship such samples by air. Also consult with the federal code of regulations (49CFR, Parts 100-185) on specific regulations on the shipment and transportation of various materials.

C. EPA Method TO-17

EPA Method TO-17 (*Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*, USEPA, 1999) is another method designed for collecting and analyzing VOCs in ambient air samples which is also used for soil gas analysis. A volume of air (or soil gas) is pulled through a sorbent tube to collect the VOCs followed by thermal desorption of the VOC onto the GC column for separation and analysis by the mass spectrometer. Other detectors or combinations of detectors such as ECD/FID in series can be used with this method provided that the criteria specified in Section 14 of the method are met.

Method TO-17 is primarily a sampling method. Analysis of samples follows the analytical approach in USEPA Method TO-15. The use of sorbent tubes requires

additional quality control measures. Freshly packed or new sorbent tubes must be conditioned before use. Conditioning entails heating the tubes at specific temperatures with a set gas flow (See Table 2 of method). Tubes can be reused for multiple thermal desorption cycles until the “safe sampling volume” validation procedures fails (USEPA, 1999, Method TO-17, Section 13.1.2).

For calibration, either gas (vapor)-phase or liquid standards can be used. Liquid standards are directly injected into the sorbent tubes for calibration. No calibration validation with gas-phase standards is needed if liquid standards are used.

Furthermore, “sample tubes awaiting analysis on an automated desorption system must be completely sealed before thermal desorption to prevent ingress of VOC contaminants from the laboratory air and to prevent losses of weakly retained analytes from the tube.” (USEPA, 1999, Method TO-17, Section 8.2.1.2)

Because of the manner by which gaseous samples are collected, this method has several inherent advantages over Methods TO-15 and 8260. One advantage is the ability to collect and concentrate a larger volume of sample. Consequently, lower reporting limits can be achieved if the entire VOCs volume of sample trapped on the sorbent tube is desorbed completely as a single aliquot of sample. In comparison, only a smaller sub-sample is usually analyzed for TO-15 at a time; therefore, the reporting limits are more elevated.

However, there are disadvantages in using TO-17. Some of the perceived disadvantages in using sorbent tube as a collection method include the inability to repeat an analysis on the same sample, potential mass spectrometer (MS) overload due to desorption of concentrated sample and column breakthrough. The unfamiliarity of practitioners in handling and collecting soil gas samples onto sorbent tubes is another potential disadvantage, since samples are mostly collected in canisters and syringes in the United States. Sorbent tubes are used less frequently for sampling in the United States whereas they are used widely in the European countries.

With Method TO-15, additional analysis on the same sample can be easily performed by withdrawing another sample aliquot from the sample canister. With Method TO-17, once all the compounds are desorbed from the sorbent tube, the sample is completely used. Repeating a sample analysis is possible only if multiple (duplicate) sorbent tubes are collected. Multiple sorbent tubes can be collected concurrently if several sorbent tubes are manifolded in parallel during sampling. Nevertheless, recent advances in thermal desorption (TD) technology have made it possible to split sample into fractions for repeat runs from the same sorbent tube.

For quantification, the volume of air passing through the cartridge must be measured and documented. Moisture can be a problem with sorbent cartridges but it can be managed by using alternative sorbents, sample splitting or dry purge (USEPA, 1999, Method TO-17, Section 7.2). The use of in-line water traps is not recommended

since the traps may absorb target analytes. Other issues with TO-17 include interferences from sorbent artifacts (USEPA, 1999, Method TO-17, Section 7.1). There is no single “universal” sorbent that can be used for all possible VOCs. The choice of sorbent depends on the target VOCs. However, “multi-bed (sorbent)” tubes are also available that can be used to sample for a wide range of target compounds.

Method TO-17 should not be used with highly concentrated soil gas samples since there are no provisions for screening or diluting samples. The concentration of VOCs or SVOCs should be predetermined by another active (or passive) soil gas method prior to deployment. Otherwise, concentrated soil gas samples will saturate the MS if completely desorbed into the GC. Field screening of soil gas sample with EPA 5035/8260 or other available techniques where appropriate are recommended to provide information concerning the soil gas concentration encountered at specific location.

D. EPA Method TO-13A

EPA Method TO-13A (*Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)*) is designed for the sampling and analysis of polycyclic aromatic hydrocarbons (PAHs) in ambient air (USEPA, 1999). Since there is no specific method designated for semi-volatile organic compounds (SVOC) in soil gas, Method TO-13A has been used for this purpose. Samples are collected/adsorbed onto a combination of filter and sorbent cartridges followed by solvent extraction, cleanup (if needed) and concentration before analysis by GC/MS. Again, since a soil gas sample is treated in the same manner as an ambient air sample, there should be no modification needed to analyze soil gas samples with this method. One consideration for this method is the necessary volume needed to meet the required reporting limits considering the amount of vapor that can be collected from soil gas. The required flow rate of sampling need to be calculated given the capacity of the sampling tube is also a consideration.

