

Work Plan for Evaluation of Sub-Surface Vapor Intrusion Con Edison MGP Sites

Prepared by:

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RETEC Project Number: CECN1-16017-100

Prepared for:

**Consolidated Edison Company of New York, Inc.
32-01 20th Avenue, Building 136
Astoria, New York 11105**

June 26, 2002

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August 8, 2001

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1 Introduction and Program Objectives

Consolidated Edison Company of New York, Inc. (Con Edison) intends to initiate a program to evaluate sub-surface vapor intrusion that may be associated with its former Manufactured Gas Plant (MGP) sites.

The subject MGP sites include properties at which gas production occurred as well as those at which only gas holders were present and gas production operations did not occur. Most of these sites are in densely populated areas and many have apartment buildings, residences, commercial or public buildings on or adjacent to the former MGP facilities. It is anticipated that most of the buildings will have basements or crawlspaces, and that some of the buildings will be slab-on-grade construction. Preliminary Site Assessments are planned but have not yet been implemented for most of the sites. However, Site History Reports are available which give information regarding the former MGP operations and current conditions, including depth to groundwater of nearby wells.

The program will involve initial screening of sensitive properties on or adjacent to MGP sites. The goal of the program is to develop data that point to one of the following scenarios:

1. There are no indications of MGP impacts to soil, groundwater or air at the site. Consequently, there is no indication of a risk of vapor intrusion associated with the MGP site.
2. There are indications of MGP impacts to soil or groundwater. However, the potential migration pathway between MGP site impacts and indoor human receptors appears to be incomplete.
3. The potential pathway is possibly complete, however indoor air concentrations of hazardous constituents, including MGP constituents and other sources, are below site ambient concentrations or published background concentrations.
4. The potential pathway may be complete. Indoor air concentrations of hazardous constituents are above ambient or published background conditions, however, non-MGP sources predominate. Constituents identified as having an MGP source are a small fraction of the total concentrations and are below to site ambient concentrations or published background concentrations.
5. The potential pathway may be complete, and indoor air concentrations of MGP source constituents are higher than site ambient or published background concentrations.

The purpose of this Work Plan is to provide practical guidance for conducting the field and laboratory work associated with Con Edison's MGP site screening program. The Work Plan also provides important considerations for interpretation of results. However, the interpretation of a particular set of data will necessarily take into account numerous site-specific factors. Therefore, this Work Plan reflects this site-specific aspect of interpretation.

The remainder of the document is organized as follows:

- Section 2 presents the sequence of investigation activities that form a phased approach to the assessment of potential air quality impacts.
- Section 3 describes the sampling methods to be employed during this program, including procedures for collection of soil gas, indoor air, and ambient air samples.
- Section 4 describes the recommended analytical methodologies and presents analyte compound lists for the program. An approach to conducting optional forensic analyses that may be used during secondary phases of assessment is also provided in this section.
- Section 5 presents data quality objectives for the sampling and analysis activities.
- Section 6 presents important considerations for interpretation of results.
- Section 7 provides a brief description of engineering controls and other measures that could be used to mitigate vapor intrusion into buildings.
- Section 8 lists reference documents cited in this Work Plan.

2 Phased Approach to Air Quality Assessments

This section describes a general approach to the sequence of activities that may be conducted to provide a rapid screening-level assessment of the intrusion of vapors into buildings near MGP sites. The work will proceed in a stepwise manner so that the appropriate and necessary information is obtained, while minimizing disruption to the property owners, users, and inhabitants.

A flowchart is presented in Figure 2-1 which indicates a typical sequence of activities in this phased approach. It is important to emphasize that site-specific factors, such as ease of access into buildings, subsurface obstructions such as utilities, and seasonal depth to groundwater may alter the exact sequence of activities. The general sequence entails performing an initial inspection of the building and grounds (if access is granted) and sampling of soil gas (both outside and beneath the building) early in the program. This would be followed later by indoor air sampling, if warranted. The benefit of this phased approach is that the soil gas sampling results will provide an accurate representation of the vapors in the soil matrix (if present), unhindered or affected by interference from materials or activities currently or historically stored, used and/or performed in the buildings (fuel oil storage, smoking, paint/paint cleaner, glues/adhesives, oils, caulking, etc.) that could be detected in the indoor samples. Note that without soil gas data, it is not always possible to make a satisfactory interpretation of the meaning of the indoor air results with respect to sources outside the building.

The remainder of this section presents the steps outlined in the flowchart. Sections 3 and 4 provide more detail regarding the methods to be employed for sampling and analysis, respectively.

The selection of buildings to be investigated should be based on their proximity to the former MGP site and the possible presence of tar-like materials, heavily impacted soils or contaminated groundwater in the subsurface.

Step 1. Identify potentially affected buildings. Evaluate whether any buildings are on or in close proximity to the MGP site, and are therefore potentially affected by tar-like materials, heavily contaminated soils or MGP-impacted groundwater. If buildings exist in close proximity to areas with potential sources of MGP contamination and a potential migration pathway exists, then the assessment will proceed. Additional buildings may be identified as potentially affected based on additional environmental investigations.

Step 2. Conduct a building inspection. If access is granted, then this step will be conducted during an initial site reconnaissance visit. The inspection will follow a protocol which will include noting the building structure, environmental conditions, unusual odors, interviews with occupants, and an inventory of potential indoor sources. The basement or crawlspace of the building will be inspected to assess whether groundwater is present in sumps or seeps and to estimate the depth below grade of the building floor slab. If groundwater is present, arrangements will be made for a water sample to be collected and analyzed for MGP constituents. If no volatile or semi-volatile organic compounds are present in this groundwater, no further evaluation of soil gas or indoor air quality in that building will be required at this time. Further general investigation of the site will yield more information regarding the seasonal fluctuation of groundwater and the need to conduct additional evaluation of vapor intrusion. If volatile or semi-volatile organic compounds are present in the groundwater above action levels, then arrangements will be made to conduct indoor and ambient air sampling (Step 4). If a vadoze zone is present beneath the building, then soil gas sampling will be conducted for the building as the next investigation step.

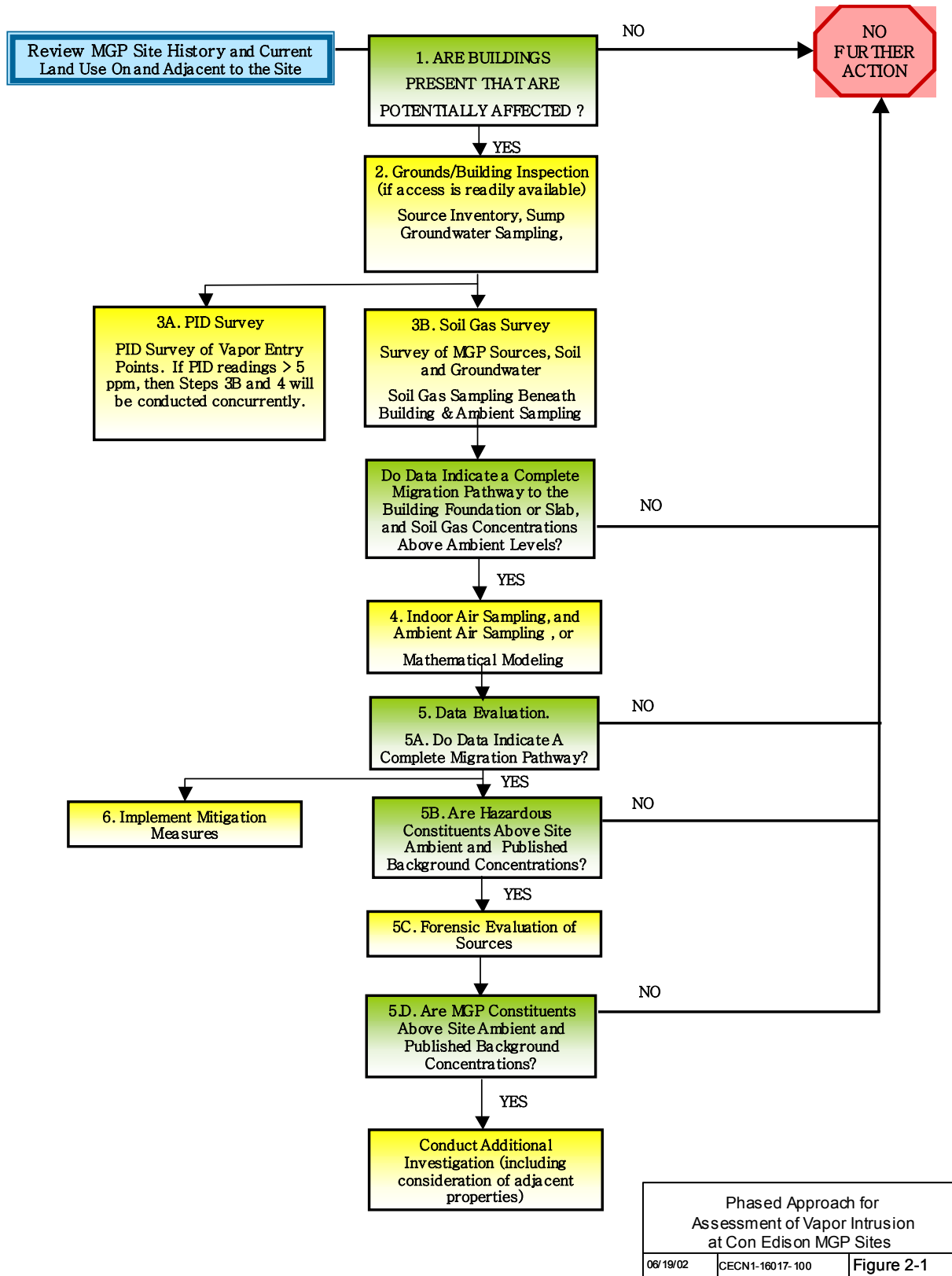
Step 3. Conduct a soil gas survey for the building. After a utility clearance is conducted, soil gas samples will be collected from soils between the location of the MGP source areas and the building being investigated. Soil gas sampling will also be conducted through the building or basement slab, (if permission is granted by the building owner). Ambient air sampling will be conducted to provide data for comparison purposes. A photoionization detector (PID) survey of potential vapor entry points will be conducted. If PID readings of vapors flowing from entry points are greater than 5 ppm, then indoor air sampling will be conducted in addition to soil gas sampling. If no target analytes are detected in the soil gas above the concentrations of concern, then no further evaluation of soil gas or indoor air quality in that building will be required at this time. Further general investigation of the site will yield more information regarding the seasonal fluctuation of groundwater and the need to conduct additional evaluation of vapor intrusion will be considered as this information is developed.

Step 4. Conduct Indoor Sampling. If warranted by the results of the site reconnaissance or the soil gas sampling, ambient air samples and indoor air samples from the basement and first floor living space will be collected either on the same day or subsequent to the soil gas survey, assuming access and approval of the owner is granted.

Step 5. Evaluate Results. All analytical results, site history information, and building inspection information will be brought together to evaluate whether hazardous constituents in indoor air are above site ambient and published background concentrations, and if so, whether they are associated with MGP sources. The outcome of this evaluation will be a decision to either conduct additional soil vapor investigation activities (including assessment of adjacent

buildings), evaluate engineering controls or other mitigation measures to be implemented for the building, or to conclude that no further assessment is required.

Figure 2-1 Phased Approach for Assessment of Vapor Intrusion at Con Edison MGP Sites



3 Sampling Methods

This section provides general guidance regarding the field methods to be used for the program. Methods are described for building inspection activities, basement groundwater sampling, soil gas sampling (outdoor and beneath the building), indoor air sampling, and ambient air sampling. Detailed procedures will be followed using standard operating procedures (SOPs). Analytical methods are described in Section 4.

3.1 Building Inspection

To collect background information on buildings where approval has been granted from the owner, Con Edison intends to conduct the following: interview the occupants of each of the buildings; walk through the building and the basement, and examine the crawl space, or concrete slab on grade; and document the results. The survey data and sampling protocol are based in part on the United States Environmental Protection Agency's (U.S. EPA's) publication, *Assessing Potential Indoor Air Impacts for Superfund Sites* (U.S. EPA, 1992) and the NYSDOH *Indoor Air Sampling & Analysis Guidance* (NYSDOH, 2001).

The information gathered will be documented on the NYSDOH Indoor Air Quality Questionnaire and Building Inventory forms, provided in Appendix A.

3.1.1 Resident Interviews

At least one resident/occupant from each building will be interviewed to determine the specific types of products containing volatile organic compounds (VOCs) that are used within the building, and building conditions that may have a bearing on the assessment. The interview will include the following items.

- Length of time the resident has lived at the building
- Time each resident spends in the basement, if present
- If any residents smoke tobacco products in the building and the frequency
- Products containing VOCs that are used in the residence for cleaning, maintenance, or hobbies
- Frequency of use of each product containing VOCs
- Methods of handling and disposing of products containing VOCs

- Type of and location of heating, cooking and clothes drying systems used in the building
- Recent remodeling or redecorating activities
- Groundwater sumps, wells or cistern and associated piping present in or near the building (status)

3.1.2 Indoor Survey

To account for sources other than soil vapor, a survey of the building and basement (if present) will be conducted. In an effort to identify and document these possible sources, the following items will be noted during the indoor survey.

- Age of the building
- Physical dimensions and layout of the building/basement
- Furnace location and type of fuel used
- Other appliances and type (e.g., hot water heaters, dryers, stoves, etc.)
- Stored volatile materials (e.g., paints, thinner, gasoline, etc.)
- Gasoline-powered engines (e.g., lawnmowers, generators, etc.)
- Condition and type of walls and floor
- Floor drain location and discharge
- Basement wall/floor joints and sumps
- Other utility conduits entering the basement
- Air intake locations for combustion appliances
- Garage location (attached or not) and contents (autos, etc.)
- Evidence of recent remodeling or redecorating activities (e.g., carpet, tile, painting, drywall, drapery, furniture, etc.)
- Type of ventilation active during sampling (open windows, fans, etc.) and general pressure differential between basement and first floor and between indoors and outdoors.

- Visual inspection for a sump, well or cistern present near or in the building

Items that can alter pressure differentials such as bathroom, kitchen or other exhaust fans, elevators, etc.

The following environmental factors will be documented because they may affect the concentrations of vapors present in the building and basement, crawl space, or concrete slab:

- Indoor and outdoor air temperatures (measured with a thermometer)
- Frozen or wet surface soils (observed)
- Wind speed and direction (from local meteorological station)
- Barometric pressure (from local meteorological station), and trend (rising or falling).

3.2 Basement Groundwater Sampling

Standard water sampling methods will be used to collect water samples from building sumps or seeps. If possible, through the interview process and observations, the source of the water will be ascertained, whether it is primarily drainage water which appears intermittently and in association with rain events, or whether it is groundwater which appears seasonally. Soil Gas Sampling

The soil gas sampling procedures will conform to the protocols described by ASTM Method D5314-92 and following the contractor's SOP.

A utility marking and clearance will be conducted and a site-specific health and safety plan (HASP) will be prepared during the planning stage of this activity, in advance of any intrusive field work.

3.3 Preliminary Survey of MGP Sources, Soil, and Groundwater

If initial environmental characterization of the site has not yet been performed, then Geoprobe or other equivalent methods will be used to collect soil and groundwater samples in addition to soil gas samples for rapid initial screening characterization. Subsurface stratigraphic and hydrogeologic information as well as information regarding MGP source materials obtained during this activity will be used to help interpret the soil gas results and determine the location of additional soil gas samples, if necessary.

Soil stratigraphy, which is critical to the assessment of soil gas migration, will be carefully logged. Samples of important soil units may be collected for grain size analysis and other sensitive parameters used in mathematical models of soil gas migration. The following procedure will be used to guide the initial characterization:

1. Borings will be continuously sampled and logged for stratigraphy.
2. Borings will not be advanced through subsurface structures. If concrete or brick material is encountered indicating a former structure, or if a clay layer is encountered, the borings will not be continued and the bottom of the boring will be grouted.
3. Borings will advance to the water table, then stopped. If the water table has not been encountered at 15 feet bgs, the boring will be stopped.
4. Two samples with the highest headspace PID readings or visual impact will be collected for soil samples and analyzed by methods listed in Section 4.
5. Collect a grab water sample. Analyze by methods listed in Section 4.

3.3.1 Location and Number of Samples

Soil gas sampling will be conducted to determine the nature and extent of soil gas impacts between historic MGP source areas and the building being investigated.

Preferential pathways of soil gas migration, including natural features (such as shallow rock or vertically fractured soil) or manmade features (such as utility trenches) will be noted. Soil gas sampling will include these areas, if sampling within these features can be safely accomplished.

Non-transmissive zones, such as clay layers, will be avoided, and transmissive zones, such as sand and gravel layers, will be targeted.

Soil gas samples will be taken from the vadoze zone, above the capillary and saturated zones. At some sites a very narrow vadose soil may be present. The soil gas sample will be obtained from the elevation of the basement floor if ground water elevations permit, or just above the water table and capillary fringe if the ground water is higher than the basement elevation. If groundwater is extremely shallow, it may not be possible to collect a soil gas sample.

Sampling may be done at several locations laterally between the MGP source and the building, including immediately adjacent to the building (within five feet) if possible. This will allow investigation of lateral attenuation of soil gas concentrations.

If stratigraphy allows, sampling will be conducted at several depths to investigate vertical attenuation of soil gas concentrations.

3.3.2 Sampling Equipment and Methods

To collect soil gas samples, 1 ¼ inch metal probing rods will be driven into the ground to the required depth via a hand held driver or Geoprobe device. The space between the probing rod and the surrounding soil column will be filled with granular bentonite, which will be hydrated to form an airtight seal so no aboveground air may impact the sample. Once the required depth is reached, a screened soil gas sample point at the tip of the leading rod attached to the sample cylinder with 1/8 inch tubing will be opened and soil vapor samples will be collected. Soil gas samples will be collected in stainless steel canisters over approximately 30 to 60 minutes by drawing air through the slotted screen and tubing. A vacuum gauge will be used to check both the initial and final vacuum in the canisters. The sample probe will be installed and removed the same day that the sample is collected.

3.3.3 Sampling Conditions

Atmospheric conditions will be taken into account when scheduling the soil gas sampling activities. If possible, these activities, as all soil gas and indoor air assessment activities, will be done during falling barometric pressure conditions so to take advantage of an upward soil gas pressure gradient which would lead to measurements under conservative, worst-case conditions.

Optional additional soil gas sampling may be conducted during or immediately after heavy rainfall events, with the intent of sampling below the temporary surface confining layer produced by heavy rain

3.3.4 Soil Gas Sampling From Beneath the Building

The number and spacing of samples will depend on several site-specific factors, including the location and proximity of former MGP features, the building floorplan, uses of specific areas, access, building construction history, perimeter versus interior areas, and vapor entry pathways such as utility corridors. However, a typical baseline would be 2 samples per 10,000 square feet for this screening program.

The soil gas sampling procedures will conform to the protocols described by ASTM Method D5314-92, provided in Appendix B. If the basement of the building is constructed of poured concrete, a hole will be drilled through the slab and a sample of the soil gas from beneath the slab will be collected using a 1 ¼ inch OD stainless steel probe. The probe assembly will contain a slotted screened portion and will be connected to a length of disposal Teflon tubing. The screen will be exposed to the soil when an expendable drive point

head is detached from the bottom of the probe assembly and the probe is pulled-back to a depth of two feet below the concrete floor. Approximately 0.5 feet of slotted screen will then be exposed for collection of the soil gas sample (2.5-2.0 feet bgs). The sample probe intake will be in communication with the slab/soil interface so that potentially intruded soil air is sampled. The annulus around the probe assembly at the concrete floor will be sealed with granular bentonite, which will be hydrated to form an airtight seal. Soil gas air samples will be collected in stainless steel canisters over a 30 to 60 minute period by drawing air through the slotted screen and tubing. A vacuum gauge will be used to check both the initial and final vacuum in the canisters. The sample probe will be installed and removed the same day that the sample is collected.

If the inspection of the basement indicates that a competent slab does not exist (i.e. dirt floor, cracks in the slab, etc.) then a soil gas sample will still be collected, but from a minimum soil gas probe depth of five feet. The condition of the floor will be documented.

3.3.5 CGI Screening Procedure

Prior to PID screening, an inspection of natural gas lines and appliances and a check for natural gas leaks using a combustible gas indicator (CGI), or equally sensitive instrument, may be conducted. In addition to being potentially explosive, natural gas is also contains trace concentrations of benzene and should be eliminated as a possible non-MGP source. Should any natural gas leaks be detected, further sampling will not be performed until the identified leaks are repaired.

3.3.6 PID Screening Procedure

A PID with a high energy light source such as 10.6 eV, will be used to screen the potential vapor intrusion points in the building and the basement, crawl space, or concrete slab for VOCs. Samples will also be collected near possible sources of VOCs including furnaces, drains, basement wall/floor joints, floor sumps, and stored VOC products.

The information gathered will be documented on the Building Survey and Air Sampling form (Appendix A).