E. Scan vs. SIM Mode

With GC/MS Methods, there are two data acquisition modes: Scan and Selected Ion Monitoring (SIM). The most common mode is the Scan mode in which the detector scans from high to low across a range of masses continuously. This mode provides the sample mass spectrum by which compound identification is made against a spectral library. In SIM (Selected Ion Monitoring) mode, only a few selected ion fragments (or masses) are monitored. Because the detector concentrates its time only on selected masses, the sensitivity is maximized. SIM mode has the advantages of having lower reporting limits and overcoming background problems. The only limitation of using the SIM mode is fewer compounds are identified.

F-4 MODIFIED GC METHODS

Regular gas chromatography (GC) methods are also being used for the analysis of soil gas samples. These methods should be used only for routine monitoring of VOC contamination at well-characterized sites and should not be used for the initial characterization of contaminated sites. Routine monitoring involves the analysis of sites where the contaminants, and to some extent their concentrations, are known. However, there will be instances when new unknown compounds may be detected. In those cases, any new compounds should be confirmed by analysis with a GC/MS method. On a routine basis, at least 10 percent of the positive results from regular GC analysis should be confirmed by analysis with a GC/MS method.

Two primary GC methods associated with soil gas analysis are EPA Methods 8015 and 8021. Various versions of each method exist in the SW-846 manual (SW-846, 1996). Laboratories should use the most updated versions of the method as they will contain the most up-to-date practices and information. Regardless of which version of the method is being employed, laboratories should clearly state in their analytical reports which version of the method was used.

A. EPA Method 8015 (8015, 8015A, 8015B, 8015C & 8015D)

EPA Method 8015 (*Non-halogenated Organics by Gas Chromatography*) is used to determine the concentration of nonhalogenated organic compounds (both volatile and semivolatiles), triethylamine and petroleum hydrocarbons (i.e., gasoline range organics (C₄-C₁₂) and diesel/motor oil range organics (C₁₂-C₃₂)) (SW-846, 1996). Samples are introduced into the GC by one of the following methods: (1) purge-and-trap; (2) equilibrium headspace; (3) direct injection; (4) injection of azeotropic distillation concentrate; (5) injection of vacuum distillation concentrate; or (6) injection of solvent extraction concentrate. A flame ionization detector (FID) is used with this method. In order to apply this method to soil gas samples, the same types of modifications described for Method 8260B/C should also be used. Samples are either injected into a purge-and-trap sparger filled with water and purged or directly injected into the GC.

B. EPA Method 8021 (8021, 8021A & 8021B)

EPA Method 8021B (*Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors*) is used to determine the concentration of volatile organic compounds (both halogenated and aromatic) (SW-846, 1996). Samples are introduced into the GC by one of the following methods: (1) direct injection; (2) purge-and-trap; (3) headspace or (4) injection of vacuum distillation concentrate. Both a photoionization detector (PID) and a Hall electrolytic conductivity detector (HECD) are used with this method in either series or as a single detector. In order to apply this method to soil gas samples, the same types of modifications described for Method 8260B/C should also be used.

F-5 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

QA/QC requirements for soil gas testing are either outlined in the specific project Quality Assurance Project Plan (QAPP) or the specific modified EPA Method being employed. Soil gas analytical laboratories, at minimum should comply with those QA/QC requirements and add additional checks as needed.

QA/QC FOR SOIL GAS TESTING

The following are the minimum QA/QC protocols that should be included with soil gas testing. Most of these QA/QC protocols are required with EPA methods and as well as laboratory certification (see later).

- **Daily Tune**: For GC/MS methods, laboratories should conduct the daily tune (i.e., BFB for VOCs and DFTPP for SVOC) as specified in the respective method. The instrument must meet the tuning criteria before sample analysis.
- **Initial Calibration**: The calibration curve should consist of a minimum of 5 points. The maximum percent relative standard deviation (%RSD) for each target compound should not exceed 30%.
- **Daily Calibration (Continuing calibration)**: The calibration curve for each compound of interest should be verified with each analytical batch or once every 12 hours, whichever is more often. Verification is conducted by analyzing the mid-point calibration standard. The results from the mid-point standard should be within 20% (percent difference) of the initial calibration in order to assume the calibration curve is valid.
- **Method Blanks**: Method blanks are used to evaluate contamination from the analytical process. This is a sample prepared by the analytical laboratory using an analyte-free matrix (for soil is humidified laboratory grade ultra pure air) and carried through the entire sample preparation and analytical procedure.
- **Container Blanks**: (This was called the "Method Blank" in the previous version of the soil gas advisory.) If sampling containers (e.g., glass syringes, glass bulbs) are reused/recycled, then at least one (1) decontaminated sample container per 20 samples or per batch, whichever is more often, should be analyzed as a container blank sample to verify the effectiveness of the decontamination procedures. Additional note: Other components of the sampling stream (e.g., fittings/valves) that are subject to carryover/contamination should also be monitored.
- **Trip Blanks**: (ONLY REQUIRED IF SAMPLES ARE COLLECTED IN TEDLAR[®] BAGS OR SORBENT TUBES FOR TO-17 ANALYSIS) Whenever VOC samples are shipped offsite for analysis, a minimum of one (1) trip blank per day should be