3.4 Indoor Air Sampling

If the results from investigation of soil gas indicate the potential for migration of volatile organic compounds from the site subsurface to indoor air or if MGP-related contaminants are identified in the building's sump water, a set of air samples will be collected from within the building, and from ambient air outside the building. The indoor sampling program will be conducted in

general accordance with the NYSDOH Indoor Air Sampling & Analysis Guidance (NYSDOH, 2001). The guidance document is included as Appendix C.

Samples of indoor air will be collected from the basement and first floor living/work space of the building. An attempt will be made to conduct indoor air sampling for a group of buildings within one general location during the same day (depending on access requirements from the home owners), so that only one ambient air sample will be needed.

Indoor air samples will be collected over a one-hour period in 6-liter Summa canisters by drawing air through Teflon tubing. The end of the tubing will be placed approximately three feet above the floor level. A vacuum gauge will be used to check both the initial and final vacuum in the canisters. Indoor air temperature will be recorded at the time of sample collection.

3.5 Ambient Air

3.5.1 Duration, Location and Number of Samples

One ambient air sample will be collected concurrently with each set of indoor air samples. The sample will be collected upwind, or on each air intake side of the building being sampled. Because outdoor air concentrations are subject to more short-term variability than indoor samples, the ambient air samples will be taken over a one to eight hour period. The ambient air sampling will begin at least one hour prior to the indoor air sampling event, in accordance with EPA guidance (EPA, 1992). This will allow sampling of the air that is most representative of air entering the building and remaining present during indoor air sampling.

To the extent possible, ambient air samples will be collected from open areas and away from extraneous point sources such as car exhausts or fuel tanks. Ambient air samples will be collected at the approximate midpoint of the ground story level of the building, usually about five feet above the ground surface, and about 5 to 15 feet away from the building (EPA, 1992). Outdoor barometric air pressure and air temperature will be collected at the beginning, midpoint and end of ambient air sampling event.

3.5.2 Sampling Equipment and Methods

To avoid the introduction of extraneous variables, ambient air sampling will be done using the same equipment and methods as indoor air sampling, except that a longer sampling time may be used in the ambient air sampling depending on the site-specific conditions.

3.5.3 Sampling Conditions

Atmospheric conditions will be noted, including general weather conditions, temperature, the presence of a temperature inversion, humidity, wind direction, wind speed, barometric pressure and trend (rising or falling). Environmental conditions such as unusual vehicle traffic will also be noted.

4 Analytical Methods

The screening program described in this Work Plan is designed to identify whether hazardous organic vapors associated with the MGP site are present in soil gas beneath buildings or in the indoor air of buildings adjacent to the source areas of MGP contamination. The primary volatile chemicals of interest are benzene, ethylbenzene, xylenes, toluene (BTEX) and naphthalene which are components of MGP tars that are known to have health impacts. Possible sources of indoor BTEX and naphthalene may include soil vapor, non-MGP related indoor sources and ambient air.

The goal of the indoor air and soil gas sampling is to evaluate the potential for migration of MGP-related contaminants into indoor air by measuring levels low enough to compare to background indoor air levels and ambient outdoor air. The goal of basement sump water analysis is to identify MGP contaminants that may be present in the groundwater beneath the site and could result in exposure.

4.1 Sump Water and Groundwater

Basement sump water samples will be analyzed by the following methods:

- VOCs : ASP-OLM04.2 TCL VOCs
- SVOCs: ASP-OLM0.42 TCL SVOCs
- Metals: ASP-ILM04.1 TAL Metals
- Total Cyanide: ASP-ILM04.1 Cyanide
- pH

If sufficient water is available, add the following:

- Available Cyanide by EPA method OIA-1677
- Individual cyanide complexes by DinexAN-55

Note that although metals and cyanide are not technically important for vapor intrusion, they would be part of the Preliminary Site Assessment (PSA) of the former MGP site, and would enable use of these data in a future PSA report.

4.2 Soil

Soil samples collected during initial site characterization will be analyzed by the following methods:

- VOCs ASP-OLM04.2 TCL VOCs
- SVOCs ASP-OLM04.2 TCL SVOCs
- Metals ASP-ILM04.1 TAL Metals
- ASP-ILM4.1 Cyanide
- pH

If sufficient sample is available, conduct grainsize analysis by ASTM methods.

4.3 Indoor Air, Ambient Air and Soil Gas

Indoor, ambient and soil gas air samples will be analyzed for standard volatile organic compounds using EPA Method TO-15. RETEC has developed an optional extended analyte list will include indicator hydrocarbons believed to be associated with either coal tar, diesel fuels or gasoline. Interpretation of the results may enable the identification of these different sources. The target compounds and reporting limits for the extended analyte list are presented in Table 4-1. The remaining constituents in the optional extended analyte list will be determined using EPA Method TO-15 for Ozone Precursors.

Table 4-1 Extended Target Analyte List for Soil Gas and Indoor Air Samples

Hydrocarbon	CAS Number	Reporting Limit RL	
ppbV			
n-alkanes			
	Butane	106-97-8	5
	Pentane	109-66-0	2
Petrol.	Hexane	110-54-3	2
	Heptane	142-82-5	2
	Octane	111-65-9	2
	Nonane	111-84-2	2
	Decane	124-18-5	2
	Undecane	1120-21-4	2
branched alkanes			
	2,4-Dimethylpentane	108-08-7	2
	2,2-Dimethylbutane	75-83-2	5
	3-Methylhexane	589-34-4	2
	2,3-Dimethylbutane	79-29-8	2
	2-Methylheptane	592-27-8	2
	2-Methylhexane	591-76-4	5
	2-Methylpentane	107-83-5	2
	3-Methylpentane	96-14-0	2
	Isobutane	75-28-5	5
	3-Methylheptane	589-81-1	2
	2,3,4-Trimethylpentane	565-75-3	2
Petrol.	Isopentane	78-78-4	5
	2,3-Dimethylpentane	565-59-3	2
	2,2,4-Trimethylpentane	540-84-1	5
cycloalkanes			
	Cyclopentane	287-92-3	2
	Methylcyclopentane	96-37-7	5
	2,3-Dimethylhexane	584-94-1	2
	2,5-Dimethylhexane	592-13-2	2
	2,2,5-Trimethyl-hexane	3522-94-9	2
Petrol.	Cyclohexane	110-82-7	2
	Methylcyclohexane	108-87-2	2
Alkenes, alkynes & diolefins			
0.5			
	cis-2-Butene	590-18-1	2
	cis-2-Pentene	627-20-3	2
	1-Pentene	109-67-1	2
	1-Butene	106-98-9	5
	trans-2-Pentene	646-04-8	2
	1-Hexene	592-41-6	5
	Isoprene	78-79-5	2
	trans-2-Butene	624-64-6	2
Aromatics & heterocycles			
	2-Ethyltoluene	611-14-3	2
	Propylbenzene	103-65-1	5
	1,3-Diethylbenzene	141-93-5	2
	m,p-Xylene	136777-61-2	2
	1,4-Diethylbenzene	105-05-5	2
	4-Ethyltoluene	622-96-8	5
	Benzene	71-43-2	2
MGP	Thiophene	110-02-1	2
	Toluene	108-88-3	2
	Ethyl benzene	100-41-4	2
	o-Xylene	95-47-6	2
MGP	Styrene	100-42-5	2
	3-Ethyltoluene	620-14-4	5
	Cumene	98-82-8	5
	1,3,5-Trimethylbenzene	108-67-8	2
	1,2,4-Trimethylbenzene	95-63-6	2
	1,2,3-Trimethylbenzene	526-73-8	2
	Indane	496-11-7	2
MGP	Indene	95-13-6	5
	Naphthalene	91-20-3	2

5 Quality Assurance/Quality Control

All samples collected during this program will be analyzed using a laboratory that has a current NYS Environmental Laboratory Approval Program (ELAP) certification for air, water and soil analyses. The remainder of this section discusses the data quality objectives for this program.

5.1 General Precautions

To prevent sampling interference, sampling personnel will not pump gasoline or use permanent marking pens during the sampling days (NYSDOH, 2001). All other similar activities will be avoided and extreme care will be taken to ensure that high quality data are obtained.

5.2 Indoor, Ambient and Soil Gas Air

All site sampling will be conducted using standard operating procedures (SOPs) prepared for indoor, ambient or soil gas air. Detailed information on the time and location will be collected for each sample and the information will be recorded on the building information form. Once samples are collected they will be stored according to the method protocol and delivered to the analytical laboratory as soon as possible. Samples should not exceed recommended holding times prior to being processed by the laboratory. Laboratory procedures for sample accession and chain of custody will be followed.

The outdoor barometric air pressure and temperature will be collected at the beginning, midpoint and end of each workday at the site location. For indoor air samples, the indoor air temperature will be recorded at the time of sample collection. One quality control duplicate will be collected from a location selected in the field for every 10 samples collected or every sampling day during which less than 10 samples are collected. One field blank will be collected for every sampling event. All data will be documented on standard chain of custody records, field data sheets or site log books according to the sampling SOPs.

All instrumentation will be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the sampling plan SOP. Equipment checkout and calibration activities must occur prior to site sampling and must be documented. All canisters shall be certified clean by GC/MS analysis before being used in the field. Certification of cleaning and evacuation will be noted prior to collection of samples. A vacuum gauge will be used to check both the initial and final vacuum in the canisters. The initial vacuum prior to use will be checked to ensure mechanical integrity of the canister, and should be approximately 30 inches mercury (in Hg). The

final vacuum should read from approximately 2 to 10 in Hg. Site name, sample location, number, and date will be recorded on a chain of custody form and on a blank tag attached to the canister. Sample holding times for canisters is 14-days.

If property access and scheduling permit, the soil gas sampling will be performed after the on-site borings have been performed, so that the soil and water conditions have been established, as described in Section 3. This will also aid in the interpretation of data collected from any basement sump water samples obtained during the investigation.

5.3 Sump Water

All site sampling will be conducted using standard operating procedures (SOPs) prepared for collection of indoor sump waters. Detailed information on the time and location will be collected for each sample and will be recorded on the building information form. Once samples are collected they will be stored according to the method protocol and delivered to the analytical laboratory as soon as possible. Samples will not exceed recommended holding times prior to being processed by the laboratory. Laboratory procedures for sample accession and chain of custody will be followed.

5.4 Hydrocarbon Fingerprint Characterization

Characterization of the volatile hydrocarbon fingerprint associated with MGP residuals in the subsurface may be performed on a sample of NAPL or heavily contaminated soil collected from the saturated or vadose zone near the MGP source. The purpose of this analysis is to confirm the identity of constituents of volatile organic compounds that have the potential to volatilize and migrate into buildings. The procedures for this characterization, as described in this section, are in development and are subject to change.

One sample of NAPL or heavily contaminated soil will be collected from each of three borings or monitoring wells at a site. Product samples will be collected using disposable polyethylene bailers or soil samples will be collected from borings according to the procedures specified in the contractors SOP. Glass sample jars (250-ml) will be completely filled with the NAPL or soil, allowing no headspace above the sample in which constituents could volatilize. Samples will then be shipped to an approved analytical laboratory for advanced forensic hydrocarbon analysis.

Headspace analysis will be conducted using a chamber maintained at constant temperature of 50°C (122°F) to maximize volatilization from the product into the headspace. This will provide an overly conservative, “worst case” volatilization scenario, since subsurface temperatures are typically 5° to 12° C (40° to 55° F). The 50-g sample will be placed in a 1.5-liter jar and the

volatile components will be allowed to come to static equilibrium with the jar headspace. The jar will then be evacuated using 1-liter Summa canister using ultra-high purity nitrogen for purging.

6 Interpretation of Results and Reporting

6.1 Limitations

The screening program described in this Work Plan is designed to provide rapid initial assessments of vapor intrusion. The interpretation of results and the conclusions drawn will therefore be considered tentative until the Preliminary Site Assessments for the MGP sites are completed and a more comprehensive understanding of the site conditions is established. In some cases, additional investigation may be necessary. For example, if groundwater levels fluctuate greatly at a specific site and are at a seasonal low point during soil gas sampling, it may be important to conduct additional soil gas sampling in six or nine months to obtain data during the seasonally high groundwater condition.

6.2 Evaluation of Soil Gas Sampling Results

Soil gas sampling results will be evaluated in comparison to New York State indoor air concentrations of indicator constituents. The New York State indoor air concentrations are provided in Table 6-1. This evaluation will be used to determine if indoor air sampling is warranted. Site-specific factors, such as preferential pathways, subsurface stratigraphy, and depth to groundwater will be taken into account in this evaluation, so that appropriate and representative soil gas results are used to make this determination.

In some cases, mathematical modeling will be used in lieu of indoor air sampling to estimate indoor air concentrations. This method will be especially useful where access for indoor air sampling is not granted by the owner, and where obvious non-MGP sources of hazardous vapors are anticipated to confound indoor air sampling results. Additional evaluation of adjacent properties may also include the use of modeling to guide the investigation and determine priorities. The Johnson and Ettinger mathematical model, with site specific inputs, will be used (EPA, 2001).

It should be noted that at some sites, physical and biological attenuation of soil gas concentrations appears to be significant, resulting in a thousand-fold decrease in benzene concentrations through as little as two vertical feet of vadoze zone immediately beneath a building (Fischer, et al, 1996). Lateral attenuation has also been observed (EPA, 2001). Therefore, elevated soil gas concentrations at an MGP site do not necessarily indicate vapor intrusion into nearby buildings.

6.3 Evaluation of Indoor Air Sampling Results

The evaluation of indoor air sampling results is complicated by the presence of multiple sources of hydrocarbons that are similar to those associated with MGP impacts. If indoor air sampling results show that indoor air concentrations of hazardous indicator constituents are above typical New York State indoor air concentrations, and multiple sources are suspected, then a forensic examination of the laboratory data will be conducted. Identification of sources and allocation of concentrations will be attempted, as described in Sections 4 and 5, to determine whether or not the concentrations of hazardous indicator constituents associated with MGP impacts exceed the median New York State indoor air concentrations

6.4 Reporting

Con Edison will provide copies of the laboratory data generated under this Work Plan upon receipt of the data to the NYSDEC, NYSDOH, NYCDOH, NYC Board of Education and other appropriate stakeholders. The results of the vapor intrusion assessments at each targeted MGP site will then be summarized in a report to be submitted to the NYSDEC, NYSDOH, NYCDOH, NYC Board of Education and other appropriate stakeholders. The report will include the completed building inspection forms, sampling logs, analytical laboratory reports, and data evaluation procedures and recommendations.

7 Potential Mitigation Measures

While it is beyond the scope of this Work Plan to develop detailed plans for mitigation measures, this section lists actions which can be taken if it is deemed necessary to decrease concentrations of MGP-related vapors inside buildings.

Potential mitigation measures include removal or containment of the source(s) of MGP-related vapors, placement of vapor barrier materials in the building, installing or modifying the building ventilation system, and depressurization of the soil in the vadoze zone beneath and/or adjacent to the building.

8 References

- Fisher, et al, 1996. Factors Affecting Indoor Air Concentrations of Volatile Organic Compounds at a Site of Subsurface Gasoline Contamination. Environ. Sci. Technol. 1996, Vol 30, No. 10. 2948-2957.
- NYSDOH, 2001. Indoor Air Sampling & Analysis Guidance, New York State Department of Health, August 8, 2001.
- U.S. EPA, 1992. Assessing Potential Indoor Air Impacts for Superfund Sites, United States Environmental Protection Agency.
- U.S. EPA, 2001. User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapor Intrusion into Buildings (Revised). Office of Emergency and Remedial Response. December.

Appendix A

Indoor Air Quality Questionnaire and Building Inventory Forms

NEW YORK STATE DEPARTMENT OF HEALTH
DIVISION OF ENVIRONMENTAL HEALTH ASSESSMENT
BUREAU OF TOXIC SUBSTANCE ASSESSMENT

INDOOR AIR QUALITY QUESTIONNAIRE AND BUILDING INVENTORY

This form must be completed for each residence involved in indoor air testing.

Preparer's Name _____ Date Prepared _____

Preparer's Affiliation _____ Phone No. _____

1. OCCUPANT

Name: _____

Address: _____

County: _____

Home Phone No. _____ Office Phone No _____

2. OWNER OR LANDLORD:

(If different than occupant)

Name: _____

Address: _____

Phone No. _____

A. Building Construction Characteristics

Type (circle appropriate responses): Single Family Multiple Dwelling Commercial

Ranch
Raised Ranch
Split Level
Colonial
Mobile Home

2-Family
Duplex
Apartment House _____ Units
Number of floors _____
Other specify _____

Residence Age _____ General Description of Building Construction Materials _____

Is the building insulated? Yes / No How air tight is the building _____

OSR-3 (continued)

B. Basement construction characteristics (circle all that apply):

1. Full basement, crawlspace, slab on grade, other _____
2. Basement floor: concrete, dirt, other _____
3. Concrete floor: unsealed, painted, covered; with _____
4. Foundation walls: poured concrete, block, laid up stone, other _____
5. The basement is: wet, damp, dry _____ Sump present? y / n _____ Water in sump? y / n _____
6. The basement is: finished, unfinished _____
7. Identify potential soil vapor entry points (e.g., cracks, utility ports, etc.)

8. Describe how air tight the basement is _____

C. HVAC (circle all that apply):

1. The type of heating system(s) used in this residence is/are:
Hot Air Circulation Heat Pump
Hot Water Radiation Unvented Kerosene Heater
Steam Radiation Wood stove
Electric Baseboard Other (specify) _____
2. The type(s) of fuel(s) used is/are: Natural Gas, Fuel Oil, Electric, Wood, Coal Solar
Other (specify) _____.
3. Is the heating system's power plant located in the basement or another area: _____.
4. Is there air-conditioning? Yes / No Central Air or Window Units?
Specify the location _____
5. Are there air distribution ducts present? Yes / No
6. Describe the supply and cold air return duct work in the basement including whether there is a cold air return, the tightness of duct joints

OSR-3 (continued)

D. Potential Indoor Sources of Pollution

1. Has the house ever had a fire? Yes / No
2. Is there an attached garage? Yes / No
3. Is a vehicle normally parked in the garage? Yes / No
4. Is there a kerosene heater present? Yes / No
5. Is there a workshop, hobby or craft area in the residence? Yes / No
6. An inventory of all products used or stored in the home should be performed. Any products that contain volatile organic compounds or chemicals similar to the target compounds should be listed. The attached product inventory form should be used for this purpose.
7. Is there a kitchen exhaust fan? Yes / No Where is it vented? _____
8. Has the house ever been fumigated? If yes describe date, type and location of treatment.

E. Water and Sewage (Circle the appropriate response)

Source of Water

Public Water Drilled Well Driven Well Dug Well Other (Specify) _____

Water Well Specifications:

Well Diameter _____ Grouted or Ungouted _____
Well Depth _____ Type of Storage Tank _____
Depth to Bedrock _____ Size of Storage Tank _____
Feet of Casing _____ Describe type(s) of Treatment _____

Water Quality:

Taste and/or odor problems? y / n If so, describe _____

How long has the taste and/or odor been present? _____

Sewage Disposal: Public Sewer Septic Tank Leach Field Other (Specify) _____

Distance from well to septic system _____ Type of septic tank additive _____

OSR-3 (continued)

F. Plan View

Draw a plan view sketch for each floor of the residence and if applicable, indicate air sampling locations, possible indoor air pollution sources and PID meter readings.

OSR-3 (continued)

G. Potential Outdoor Sources of Pollution

Draw a sketch of the area surrounding the residence being sampled. If applicable, provide information on the spill location (if known), potential air contamination sources (industries, gas stations, repair shops, landfills, etc.), outdoor air sampling location(s) and PID meter readings.

Also indicate compass direction, wind direction and speed during sampling, the locations of the well and septic system if applicable, and a qualifying statement to help locate the site on a topographical map.

Household Products Inventory

Occupant / residence _____

Investigator: _____ Date: _____

Product description (dispenser, size, manufacturer ...)	VOC Ingredients	PID Reading

Appendix B

ASTM Method D5314-92

Standard Guide for Soil Gas Monitoring in the Vadose Zone¹

This standard is issued under the fixed designation D 5314; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers information pertaining to a broad spectrum of practices and applications of soil atmosphere sampling, including sample recovery and handling, sample analysis, data interpretation, and data reporting. This guide can increase the awareness of soil gas monitoring practitioners concerning important aspects of the behavior of the soil-water-gas-contaminant system in which this monitoring is performed, as well as inform them of the variety of available techniques of each aspect of the practice. Appropriate applications of soil gas monitoring are identified, as are the purposes of the various applications. Emphasis is placed on soil gas contaminant determinations in certain application examples.

1.2 This guide suggests a variety of approaches useful to successfully monitor vadose zone contaminants with instructions that offer direction to those who generate and use soil gas data.

1.3 This guide does not recommend a standard practice to follow in all cases nor does it recommend definite courses of action. The success of any one soil gas monitoring methodology is strongly dependent upon the environment in which it is applied.