collected and analyzed for target compounds. Trip blanks, consisting of humidified laboratory grade ultra pure air, are prepared to evaluate if the shipping and handling procedures are introducing contaminants into the samples and if cross-contamination in the form of VOC migration has occurred between the collected VOC samples. The trip blank containers and media should be the same as the site samples. For passivated stainless steel canisters (e.g., SUMMA[®] canisters), trip blanks are not necessary since it is unlikely that VOCs will migrate in or out of or between canisters unless a specific canister is not tightened properly by the sample handler. Additionally, EPA Method TO-15 does not have specific trip blank requirements. Therefore, trip blanks are not recommended if samples are collected in passivated stainless steel canisters unless specified in the QAPP or by the project manager.

- Duplicate Samples: At least one duplicate sample per 20 samples or per batch, whichever is more often, should be collected and analyzed. Duplicate samples should be collected in separate containers at the same location and depth. A duplicate sample can be collected by use of a splitter (T) at the point of collection to divide the sample stream into two separate sample containers. This sample analysis is designed to evaluate the reproducibility (precision) of the sampling process.
- Replicate Samples: At least one replicate sample per 20 samples or per batch, whichever is more often, should be re-analyzed by the laboratory to assess analytical precision. This is not to be confused with the duplicate sample mentioned above. This is designed to evaluate the reproducibility (precision) of the laboratory's analytical ability.
- Matrix Spike/Matrix Spike Duplicates (MS/MSD): Although MS/MSD samples are required with the EPA 8000 series method, there is no practical approach to apply this requirement to soil gas samples. For really true MS/MSD samples, spike compounds must be added to the sample during the collection process. With soil gas samples, this is not technically feasible. The addition of a spike into the sparger with modified EPA Method 8260B/C does not duplicate the actual condition of the sample as it is collected, processed and analyzed. Therefore, the requirement for MS/MSD with modified EPA Method 8260B/C is discretionary. There is no requirement for MS/MSD with EPA Method TO-15 as the analysis of MS/MSD with TO-15 is impractical. Spike compounds are added at the same time when the sample is transferred into the concentrator. This does not truly assess the impact of the matrix on the recovery of the target compounds. Therefore, the need for MS/MSD with Method TO-15 is at the discretion of the parties involved in the project and should be based on the data quality objectives.
- Laboratory Control Sample (LCS): LCS is required with the EPA 8000 series methods. LCS is a sample made with an aliquot of a clean (control) matrix similar to the sample matrix spiked with compounds that are representative of the target analytes. It is used to document laboratory performance. This is similar to MS/MSD without the possibility of any matrix interference. For soil gas analysis, this QA/QC

sample is not necessary since the “clean” matrix is humidified laboratory grade ultra pure air. When prepared as such, this is equivalent to the daily calibration (continuing calibration) sample. Therefore, it would be redundant to analyze this QA/QC sample. This QA/QC sample is optional depending on the requirement of the project QAPP and the project manager. Methods TO-13, TO-15 and TO-17 do not have any requirements for LCS sample analysis.

- Surrogates: The use of surrogates in soil gas analysis is discretionary. EPA Method 8260B/C requires surrogates whereas Method TO-15 does not. The introduction of surrogates into soil gas samples can present some logistical challenge. Surrogates are designed to monitor recoveries of target analytes. Therefore, they should be introduced at the point of sample collection in order to fully assess the recovery process. Depending on the type of containers being used to collect soil gas samples, the introduction of surrogates can be problematic.

For most laboratories that use modified EPA Method 8260B/C, the surrogates are usually added to the water in the sparger either before or after the soil gas sample has been forced into the water. Vapor-phase surrogates (which are available for air analysis) can be theoretically added into soil gas sample aliquot in a gas-tight syringe just before injecting into the sparger. However, few if any laboratories are using this practice for various reasons. For laboratories using EPA Method TO-15, the surrogates are added to the sample loop at the same time the soil gas sample is being loaded onto the concentrator. In both instances, the surrogates are added after the sample has already been collected. There is a gap between when the sample is collected and when the sample is analyzed where there are no surrogates to monitor the process.

Some laboratories add “vapor surrogates” immediately after sampling to samples collected in glass bulbs. The “vapor surrogates” are liquid surrogates that have been injected into a glass bulb, allowed to expand, and aliquots of the “vapor surrogates” are injected into the glass bulb with the soil gas sample. Cautions should be exercised when preparing “vapor” internal standards or surrogates with liquid standards in either Tedlar[®] bags or glass bulbs. Make sure the internal standards or surrogates have completely vaporized before aliquots are taken. Droplets of liquid standards or surrogates can adhere to the internal surface of the bags or bulbs. This practice is not recommended because of the inherent difficulty in preparing the surrogates or standards. Commercially prepared surrogates or standards should be used. Due to variations with where and when the surrogates are added to the soil gas samples, laboratories are advised to note in their final analytical reports the exact step in the process where the surrogates (if used) are added so the results can be evaluated accordingly.