1.4 Concerns of practitioner liability or protection from or release from such liability, or both, are not addressed by this guide.

1.5 This guide is organized into the following sections and subsections that address specific segments of the practice of monitoring soil gas:

Section

4	Summary of Practice
4.1	Basic principles, including partitioning theory, migration and emplacement processes, and contaminant degradation
4.7	Summary Procedure
5	Significance and Use
6	Approach and Procedure
6.1	Sampling Methodology
6.5	Sample Handling and Transport
6.6	Analysis of Soil Gas Samples
6.7	Data Interpretation
7	Reporting

1.6 *This guide does not purport to set standard levels of acceptable risk. Use of this guide for purposes of risk assessment is wholly the responsibility of the user.*

¹ This guide is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Ground Water and Vadose Zone Investigations.

Current edition approved Nov. 15, 1992. Published January 1993.

1.7 The values stated in either inch-pound or SI units are to be regarded separately as the standard. The values given in parentheses are for information only.

1.8 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

2. Referenced Documents

2.1 ASTM Standards:

- D 653 Terminology Relating to Soil, Rock, and Contained Fluids²
- D 1356 Terminology Relating to Atmospheric Sampling and Analysis³
- D 1357 Practice for Planning the Sampling of the Ambient Atmosphere³
- D 1452 Practice for Soil Investigation and Sampling by Auger Borings²
- D 1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors³
- D 1914 Practice for Conversion Units and Factors Relating to Atmospheric Analysis³
- D 2652 Terminology Relating to Activated Carbon⁴
- D 2820 Test Method for C₁ Through C₅ Hydrocarbons in the Atmosphere by Gas Chromatography³
- D 3249 Practice for General Ambient Air Analyzer Procedures³
- D 3416 Test Method for Total Hydrocarbons, Methane, and

² *Annual Book of ASTM Standards*, Vol 04.08.

³ *Annual Book of ASTM Standards*, Vol 11.03.

⁴ *Annual Book of ASTM Standards*, Vol 15.01.

Carbon Monoxide (Gas Chromatographic Method) in the Atmosphere³

D 3584 Practice for Indexing Papers and Reports on Soil and Rock for Engineering Purposes²

D 3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions³

D 3670 Guide for Determination of Precision and Bias of Methods of Committee D-22³

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)³

D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method³

D 4220 Practices for Preserving and Transporting Soil Samples²

D 4490 Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes³

D 4597 Practice for Sampling Workplace Atmospheres to Collect Organic Gases or Vapors with Activated Charcoal Diffusional Samplers³

D 4696 Guide for Pore-Liquid Sampling from the Vadose Zone²

D 4700 Guide for Soil Core Sampling from the Vadose Zone²

D 5088 Practice for the Decontamination of Field Equipment Used at Non Radioactive Waste Sites⁵

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods⁶

E 260 Practice for Packed Column Gas Chromatography⁷

E 355 Practice for Gas Chromatography Terms and Relationships⁷

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography⁷

E 697 Practice for Use of Electron-Capture Detectors in Gas Chromatography⁷

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *capillary fringe*—the basal region of the vadose zone comprising sediments that are saturated, or nearly saturated, near the water table, gradually decreasing in water content with increasing elevation above the water table. Also see Terminology D 653.

3.1.2 *contaminant*—substances not normally found in an environment at the observed concentration.

3.1.3 *emplacement*—the establishment of contaminant residence in the vadose zone in a particular phase.

3.1.4 *free product*—liquid phase contaminants released into the environment.

3.1.5 *free vapor phase*—a condition of contaminant residence in which volatilized contaminants occur in porosity that is effective to free and open gaseous flow and exchange, such porosity generally being macroporosity.

3.1.6 *liquid phase*—contaminant residing as a liquid in vadose zone pore space, often referred to as “free product.”

3.1.7 *macroporosity*—large intergranular porosity with large pore throats, including soil cracks, moldic porosity, animal burrows and other significant void space.

3.1.8 *microporosity*—intragranular porosity and microscopic intergranular porosity with submicroscopic pore throats.

3.1.9 *occluded vapor phase*—condition of contaminant residence in which volatilized contaminants occur in porosity that is ineffective to free and open gaseous flow and exchange, such porosity generally being microporosity; frequently termed dead-end pore space.

3.1.10 *partitioning*—the act of movement of contaminants from one soil residence phase to another.

3.1.11 *soil gas*—vadose zone atmosphere.

3.1.12 *solute phase*—a condition of contaminant residence in which contaminants are dissolved in ground water in either the saturated or the vadose zone.

3.1.13 *sorbed phase*—a condition of contaminant residence in which contaminants are adsorbed onto the surface of soil particles or absorbed by soil organic matter.

3.1.14 *vadose zone*—the hydrogeological region extending from the soil surface to the top of the principal water table.

4. Summary of Guide

4.1 Soil gas monitoring in the vadose zone is a method used to directly measure characteristics of the soil atmosphere that are frequently utilized as an indirect indicator of processes occurring in and below a sampling horizon. Soil gas monitoring is used as a method to suggest the presence, composition, and origin of contaminants in and below the vadose zone. Among other applications, this method is also employed in the exploration for natural resources, including petroleum, natural gas and precious metals. Soil gas monitoring is a valuable screening method for detection of volatile organic contaminants, the most abundant analytical group of ground-water contaminant compounds (1).⁸

4.2 *Basic Theoretical Principles*—The processes indicated by the soil gas monitoring method are partitioning, migration, emplacement and degradation. Partitioning represents a group of processes that control contaminant movement from one physical phase to another, these phases being liquid, free vapor (that is, through-flowing air (2)), occluded vapor (that is, locally accessible air and trapped air (2)), solute and sorbed. Migration refers to contaminant movement over distance with any vertical, horizontal or temporal component. Emplacement refers to establishment of contaminant residence in any phase within any residence opportunity. Degradation is the process whereby contaminants are attenuated by oxidation or reduction in the vadose zone, either through biogenic or abiogenic processes. Soil gas monitoring measures the result of the interaction of these processes in a dynamic equilibrium. Measurement of these processes in static equilibrium is unrealistic.

4.3 The following subsections provide detailed information

⁵ Annual Book of ASTM Standards, Vol 04.09.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Annual Book of ASTM Standards, Vol 14.01.

⁸ The boldface numbers given in parentheses refer to a list of references at the end of the text.

on partitioning, migration, emplacement and degradation. Sub-section 4.4 provides a summary procedure for soil gas sampling. Users of this guide who do not wish to study details of partitioning, migration, emplacement and degradation at this time may skip to 4.4.

4.3.1 Partitioning is the initial step by which contaminants begin to move away from their source. Partitioning occurs in water saturated and unsaturated environments. This group of processes is complex and difficult to quantify when considered in the vadose zone due to the unique makeup of the vadose matrix, i.e. air-filled porosity (microporous and macroporous), pore water, free product, solid-phase soil organic matter, clay and discrete inorganic soil particles. Important individual processes of partitioning are dissolution, volatilization, air-water partitioning, soil-water partitioning and soil-air partitioning (3).

4.3.2 Dissolution is the process whereby volatile contaminants move between the liquid phase (free product) and the solute phase (dissolved in water). At equilibrium, the product of the mole fraction of a particular compound in the liquid phase and the activity coefficient of that compound in the liquid phase is equal to the product of the mole fraction of that compound in the solute phase and the activity coefficient of that compound in the solute phase. This process is more clearly described by the following expression:

$$X_I^L \Gamma_I^L = X_I^W \Gamma_I^W \quad (1)$$

where:

X_I^L = the mole fraction of compound (I) in the liquid (L) phase (free product),

X_I^W = the mole fraction of compound (I) in the solute (W) phase (dissolved in water),

Γ_I^L = the activity coefficient of compound (I) in the liquid (L) phase (free product), and

Γ_I^W = the activity coefficient of compound (I) in the solute (W) phase (dissolved in water).

Dissolution equilibrium is therefore influenced by concentration of the subject compound in both the free product contaminant mixture and water. The most common practical application of expression (Eq 1) in soil gas monitoring is in hydrocarbon detection. Simplification of (Eq 1) is achieved by the following:

assume:

$$\Gamma_I^W = 1/S_I,$$

where:

S = the solubility of compound (I) in water

and:

$\Gamma_I^L = 1$, acceptable for hydrocarbons (3),

then:

$$X_I^W = X_I^L S_I \quad (2)$$

4.3.2.1 Dissolution equilibrium is impacted by the presence of liquid phase cosolvents, such as gasoline additives, at low concentrations in liquid phase mixtures. This change in dissolution equilibrium can enhance the solubility of certain liquid phase components in water beyond what is indicated by partitioning coefficient data generated in the laboratory. This can have significant impact on downstream concentrations of the contaminant(s) in the soil atmosphere.

4.3.2.2 The effects of temperature upon dissolution equilibrium are generally insignificant for aliphatic hydrocarbons between 15 and 50°C (4), the temperature range from which most soil gas samples are recovered. However, temperature effects upon dissolution equilibrium can be significant for other common families of contaminant compounds within similar temperature ranges (5). These effects must be considered when planning or interpreting the results of a soil gas survey.

4.3.2.3 Dissolution equilibrium is altered by changes in water salinity. Modest decreases in the solubility of contaminants in water are to be expected with increases in salinity of the solution.

4.3.2.4 The rate of dissolution is strongly dependent upon the partitioning coefficient of the particular contaminant of interest and the amount of mixing of the liquid phase and water (3). For example, partitioning of a particular contaminant into ground water is accelerated by frequent water level fluctuations within a contaminated capillary fringe. The downstream implications for subsequent partitioning of the contaminant from the solute to the vapor phase for eventual soil gas recovery are obvious.

4.3.3 Volatilization is the process during which volatile contaminants move between the liquid phase (free product) or solute phase and a vapor phase, either the free vapor phase or the occluded vapor phase or both. Contaminant mixtures can contain compounds with a considerable range of vapor pressures that can contribute contaminants to the soil atmosphere by volatilization. This atmosphere will exhibit a composition similar to that of the parent contaminant but lacking in those constituents with the lowest vapor pressures. The likelihood of the presence of a particular contaminant introduced into the soil atmosphere by volatilization can be estimated by considering the partial pressure of that contaminant in a vapor phase. This partial pressure is equal to the product of the mole fraction concentration of the subject component in the liquid contaminant solution, the activity coefficient of the subject component and the vapor pressure of the pure component. This concept is more clearly expressed as follows:

$$P = X_I \Gamma_I P^o \quad (3)$$

where:

P = the partial pressure of the subject contaminant compound in the vapor phase,

X_I = the mole fraction concentration of contaminant (I) in the liquid contaminant solution,

Γ_I = the activity coefficient of the subject contaminant in the liquid contaminant solution, and

P^o = the vapor pressure of the pure component.

4.3.3.1 The quantity of contaminant volatilized into a vapor phase and the rate of that process is strongly dependent upon temperature. Rate of volatilization is also controlled by the rate of transport of contaminant vapors from the liquid phase-vapor phase interface (3). This rate is probably higher when macroporous flow paths are available for vapor phase transport, and is promoted by a number of driving forces. These are concentration gradient, density gradient between soil atmosphere and contaminant-saturated soil atmosphere, convection currents related to temperature gradient, barometric pressure

pumping and introduction of water onto the liquid phase-vapor phase interface.

4.3.4 Air-water partitioning is the process by which volatile contaminants move between the solute phase and a vapor phase, either the free vapor phase or the occluded vapor phase or both. For dilute solutions, air-water partitioning is controlled by Henry's law, which states that the vapor pressure of a volatile compound above a dilute aqueous solution of that compound is equal to the product of the Henry's law constant and the mole fraction of that compound in the aqueous solution. Henry's law may be represented as:

$$P_I = kX_{I(aq)} \quad (4)$$

where:

P_I = vapor pressure of compound (I) above a dilute aqueous solution of (I),

k = the Henry's law constant for compound (I) at a given temperature, and

$X_{I(aq)}$ = the mole fraction of the subject contaminant compound in the aqueous solution.

Care must be exercised in using Henry's law to approximate contaminant vapor pressures because of unknowns related to the concentration of contaminants in solution and the contribution of other partitioning processes. Some available literature pertaining to soil gas surveying places emphasis on Henry's law constant at 25°C and atmospheric pressure as a primary controlling factor in determining the suitability of a particular volatile contaminant to the soil gas monitoring method. Such emphasis may be inappropriate when, for example, free product is the source of contaminant vapors or when contaminants have not reached ground water. Care must also be exercised in noting the units in which Henry's law constants are expressed, as these vary from source to source. Volatile but very highly water soluble compounds behaving according to Henry's law may not be detectable in soil gas because of their persistence for residence in the solute phase (6).

4.3.5 Soil-water partitioning is the process by which volatile contaminants move between the sorbed phase and the solute phase. This process is generally underestimated in its importance to the success or failure of contaminant recovery by soil gas sampling, especially when utilizing the majority of active soil gas sampling techniques generally available to field personnel.⁹ There is uncertainty with respect to factors controlling soil-water partitioning, creating doubt as to the reliability of soil sorption data in most applications. Problems with soil sorption data include variability in measurement protocols, the variable nature of organic matter in soils, the effect of dissolved organic matter, unusual pH effects and the effect of salinity, among others (3).

4.3.5.1 The contribution of soil-water partitioning to contaminant phase residence equilibria is strongly controlled by sorbed contaminant concentration in soil, soil makeup, vadose zone pore water content, and soil porosity configuration. Important variables in soil makeup are the quantity, type and distribution of clay in soil and the quantity, type and distribu-

tion of soil organic matter. These variables impact the surface area available to sorptive processes, that is, the storage capacity of the soil for contaminants in the sorbed phase, and the pH of the sorption environment. Variations in vadose zone pore water content directly affect the storage capacity of the soil for contaminants in the solute phase. Soil porosity configuration, principally microporosity versus macroporosity, is critical to the rate of soil-water partitioning due to the contrast in surface area between micropores and macropores and the related storage capacity of this porosity for both pore water and sorbed contaminants.

4.3.6 Soil-air partitioning is the process by which volatile contaminants move between the sorbed phase and a vapor phase, either the free vapor phase or the occluded vapor phase or both. Like soil-water partitioning, this process is underestimated in its importance to the recoverability of contaminants by many soil gas sampling techniques. In vadose zone horizons with very low pore water contents, soil-air partitioning can yield vapor phase contaminant composition that differs from free product composition. In vadose zone horizons with higher pore water content, the responsibility for this compositional inconsistency is shared, largely with soil-water partitioning. In wet soil conditions, threshold soil water content values exist for trapped soil atmosphere content to become significant (7), suggesting that responsibility for this compositional inconsistency can be largely attributed to occluded phase residence. Additional important variables are soil clay content, type and distribution, and soil organic matter content, type and distribution. Studies have demonstrated significant impact of soil organic matter and clay content on volatile organic compound emissions from soils (8). Due to the strong control on vapor phase contaminant content by the soil-air partitioning process, it is unreasonable to expect soil contaminants with high affinity for sorption to be efficiently recovered by most soil gas sampling techniques.

4.4 Migration of contaminants in the vadose zone, that is, unsaturated flow, is highly complex and is controlled by soil characteristics, contaminant composition and contaminant phase (9). Migration through unsaturated matrix can occur through a variety of diffusion, dispersion and mass transport mechanisms which behave in a manner unique to saturated flow.

4.4.1 A major division in migratory behavior of contaminants is defined by their solubility or immiscibility in water. Contaminants are often introduced into the soil as liquid mixtures, the components of which immediately begin to partition into other phases upon soil entry. Contaminants that establish soil residence behind a migratory front change in composition with distance from their point of entry. As contaminant migration continues, pathways for individual components can become divergent, such that the composition of the liquid mixture continues to change as migration proceeds. Eventually, migration of liquid mixtures may reach ground water. This can be retarded if the contaminants partition into other phases before reaching ground water and if contaminant vapor is less dense than the uncontaminated soil atmosphere. Transport of contaminants by downward percolation of meteoric waters and upward movement of ground water

⁹ See 6.2 for a discussion of active soil gas sampling techniques.

accelerate the contact of contaminants with ground water. When these contaminants do reach ground water, a radically different set of migration mechanisms begins to govern contaminant transport via saturated flow. Further divergence of contaminant pathways is dependent upon the tendency of each component of the contaminant mixture to float on ground water, become dissolved in ground water or sink to an impermeable layer within the aquifer. Detailed descriptions of these phenomena are available in the literature (10).

4.4.2 The impact of migration processes on soil gas measurement is significant. Although it is impractical to estimate actual migration mechanisms by modelling prior to most soil gas monitoring efforts, a rudimentary knowledge of site characteristics can guide investigators to realistic interpretations of soil gas data expressing unusual or highly variable compositions. More thorough knowledge of relevant site characteristics, such as the presence or absence of barriers to vertical or horizontal migration, that is, foundations, buried pavement, or perched ground water, as well as preferential pathways for contaminant migration, that is, backfill rubble, utility vaults, storm sewers or soil cracks, can assist investigators to assess the migration impact on soil gas survey design.

4.5 The vadose zone is a highly complex soil-air-water-hydrocarbon system with abundant opportunity to store contaminants in all phases. Contaminants partition according to their physical properties and the residence opportunity presented to them along their migratory path. This process has been described as an *in situ* chromatographic-like separation of contaminants (11). Emplacement, or the establishment of contaminant residence, is a highly dynamic process. Contaminants move from one phase to another as changes occur in both chemical and physical equilibria. Important changes impacting phase residence change include temporal variations in moisture content, soil temperature and level of microbial activity.

4.5.1 One interesting example of disruption in equilibrium conditions is the act of sampling soil gas. Many soil gas sampling systems rely on large volume recovery of soil gas to provide a sample that is believed to be representative of the soil atmosphere *in situ*. Movement of this soil gas by convective flow through unsaturated soils can cause upward changes in vapor phase contaminant concentration at the expense of other phases.

4.5.2 In natural systems, temporal increases in soil moisture cause gradual increases in solute phase emplacement at the expense of other phases. It is unrealistic to attempt to characterize a static soil gas equilibrium in the vadose zone because this equilibrium is never achieved. For this reason, soil gas data sets based on specific contaminant concentrations and generated at different times are usually not comparable for the absolute values generated by each temporal sampling event. Qualitative comparison of data generated by the same soil gas method and performed at different times is permissible. Generation of a single data set by reconnaissance soil gas sampling and subsequent infilling of data to form a single data set is strongly discouraged.

4.5.3 Attempts to compensate for temporal variations in phase equilibria have been attempted by collecting samples that approximate replicates at known locations and adjusting

succeeding data up or down to compensate for observed changes. This procedure is also strongly discouraged, because the number of variables affecting observed changes are too great. Moreover, the ability or willingness of most investigators to determine the most significant effects upon phase equilibria is insufficient to be of use.

4.5.4 Data sets generated by different soil gas sampling techniques may not be comparable as a direct result of differences in efficiency of recovery of contaminants from specific phases. Not only can these data sets differ in measured contaminant concentration, but they can vary substantially in composition as well.

4.6 Degradation of contaminants occurs in the vadose zone through oxidation or reduction reactions that can be biogenic or abiogenic in nature. This process can occur both aerobically and anaerobically to mitigate contaminant levels. Degradation is most often recognized in shallow, permeable soils where favorable conditions exist for oxidation of labile compounds, however other vadose environments can be conducive to degradation. Specific environmental conditions are required for degradation processes to occur. For abiogenic degradation, redox potential and soil pH can be rate controlling factors. For biodegradation, necessary environmental conditions include the presence of microorganisms capable of adaptation to the contaminant as substrate, conditions favorable to population increases of these microorganisms and migration pathways for contaminants to come in contact with these microorganisms. Most soils contain naturally occurring populations of various microorganisms that can degrade petroleum products (12). Contaminant biodegradation is known to occur in ground water (13) and in soils (14) prior to contaminant partitioning into a vapor phase. Contaminant biodegradation rates for some compounds are highly variable and are controlled by a number of kinetic factors influencing the distribution of microorganisms responsible for degradation. These include aerobic versus anaerobic environments, contaminant type and temperature (15, 16).

4.6.1 Degradation rate can approach, equal or periodically exceed the rate of contaminant emplacement into the vadose zone, such that contaminants are not detectable by soil gas monitoring. This mechanism can result in soil gas data which are not representative of an underlying contaminated condition (17).

4.6.2 Labile contaminants can be degraded to compounds that may or may not be detectable in soil gas. Aerobic degradation can produce carbon dioxide which can be monitored as an indirect indicator of the presence of contaminants (18), or organic acids and phenols (13) that are not routinely detectable in active whole air soil gas samples. In alternative to whole air methods, use of an appropriate adsorption medium may facilitate recovery of such compounds for analysis by desorption and gas chromatography-mass spectroscopy. Anaerobic degradation can produce compounds including methane, ethylene, propylene, acetylene, and vinyl chloride which also can be monitored as an indirect indicator of the presence of contaminants. Caution must be used in attributing elevated levels of these compounds to biodegradation, because

competitive processes can confuse the interpretation of absolute concentration values and potential sources.