- Reporting Limit Verification: The Reporting Limit (RL) is defined as the limit of quantification reported by the analyzing laboratory. The RL should not be lower than the lowest calibration point. The RL should be validated periodically (recommended

with each batch of samples) by spiking a blank sample at the RL level. There is no limit on the number of samples per batch for RL verification. Once per day is sufficient.

- **Acceptance Limits:** Laboratories should establish their own acceptance levels (limits) for their QA/QC parameters (i.e., percent recoveries for surrogates, matrix spikes, laboratory control samples and percent relative difference for duplicates, etc.) based on laboratory performance. The limits should be evaluated and updated periodically. For guidance on establishing acceptance limits, consult EPA Method 8000B (December 1996), Section 8.0 (SW-846, 1996).
- **Standard Operating Procedures:** Laboratories should have detailed written Standard Operating Procedures (SOP) for their soil gas sampling and testing procedures. Copies of the SOP should be available in the laboratory for review and reference. The SOP should be reviewed on annual basis and updated as needed. Field procedures, including sampling procedures, can be written as a separate SOP from the laboratory analytical procedures.

F-6 DETECTION LIMITS vs REPORTING LIMITS

For the purpose of this Advisory, Detection Limit (DL) is defined as the “*the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte*” (SW-846, Chapter One, Quality Control, Revision 1, July 1992). Reporting Limit (RL) is defined as the lowest concentration of an analyte that can be detected in a sample by the given analytical procedure taking into account sample matrix, interferences, dilution factor and the lowest point of the calibration curve. Laboratories should use RL in their analytical reports since it is a more reliable indicator of the limit of detection.

F-7 REPORTING LIMITS

The appropriate RLs to be used on a specific project should be based on the project data quality objectives (DQOs) taking into consideration various factors. The project manager and the parties involved with the project should consider factors such as: sampling protocols, analytical method(s) to be used, list of target compounds and other DQO need for risk assessment.

Table F-4 delineates the reporting limits of the common soil gas analytical techniques. The ranges in this table are based on the survey of analytical laboratories conducted by the Soil Gas Advisory Workgroup. For the reporting limits of other methods/techniques, consult with the analytical laboratory.

Table F-4: Reporting Limits

Analytical Method/Technique	Reporting Limit Range*	Comments
Modified EPA 8260B/C: Direct injection of soil gas into sparger with water.	20 – 5000 $\mu\text{g}/\text{m}^3$ (0.02-5 $\mu\text{g}/\text{L}$) (most compounds at 1000 $\mu\text{g}/\text{m}^3$ (1.0 $\mu\text{g}/\text{L}$) or lower.)	Sample size dependent. Most samples are 5-250 cc (mL).
Modified EPA 8260B/C: Direct injection of soil gas into GC column.	100 – 1000 $\mu\text{g}/\text{m}^3$ (0.1-1.0 $\mu\text{g}/\text{L}$) or 10 – 700 ppbv	
Modified EPA TO-15 (Conventional GC/MS system).	Scan Mode: 0.5 – 20 ppbv or 0.7 – 200 $\mu\text{g}/\text{m}^3$ (0.0007 – 0.20 $\mu\text{g}/\text{L}$) SIM Mode: 0.0025 – 0.02 ppbv or 0.004 – 0.20 $\mu\text{g}/\text{m}^3$ (4×10^{-6} – 2×10^{-4} $\mu\text{g}/\text{L}$)	
Modified EPA TO-15 (Using portable GC/MS system (e.g., Hapsite®)).	3 – 10 ppbv or 4 – 100 $\mu\text{g}/\text{m}^3$ (0.004 – 0.10 $\mu\text{g}/\text{L}$) (most at 5 ppbv)	

* The “ppbv” ranges in the table are approximations based on the average molecular weights of target analytes. The actual reporting limit ranges is dependent on the molecular weight of the compound of interest. See discussion on reporting units.

The analytical method should be selected with the specific reporting limits needed for the site investigation. For risk assessment purposes, the reporting limits should be the California Human Health Screening Levels (CHHSLs) for soil gas, or lower if cumulative health effects are of a concern. For compounds that are not on the CHHSL listing, the analytical method should be selected that can achieve the reporting limits for risk-based decision making.

F-8 REPORTING UNITS

Laboratories using modified EPA Method 8260B (and other 8000 series methods) generally report results in micrograms per liter ($\mu\text{g}/\text{L}$). Data users and laboratories are strongly cautioned that $\mu\text{g}/\text{L}$ for gas is not equivalent to $\mu\text{g}/\text{L}$ for aqueous samples. It is particularly critical that the distinction is made since the calibration curve for modified Method 8260B is built on liquid calibration standards and calculated as $\mu\text{g}/\text{L}$ for liquid. Results for soil gas samples are also reported in $\mu\text{g}/\text{L}$ but they are not equivalent to the liquid (aqueous) matrix unit. Analytical laboratories must take this into account when they report soil gas sample results. All parties should be aware of this. All final soil gas data must be reviewed and verified that they are calculated correctly and reported in the proper unit.

To avoid confusion, it is recommended that analytical laboratories that use modified EPA Method 8260B/C report soil gas results in “ $\mu\text{g}/\text{m}^3$ ” rather than “ $\mu\text{g}/\text{L}$ ”. Note that “ $\mu\text{g}/\text{m}^3$ ” is not equivalent to “ $\mu\text{g}/\text{L}$ ”. For example (*Benzene in air/soil gas with molecular*

weight=78.11):

$$1.0 \mu\text{g/L Benzene} = 1000 \mu\text{g/m}^3 \text{ Benzene} = 315 \text{ ppbv Benzene}^*$$

$$*\text{ppbv} = [(\mu\text{g/L}) \times (RT)] \times 1000 / (\text{MW}) \times P \text{ or}$$

$$\text{ppbv} = [(\mu\text{g/m}^3) \times (RT)] / (\text{MW}) \times P$$

Where:

$$\begin{aligned} \mu\text{g/L} &= 1.0 \\ \mu\text{g/m}^3 &= 1000 \\ R &= 0.0825 \text{ L-atm/mole}^\circ\text{K (Ideal Gas Law Constant)} \\ T &= 298^\circ\text{K (Standard Temperature)} \\ 1000 &= \text{Conversion of } 1 \text{ m}^3 = 1000 \text{ L} \\ \text{MW} &= 78.11 \text{ (Molecular Weight of Benzene)} \\ P &= 1 \text{ atm (Standard Pressure)} \end{aligned}$$

Laboratories using TO methods generally report results in parts per billion by volume (ppbv). The unit "ppbv" is strictly a gas unit and there should not be any confusion.

F-9 COMPARING RESULTS

A quick and simple way to evaluate the comparability of results from two different methods is to calculate the Relative Percent Difference (RPD) of the results. The RPD is calculated according to the formula:

$$\text{RPD} = 100 \times |C_1 - C_2| / [(C_1 + C_2) / 2]$$

where:

C_1 = Result from the first method

C_2 = Result from the second method

It is generally accepted that if two results have a RPD of 25% or less, then they are considered to be comparable.

The variability in soil gas results comes from a number of sources. Although laboratories may use the same method for their analyses, there will be variations in their instrumentation (i.e., manufacturer), sample introduction technique, analyst skill, experience and practices. For soil gas, there will be differences in sample collection methods and in sample containers. Finally, there will be a variation in the sample matrix. A replicate sample collected immediately after the original sample may not be the same due to spatial and temporal differences.

In instances where soil gas results from the same source analyzed by two different methods (e.g., modified 8260B/C and TO-15) are disparate (>25% RPD), it is important

to validate the results first before any conclusions are made. Validation would involve reviewing the sampling procedures, collection containers, sample introduction technique (i.e., purge-and-trap or mass flow controller, etc.), QA/QC, etc. Any differences noted should be scrutinized to explain the differences in results. All QA/QC results should be reviewed to make sure the parameters are within the established control limits. More importantly, the calculations should be checked. Results from modified 8260B/C should be reviewed to make sure the proper units are used and properly calculated for soil gas (see section above on reporting units).

Finally, the characteristics of the specific compounds should be checked where the results do not agree. For example, Naphthalene is known to have poor recovery if vapor samples are collected, transferred or stored in glass vessels such as glass bulbs or air-tight syringes. Naphthalene purges well if liquid standard is used in the purge-and-trap. However, vapor phase naphthalene standard will purge poorly due to adsorption onto the glass syringe used to transfer into the purge-and-trap. Highly volatile VOCs such as the Freons are well-recovered with modified 8260B/C compared to TO-15. Some compounds are better analyzed by one method than the other. If the discrepancies cannot be explained after validation, then it may be necessary to resample and reanalyze.

To avoid discrepancies, sites can be initially evaluated for soil gas with any one of the available analytical methods described above. If soil gas is detected at a site, and it is determined that further characterization is needed, the analytical method used should take into consideration the factors previously discussed. Consultants, regulators or other parties involved in the process need to decide which method(s) to use based on many considerations including: sampling method, sampling containers, target compounds list, laboratory equipment available (e.g., the limited number of mobile labs have the capability for TO-15) and most importantly data quality objectives. However, all final risk assessment and risk management decisions should be based on the results from analyses using a GC/MS method.

All soil gas samples for decision-making purposes should be of the highest quality, even those samples used to “screen” sites initially. If the initial sampling shows “clean” results but the samples are biased low due to inappropriate DQOs, then potential contamination might be overlooked.

F-10 METHOD REFERENCES IN ANALYTICAL REPORTS

The analytical method used to test soil gas samples should be clearly identified in the laboratory reports.