4.6.3 Biodegradation of contaminants in the vadose zone can proceed naturally by adaptation of indigenous microbial populations to metabolize contaminants as primary substrate, or by introduction of foreign populations which have been preconditioned to metabolize contaminants of interest. Case histories demonstrate the absence of certain compounds in soil gas contaminant suites for which biodegradation has been named as the responsible process (17, 19, 20). Such cases address the attenuation or complete absence of simple aromatic hydrocarbons, some of which are halogenated, in soil gas. This phenomenon may be controlled by the availability of oxygen as has been demonstrated in the laboratory (13). Other compound classes can exhibit similar effects.

4.6.4 Other processes may share responsibility for the actual or apparent absence or attenuation of some contaminants in soil gas sample sets. In some cases where attenuation of contaminant concentration is attributed to degradation, combinations of high soil clay, organic matter and pore water content can reduce the recovery efficiency of certain soil gas sampling techniques for certain contaminants such that contaminant concentrations fall below detection limits. Care must be exercised in attributing a lack of contaminants in soil gas samples to degradation.

4.7 Summary Procedure for Soil Gas Sampling—Vadose zone monitoring methods have a set of procedures, both general and specific, that must be consistently followed in order to provide maximum data quality and usefulness. Soil gas monitoring is no exception, with six primary procedures common to all soil gas monitoring techniques. The procedures are a planning and preparation step including definition of data quality objectives, the act of sampling soil gas in the field, handling and transporting the sample, sample analysis, interpretation of the results of analysis, and preparation of a report of findings.

4.7.1 The planning and preparation step begins with the formulation of project objectives, including purpose of the survey, appropriate application of the data to be collected and data quality objectives.

4.7.2 Data can vary in quality due to sampling methodology, sample preparation, analytical procedures, laboratory quality control, and available documentation. Quality assurance programs include all of the activities necessary to provide measurement data at a requisite precision and bias (see Practice 1357). Quality assurance objectives for soil gas monitoring are similar to those for atmospheric air monitoring. The overall quality assurance objective for measurement data is to ensure that data of known and acceptable quality are provided. In order to meet these objectives, data quality objectives should be defined for data measurements in support of the soil gas data interpretation. These are comparability, completeness, representativeness, bias and precision. The comparability of the data collected refers to the ability to interpret the results in light of previous data collection efforts. Completeness refers to the number of samples collected and analyzed compared to the planned number of samples. Representativeness is a measure of the degree to which analytical results reflect true field

conditions. Field contamination and sampling intensity are two factors affecting representativeness. Bias is a generic concept of exactness related to the closeness of agreement between the average of one or more test results and an accepted reference value (see Practice E 177). The precision of a measurement process is a generic concept related to the closeness of agreement between test results obtained under prescribed like conditions from the measurement process being evaluated. Overall precision and bias targets for chemical contaminant measurements can be set at 10 % allowable deviation with 90 % confidence limits. In all of these quality assurance activities one must take into consideration that factors including geophysical conditions and definition of sampling volume in the vadose zone often have higher variability than analytical equipment calibration procedures.

4.7.3 Table 1 provides suggested quantitative limits for data quality objectives.

4.7.4 The planning and preparation step continues with the evaluation of available information already gathered for the project area. These efforts culminate in the selection of an appropriate soil gas monitoring method and a survey design which best fits the project objectives within budgetary constraints. Prior to actual field work, investigators must obtain the necessary permits and landowner permission for property access. When a survey area is pending sale, investigators should obtain written permission to conduct the survey from both the buyer and the seller. Moreover, when a soil gas survey is being performed as a service, no work should proceed on the survey without a fully executed consulting agreement between the investigator and the client for whom the survey is being conducted.

4.7.5 Actual field work consists of recovery of soil gas samples. The method selected should be based upon site specific factors and dictated by the project objectives. A detailed discussion of soil gas sampling methods is provided in 6.1.

4.7.6 As samples are being recovered, they must be handled and transported in such a way as to assure preservation prior to analysis. A detailed discussion of sampling and transport is located in 6.5.

4.7.7 The presence of contaminants is determined through analysis of the soil gas samples. This step is controlled to a large degree by the QA/QC objectives of the survey. A discussion of sample analysis is provided as 6.6.

4.7.8 Data interpretation is largely an iterative process of review of the raw soil gas data out of context, a review of the

TABLE 1 Suggested Quantitative Limits for Data Quality Objectives

QA/QC Objective	Measure	Formula	Limit
Accuracy	Laboratory standard	Standard recovery	90 to 110 %
Precision	Field replicate	Relative standard deviation	< 20 %
	Laboratory replicate	Relative standard deviation	< 20 %
Representativeness	Air blank	Bias	< 10 %
	Cross contam. blank	Bias	< 10 %
Completeness	Completion (%)	Relative compl.	> 90 %
Comparability	Prof. judgment	NA	NA

soil gas data in context of other site characteristics and the formulation of conclusions based upon all known information. A discussion of soil gas data interpretation is located in 6.7.

4.7.9 Finally, a report of findings is generated in a format that is selected to be appropriate to the requirements of the end users. Section 7 provides options that can be addressed in reporting as well as recommendations of topics that should be included in all soil gas summations.

5. Significance and Use

5.1 *Application of Soil Gas Monitoring*—Soil gas monitoring is an extremely versatile method in that it can be adapted to conform to the requirements of dissimilar industries for a wide variety of applications. A number of soil gas techniques have been utilized in the agricultural (21), petroleum (22, 23) and minerals (24) industries. Certain applications have been exercised for well over 50 years. Soil gas monitoring has been utilized in research efforts, including the monitoring of underground coal gasification retorts (25). Application to the environmental industry is comparably recent but very effective as a rapid and relatively inexpensive method of detecting volatile contaminants in the vadose zone. Field screening, of which soil gas monitoring is a basic component, has been demonstrated to be effective for selection of suitable and representative samples for other more costly and definitive monitoring methods (26). Soil gas monitoring is useful to assess the extent of ground water contamination for certain contaminants and field environments (27). Soil gas monitoring is also a viable method of monitoring subsurface contaminant discharges from underground storage tanks (28). New applications of the soil gas monitoring are periodically developed and published in the referenced literature. The method may be useful in the study of unsaturated flow. In most instances, the method can make use of very light-weight, portable and inexpensive tools made from commonly available materials. Soil gas monitoring has become a widely accepted method for locating subsequent environmental monitoring and remediation activities such as ground water monitoring wells, contaminant product recovery wells or excavations to recover contaminated soil. Soil gas monitoring has made a significant contribution to ground water monitoring and remedial planning on sites that fall under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (29). This method is highly useful at the initiation of Phase II environmental assessment action in determining the presence of volatile organic contamination of real property in a pending sale.

5.1.1 In any application, soil gas monitoring can be performed over a wide range of both spatial and temporal designs. Spatial designs include soil gas sampling in profiles or grid patterns at a single depth or multiple depths. Multiple depth sampling is particularly useful for contaminant determinations in cases with complex soil type distribution and multiple sources. Depth profiling can also be useful in the determination of the most appropriate depth(s) at which to monitor soil gas, as well as the demonstration of migration and degradation processes in the vadose zone. Temporal designs include the long-term monitoring of the vadose zone for the appearance of volatile organic contaminants from known potential sources such as underground storage tanks and solid waste landfills.

Temporal designs are especially useful in monitoring the effectiveness of contaminant remediation efforts.

5.1.2 Soil gas monitoring in the vadose zone is an ideal reconnaissance tool and screening technique in most applications. However, site specific and contaminant specific limitations can cause this technique to be unsuccessful in meeting project objectives. Caveats exist in all soil gas monitoring procedures that can frustrate efforts to successfully apply the method to any application.

5.2 *Limitations*—The most significant limitation on soil gas monitoring is the inability to utilize the method as a stand alone technique. Soil gas monitoring does not provide repeatable quantitative information over time due primarily to the dynamic nature of phase equilibria in the vadose zone and secondarily to unavoidable inconsistencies in sampling practice. As a result of geologic variability in the vadose zone and the multitude of unique sampling devices currently being used in the field, quality assurance and quality control protocol, discussed in 6.4, cannot provide the rigor required as in a test method. For these reasons, soil gas data in itself cannot be used to provide definitive answers about the location or absence of buried contaminants. Moreover, the success of any soil gas monitoring method is strongly dependent upon effects related to geologic variation and moisture content in the sampling horizon as well as the physical properties of the target contaminants.

5.2.1 False negative results can occur as a direct result of the incompatibility of a specific procedure with the properties of the sampling horizon or the target contaminants, or both. Soil gas data cannot be used to establish bulk volume or the commerciality of buried petroleum, natural gas, or ore bodies.

5.2.2 With the necessary analytical procedures, soil gas can be examined for compositional anomalies, a very useful technique for multiple source problems. In some instances, contaminant occurrences are limited to single species (compounds, mercury, etc.), however more often than not the contaminant source is a mixture of organic chemicals that have a unique chemical compositional character consisting of both normally evaluated priority pollutants and nonpriority pollutant chemicals that may be overlooked. By identifying and using compositional information, many problematic site situations such as degradation can be minimized by targeting the more refractory compounds associated with the contaminant occurrence. This interpretive method is impossible to model for an industry wide application due to variation in methods and technique.

5.2.3 A basic limitation of the technique is that due to the ease of procurement and use of soil gas sampling devices, there is a tendency for inexperienced personnel to oversimplify any and all aspects of the method. Investigators must consider the experience level and technical ability of personnel who acquire soil gas samples and attempt to interpret the results. Certain procedural facets are not trivial, as discussed in Section 6. The results of certain techniques tend to be affected by minor variations in procedure despite apparent adherence to a “Standard Operating Procedure.”

5.2.4 Atmospheric air contamination is not a trivial problem

corrected by simple device-oriented field practice. Many sampling systems recover very large volumes of “soil gas” that may actually represent a mixture of soil gas and atmospheric air. This mixing occurs through the introduction of ambient air adjacent to the sampling device and through macroporous pathways in the soil which are far from the sampling device. Some environmental investigators avoid the impact of this problem by reasoning that contaminant quantities in the soil are so great that they are detected despite atmospheric mixing. For qualitative approaches with non-rigorous quality assurance/quality control (QA/QC) objectives this mixing problem can be insignificant. For detection of compounds that exhibit only marginal partitioning preference for the free vapor phase, the mixing problem can be a fatal flaw in procedure. Moreover, contaminant concentration and composition investigations can be rendered useless by variations in the magnitude of mixing at various sample locations and depths in a survey area.

5.3 Comments on Limitations of Soil Gas Monitoring—Many investigators believe that soil gas monitoring is not an effective vadose zone monitoring method for certain volatile organic applications, in certain geographic regions or during certain seasons of the year, or both. The applicability of soil gas monitoring is controlled by physical and chemical properties and processes in the subsurface and not by factors that are obvious at or above the surface. For example, one common misconception is that soil gas monitoring is not effective during the winter season. The impacts upon soil gas measurement of elevated soil pore water content, reduced vadose zone temperature and the presence of frost, typical of numerous regions in winter, are obvious for many facets of most soil gas monitoring methods. Modification of standard operating procedure, such as an increase in sampling depth, or selection of another soil gas monitoring method altogether can minimize the negative impacts of seasonal field conditions. It is important to understand that the responsibility for success or failure in soil gas monitoring can reside as much in the planning phase of a survey, including the method chosen, as in factors controlling the chemical and physical processes at work in the subsurface. Even with apparently ideal field conditions and with a carefully planned survey, soil gas monitoring can succeed or fail due to unknown factors controlling contaminant migration and emplacement. Soil gas monitoring is no different than any other measurement method, in that investigators must maximize effort in planning and implementation of procedure to maximize the likelihood of success.

6. Approach

6.1 Sampling Methodology—Soil gas sampling methodology has evolved over time and through practice in several industries. The equipment with which to perform this monitoring technique is highly varied, although it may be categorized into basic types (see 6.2.2). The literature provides numerous discussions about the design of some of this equipment (10, 30, 31, 32, 33). The selection of a soil gas sampling method involves consideration of three primary issues. These are the type of sampling system, the methodology of application of that sampling system and the rigor of the field QA/QC protocol. Each of these issues is discussed in this guide, however, no single method or procedure is recommended to the

reader due to the variation in site specific factors. As many as one hundred unique soil gas sampling systems exist that arise from variations or combinations, or both, of the many facets described in this guide. Some systems are highly versatile for numerous applications. Others are functional for more limited or specific applications. Informed investigators must assume the responsibility of selecting the technique most appropriate to the subject application, whether that technique is commercially available from contractors or equipment suppliers, or reliant upon the ingenuity of the investigator in the field utilizing commonly available materials. Success in choosing an appropriate sampling device or an entire sampling system is dependent upon the investigator’s level of understanding of vadose zone processes, contaminant properties and appropriate applicability of the soil gas method.

6.1.1 The application of any of these methods must be controlled by strict adherence to a standard operating procedure. Occasional deviations as dictated by unusual field conditions should be recorded in the project field notebook. Inadvertent minor deviations in field procedure can result in misinterpretation of the data acquired.

6.2 Sampling Systems—Six basic sampling systems exist. These are based upon the collection of soil gas by a whole-air or sorbent method in an active or passive approach, or upon the principle of collection of a soil or water sample for subsequent sampling of a contained headspace atmosphere. Contained atmosphere methods do not yield samples representative of in situ vadose zone atmospheres.

6.2.1 Whole-air methods sample the soil atmosphere as a mixture of gases, including contaminant and noncontaminant vapors. Sorbent methods sample contaminants adsorbed onto a collection medium exposed to a whole-air sample stream. Active methods are those that obtain a soil gas sample by positioning a sampling device in the subsurface and the withdrawal of soil atmosphere through the device from the sampling horizon. Passive methods are those that obtain a soil gas sample by placing a collection device in the soil or on the soil surface, and allowing the atmosphere within the device to come into compositional equilibrium with the soil atmosphere. Four of the six basic sampling systems arise from these approaches, namely the whole air-active approach, the sorbed contaminants-active approach, the whole air-passive approach, and the sorbed contaminants-passive approach. Two additional systems exist that are based respectively upon the collection of a soil or water sample for subsequent sampling of a small volume headspace atmosphere.

6.2.2 Whole Air-Active Approach—This method of soil gas sample collection involves the forced movement of bulk soil atmosphere from the sampling horizon to a collection or contaminant device through a probe or other similar apparatus (10, 34). Contained samples of soil atmosphere are then transported to a laboratory for analysis, or the sampling device is directly coupled to an analytical system. Whole air-active sampling is best suited to soil gas monitoring efforts where contaminant concentrations are expected to be high and the vadose zone is highly permeable to vapor. Probes exist that must utilize pre-existing holes or that can penetrate the vadose zone by driven means. These devices can be very simple and

light-weight for low cost mobilization (35), or they can be affixed to vehicle mounted drills or hammers useful for larger, more complex surveys at a higher cost of mobilization. The whole air-active technique can be combined with other monitoring methods such as soil monitoring for engineering purposes (36) in some survey environments. The success of this practice can be highly site-specific.

6.2.2.1 Ground probes can be of small to large internal volume. The development of sampling devices with smaller internal volumes equating to smaller purge volumes is a significant improvement, providing samples which are more representative of soil atmosphere, and a greater ease of equipment decontamination between usages. Sample size can vary from a few millilitres to many tens of litres depending upon the sample rate through the probe, the vapor storage capacity of the soil and the ability of the soil to deliver vapor to a probe under vacuum.

6.2.2.2 The success of the active approach is strongly dependent upon soil clay, organic matter and moisture content. Driven probes tend to destroy natural soil permeability around the body of the probe due to soil compaction concurrent with insertion. This can be a severe limitation in moist, heavy clay soils. In very dry, cemented soils, driven probes can create radial fractures that can enhance soil permeability to vapor concurrent with insertion. These fractures can communicate atmospheric air with soil atmosphere, a limiting factor for obtaining representative, large-volume soil gas samples. The effect can be so severe as to lower recovered contaminant concentrations in the soil gas sample below the limits of analytical detection. This is especially true for highly sorptive or water soluble compounds, or both. Some investigators have attributed the poor recoveries of these compounds exclusively to other processes, that is, degradation (21, 37).

6.2.2.3 Methods requiring a pre-existing hole for probe insertion (38) made with a commercially available “slam bar” can provide supportable contaminant data where contaminant concentrations and soil permeability to vapor are high, however the act of making a hole with a “slam bar” and subsequent removal of the “slam bar” can encourage soil contaminant venting and lower sample representativeness. Insertion of the sampling probe into this hole further degrades representativeness by additional venting of contaminants as the probe displaces the atmosphere in the hole upon insertion. Purging of the probe prior to sampling under conditions of low soil permeability and low contaminant concentration may lower contaminant levels below the limits of analytical detection. Methods requiring a pre-existing hole for probe insertion are not recommended for soil gas sampling from soils with high clay and moisture contents.

6.2.2.4 Excellent discussions of numerous whole air-active sampling systems may be found in the literature (10, 21, 37, 39). Investigators must consider the caveats and limitations of the whole air-active approach when selecting a certain method for a specific application.

6.2.3 *Sorbed Contaminants-Active Approach*—The sorbed contaminants-active method of soil gas sample collection also involves the forced movement of bulk soil atmosphere from the sampling horizon through a probe or other similar apparatus,

but to a collection device designed to extract and trap sample stream contaminants by adsorption (40, 41). This system is well suited to sites where the soil may be highly permeable to vapor and where the contaminant concentration may be lower than required for successful whole-air surveys. Sorbent devices are designed to concentrate the components of interest and remove some of the soil gas components known to interfere with sample analysis.

6.2.3.1 Contaminant trapping is accomplished by use of an adsorbent collection medium such as charcoal or a carbonized molecular sieve adsorbent (43, 44), as well as porous polymers, silica gel and activated alumina (10). This approach is especially amenable to the detection of nonpolar volatile organic compounds. Organic compounds that are reactive, oxygenated or are gaseous at room temperature are either not adsorbed by or are not efficiently desorbed (42) from charcoal. Sorbent collection devices are commercially available or can be specially prepared with an appropriate sorbent material that concentrates desired compounds for future analysis. Colorimetric detector tubes are available which will provide an indication of the presence of target compounds at the time of sampling. These devices are limited in application by the high concentration requirements for many compounds and the compound-specific nature of these tubes.

6.2.3.2 The effectiveness of the sorbed contaminants-active approach can be limited by high vadose zone clay and water content, reducing the ability of the soil to transmit vapor through the sorbent trap. Commercially available sorbent traps come with information suggesting maximum, minimum and optimum sampling rate through the trap. Soil characteristics can limit flow rate to a point below the minimum recommended rate, affecting the performance of the trap and the reproducibility of adjacent samples. Interaction of the sorption media with target compounds during desorption in the laboratory can form artifacts, restricting the interpretive value of the data. Some sorption media are prone to irreversible adsorption (see Definitions D 2652). Some may be affected by high soil gas relative humidity. Humidity greater than 60 % (very common for soil gas) can reduce the adsorptive capacity of activated charcoal to 50 % for some chemicals. Presence of condensed water in the sample tube will indicate a suspect sample (see Practice D 3686). Anticipation of these problems is recommended for all sorbent techniques, and a thorough quality control plan should be designed and implemented as is discussed in 6.4 of this guide.

6.2.3.3 Special sample preparation is required for samples adsorbed onto a trapping medium. This preparation step consists of the thermal or solvent desorption of the contaminants from the trapping medium. Proper practice will promote needed accuracy and precision in the determination of contaminant concentrations above specified values (see Practice D 3687).

6.2.4 *Whole Air-Passive Approach*—This method of soil gas sample collection involves the entry of bulk soil atmosphere or soil atmosphere components from a near-surface sampling horizon to a collection or containment device through a flux chamber or other similar apparatus (30). Enclosure devices sample vaporous emissions from a known soil surface

area capped by a chamber. The volume of the chamber is continuously swept by injection of a gas of known composition, and the resultant carrier gas-contaminant mixture is collected for analysis. The rate of emission or “flux” of contaminants can be calculated if flow rate of injected gas and contaminant concentration in the sample are determined.

6.2.4.1 The whole air-passive approach is useful to some very specific applications. This method may be used, for example, to monitor contaminant emissions from soil or water to assess the health hazard risk of such emissions to the general public. Determination of the extent of contamination by volatile organic compounds has been performed with whole air-passive devices, however the application of other types of systems is far more common.

6.2.4.2 A key to successful operation of a whole air-passive system is that the system is able to recover volatile compounds as they are emitted from the vadose zone. The effects of changes in barometric pressure, soil temperature and soil moisture content are not quantifiable from site to site due to site specific variables controlling vapor phase contaminant migration and the rate of contaminant partitioning into the vapor phase. The presence of contaminants or naturally occurring organic matter floating on surface water may impact the rate of entry of certain vapor phase contaminants into the chamber.