Since soil gas samples are analyzed by modifying existing air, water or water methods, analytical laboratories should reference the analytical methods as “modified” versions of the methods in laboratory reports. For example, “Modified EPA 8260B” should be used as the method reference instead of “EPA 8260B” for soil gas results.

F-11 LABORATORY CERTIFICATION

All laboratories performing soil gas testing should be certified. According to the California Health and Safety Code Section 25356.1.5(e) [*Response action criteria, risk assessment*], exposure assessments shall include the development of reasonable maximum estimates or exposure to VOCs that may enter existing or future structures on a site. Section 25358.4 requires that analysis of any material that is required to show compliance with Chapter 6.8 of the Health and Safety Code shall be performed by a laboratory accredited by the Department of Public Health pursuant to Article 3 of Chapter 4 of Part 1 of Division 101.

Soil gas testing laboratories can obtain certification from the California Department of Public Health's Environmental Laboratory Accreditation Program (ELAP) for all analytical methods they are using for soil gas testing. Certification assures that the laboratories have the requisite facilities, equipment and personnel to perform the testing and have demonstrated competence and compliance with the methods being certified.

In addition, certification entails the validation of the analytical method as well as periodic checks with performance evaluation (PE) or blind samples (where available) to assess laboratory continued competence with the method.

Soil gas certification for EPA Methods 8015, 8021, 8260, TO-13A, TO-15 and TO-17 is available from ELAP.

National Environmental Laboratory Accreditation Program (NELAP) accreditation for EPA Methods TO-13A, TO-15 and TO-17 should be accepted in lieu of California ELAP certification for soil gas testing.

Laboratories that have either certification from ELAP or NELAP for EPA Methods 8015, 8021 or 8260B (for either soil or water matrices) should obtain separate certification from ELAP for soil gas work with those methods.

Laboratories seeking certification for modifications of methods not discussed in this guidance document need to obtain written approval for the alternate test method to be used from the California Environmental Protection Agency, Environmental Chemistry Laboratory pursuant to ELAP regulations.

F-12 REFERENCES

DiGiulio, C. Paul, R. Cody, R. Willey, S. Clifford, R. Mosley, A. Lee, K. Christensen and R. Costa, 2006a. *Comparison of Geoprobe PRT and AMS GVP Soil-Gas Sampling Systems with Dedicated Vapor Probes in Sandy Soils at the Raymark Superfund Site*. EPA/600/R-06/111. National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, November. <http://www.epa.gov/ada/pubs/report.html>.

Hartman, B. 2006. *How to Collect Reliable Soil-Gas Data for Risk-Based Applications-Specifically Vapor Intrusion; Part 4-Updates on Soil-Gas Collection and Analytical Procedures*, LUSTLine Bulletin 53, September 2006.

Smith, Roy-Keith, 2003. *Guide to Environmental Analytical Methods*, 5th Edition. Genium Publishing Corporation, 2003.

SW-846, 1996: *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846: Methods 8000B, 8015, 8021, 8260B, Various Revisions, U.S. Environmental Protection Agency, Washington, D.C., 1996. SW846 On-line: <http://www.epa.gov/sw-846/sw846.htm>

USEPA, 1999: *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. Methods TO-13, TO-15, TO-17, Second Edition, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1999; EPA 600/625/R-96/010b.

APPENDIX G

BAROMETRIC PRESSURE, RAINFALL, and SOIL DRAINAGE

Barometric Pressure Fluctuations

Soil Gas

Massmann and Farrier (1992) evaluated the significance of barometric pressure fluctuations on the transport of atmospheric gas into the vadose zone. They examined situations in which barometric fluctuations will yield a significant affect on the vadose zone. Model calculations showed that fresh air may migrate several meters into a highly permeable subsurface during large barometric pressure cycles and the depth of penetration increases as the thickness and permeability of the vadose zone increases. Massmann and Farrier (1992) thus suggested that the concentration of volatile contaminants may be lower when barometric pressures are high and that soil gas measurements will show the largest fluctuations during times of rapidly rising or falling barometric pressures. During these large barometric pressure changes, as indicated by Figure 8 of their paper, soil gas at 1.5 meters (5 feet) may be diluted with atmospheric air by 30 to 50 percent.

Surface Flux

Clements and Wilkening (1974) demonstrated empirically that atmospheric pressure changes of one to two percent associated with the passage of frontal systems will produce changes in the flux of radon from the subsurface by 20 to 60 percent. The actual magnitude of the change in the radon flux depends upon the rate of change of the barometric pressure and its duration. The effect of pressure changes to VOC concentrations in soil gas is expected to be similar.

Rainfall Events

Surface flux

Kienbusch and Ranum (1986) evaluated the affects of rainfall on the collection of flux chamber measurements on open ground. In tests at a simulated landfill, water was added to dry soil cells to simulate rainfall. Trace precipitation (0.01 inches) had no effect on measured emission fluxes from the ground. Heavier rainfall (0.4 inches), however, did have an effect. The emission flux was decreased by 90 to 95 percent and the reduction in emissions lasted for over eight days. These results are consistent with other field observations (Radian Corporation, 1984; Eklund, 1992).