6.2.4.3 The whole air-passive method is limited in application primarily due to the great degree of dilution of contaminants in the sample stream by injected gas. This can decrease method sensitivity by lowering contaminant concentrations to levels below the detection limits of the analysis method chosen. Further decrease in method sensitivity results from the fact that soil gas contaminant concentrations are generally lower at the surface than even at nominal depths. Soil characteristics such as high water saturation, soil cements, clay content and organic matter content will negatively impact results of these systems by restricting the rate of contaminant flux to the chamber.

6.2.4.4 Additional limitations exist. Certain devices limit flux rates into the chamber due to aspects of design. Soil macroporosity such as desiccation cracks extending beyond the collecting device will vent soil vapors to the atmosphere that will not be collected by flux chambers unless monitoring locations are biased to include these features.

6.2.5 *Sorbed Contaminants-Passive Approach*—This method of soil gas sample collection involves the passive movement of contaminants in soil to a sorbent collection device over time. Passive samplers that have been applied to sampling soil gases of environmental concern include occupational health volatile organic compound monitors (44) and a sampler originally developed for detecting the presence of hydrocarbons in petroleum exploration (33, 46). Both devices use charcoal as a sorbent; the former as a flat film and the latter coated on a wire. Passive samplers are housed in containers up to several inches in diameter, depending upon the design. They are placed open end down in holes that are usually less than 5 ft (1.5 m) deep, that are then backfilled (32). These monitors are generally left in place from two to ten days, although certain passive collectors can be left in place for a period of 30 days or more for certain applications. For at least one device,

exposure efficiency can be determined.

6.2.5.1 The sorbed contaminants-passive approach can be employed in a wide range of geological conditions. Frozen ground and high water saturation may not limit the ability of the monitors to collect contaminants (46), although the composition of the contaminant suite may be impacted by related alterations in partitioning equilibria.

6.2.5.2 The sorbed contaminants-passive approach depends upon the ability of contaminants to move through the vadose zone to the passive collection device. Numerous adsorption media can be used to collect contaminants (see 6.2.4). The principle of passive-sorbent monitors relies on adsorbent reduction of the equilibrium concentration of contaminants around the monitor over time, therefore creating a concentration sink, that is, a continuous state of disequilibrium, in the vicinity of the monitor. This can encourage continued migration of contaminants toward the monitor when conditions for contaminant partitioning into the vapor phase are favorable. Migration of contaminants in the vadose zone toward a passive-sorbent device is strongly controlled by vadose zone character and the chemical and physical properties of the subject contaminants. Contaminants may move from a few feet to thousands of feet, or not at all.

6.2.5.3 Many investigators attribute the principle mechanism of contaminant migration to a passive-sorbent device to diffusion, that is, the movement of organic vapor or gas molecules from a region of high concentration to a region of low concentration as described by Fick’s law (see Practice D 4597). Fick’s law of diffusion states that for a constant concentration gradient, the mass of material transferred to the sampling layer can be expressed as:

$$M = \{DA(C - C_o)t\}/L \quad (5)$$

where:

- M = mass of the material, ng,
- D = diffusion coefficient, cm^2/min ,
- A = cross sectional area of diffusion cavities, cm^2 ,
- L = length of diffusion path, cm,
- C = concentration at face of sampler, ng/cm^3 ,
- C_o = concentration at adsorbing layer surface, ng/cm^3 , and
- t = exposure time, min.

6.2.5.4 The cross sectional area of a diffusion cavity, the length of the diffusion path and the quantity $(C - C_o)$ are impossible to accurately measure for soil gas contaminants interacting with a passive-sorbent sampler. There is some debate as to whether passive samplers measure flux or total contaminant concentration (32) in the vicinity of the trap. Due to the fact that the mass of the material transferred to the sampler by diffusion, a key measurement, cannot be determined, the debate will no doubt continue. It is reasonable to assume that a combination of processes is responsible for contaminant migration to sorbent traps, including diffusion, dispersion and mass transfer. All migration processes are impacted by partitioning equilibria.

6.2.5.5 Ambient air represents an atmospheric contaminant concentration sink that encourages a strong vertical vector of contaminant migration. This prevailing upward movement of contaminants from sources at depth results in contaminant concentration gradients throughout the vadose zone. The

sorbed contaminants-passive method makes use of this contaminant flux (see 6.2.4) to collect long-term, nondisruptive samples of volatile contaminants. The method can collect contaminants which are compositionally representative of the contaminant mixture favoring the vapor phase. The quantity of volatile organic compounds trapped by these devices is proportional to the concentration gradients of contaminants present near the collection device and the affinity of the contaminant(s) for the collection medium.

6.2.5.6 As with active sampling protocols, specific issues exist affecting the function and calibration of passive monitors. Soil gas, even in the drier climates, will be at a relatively high humidity condition. This humidity can affect the collection efficiency of the adsorbent media. In soils of low permeability, contaminants commonly move very slowly. This can create a condition of near-zero contaminant concentration in the soils immediately adjacent to the monitor if the sorptive potential of the monitor is higher than that of the soil. When soil contaminant concentrations are rapidly depleted, that is, as the result of invasion of the sampling horizon by meteoric water, the passive monitor can source contaminants back to the soil.

6.2.5.7 The sorbed contaminant-passive approach to soil gas monitoring is not immune to the migration, emplacement and degradation factors affecting all soil gas monitoring techniques. It is not possible to measure the efficiency of passive-sorbent monitoring devices because the bulk volume of soil gas affected by the sorbent trap cannot be measured. Care must be taken not to contaminate the sorbent samples during installation or by backfilling with contaminated soil. Such care is comparable to potential problems for any measurement method in which a contaminated layer is penetrated.

6.2.6 *Soil Sampling for Subsequent Headspace Atmosphere or Extraction Sampling*—This method examines contaminants that are present in a headspace atmosphere above a contained soil sample. Note well that this headspace atmosphere is not true soil gas (see 3.1.11), but is an artificial atmosphere formed above a potential contaminant source, that is, the soil sample. Contained atmosphere methods do not yield samples representative of in situ vadose zone atmospheres. Headspace atmospheres differ from in situ vadose zone atmospheres in that large percentages of vapor phase and moderate percentages of solute and sorbed phase contaminants can be lost in the act of soil sampling. This method is not generally recommended for a broad spectrum of cases due to numerous limitations and caveats. In comparison to other methods described in this guide, soil sampling for subsequent headspace atmosphere or extraction sampling can be a relatively poor method for determining many of the more volatile contaminants. Headspace atmospheres contain residual sorbed and solute phase contaminants that have partitioned to the vapor phase in the contained environment; most headspace approaches are reasonably efficient in recovery of some fraction of sorbed and solute phase contaminants. Contaminants in these phases in situ are recovered from a headspace after they have partitioned into the vapor phase. Recovery efficiency of contaminants in the vapor phase in situ ranges from moderate to poor.

6.2.6.1 Important criteria exist to consider when selecting a device that will provide suitable samples (see Guide D 4700).

The equipment required is simple and readily available. Some commonly used augers are not suitable for soil sampling in support of subsequent headspace atmosphere sampling due to soil disturbance. Depths of auger investigations are limited by ground water conditions, soil characteristics and the equipment used (see Practice D 1452). Suitable procedures for some methods are described in the literature (47, 48). Current soil preservation practice may not apply (see Practice D 4220).

6.2.6.2 Limitations and special procedures exist for the application of soil sampling for subsequent headspace gas analysis. Filling head space with solvent can support a subsequent solvent extraction procedure. Some investigators minimize the effects of devolatilization by rapidly recovering small soil core plugs with polypropylene syringes which have been modified to accommodate recovery of soil plugs. Investigators also attempt to maximize partitioning of contaminants into the vapor phase by adding buffering solutions or sodium sulphate and phosphoric acid to the vial prior to sealing, in order to shift the activity coefficients of the subject contaminants to favor the vapor phase. Aqueous suspensions of solvent slurries of soil can be ineffective for the determination of high molecular weight labile compounds. Their persistence in soil is the result of physical entrapment in soil microporosity (49). Recovery efficiency of contaminants in soil headspace can be greatly enhanced by pulverization of the soil (50) in a ball mill or other similar apparatus. The method is biased toward recovery of contaminants in the sorbed, solute and occluded phases in situ due to the loss of pore space gas in preference to contaminants adsorbed onto the soil particles or trapped in soil micropores. Contaminant degradation, especially biodegradation, in the container is encouraged by the creation of an aerobic, moist environment during sample handling and transport prior to analysis. However, a simple method to minimize the effects of biodegradation can be achieved by storing samples, when necessary, at approximately 4°C in the dark.

6.2.6.3 Acid extraction of volatile organic compounds is widely used in geochemical exploration for petroleum and natural gas. Soil samples are placed in a closed vessel, heated and evacuated to remove vapor phase contaminants. The addition of acid to the evacuated chamber causes release of hydrocarbons believed to be bound to the soils by carbonates (22). Hydrocarbons are determined by analysis of resulting vessel atmospheres. Refinements to this method have been developed (48), however the method is designed not to determine compounds in the vapor, sorbed, or solute phases. Method sensitivity is therefore greatly reduced.

6.2.7 *Soil Pore Liquid Headspace Gas Approach*—In the vadose zone, soil gas monitoring can be accomplished in combination with soil pore liquid sampling through the use of a suction lysimeter, a pan lysimeter or a free drainage glass block sampler. The suction lysimeter installed in the vadose zone is most commonly employed for this purpose. Temporally designed surveys are ideally suited to this method.

6.2.7.1 After a lysimeter has been installed for some period of time, initial aliquots of vapor sampled from a soil pore liquid sampler will be in compositional equilibrium with solute phase contaminants when pore liquid tensions are within the operating range of the lysimeter and if pore sizes are not so great as

to cause loss of hydraulic contact between the soil and the porous segment of the lysimeter. Subsequent aliquots of soil gas may compositionally resemble soil vapor in situ if soil atmosphere enters the porous segment of the sampling device. When the lysimeter cannot recover a pore liquid sample, the soil gas recovered will be compositionally similar to soil vapor in situ.

6.2.7.2 The most common effort to recover soil gas from a suction lysimeter occurs when polytetrafluoroethylene (PTFE) porous segments are employed in sampling environments with high soil moisture tensions (low moisture contents). At tensions above 60 to 80 centibars, soil pore liquid samples cannot be collected (see Guide D 4696). However, soil gas can be recovered through the porous segment and collected at the surface. This alternative sampling effort can monitor soil vapor contaminants utilizing an otherwise unsuccessful procedure until soil moisture contents increase or until an alternative soil pore liquid sampler can be installed.

6.2.7.3 This technique is limited by the relative expense and complexity of installation of the sampling devices as a primary soil gas sampling method. The completeness criterion for quality assurance is difficult to satisfy due to the inability to anticipate the performance of the soil pore liquid sampler with respect to vapor recovery. Moreover, compositional bias toward solute phase contaminants and contaminants volatilized from free product is likely in soil gas samples recovered concurrently with soil pore liquid samples.

6.3 *Methodology in Application of a Sampling Technique*—The likelihood of success of the soil gas sampling technique selected is controlled in part by the methodology in application of that sampling technique. This methodology should be guided by the objectives of the subject project and the perceived spatial and temporal array of the potential sampling targets.

6.3.1 *Grids*—Many problems suitable for soil gas monitoring are best solved by obtaining data distributed over a geographic area. Sampling in grid patterns of variable design and spacing can be a very effective way to provide data coverage over a large area for a very low cost of acquisition. Common applications of soil gas grid sampling are environmental contaminant assessments, exploration for natural resources and the siting of locations for other monitoring or exploratory techniques. Compositional analyses in conjunction with properly designed grid systems are often fundamental to successful evaluation of soil gas monitoring.

6.3.1.1 Grid spacing provides for the location of soil gas samples in grid cells. The selection of grid cell size is strongly dependent upon the relationship between project confidence level requirements and cost budget. Small survey targets and complex vadose zone geology require decreased spacing between soil gas sample locations for grid methodology to be successful. Some applications, for example, defining the boundaries of contaminated soil or ground-water contaminant plumes, may require the grid cell area to be as small as 100 to 400 ft² (9 to 37 m²). Most applications to natural resource exploration monitor naturally occurring volatile compounds in soil atmospheres, requiring closely spaced grids to increase the signal to noise ratio. However, a closely spaced exploratory

grid equates to a broadly spaced grid for environmental application in most situations. Common petroleum exploration grid spacing utilizes a grid cell area of approximately 250 000 ft² (23 000 m²), however grid cells can range from 10 000 to 1 000 000 ft² (9 to 90 000 m²) depending upon perceived reservoir target area. Widely spaced grid sample arrays are useful in reconnaissance applications such as the establishment of contaminant baselines or evaluation of the exploration potential of a geologic basin. Grid cells for such purposes can be as large as a square mile or more.

6.3.1.2 The tendency exists for investigators with constrained budgets to utilize overly large grid cell spacings. This action normally results in inadequate, over-interpreted data supporting meaningless conclusions. Care must be taken to avoid this caveat.

6.3.1.3 Grid arrays can be designed as regularly spaced and predetermined locations for soil gas sampling or they can be irregularly spaced and continually field modified. Predetermined and widely spaced grid patterns are most useful for reconnaissance work, while closely spaced, irregularly situated or field modified soil gas grid sample sites, or both, are commonly used when targeting contaminant plume boundaries, contamination from underground storage tanks or other detail work.

6.3.1.4 Multiple depth sampling, discussed in 6.3.3, when coupled with a soil gas grid sampling methodology, can provide useful data in complex geologic settings and sites with multiple contaminant sources. Computer mapping of closely spaced three-dimensional soil gas grids can provide the investigator with horizontal or vertical cross sections through the subject site, making difficult observations possible.

6.3.2 *Profiling*—Profiling is a soil gas sampling methodology useful to test a linear array for the existence of contaminants. Profiling is most often performed by sampling at closely spaced intervals in a linear array and is displayed as contaminant concentration or composition versus distance sampled on an $X - Y$ plot. Concentration data are often displayed logarithmically on the ordinate (Y) axis, while single components or ratios of compositional data are often displayed linearly on the ordinate axis.

6.3.2.1 For environmental applications such as leak detection along the length of a pipeline or monitoring of contaminant encroachment across a property boundary, soil gas samples are recovered along a profile at intervals from 25 to 100 ft (8 to 30 m) (23). Profiling for natural resource exploration can be performed at sample intervals from 50 to 500 ft (15 to 50 m), depending upon the application.

6.3.2.2 Profiling is useful as a corroborative tool for other monitoring or exploration methods. For example, a soil gas sample profile acquired coincident with a seismic profile can suggest primary contaminant migration pathways or the boundaries of confining layers in shallow, complex geologic settings. This technique has been demonstrated as highly effective in reducing exploratory risk prior to drilling for petroleum and natural gas, by suggesting the presence of hydrocarbon seepage coincident with structures with reservoir potential defined by the seismic method (51).

6.3.2.3 Soil gas profiling is also a convenient methodology

effective in comparative evaluation of multiple soil gas sampling techniques. Due to variations common to the dynamic equilibrium conditions over small spatial and temporal intervals in the vadose zone (see 4.1), comparisons of multiple soil gas techniques using only one or a few soil gas samples recovered from nearly identical locations will not result in a valid comparison. However, a visual overlay of soil gas profiles resulting from the implementation of the various sampling techniques can provide a rapid and definitive comparison as to the efficiency of recovery of subject contaminants by a particular sampling system in a specific sampling environment. Similarly, comparison of profiles obtained by using the same soil gas sampling system can provide a direct measurement of system accuracy for quality control purposes.

6.3.2.4 Some investigators compare geographically coincident profiles obtained with the same sampling system at times differing by days or even years in order to generate a data correction factor in order to enhance data comparability. This practice is strongly discouraged. Factors not anticipated in this practice such as the effects of the dynamic equilibrium in the vadose zone, unavoidable changes in procedure due to personnel substitutions, contaminant movement or cultural influence on the sampling environment can have impact on results that are far more significant than the apparent correction.

6.3.3 *Multiple Depth Sampling*—Methodologies encompassing multiple depth sampling normally have one of two goals, that is, to monitor changes in soil gas contaminant fractions versus depth, and to closely follow a single sampling horizon for an entire soil gas grid or profile.

6.3.3.1 When the goal of a survey is to monitor contaminants over varying depths, some sampling systems can recover soil gas samples as probes are advanced deeper into the vadose zone. This practice is helpful in determining the optimum sampling depth for a particular site or to demonstrate the presence or absence of soil atmosphere contamination in a certain horizon. Soil gas contaminant concentrations often increase with depth as the sampling horizon approaches contaminated ground water or other source of soil gas contaminants (52). Caution must be exercised when soil gas sampling tools are advanced to increasing depths due to the fact that cross contamination of some or all of the sampling system is unavoidable. This situation limits quality control for this type of multiple depth sampling. Attempts to eliminate cross contamination in multiple depth sampling by replacement or decontamination of sampling equipment with each new sample aliquot also result in limited quality control. Tool withdrawal and tool reinsertion result in venting of the sampling environment via an open hole. The open hole behaves as a macroporous pore space, allowing enhanced partitioning into the vapor phase and convective migration to the atmosphere. The end result is a reduction in representativeness for each subsequently recovered soil gas sample.

6.3.3.2 Multiple depth sampling can also be used to focus a sampling program into a single geologic unit or suite of units without regard to depth. This practice is helpful at sites with complex lithologic changes in the vadose zone. Samples can be recovered from lithologies with greater permeability to vapor or greater storage capacity for vapor when bias in sampling

depth is necessary to accomplish project goals. This practice involves greater effort and expense than most methodologies due to the necessity to establish the presence, thickness and depth of the target horizons prior to soil gas sampling. The most common application of this methodology is the sampling of soil gas at the top of the capillary fringe.

6.3.4 *Time Variant Methodologies*—Monitoring soil gas in the vadose zone over time can suggest process rates of contaminant partitioning, emplacement, migration and degradation. Practical application of this methodology includes the monitoring of the effectiveness of remedial air-injection systems, the appearance of contaminants sourced from underground storage tanks, the encroachment of contamination onto a subject property from an abutting property and the mitigation of soil and ground-water contamination by microorganisms.

6.3.4.1 Some investigators and regulators with responsibilities at more than one location delegate seemingly simple time variant soil gas monitoring tasks to local personnel. Numerous problems with time variant monitoring can arise in the field as the result of poor system maintenance and record keeping by inexperienced or unmotivated personnel (property owners or parties responsible for contamination).

6.3.4.2 Certain maintenance problems are easily corrected, that is, cleaning bacteria and other foreign matter from detectors or replacing damaged components. Other maintenance problems can be fatal flaws in the methodology. These are principally related to ice formation in the sampling system and destruction of system integrity due to soil frost heaving.

6.3.5 *Combination of Soil Gas Monitoring With Other Vadose Zone Monitoring Techniques*—Soil gas monitoring is not a stand-alone technique. Corroborative support of this reconnaissance and screening tool by other vadose zone monitoring techniques is strongly encouraged. The possible combinations of the various vadose zone techniques with soil gas surveys are numerous. Soil gas can commonly be used as a reconnaissance tool to locate other monitoring devices such as lysimeters, neutron probes or ground water monitoring/sampling wells. Limits upon such combinations are controlled by budgetary constraints and the investigator's imagination.

6.4 *Field QA/QC*—Quality assurance and quality control procedures (QA/QC) are essential to establishing support for any interpretation of measurement data. Soil gas monitoring data requires a thorough QA/QC protocol confirming that data have been generated to satisfy the data quality objectives for the survey. This requirement is well known, however few investigators subject their soil gas data sets to the rigors of such protocol. Conclusions based upon data of unknown quality may be without merit. Justification for interpretations based upon data of unknown quality is not possible.

6.4.1 QA/QC requirements are dependent upon the data quality objectives defined in the planning phase of the survey. For example, simple contaminant audits require a less demanding QA/QC protocol than contaminant source identification. The goals of the QA/QC effort must be understood by field personnel to assure effective implementation of field QA/QC. A document control officer who is a member of the field team can provide this assurance.

6.4.2 Persons collecting descriptive data should not be

varied during a soil gas survey. Soil descriptions, for example, can be somewhat subjective when estimations are made as to soil moisture or clay content. Changes in field personnel can translate into apparent changes in soil lithology that are merely functions of this subjectivity. The document control officer can review field records to discover any obvious errors related to descriptive data.

6.4.3 The results of a soil gas survey are highly sensitive to procedure. Field personnel should closely follow a standard operating procedure. This procedure should include the method(s) selected for the survey including the sampling system, means of sample collection, handling and transport of samples and field based equipment decontamination. A standard practice for equipment decontamination is essential to maximize the integrity of samples that may undergo chemical analyses (see Practice D 5088). Any deviations in the standard operating procedure should be recorded by the document control officer in a field notebook, with notes outlining the justification for the deviation. Data comparability can be severely compromised by deviations from the standard operating procedure.