Soil Drainage

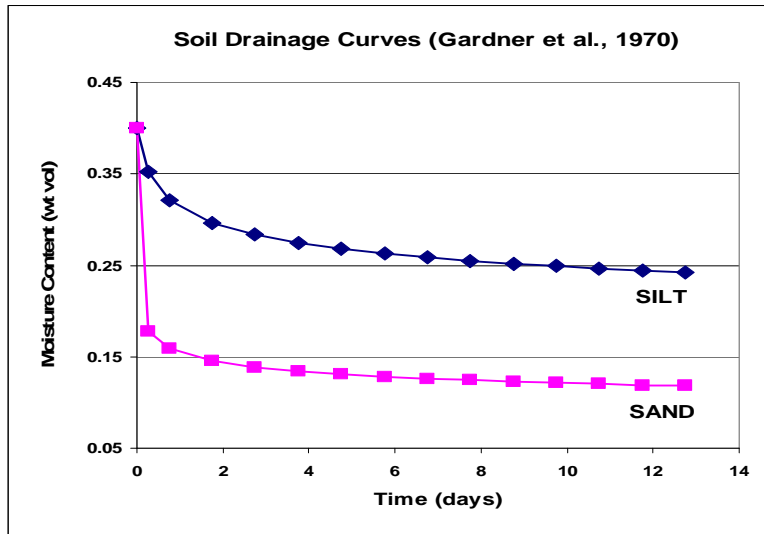
Gardner et al. (1970) derived approximate solutions for unsaturated flow following

irrigation. Their solutions can be used to evaluate the impact of rainfall on subsurface moisture conditions. The drainage of soil by gravity following infiltration of one centimeter of water for two soil types, sand and silt, is shown in Figure 1. The figure demonstrates that these two soil types drain within approximately five days. Additionally, Sisson et al. (1980) derived a one-dimensional unsaturated flow equation by assuming a unit gradient approximation. The estimation of the rate of drainage for a silty sand is shown in Figure 2. The figure shows that silty sand drains within about five days, agreeing with the approximations by Gardner et al. (1970).

REFERENCES

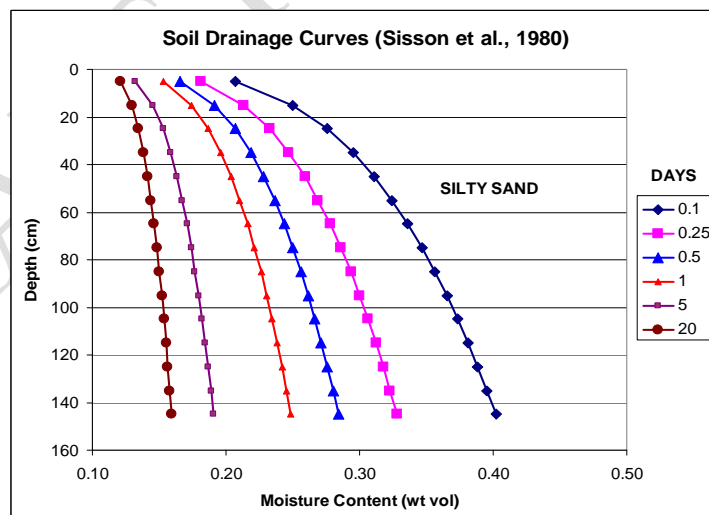
- Auer, L. H., N. D. Rosenberg, K. H. Birdsell, and E. M. Whitney. 1986. The Effects of Barometric Pumping on Contaminant Transport. *Journal of Contaminant Hydrology*, v. 24, p. 145 - 166.
- Clements, W. E., and M. Wilkening. 1974. Atmospheric Pressure Effects on ^{222}Rn Transport across the Earth-Air Interface. *Journal of Geophysical Research*, v. 79, n. 33, p. 5025 - 5029.
- Eberling, B., F. Larsen, S. Christensen, and D. Postma. 1998. Gas Transport in a Confined Unsaturated Zone during Atmospheric Pressure Cycles. *Water Resources Research*, v. 34, p. 2855 - 2862.
- Gardner, W. R., D. Hillel, and Y. Benyamini. 1970. Post-Irrigation of Soil Water, 1. Redistribution. *Water Resources Research*, v. 6, n. 3, p. 851 - 861.
- Kienbusch, M., and D. Ranum. 1986. Validation of Flux Chamber Emission Measurements on a Soil Surface. Draft Report to EPA-EMSL, Las Vegas, under EPA Contract No. 68-02-3889, Work Assignment 69, June 1986.
- Nilson, R. H., E. W. Peterson, K. H. Lie, N. R. Burkhard, and J. R. Hearst. 1991. Atmospheric Pumping: A Mechanism Causing Vertical Transport of Contaminated Gases through Fractured Permeable Media. *Journal of Geophysical Research*, v. B13, p. 21,933 - 21,948.
- Massmann, J., and D. F. Farrier. 1992. Effects of Atmospheric Pressures on Gas Transport in the Vadose Zone. *Water Resources Research*, v. 28, n. 3, p. 777 - 791.
- Radian Corporation. 1984. Soil Gas Sampling Techniques of Chemicals for Exposure Assessment – Data Volume. Report to EPA-EMSL, Las Vegas under EPA Contract No. 68 -02-3513, Work Assignment 32, March 1984.
- Sisson, J. B., A. H. Ferguson, and T. Th. van Genuchten. Simple Method for Predicting Drainage from Field Plots. *Soil Science Society of America Journal*, v. 44, p. 1147 - 1152.