6.4.4 Field based equipment decontamination can have impact on data quality. This results from the potential for cross contamination of samples due to poorly controlled field cleaning procedure or difficulties presented by the inconvenience of field decontamination. Field based equipment decontamination should not be considered a method of choice, but if unavoidable, must be performed with the data quality objectives for the survey as driving forces for procedure.

6.4.5 Bias of soil gas data describes a situation of consistently lower-than-actual or higher-than-actual soil gas contaminant concentration measurements (32). The bias of a measurement process is a generic concept related to consistent or systematic difference between a set of test results from the process and an accepted reference value of the property being measured (see Practice E 177). Bias can be imparted to the data through sample site selection, that is, exposure of a sampling device to an environment of enhanced contaminant concentration due to a preferential contaminant migration pathway, or exposure of a sampling device to an environment devoid of contaminants due to barriers to contaminant migration. Bias may also result from malfunction of the sampling system, contaminant degradation or numerous other factors. False positive or false negative values can result, lowering the value of the soil gas data set.

6.4.6 Table 2 summarizes some common problems in soil gas monitoring that can result in biased results.

6.4.7 A sampling program must be conducted during the survey to support evaluation of both the sampling system in the field and the analytical system employed. These samples are known as QA/QC samples. The type and magnitude of QA/QC sampling depends upon the purpose of the soil gas survey and the requirements for data quality attendant to it. It is the responsibility of the investigator to determine the appropriate rigor of field QA/QC protocol. The variation in QA/QC protocol from survey to survey is controlled by the purpose and magnitude of the survey, and can vary to a great degree.

6.4.8 The types of field QA/QC samples are field blanks, travel blanks, sample container blanks, sample probe blanks

TABLE 2 Summary of Possible Causes of False Positive and False Negative Values^A

Result	Causes
False negatives, that is, falsely low values	Barriers to gaseous diffusion, such as perched water, clay lenses, impervious man-made debris, saturation of soil pores with water (as from rain), low subsurface temperatures. Biological or chemical degradation. Leakage or blockage in the sample train, improper purge procedure, loss of sample from sample container, problem with analytical system.
False positives, that is, falsely high values	Contamination in sampling train, sample container, or analytical system. Contribution of volatile organic contaminants from vegetation. Significant contamination in overlying soil.

^ASee Ref (32).

and sample replicates. Other types of QA/QC samples are analytical in nature and are discussed in 6.6.

6.4.9 Field blanks are samples of ambient air or nitrogen recovered from the sampling system which are recovered to determine contamination of samples by ambient atmospheric air, or, to act as system blanks to test for contamination of the sampling system. Field blanks are used to provide an indication of the probability of leakage in the sampling system or the breakthrough of atmospheric air to the sampling device through macroporous migration pathways in the vadose zone such as soil cracks or moldic porosity. If nitrogen is employed instead of atmospheric air, field blanks can have higher contaminant levels than soil gas. This is especially true for petroleum hydrocarbons in urban environments. At least one field blank should be recovered for each ten soil gas samples, or at least one field blank per sample batch or container type (53).

6.4.10 Travel blanks are the contents of a sample container handled in the same manner as those containers holding samples, except that there has been no sample inserted into the travel blank. The purpose for travel blanks is to audit sample integrity for loss due to sample handling and transport. Travel blanks are useful when analysis is performed at an off-site laboratory. The results obtained by analysis of travel blanks can be used to indicate a potential need to modify sample handling and transport procedure. At least one travel blank should be included in each batch of samples.

6.4.11 Sample container blanks are obtained by sampling the contents of a clean sample container to ensure that residual contaminants are not present in the container prior to sample collection. If contamination is detected in the cleaned containers, the decontamination procedure must be modified to remedy the problem. Sample container blanks should be collected and analyzed prior to each use of a sample container.

6.4.12 Sample probe blanks, consisting of carrier gas or atmospheric air contrasted to atmospheric air blanks, are drawn through the sampling device and recovered in the same manner as soil gas. The purpose for sample probe blanks is to check for the presence of sample train contaminants that would impact data quality. If contaminants are detected in sample probe blanks, the decontamination procedure must be modified to remedy this condition. Sample probe blanks should be collected and analyzed prior to each use of a probe and/or other components of the sampling system.

6.4.13 Field replicates are recovered as separate soil gas samples collected from the same sample site into multiple containers. Field replicates can be used to estimate the combined precision of sampling and analysis. The recovery of field replicates is not a common practice. When field replicates are demanded by a client or as dictated by a particular situation, field replicates should be recovered as often as is economically and practically possible, however, in no instance should the number of replicates fall below ten percent of the total number of soil gas samples (53).

6.4.14 Sample spiking, or the addition of a known quantity of a known compound or mixture to the soil gas sample, is sometimes performed in the field to provide internal checks of analytical quality. Sample spiking in the field is not recommended due to measurement uncertainties in the field. Moreover, caution must be exercised with this procedure because of the potential for contaminant interaction with the known compound(s).

6.4.15 A paperwork audit is recommended at the end of each working day or at the conclusion of recovery of each batch of samples recovered. The paperwork audit should be conducted by the document control officer and include evidence of an equipment inventory, sample inventory including QA/QC samples, review of field notes and chain-of-custody documentation.

6.4.16 Chain-of-custody documentation is recommended at all times, and is mandatory for soil gas surveys when samples are transmitted to an off-site laboratory. It is recommended for soil gas surveys when sample custody is transferred to someone other than the field team leader for any reason. Chain-of-custody documentation assures that samples have not been altered or mishandled prior to analysis. This procedure is mandatory for sample handling and transport in situations where there is likely to be a cost recovery effort or demonstration of contaminant responsibility in a court of law.

6.5 *Sample Handling and Transport*—Soil gas sampling and analysis usually involve the monitoring of contaminants at very low levels. Consideration of sample handling and transport is not trivial to this exercise.

6.5.1 The period of sample handling and transport represents the greatest opportunity for loss or gain of contaminants from or to sample containers. Loss occurs by contaminant condensation within the sampling train, sorption onto materials within the sampling train, solution into condensed water in the sampling train, chemical changes or leakage to the atmosphere through defects in the sampling apparatus or sample container. Gain of contaminants from sources other than the sampling horizon can occur through related mechanisms working in reverse. Both processes can severely limit the value of data obtained from a survey, and they must be minimized.

6.5.2 In general, the time between sample collection and analysis should be minimized. Investigators should protect samples against light and heat, and exercise precautions against leaks (see Practice D 1605).

6.5.3 *Acceptable Materials*—Investigators are responsible for selecting materials for soil gas sampling, transfer and containment that will not impact sample integrity. Containers that have parts made from porous or synthetic materials such as

PTFE, rubber or many plastics are likely to retain or contribute contaminants to soil gas samples. Corrosive metals such as steel or brass become difficult to decontaminate upon corrosion due to the increased surface area of the corroded material and its enhanced sorptive capacity. Septa of any material will be responsible for measurable contaminant loss over time due to leakage. Acceptable materials can be conveniently decontaminated prior to soil gas recovery. Materials that cannot be decontaminated effectively between samples must either be replaced between samples, considered in QA/QC planning as a survey limitation or abandoned in favor of more suitable materials.

6.5.4 *Integral Systems*—Problems of sample handling and transport are minimized by integration of the sampling and analytical system. For example, a whole air-active sampling system can be coupled directly to a portable VOC (volatile organic compound) analyzer. The sample stream is fed directly to the intake port of the analyzer and passed through the detector. If there are no system malfunctions in the sample path, problems of sample degradation become trivial.

6.5.4.1 Care must be exercised with integral systems, however. The dead volume of integral systems is much higher than separate sampling and analytical systems. If the sampling system is not capable of delivering constant sample flow rates at or exceeding the requirements of the analyzer employed, data accuracy and comparability can be seriously affected. Moreover, a large sample volume is required merely to purge the sample system. In soils with moderate moisture contents or even nominal clay contents, it may not be possible to recover the volume of soil gas required to purge the system without serious negative impact to the composition of the soil gas sample recovered. Vapor phase contaminants can be lost to purge volume and atmospheric breakthrough can occur, leading toward a false negative result. Although this problem may not be apparent in seriously contaminated environments, it can become a fatal flaw at low contaminant levels.

6.5.4.2 Cross-contamination is a concern with integral systems. Many integral systems employ common elements from sample to sample, namely tubing, flow meters and analyzer components. Overcoming persistent contaminants can be difficult in integral systems, especially when high soil humidity and cold weather complicate the field effort.

6.5.5 *Transfer of Samples from Sampler to Container*—The method of transfer of samples from sampling device to containers is largely dependent upon the volume of soil gas recovered.

6.5.5.1 Small volume samples are commonly recovered by syringe for immediate injection into an analyzer or small volume container. Glass gas-tight chromatography syringes are employed when rigorous QA/QC protocol is required and samples are injected into the analyzer immediately upon recovery. These syringes must be decontaminated prior to recovery of each sample aliquot. Disposable syringes are employed when samples are to be transferred to a small volume container for transport. They are inexpensive, commercially available and convenient to use. However, disposable syringes can present a disposal problem. They should be inventoried prior to use and destroyed after use, the number destroyed

equalling the number inventoried and used. Destruction includes smashing the syringe cylinder and clipping the needle.

6.5.5.2 Hand pumps are also used to transfer samples into tedlar bags or glass bulbs. Hand pumps are preferably installed behind the analyzer or container in the sample train to avoid contribution from or loss of contaminants to the hand pump. Hand pumps commonly contain petroleum-based lubricants which will contribute to the hydrocarbon content of soil gas. These devices must be placed at the end of the sample train or abandoned in favor of another tool.

6.5.5.3 Large volumes of soil gas are commonly recovered by hand or mechanical pumps installed at the end of the sample train. Large volume systems can be metered for soil gas flow rate, which is controlled by the capacity of the vadose zone sampling horizon to transmit vapor to the sampling device, the volume and configuration of the sampling system and the requirements of the analyzer or sorptive trap employed.

6.5.5.4 Small volume sampling is quite sensitive to variations in sample transfer technique. Septum coring by syringe is a common problem that restricts flow of soil gas through the needle. Coring can be corrected by decreasing the needle size and using a relatively hard septum material. Coring does not occur with side-port needles, a high-cost alternative. Needles of 25 to 27 gage seldom core septa. However, flow rates through these small gage needles are slow enough to require great care in consistency of sampling rate to minimize septum bleeding during sampling. This consistency is highly subjective and must be obtained through experience. Polypropylene disposable needles may provide opportunity for contaminant loss by sorption or gain by contribution to the soil gas sample. This can be minimized by using the polypropylene syringe to purge the sampling device prior to sampling, thereby reducing the potential for loss or gain of contaminants to that of the sampling device. Luer-lock needles should be checked for tightness by twisting prior to each use.

6.5.5.5 Tubing is commonly used in large volume sampling. For low level detection, tubing can present a cross contamination problem if not replaced in the sampling train prior to sampling at a new location. Some particulate matter and condensate may be trapped in tubing prior to entry into the flow meter and analyzer by looping the tubing into three or four small diameter loops at a point near the sampling device. This can eliminate the need for water traps or particulate filters in the system that can contribute to system loss or gain of contaminants.

6.5.5.6 Vacuum can be employed to transfer soil gas from a sampler to a container. Evacuated glass bulbs, some containing adsorbents or absorbing liquids (see Practice D 1605), can be affixed to an in-place and purged sampling device and allowed to come to pressure equilibrium. Care must be exercised in recovery of the gas sample from a vacuum cylinder. Upon recovery, the sample is immediately subjected to negative pressure and atmospheric contamination of the sample is encouraged.

6.5.6 *Sample Collection: Containers*—A wide variety of sample containers is employed by field investigators. Container selection is based upon the physical properties of the contaminants sampled, the volume of the sample recovered, the

physical properties of suspected contaminants, the sampling system employed, the anticipated sample holding time prior to analysis and the analytical method chosen. Container type for a soil gas survey should be held constant within the survey. A change in container type can impart bias to a portion of the data due to sorptive or desorptive processes related to container type.

6.5.6.1 Whole air samples can be contained in any device made of suitable materials (see 6.5.3) that conveniently satisfy survey, handling, transport and analytical requirements. Certain containers require special handling practice. The literature provides discourse on atmospheric sampling bags (54).

6.5.6.2 Sorbent traps are commonly self-contained. Care must be exercised to select a trapping device that is compatible with the properties of the target compounds and the technique of desorption chosen. Good practice for use of these devices, including handling and desorption procedure is required for successful implementation of sorbent traps when sampling organic compound vapors (see Practice D 3686).

6.5.6.3 Table 3 provides an inventory of sample containers, their applications, advantages and limitations (32).

6.5.6.4 Containers exist that provide for both whole-air and sorbent fractions as well as removal of sample by displacement (see Practice D 1605). Some are convenient for field use, however most are too complex or fragile to be of effective use for a field screening technique requiring rapid mobility.

6.5.6.5 Detector tubes should not be considered as a primary containment vehicle for the purpose of storage and transport of soil gas. A discussion of detector tube application is provided in 6.6.1.

6.5.6.6 Containers for soil samples to be preserved for a subsequent headspace analysis range from glass sample vials to metal cans. The choice of container for soil headspace determination is dependent upon the method of sampling chosen. For soil samples obtained by backhoe, bucket auger or other destructive technique, that is, a disturbed sample, extrusion into a sample vial is not necessary since most of the highly volatile components have already been lost through the act of soil sampling. Metal cans should be made from a material that does not rust. Coating materials and sealing waxes are likely to react with or adsorb soil contaminants, presenting limitations to the value of the data collected. Glass containers with screw threads or crimped seals are difficult to use for soil headspace methods due to the inability of investigators to consistently, thoroughly and rapidly clean the threads or crimp surfaces of all containers prior to capping.

6.5.6.7 Soil pore liquid headspace samples are whole-air or whole-air plus pore liquid samples. They may be contained in most devices suitable for whole-air containment, however investigators are cautioned to select containers from which a vapor sample can be extracted for analysis independently of the liquid present.

6.5.7 *Sample Processing*—Some investigators process soil vapor samples prior to analysis. Processing is performed in an effort to control sample degradation in containers. Efforts to check this degradation by sample processing include refrigeration, pressurization, and pasteurization. As a general practice, sample processing is strongly discouraged. Refrigeration may

TABLE 3 Soil Gas Sampling containers^A

Type	Applications	Advantages	Limitations
Stainless steel canisters	Collection of samples for delayed analysis	Durability Ease of sample handling Can be re-used Sample holding time longer than that for other whole-air sample containers Sample volume measurement not required Desorption not required Allows replicate analysis	Expense Requires vacuum pump or gage Can be difficult to decontaminate
Glass bulb	Collection of samples for delayed analysis	Glass is more inert than other sample container materials Septa possible Allows replicate analyses	Easily breakable Leakage through stopcocks or septa possible Adsorption to PTFE or other parts
Bag	Collection of samples for delayed analysis Sampling of very high vapor pressure compounds for which absorption methods are unsuitable	Bulk loss of sample is readily apparent Containers are light-weight and easy to handle Sample volume measurement not required Desorption not required Allows replicate analyses	Expense Some compounds may be lost through or adsorbed to bag walls Some container materials may contaminate samples Containers cannot be easily re-used Leaks in valves
Syringe ^B	Collection of samples for on-site analysis	Ease of sample collection Does not require special equipment to introduce sample into GC Desorption not required Ease of handling	PTFE plungers can adsorb sample Holding time short due to leakage or absorption Sample volume smaller than for other containers
Sorbent sampler	Allows concentration of low level samples If samples are solvent-desorbed, allows analysis of liquid sample	Relatively long holding time	Requires precise sample volume measurements Sorbent type must be tailored to compounds to be measured; adsorption behavior of each compound for solvent used must be accounted for Requires desorption (thermal or solvent) for analysis

^ASee Ref (32).

^BSyringes may also be used to transfer samples from the sampling device to a container for off-site analysis.

be somewhat effective in controlling sample degradation; however, the best method is to limit or avoid soil gas sample storage whenever possible. The limited shelf life of soil gas samples is discussed in 6.5.9.

6.5.7.1 Extraction is a sample processing step used to remove soil contaminants from soil cores or other similar samples. This technique can efficiently recover contaminants from all residence phases, not just the vapor phase. As a result, the technique yields samples that are not representative of soil atmosphere contaminant suites.

6.5.8 *Sample Transport*—If samples are to be transported to an off-site laboratory for analysis, they must be properly packaged to avoid damage to sample containers. Care must be taken to keep samples from becoming overly warm or agitated during transport. Overnight air express is highly convenient if samples are properly contained, but air freight is not recommended if samples are held in containers such as gas tight syringes or tedlar bags. These containers have other limitations as discussed in 6.5.6.

6.5.9 *Sample Life*—Soil gas samples have limited shelf life even in the most effective containers. Soil gas sample life is strongly container dependent. Numerous factors limit shelf life; most involve degradation in a container. Exposure to light, heat and agitation during shipping will accelerate sample degradation. Biodegradation may occur in some sample containers if water vapor condenses in a container containing microorganisms capable of metabolizing contaminants as substrate.

6.5.9.1 The safest practice is to minimize sample storage time. This problem is greatest when off-site laboratories are

engaged to analyze the samples. Prior to recovering the soil gas samples, arrangements can be made with the selected off-site testing laboratory to schedule the necessary personnel and equipment in anticipation of sample delivery.

6.5.10 *Soil Gas Archiving*—Sample archiving in anticipation of a future analytical or descriptive requirement is a common practice. Minimal effects of degradation or loss may be noted in storing certain sorbed samples. Soil gas archiving is, however, not recommended. Although dependent upon the type of container and the storage environment, the likelihood of degradation of soil gas samples is great enough to raise concern. Insertion of standard gases into an archived sample set and spiking of archived soil gas samples with standards provides a reference to determine the likelihood or extent of sample degradation.

6.6 *Analysis of Soil Gas Samples*—Soil gas analysis procedure is based upon pre-existing protocol established for the analysis of contaminants in ambient air. A common reference practice defining terms, sampling information, calibration techniques and methods for validating results may be applied to all automatic analyzers (see Practice D 3249). Basic laboratory practice common to investigators engaged in sampling and analysis of atmospheres applies to soil gas analysis. Note that air sampling protocols and soil gas sampling protocols are not equivalent; geophysical and geochemical factors as well as definition of air sample volume contribute to this lack of equivalency. This guide includes the criteria, guidelines and recommendations for analytical segments including the mode of operation of the laboratory and data validation (see Practice D 3614).

6.6.1 *Basic Analytical Approach*—Soil gas analysis is performed to identify the presence of contaminants, their type and relative concentrations. Various analytical methods are highly general, satisfying only the most rudimentary requirements of contaminant screening. Others are sophisticated, providing identification and relative concentration information for numerous chemical compounds determined to be present in a soil gas sample. The choice of basic analytical approach in soil gas analysis is driven by the purpose of the soil gas survey, quality assurance objectives and budgetary constraints placed upon investigators.

6.6.1.1 Soil gas surveying as a field screening technique can often be effective without the commitment of expenditure for highly sophisticated techniques. This survey purpose is merely to locate other, more direct, techniques. Caution is suggested when choosing highly sophisticated analytical methods for field screening by soil gas monitoring. This selection is controlled largely by the need for the analytical method chosen to be cost-effective.

6.6.1.2 Other applications of soil gas monitoring require more thorough analytical protocol. It is not possible, for example, to suggest the locations of partitioned miscible and immiscible ground-water contaminant plumes with elementary analytical systems. Moreover, the independent monitoring of multiple classes of contaminants in soil gas normally requires analytical systems with multiple detectors. Successful soil gas monitoring for petroleum exploration requires an analytical system which can separate and identify extremely similar volatile compounds occurring at very low concentration levels.

6.6.1.3 Contaminant concentrations in soil gas can vary from levels below the detection limit of the most sophisticated equipment to percent of a whole-air sample. Ideally, the analytical system chosen has enough flexibility to determine contaminants in a wide range of concentrations. Care should be taken to select an analytical system sensitive enough to avoid false negative results which can lead to invalid conclusions. Many analytical systems are not designed to perform to specifications in very high concentration environments, requiring sample dilution prior to analysis or selection of a less sensitive method.

6.6.1.4 Of primary importance to the successful analysis of soil gas is the familiarity and experience of the analyst with the analytical system chosen. The analyst must be able to independently care for and maintain the equipment as well as recognize symptoms of procedural error. The success of an analytical effort lies wholly with operator ability and experience. Excessive machine capability cannot compensate for operator inexperience.

6.6.1.5 Soil gas may be analyzed by a number of methods, including portable VOC (volatile organic compound) analyzers, gas elution chromatography, gas chromatography-mass spectroscopy, and colorimetric and color-indicating detector tubes. Infrared spectroscopy and fiber optic chemical sensors can be applied to soil gas analysis; however, their use is currently limited and few investigators have experience with this instrumentation. In practice, gas chromatography (GC) or GC-based handheld detectors are the most widely used analytical instruments (32) for soil gas analysis. This guide uses

numerous terms relating to various GC methods for soil gas analysis. Most of the terms should apply to other GC methods (see Practice E 355).

6.6.1.6 Portable VOC analyzers used for fugitive emission screening and industrial hygiene monitoring have been adopted for soil gas analytical purposes by numerous investigators. These devices are easily transported to and from the field, require minimal operator skill, provide immediate data and serve to eliminate many sample handling and transport steps which can result in uncertainty. Portable VOC analyzers are limited in application to very low level detection due to the absence of a concentration step. They exhibit limited selectivity and do not have the ability to separate contaminant compounds, leading to potential interference. These devices also are limited in accuracy due to the inability to calibrate for the wide variety of contaminant compounds encountered in soil gas, each compound having its own character of detector response. Portable VOC analyzers contain three types of detectors. These are the flame ionization detector (FID), the photoionization detector (PID) and the infrared (IR) detector. The literature contains a thorough treatment of these devices (10, 55).

6.6.1.7 Soil gas analysis by GC is by far the most versatile and the most costly soil gas analytical method. Instrumentation can be varied to accommodate field mobility, however this is not always required. The technique provides separation of compounds in a chromatographic column, tentative identification of compounds determined to be present and a relative quantitation of compound concentration based upon comparison to a known standard. Soil gas is introduced into the GC and conveyed through a chromatographic column by a carrier gas, separating the contaminants as they pass through the column. The separation is obtained when the sample mixture in the vapor phase passes through a column containing a stationary phase possessing special adsorptive properties. As the gas stream emerges from the column, it passes through a detector, providing for measurement of a specific sample property through the recording of detector electrical response. These responses, or peaks, are recorded as a function of time. Comparison of known standard compound response time with the response time of an unknown represented by a peak results in the tentative identification of the unknown. Comparison of the magnitude of detector response to the newly identified compound versus detector response to the same compound of known concentration, a laboratory standard, results in a relative quantitation of subject compound concentration in the sample.

6.6.1.8 Gas chromatography is essentially a physical separation technique. The degree of separation depends upon the differences in the distribution of volatile compounds, organic or inorganic, between a gaseous mobile phase and a selected stationary phase that is contained in a tube or GC column (see Practice E 260).

6.6.1.9 Numerous factors can impact the ability of the GC to determine contaminants in a soil gas sample. These include column characteristics, sample flow rate, sample temperature, the composition of the carrier gas and the type of detector

employed. Instrumentation can be expanded to include multiple columns, multiple detectors, sample loops and temperature programming, all of which make an instrument more versatile, albeit at additional cost.

6.6.1.10 Simple GCs are portable analyzers with GC options. Field GCs are more advanced instruments with temperature programmable ovens and provide opportunity for multiple columns and detectors. They can be carried in mobile laboratories or established in a temporary base laboratory in the field. Research-grade instruments are normally based at off-site laboratories with strictly controlled environments. These are used when positive identification or very low detection limits are specified. The literature contains excellent comparisons of the advantages, limitations and applications of the various configurations of GCs, including instrument specifications (10, 32, 56, 57).

6.6.1.11 Detector tubes have been applied to safety and health atmospheric monitoring, agriculture and the chemical industry. These devices are designed to be compound specific, although this characteristic is dependent upon the contaminant compounds present in the sample drawn through the tube. Detector tubes may be used for short-term sampling (grab sampling; 1 to 10 min) or long-term sampling (dosimeter sampling; 1 to 8 h). Short-term sampling involves the movement of a given volume of gas through the tube by a mechanical pump. If the substance for which the detector tube was designed is present, the indicator chemical in the tube will change color (stain). The concentration of the gas may be estimated by either the length of the stain compared to a calibration chart or by the intensity of the color change compared to a set of standards (see Practice D 4490). Long-term sampling involves the movement of gas at a very slow rate through the tube by means of an electric pump. The use of long-term detector tube sampling for soil gas monitoring is limited to specific temporal survey designs.

6.6.1.12 Detector tubes are relatively inexpensive and provide immediate results. Their use is restricted to applications with few interfering compounds. Depending upon the contaminants present, they may be of low sensitivity and can be affected by humidity, normally high in soil gas, sample flow rate, temperature extremes (32), storage conditions and shelf life.

6.6.1.13 The literature contains excellent discourse on the detector tube apparatus, reagents, procedure accuracy and amenable compounds (see Practice D 4490).

6.6.2 *Specific Analytical Approaches*— This subsection discusses various detectors and methods that may be integrated into soil gas analytical instrumentation. For methods providing detector alternatives, the choice of an appropriate detector should be guided by knowledge of detector properties. Key properties are as follows (after Mayer, 1989 (32)):

6.6.2.1 *Selectivity or Specificity*—Selectivity refers to the responsiveness of the detector to the compound of interest. Detectors responding to a wide range of classes of compounds are termed universal or non-selective detectors. Those that respond to only certain classes of compounds are termed selective detectors.

6.6.2.2 *Sensitivity*—Sensitivity refers to the relationship

between the detector response and the quantity of the subject compound injected. It is the smallest detectable quantity of a compound; it is usually considered to be the amount that produces a response equal to twice the baseline noise of the detector.

6.6.2.3 *Linear Dynamic Range*—Linear dynamic range is the range over which the detector response to a compound is directly proportional to the amount of compound injected. Detectors vary in the range of component concentrations over which they are linear. Wide linear dynamic range is desirable because it simplifies quantitation of samples having widely varying ranges of concentrations.

6.6.2.4 *Stability*—Stability is a factor referring to detector responsiveness over time. Stability is controlled by numerous factors and is seldom quantified. The required frequency of instrument calibration is determined by detector stability.

6.6.3 Specific analytical approaches are as follows:

6.6.3.1 *Flame Ionization Detectors (FID)*— Flame ionization detectors generate electric current when gases containing carbon atoms are oxidized to carbon dioxide in a hydrogen flame and potential is applied across the flame. The magnitude of the electric current generated is termed the detector response. FIDs are responsive to hydrocarbon contaminants in soil gas and are commonly employed for this purpose. These detectors are durable for field application, and have a wide linear range and nearly uniform response to organic gas species. FIDs are generally unresponsive to inorganic gases and water vapor, common constituents in soil gas. FID performance can be evaluated independently of the chromatographic column (see Practice E 594). Although highly versatile, these detectors are not selective for halogenated compounds. They require supplies of fuel gas which require careful safety practices in handling and flame ignition.

6.6.3.2 *Photoionization Detectors (PID)*— Photoionization detectors employ ultraviolet radiation to ionize contaminant molecules. Positive ions and free electrons are formed which migrate to the detector electrode(s), resulting in an electric current that is proportional to contaminant concentration at the detector. PIDs are extremely sensitive to aromatic hydrocarbons due to the great efficiency of ionization of pi bonds under ultraviolet radiation. Efficiency of ionization of sigma bonds is lower, resulting in a higher PID detection limit for aliphatic hydrocarbons. The selectivity of the method can be adjusted by selecting lamps of different energies, causing a change in response of contaminants with fixed ionization potentials to changing lamp energies. Tables exist of ionization potentials of compounds within classes common to soil gas contaminants (58). Methane has an ionization potential higher than the energies of commercially available lamps, limiting the PID to detection of compounds other than methane. PIDs are further limited by their tendency to conceal the presence of low-sensitivity compounds when high-sensitivity compounds (aromatics) are present. PID response can be impacted by condensation of water vapor in the lamp.

6.6.3.3 *Electron Capture Detectors (ECD)*— Electron capture detectors are highly sensitive to and selective for compounds with electronegative functional groups such as CFCs

(chloro-fluorocarbons). The sensitivity of the detector is proportional to the number of these groups on a compound, resulting in a unique detector response to each compound. The ECD comprises a source of thermal electrons inside a reaction chamber (a radioactive source emits β radiation which ionizes the carrier gas to produce electrons). The device detects compounds with electronegative functional groups capable of reaction with thermal electrons to form negative ions. Such reactions cause a decrease in the concentration of free electrons. The detector is designed to measure changes in the concentration of these electrons inside the chamber (see Practice E 697). Calibration of the ECD is therefore linked to each compound to be determined by the detector. ECDs are also sensitive to water, oxygen and other common components of soil gas, causing potential problems in method performance. ECDs emit β radiation that should be properly vented. Operation of an ECD requires licensing under Federal regulation.

6.6.3.4 *GC/Mass Spectroscopy*—Combination of gas chromatography and mass spectroscopy results in the GC/MS method of analysis. A mass spectrometer is used to obtain a mass spectrum of each eluting compound. Positive identification of these compounds is sometimes obtained by comparison of the unknown mass spectrum to a library of known spectra. GC/MS can be extremely selective for target compounds. Use of the technique for soil gas monitoring is limited, primarily due to the cost of analyses.

6.6.3.5 *GC/Fourier Transform Infrared Spectroscopy*—This analytical method combines gas chromatography with Fourier transform infrared spectroscopy. GC/FTIR can provide a rapid identification of eluting compounds by comparison of their infrared spectra with a known spectral library. Quantitation is achieved by subsequently passing the sample through an appropriate GC detector such as the FID or ECD. This method, like GC/MS, is limited in application to soil gas monitoring by the high cost of analysis.

6.6.3.6 Other detectors are applied to soil gas analysis by GC, albeit rarely in comparison to FID, PID and ECD. They include the argon ionization detector, a nondestructive device similar in operating design to the ECD, the flame photometric detector (FPD) used to determine organic compounds containing sulfur and phosphorus, and the hot-wire (pyrolyzer) used to determine compounds containing nitrogen.

6.6.4 *Analytical QA/QC*—The validation of the analytical aspects of soil gas monitoring is fundamental to the technique. Analytical equipment and procedure must be evaluated by laboratory QA/QC, just as the sampling system, sampling plan and field procedure are evaluated by field QA/QC methods. Analytical QA/QC defines a confidence limit of performance. The utilization of well tested and uniform analytical practices is essential to the production of reliable and defensible data, the validity of which can be demonstrated at a later date through the use of written field and laboratory records (see Practice D 3614).

6.6.4.1 Most analytical QA/QC plans contain calibration steps, linearity checks, standard analyses, blank analyses, duplicate analyses and audit checks. The various analytical approaches discussed in 6.6.3 require a variety of different protocols which will satisfy the QA/QC requirements for each method. Four types of analytical QA/QC samples are required for determination of quality assurance. These are analytical reagent blanks (used to determine the potential of sample or standard contamination from a reagent), laboratory blanks (used to determine the impact potential of the laboratory atmosphere on analytical results), analytical sample replicates (used to estimate the analytical precision for samples) and analytical standard replicates (used to estimate the analytical precision for standards). Table 4 provides a summary of suggested calibration and quality control requirements for analytical systems (10).

TABLE 4 Summary of Suggested Calibration and Quality Control Requirements for Analytical Systems^A

Type of Instrument	Detector Type	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
Portable VOC (THC) Analyzer	FID	(1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Methane or other aliphatic compound	Correlation coefficient \geq 0.995	Repeat multipoint calibration after checking calibration dilution system
		(2) Zero (span) calibration	Daily	UHP Air or N ₂ /Methane	Response factor agreement within \pm 20 % of mean RF for multipoint calibration	(1) Repeat zero span calibration (2) If still unacceptable, repeat multipoint calibration
		(3) Control sample analysis	Daily, prior to testing	Methane	Measured concentration within \pm 10 % of certified concentration	(1) Repeat zero span calibration (2) Repeat control sample analysis
		(4) Drift check	Daily, at conclusion of testing	Methane	Drift value \leq 20 % of the input value	(1) Flag day's data as questionable (2) Repair or discontinue use of analyzer
	PID	(1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Benzene or other aromatic compound	Correlation coefficient \geq 0.995	Repeat multipoint calibration after checking calibration dilution system

TABLE 4 *Continued*

Type of Instrument	Detector Type	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action	
Portable Gas Chromatograph	PID	(2) Zero/span calibration	Daily	Benzene or other aromatic compound	Response factor agreement within $\pm 20\%$ of mean RF for multipoint calibration	(1) Repeat zero/span calibration (2) If still unacceptable, repeat multipoint calibration	
		(3) Control sample analysis	Daily, prior to testing	Benzene or other aromatic compound	Measured concentration within $\pm 10\%$ of certified concentration	(1) Repeat zero/span calibration (2) Repeat control sample analysis	
		(4) Drift check	Daily, at conclusion of testing	Benzene or other aromatic compound	Drift $\leq 20\%$ of the input value	(1) Flag day's data as questionable (2) Repair or discontinue use of analyzer	
	FID	(1) Multipoint calibration (zero plus three upscale concentrations) (2) Zero/span calibration	At start of program	Benzene or toluene	Correlation coefficient ≥ 0.995	Repeat multipoint calibration after checking calibration dilution system	
			Daily	UHP air or N ₂ /methane	Response factor agreement within $\pm 20\%$ of mean RF for multipoint calibration	(1) Repeat zero/span calibration (2) If still unacceptable, repeat multipoint calibration	
		(3) Control sample analysis (4) Drift check	Daily, prior to testing	Benzene	Measured concentration within $\pm 10\%$ of certified concentration	(1) Repeat zero/span calibration (2) Repeat control sample analysis	
			Daily, at conclusion of testing	Benzene	Drift $\leq 20\%$ of the input value	(1) Flag day's data as questionable (2) Repair or discontinue use of analyzer	
		(5) Retention time checks (6) Analytical blanks	Daily	Benzene or toluene	None	None	
			Daily	UHP air or N ₂	Measured concentration $\leq 5\%$ of the instrument span value	Clean/replace system components until acceptable blank can be obtained	
		(7) Sampling system blanks	Daily, plus after very high samples	Sample gas	Measured concentration $\leq 5\%$ of the instrument span value	Clean/replace system components until acceptable blank can be obtained	
			(8) Duplicate samples (9) Control point samples (10) Background samples	10 % of sampling points, minimum	Sample gas	None; provides a measure of total sampling variability	None
		After every ten samples or once per day, whichever is greater		Sample gas	None; provides a measure of temporal variability	None	
		One sample per day		Sample gas	None; provides a measure of background concentration	None	
		PID	(1) Multipoint calibration (zero plus three upscale concentrations) (2) Zero span calibration	At start of program	Benzene or toluene	Correlation coefficient ≥ 0.995	Repeat multipoint calibration after checking calibration dilution system
				Daily	UHP air or N ₂ /methane	Response factor agreement within $\pm 20\%$ of mean RF for multipoint calibration	(1) Repeat zero/span calibration (2) If still unacceptable, repeat multipoint calibration
PID	(3) Control sample analysis (4) Drift check	Daily, prior to testing	Benzene	Measured concentration within $\pm 10\%$ of certified concentration	(1) Repeat zero/span calibration (2) Repeat control sample analysis		
		Daily, at conclusion of testing	Benzene	Drift $\leq 20\%$ of the input value	(1) Flag day's data as questionable (2) Repair or discontinue use of analyzer		
	(5) Retention time checks (6) Analytical blanks	Daily	Benzene or toluene	None	None		
Daily		UHP air or N ₂	Measured concentration $\leq 5\%$ of the instrument span value	Clean/replace system components until acceptable blank can be obtained			

TABLE 4 *Continued*

Type of Instrument	Detector Type	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
		(7) Sampling system blanks	Daily (plus after very high samples)	Sample gas	Measured concentration \leq 5 % of the instrument span value	Clean/replace system components until acceptable blank can be obtained
		(8) Duplicate samples	10 % of sampling points, minimum	Sample gas	None; provides a measure of total sampling variability	None
	PID	(9) Control point samples	After every ten samples or once per day, whichever is greater	Sample gas	None; provides a measure of temporal variability	None
		(10) Background samples	One sample per day	Sample gas	None; provides a measure of background concentration	None
Off-site Gas Chromatograph	FID	(1) Multipoint calibration (zero plus three upscale concentrations)	1 per month	Propane/hexane	Correlation coefficient \geq 0.995	Repeat linearity check
		(2) Single point calibration check	Daily, prior to sample analyses	Propane/hexane	Response factor agreement within \pm 20 % of most recent average RFs for multipoint calibration	Repeat single point calibration
		(3) Retention time check	Daily, prior to sample analyses	Multicomponent standard	Agreement with preestablished relative retention times	Adjust GC conditions and repeat RT check
	FID	(4) Control sample analysis	Daily, prior to sample analyses	Sample gas	(1) Correct identification of 90 % of components (2) For 90 % of components, measured concentrations within \pm 30 % of actual concentrations	Repeat control sample analysis
		(5) Duplicate analyses	Minimum 10 % of samples (all duplicate samples will be analyzed in duplicate)	Sample gas	CV \leq 20 % for ten major sample components	Repeat sample analysis
		(6) Blank analysis	Daily, prior to sample analysis	UHP air or N ₂	Total \leq 20 ppbv-C	(1) Clean system (2) Repeat blank analysis
	PID	(1) Multipoint calibration (zero plus three upscale concentrations)	1 per month	Propane/hexane	Correlation coefficient \geq 0.995	Repeat linearity check
	PID	(2) Single point calibration check	Daily, prior to sample analyses	Propane/hexane	Response factor agreement within \pm 20 % of most recent average RFs for multipoint calibrations	Repeat single point calibration
		(3) Retention time check	Daily, prior to sample analyses	Multicomponent standard	Agreement with preestablished relative retention times	Adjust QC conditions and repeat RT check
			(4) Control sample analysis	Daily, prior to control sample analyses	Sample gas	(1) Correct identification of 90 % of components (2) For 90 % of components, measured concentrations within \pm 30 % of actual concentrations
		(5) Duplicate analyses	Minimum 10 % of samples. (Duplicate samples analyzed in duplicate)	Sample gas	CV \leq 20 % for ten major sample components	Repeat sample analysis
	PID	(6) Blank analysis	Daily, prior to sample analysis	UHP air or N ₂	Total \leq 20 ppbv-C	(1) Clean system (2) Repeat blank analysis
	ECD	(1) Quantitative standard	Daily, prior to sample analysis	Multicomponent standard	Response factor agreement within \pm 30 % of three day rolling mean RFs for all components	Repeat calibration

TABLE 4 *Continued*

Type of Instrument	Detector Type	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
		(2) Retention time check	Daily, prior to sample analyses	Multicomponent standard	None; will provide basis for comparison of FID/PID results to ECD results	None
		(3) Control sample analysis	Daily, prior to sample analyses	Sample gas	(1) Correct identification of all components (2) For 90 % of components, measured concentrations within ± 30 % of actual concentrations	Repeat control sample analysis
	ECD	(4) Duplicate analyses	Minimum of 10 % of samples (all duplicate samples analyzed in duplicate)	Sample gas	$CV \leq 20$ % for ten major sample components	Repeat sample analysis
		(5) Blank analysis	Daily, prior to sample analyses	UHP air or N ₂	Total ≤ 20 ppbv-C	(1) Clean system (2) Repeat blank analysis

^A See Ref (10).

6.6.4.2 The aspects of bias, precision, representativeness, completeness and comparability must be considered to evaluate analytical equipment performance, including the establishment of minimum detectable quantities of contaminant compounds, retention time drift and the linearity of instrument response. Bias and precision must be quantified in order to compare actual survey performance with goals established in the survey plan.

6.6.5 A data validation summary report is a common method of evaluating analytical system performance. A guide for determining parameters key to the data validation summary report is provided as follows.

6.6.5.1 *Bias*—For determination of bias, the percent recovery can be determined using the following formulas:

$$\text{recovery reproducibility} = (DCS/KCS) * 100 \quad (6)$$

where:

DCS = determined concentration of standard, and
KCS = known or certified concentration of standard.

The standard deviation of all standards analyzed can be determined as follows:

$$SD = \{(\text{sum}(\text{recovery} - i - \text{recovery} - \text{ave})^2) / (n - 1)\}^{0.5} \quad (7)$$

Finally, the range of uncertainty can be determined using the following equation:

$$\pm R = \pm t * (SD) / (n^{0.5}) \quad (8)$$

where:

t = the value of Studentized *t* at the 90 % confidence level and (*n* - 1) degrees of freedom.

The bias statements for data collected should be expressed as the average recovery plus or minus the range.

6.6.5.2 *Precision*—For the determination of precision, the relative standard deviation of replicates can be calculated using the following equation:

$$RSD - \text{pair} = SD / \text{Mean} \quad (9)$$

$$RSD - \text{ave} = \{(\text{sum}(RSD - \text{pair})^2) / (n - 1)\}^{0.5} \quad (10)$$

where:

RSD-pair = relative standard deviation for each pair of replicates, and

RSD-ave = relative standard deviation overall.

Next, the precision can be determined as follows:

$$\text{precision} = \{(t * RSD - \text{ave}) / DF\} * 100 \quad (11)$$

where:

precision = the percent precision,

t = the *t* value for *n* - 1 pairs of replicates, and

DF = the degrees of freedom = (*n* - 1).

Finally, mean value is reported with associated uncertainty:

$$x \pm (x * t * SD - \text{ave}) / (DF)^{0.5} \quad (12)$$

where:

x = reported chemical concentration, and

t = the value of *t* at the 90 % confidence level for the appropriate degrees of freedom.