FIGURE G-1



Soil drainage curves where gravity predominates as derived from Gardner et al. (1970). The figure denotes two scenarios, silt and sand, where the initial unsaturated hydraulic conductivity within the infiltration zone is 1 centimeter per day and 1000 centimeters per day, respectively. An instantaneous infiltration of one centimeter is assumed in the evaluation. The figure demonstrates that drainage to asymptotic moisture conditions occurs within about five days for these two soil types.

FIGURE G-2



Soil drainage curves as derived from Sisson et al. (1980) where a unit gradient is assumed. The figure denotes one scenario, silty sand, where the initial unsaturated

hydraulic conductivity is 100 centimeters per day. The model assumes that the vadose is saturated to 0.40 and allowed to drain. Moisture profiles are shown for five different time intervals. The figure demonstrates that drainage to near ambient moisture conditions of 0.10 occurs within about five days.

DRAFT FOR REVIEW

APPENDIX H

REPORTING FORMAT AND PARAMETERS

Recordkeeping in the Mobile Laboratory

Maintain the following records in the mobile laboratory:

1. A hard copy record of calibration standards and QA/QC standards/samples with the following information, at a minimum:
 - a. Date of receipt
 - b. Name of supplier
 - c. Lot number
 - d. Date of preparation for intermediate standards (dilution from the stock or concentrated solution from supplier)
 - e. ID number or other identification data
 - f. Name of person who performed the dilution
 - g. Volume of concentrated solution taken for dilution
 - h. Final volume after dilution
 - i. Calculated concentration after dilution
2. A hard copy of the latest and current initial calibration data for each instrument used.
3. A hard copy of the currently-use laboratory standard operating procedures.

Reporting of Soil Gas Sample Results and QA/QC Data

(1) Report all sample test results for all compounds in the analyte list and QA/QC data. Compounds may be listed by retention time or in alphabetical order. Report any unidentified or tentatively identified peaks. Submit all data in electronic format and raw data, including the chromatograms for samples and standards as requested.

(2) Report the following, at a minimum, for all calibration standards, QA/QC standards and soil gas samples:

- a. Site name
- b. Laboratory name
- c. Date of analysis
- d. Name of analyst
- e. Instrument identification
- f. Injection amount
- g. Injection time
- h. Concentrations of each analysis

- i. Laboratory quality control limits
- j. Calculated results
- k. Notes or explanation of any outliers

(3) Provide additional information, as specified, for different types of analyses. Tabulate and present in a clear legible format all information according to the following grouping:

(A). Initial calibration

- a. Standard source (**STD Lot ID No.**)
- b. Detector
- c. Retention time (**RT**)
- d. Standard mass or concentration (**Mass/Conc**)
- e. Peak area (**Area**)
- f. Response factor (**RF**)
- g. Average response factor (**RF_{ave}**)
- h. Standard deviation (**SD_{n-1}**) of RF, i.e.,

$$n$$

$$\left[\frac{\sum_{i=1}^n (RF_{ave} - RF_i)^2}{(n - 1)} \right]^{1/2}$$
 n = number of points in initial calibration
- i. Percent relative standard deviation (**% RSD**), i.e., $(SD_{n-1} / RF_{ave}) \times 100$ (%)
- j. Acceptable range of %RSD (**ACC RGE**)

(B). Daily calibration check sample

- a. Source of standard
- b. Detector
- c. Retention time (RT)
- d. Standard mass or concentration
- e. Peak area
- f. Response factor (RF)
- g. Percent difference between RF and RF_{ave} from initial calibration (**% DIFF**)
- h. Acceptable range of %DIFF (**ACC RGE**)

(C). Laboratory Control Sample (LCS). Same format as daily calibration check sample

(D). Soil gas sample

- a. Sample identification
- b. Sampling depth
- c. Purge volume
- d. Vacuum pressure
- e. Sampling date and time

- f. Injection date and time
- g. Injection amount
- h. Dilution factor (or concentration factor if trap is used)
- i. Detector
- j. Retention time (RT)
- k. Peak area
- l. Concentration in $\mu\text{g/L}$ (**Conc**) (sample results reported in ppbv or ppmv must be converted in $\mu\text{g/L}$)
- m. Total number of peaks found by each detector
- n. Unidentified peaks and/or other analytical remarks
- o. Surrogate results
- p. Control limits