6.6.5.3 *Representativeness*—Representativeness is determined by the results of the cross contamination blanks and the air blanks. The results should be presented as a bias estimate, as follows:

$$\text{bias} (\%) = \{(CCC - CA) / \text{Mean}\} * 100 \quad (13)$$

where:

CCC = concentration in cross contamination sample,

CA = concentration in air, and

Mean = mean concentration in sample set (bias may also be expressed for a single sample by substituting sample concentration).

6.6.5.4 *Completeness*—The completeness goal is 90 % or higher. Completeness is the number of samples collected that can be validated through the procedures for bias, precision, and representativeness.

6.6.5.5 *Comparability*—Comparability is based upon professional judgment and is provided through planning steps carried out prior to initiation of field work.

6.7 *Data Interpretation*—Soil gas data interpretation is an iterative process including the examination of the raw data,

selection of appropriate and useful data displays, and establishment of correlation of the data set to other vadose zone monitoring data and ground truth. Interpretation of soil gas data is not like other interpretive exercises involving measurement data, in that mathematical expressions relating soil gas contaminant concentrations to underlying soil, rock and ground-water contaminant concentrations cannot be written for most applications at a high confidence level. This is a function of a lack of site characteristics information at even the most comprehensively studied sites. Soil gas data cannot be consistently interpreted in a manner that establishes direct correlation between contaminants in a soil gas horizon and contaminants in other horizons. Processes including migration and degradation can have profound influence on the correlation of soil gas data to ground truth. Interpretive efforts excluding consideration of these influencing processes can be highly misleading. For example, the presence of contamination in an underlying horizon will not necessarily correlate to the detection of contaminants in overlying soil atmospheres, that is, the potential for a false negative result. The converse is also true, that is, the potential for a false positive result. Interpretation of GC results in the laboratory without consideration of pertinent hydrogeological information may lead to incorrect conclusions (59). However, the detection of contaminants in soil gas does suggest the existence of a contaminant source, and increases in contaminant concentration can suggest close proximity to the source or an increased quantity of the subject contaminant in the subsurface. It is the responsibility of the interpreter to examine soil gas data in context of other site characteristics, and provide an interpretation based upon sound judgment and thorough yet practical data treatment.

6.7.1 *Manipulating Data*—Soil gas data are normally interpreted as raw data. The application of correction factors is not recommended, as it is difficult if not impossible to determine if the magnitude of the correction factor is greater than that of the variance between data populations in a survey. Moreover, the need for correction factors can indicate a flaw in survey design, sampling system performance or the objectivity of the interpreter.

6.7.2 *Defining Data Subpopulations*—Soil gas monitoring seeks to define anomalous subpopulations of data that contain measurable quantities of contaminants or unusual compositions. These populations can easily be described by their contrast to normal populations, for example, contrasting populations with and without measurable contaminants. Establishment of contaminant baselines or conditions “at background” make this contrast possible. If all soil gas samples are recovered in a contaminated area, there may be no apparent contrast.

6.7.2.1 Statistical treatment of soil gas monitoring data allows the interpreter to estimate the amount of variation noted in the survey data due to errors. This practice also permits the interpreter to evaluate the data quality objectives suggested for the survey during the planning phase. Statistical treatment of soil gas data can also be of use to define anomalous data subpopulations when the boundaries of a contaminated area are not clearly defined or if the existence of multiple populations of data (that is, contaminated and uncontaminated) within a single data set is in doubt. The literature contains discourse on

statistical treatment of soil gas data (10, 60).

6.7.3 *Interpreting Soil Gas Data Profiles*—Soil gas data from survey profiles displayed on an $X - Y$ plot are an effective aid to data interpretation. This display is useful to examine the overall context for soil gas measurement data potentially indicating contamination. If the profile is displayed as a cross section through a grid pattern or as a linear array of sample points, the profile display can illustrate spatially significant groupings of data subpopulations.

6.7.3.1 It is quite common for concentration data to be highly variant within a contaminated area. Soil gas profiles can be used to show variation in spatially related data. This is one method of defining subpopulations of data indicating contamination or other anomalous characteristics.

6.7.3.2 Multiple data sets can be displayed on a single profile. Comparison of one data set to another on a single profile is a simple visual method to screen for suggested data subpopulations. Comparison of concentration data and compositional data (see 6.7.5) on a single profile can further resolve this problem.

6.7.4 *Mapping Soil Gas Data*—Soil gas data obtained by sampling at a single depth are often mapped to suggest the lateral extent of subsurface contamination. Map suites of soil gas data obtained from multiple depths can sometimes aid investigators in determining the depth to the contaminant source.

6.7.4.1 Numerous algorithms can be used to interpolate between data points, including linear, inverse distance squared, inverse distance cubed, splines and kriging. The various interpolation methods will yield similar results, suggesting a general pattern of contaminant distribution in soil gas. Kriging requires a probability model for each survey site mapping application for which it is employed, the derivation of which requires data which are not normally available for a given soil gas survey area.

6.7.4.2 Caveats exist in using computer mapping programs as interpretive aids. Difficulties can arise in treatment of adjacent data points differing in contaminant concentration by an order of magnitude and more due to vapor migration barriers, preferential vapor flow paths or changes in soil moisture or porosity content. It is possible to model these characteristics and input such a model into some computer mapping programs; however, this introduces bias into the mapping effort. Single point soil gas contaminant concentration highs may exist due to a sample density which is insufficient to resolve the cause for the single point anomaly. Contour mapping of such data may be meaningless without the complement of other information, especially detailed knowledge of site characteristics.

6.7.5 *Analyzing the Composition of Soil Gas Contaminants*—Certain applications of soil gas monitoring require detailed analyses available from off-site bench laboratories or mobile laboratories. Determination of a number of contaminant compounds in a soil gas sample set with either of these analytical systems enables the interpreter to make a comparative analysis of the changes in soil gas contaminant composition within that sample set.

6.7.5.1 Compositional analyses can range in scope from a

simple listing of the various compounds determined in each sample to thorough data treatments. Profiles of soil gas data can be constructed to illustrate the spatial relationship between two potentially different groupings of data (see 6.7.3). Cross-plots of contaminant compound concentrations are highly effective in the definition of data subpopulations, and can be used to relate contaminant types to known on-site waste streams and sources in complex settings. Known as fingerprinting, this guide compares vapor composition over a known contaminant product and the known soil atmosphere composition over that product to soil gas contaminant composition in areas being investigated on the subject site. Subtle divisions in data subpopulations can be defined by crossplots of contaminant ratios. In addition to simple ratioing, computerized multivariate pattern recognition techniques such as cluster, factor and discriminant analyses can assist in the evaluation of intra-data set compositional variations and their relationship to the physical contamination issues at a site.

6.7.5.2 Soil gas data can be examined for the appearance of target compounds determined to be present in contaminant mixtures. The success of this practice, used primarily to establish the location and extent of underlying ground water contamination, relies upon selection of appropriate target compounds and the persistence of target compounds in soil vapor.

6.7.5.3 Monitoring specific compounds in soil gas data can be utilized to determine the progress of degradation or migration of contaminants in the vadose zone and in ground water. Biodegradation has been monitored by the appearance of excessive quantities of carbon dioxide in soil gas (61).

6.7.6 *Interpretation in Context of Other Vadose Zone Monitoring*—Soil gas monitoring is not a technique that can consistently support conclusions based upon interpretations of survey results. For this reason it is strongly recommended that other vadose zone monitoring methods be used to corroborate data obtained from a soil gas survey, especially when investigators are attempting to do more than simply audit a subject site for the presence of contaminants. Useful models of contaminant emplacement and transport in the vadose zone can be constructed by combining techniques. Examples of useful combinations are soil pore liquid and soil gas monitoring or neutron probe and soil gas monitoring.

6.7.7 *Correlation With Ground Truth*— Interpretation of soil gas data is difficult without establishing some form of ground truth with which to substantiate survey results. Ground truth can be in the form of monitoring well data, for purposes of determining the extent of contamination by a ground-water contaminant plume. Examples of other forms of ground truth usable in support of soil gas data interpretation are soil cores, the presence of contaminant odors in basements, observed floating contaminants in storm sewers or utility vaults, or other field observations.

7. Data Reporting Requirements

7.1 *Purpose of Reporting*—Of primary concern in a report of findings pertaining to a soil gas survey is that the report includes the information necessary to describe the results of that survey performed for a particular application. In many instances, certain interpretative methods or data reporting

formats useful to end users for one particular application are not relevant to the needs of end users applying the information to a different application. Examples of these differing applications that require unique report subject matter are soil gas contaminant determinations for real property environmental assessments, soil gas monitoring of volatile organic contaminants from underground storage tanks and soil gas sampling as a tool useful in the exploration for natural resources. Certain applications require a thorough treatment of a significant number of factors impacting the meaning and usefulness of soil gas data interpretations. Examples of such applications include damage assessments, contaminant source identification or tests of the effectiveness of remediation. Other applications command minimum reporting requirements. An example of such an application is the monitoring of releases from underground storage tanks over time. Included in a discussion of the report objectives should be an identification of the end user category (for example, regulatory agency, land acquisition negotiations).

7.1.1 A decision must be made regarding the units expressed in reporting, that is, qualitative or quantitative. If quantitative, the appropriate expression of units in volume/volume or weight/volume must be determined. SI units are recommended for reporting of atmospheric measurement data (see Practice D 1914).

7.2 *Report Format*—Certain reporting requirements are commanded without regard to data application. In large part they are related to the QA/QC objectives, and include data comparability, representativeness, bias, precision accuracy, completeness and analytical detection limits whenever possible. At a minimum, a general discussion of the reliability of results and analytical detection limits is warranted; soil gas test data may be evaluated in the same manner as is other atmosphere test data (see Practice D 3614).

7.3 *Salient Points to be Addressed in Reporting*—The report of findings of any soil gas monitoring effort can contain discussions within any number of topics that should be selected to best suit the requirements of the end user. Selection of appropriate topics is discretionary, usually based upon a scope of work determined by prior agreement between the data provider and the data end user. Efforts to limit reporting requirements for the sake of short term time and money cost savings usually result in low-confidence level treatment of the report or an ultimate time and money cost gain, or both. Discussions that should be included when appropriate and whenever possible are provided below.

7.3.1 The purpose of the soil gas study should be stated, as well as the rationale for selection of a particular soil gas monitoring technique.

7.3.2 Selection of a particular soil gas monitoring technique is typically controlled by the chemical and physical properties of the chemical compounds of interest which are known to occur or suspected to occur on site. A discussion of the sample array in three dimensions, sampling method employed and the analytical scheme chosen in context of these properties should be provided.

7.3.3 The rationale for selection of a particular soil gas monitoring technique should always be based upon the physical properties of the vadose zone as well as the chemical and

physical properties of the compounds of interest. A discussion of the impact of these vadose zone properties on survey design should be included in the report. The regional and local hydrogeologic conditions within the survey area should be described. A discussion of the regional geology should include the physiographic province, a generalized geologic column, geologic structure and general ground water occurrence. The local conditions should be described with regard to soil type(s), moisture content in the vadose zone, soil/bedrock interface, stratigraphy and lithology, ground water bearing zones, flow directions and gradients, potentiometric levels, aquifer characteristics and ground water quality.

7.3.4 If known and appropriate, the characteristics of a contaminant source or spill should be addressed. Examples of such characteristics are contaminant composition, the likelihood of single or multiple contamination events or the reaction potential (above, within and beneath the vadose zone) of multiple contaminant mixtures.

7.3.5 Every subject of every vadose zone monitoring effort has unique characteristics. Those characteristics that could impact the results of the soil gas monitoring effort should be described to provide a meaningful context in which to interpret the soil gas data.

7.3.6 There are a number of topics common to most soil gas data reporting that are useful in the majority of applications. The regional and specific site location should be identified using a site plot plan. The site plot plan could include an insert showing the regional location. A discussion should be included regarding the physical structures at the site that may impact the location of sampling points and the migration of soil gas, for example, asphalt and concrete pads, buried pipelines and surface water impoundments. Site history must be considered, including the types of chemical compounds known or suspected to have been used at the site. These compounds should be listed with their chemical and physical properties as they relate to volatilization, solubility and other migration characteristics or soil gas recovery characteristics.

7.3.7 The site should be evaluated in the report of findings for the impact of the regional and local hydrogeologic conditions within the survey area on the results of the survey.

7.3.8 A detailed description should be given of the type of soil gas survey conducted. Details should include selection of active or passive method, whole air or passive sample collection method, sampling array, background sampling, equipment decontamination procedure employed prior to the survey, field or laboratory analytical methods and QA/QC procedures. Any unusual conditions should be noted, such as rainfall events during the course of the survey (especially when moveable soil gas chiefly originates from vadose zone microporosity), high pressure or low pressure front movement across the survey area during the course of the survey (especially when moveable soil gas chiefly originates from vadose zone macroporosity), or visual observations of contamination at sampling points.

7.3.9 If a subject property is found to be contaminated, a separate discussion of soil gas characterization of uncontaminated or nonanomalous contiguous property should be provided in the report of findings. This can be useful in highlight-

ing naturally occurring petroleum hydrocarbons in soil and in establishing a regional baseline of contamination.

7.3.10 Data collected during the field sampling and field or laboratory analyses should be compiled in table form and be included in a preliminary or final report, preferably as appendices. Such data should include a listing of sampling and analysis dates, soil/rock description at each sampling point, depth and diameter of sampling point, quantity of soil gas purged prior to sampling, quantity of sample extracted, chromatogram and/or mass spectra for each sample and a tabulation of QA/QC samples recovered.

7.3.11 The report of findings should include a discussion of the results of the QA/QC efforts, establishing performance within limits set prior to the survey. Data validation involves review of the data collected for the purpose of isolating spurious values (32). Systematic errors or bias can be detected in this review. Suggestions should be made as to the origin of the errors or bias.

7.3.12 Results of analyses should be displayed on plan maps and should include sampling point locations, physical features, contours of equal concentrations of specific compounds or compound groups (for example, alkanes) and any necessary keys or other notes to guarantee map clarity. Cross-sections showing changes in contaminant concentration with depth and concentration profiles of more than one contaminant through several sample locations can be highly useful displays. The report should include text describing each map, cross-section or profile.

7.3.13 Whenever possible, discussion should be provided that correlates soil gas data to ground truth. The most common and widely accepted form of ground truth is data from ground water monitoring wells.

7.3.14 When appropriate, the report of findings should attempt to identify the source of the contaminants encountered in the soil gas survey.

7.3.15 The report should contain a section which discusses the conclusions drawn from the results of the soil gas study and any recommendations which seem appropriate to enhance the value of conducting such a soil gas study. Conclusions should include identification of the compounds detected, if any, an assessment of the appropriateness of the soil gas study method used, and any circumstances that may have significantly impacted the results of the investigation, such as weather conditions or equipment calibration. Recommendations should address need for establishing ground truth, extension of the study to adjacent areas of interest, the need for a different soil gas study method, actions to resolve questionable QA/QC results, or need for additional chemical analyses for contaminant identification.

7.4 *Disadvantages of Real-Time Reporting*—In actual practice, many end users request real-time reporting of soil gas data obtained from field-based laboratories. Presentation of such data presents the opportunity for misunderstanding by end users who are not familiar with the caveats presented by data not examined in light of the QA/QC program or site specific factors. Real-time reporting of soil gas data is therefore not recommended.

8. Keywords

8.1 contaminant; environmental monitoring; geochemistry; ground water; Henry's law; petroleum hydrocarbon; sampling;

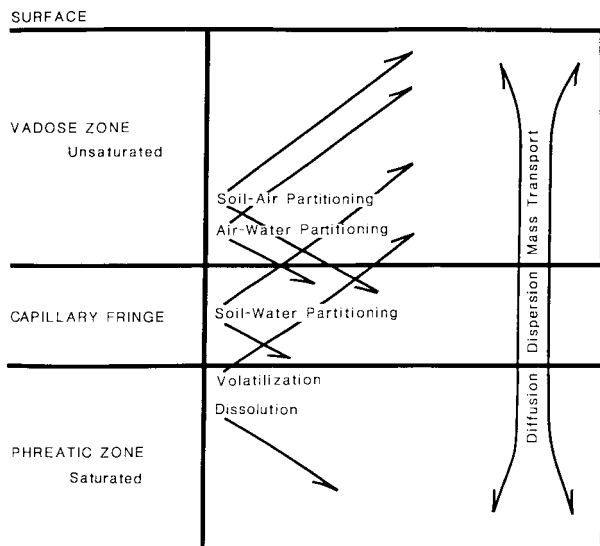
soil gas; unsaturated flow; vadose zone; vapor monitoring; volatile organic compound

APPENDIX

(Nonmandatory Information)

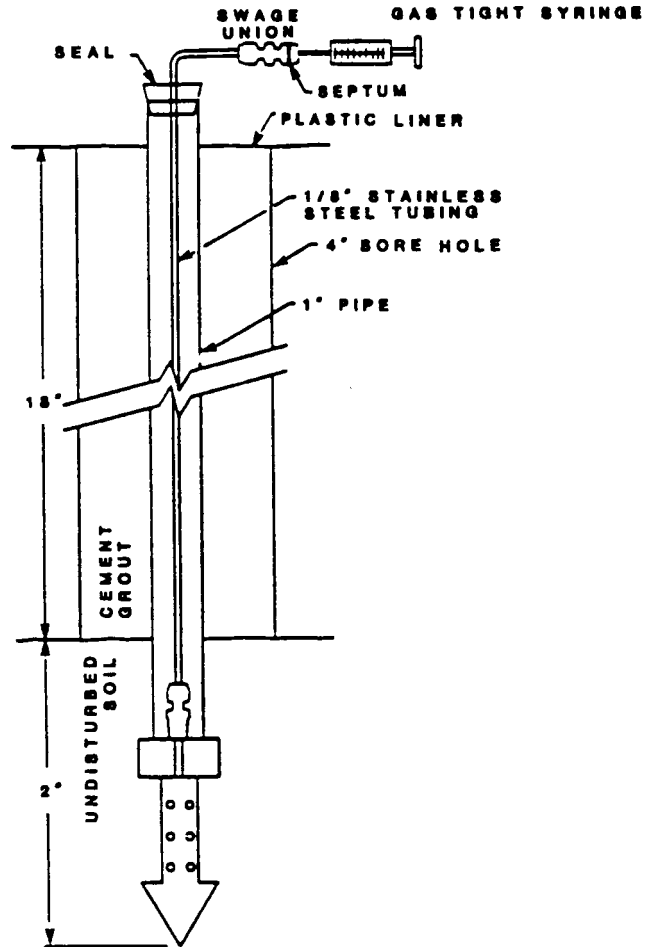
X1. SOIL GAS MONITORING

X1.1 See Figs. X1.1-X1.9.



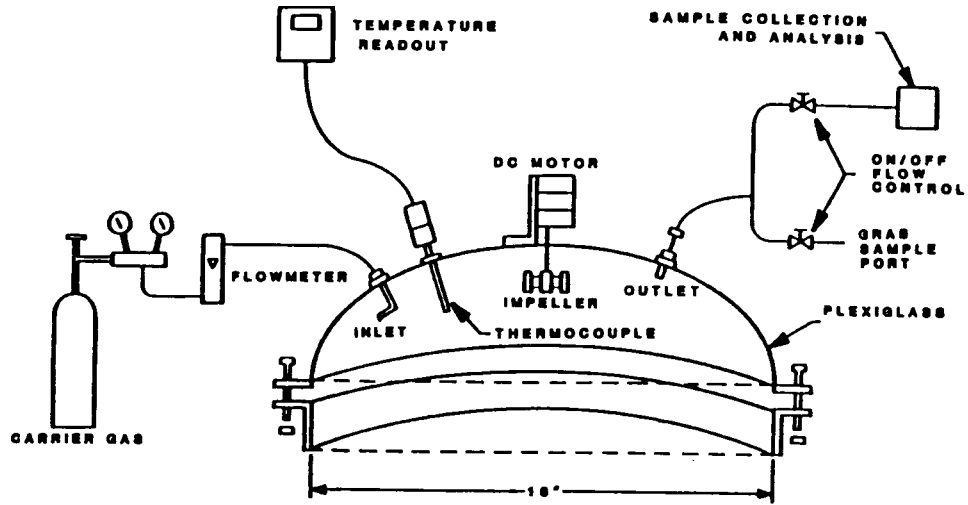
NOTE 1—The processes indicated by the soil gas monitoring method are partitioning, migration, emplacement and degradation. Partitioning represents a group of processes which control contaminant movement from one physical phase to another, these phases being liquid, free vapor, occluded vapor, solute and sorbed. Migration refers to contaminant movement over distance with any vertical, horizontal or temporal component. Emplacement refers to establishment of contaminant residence in any phase within any residence opportunity. Degradation is the process whereby contaminants are attenuated by oxidation or reduction in the vadose zone, either through biogenic or abiotic processes. Soil gas monitoring measures the result of the interaction of these processes in a dynamic equilibrium.

FIG. X1.1 Arena of Soil Gas Monitoring

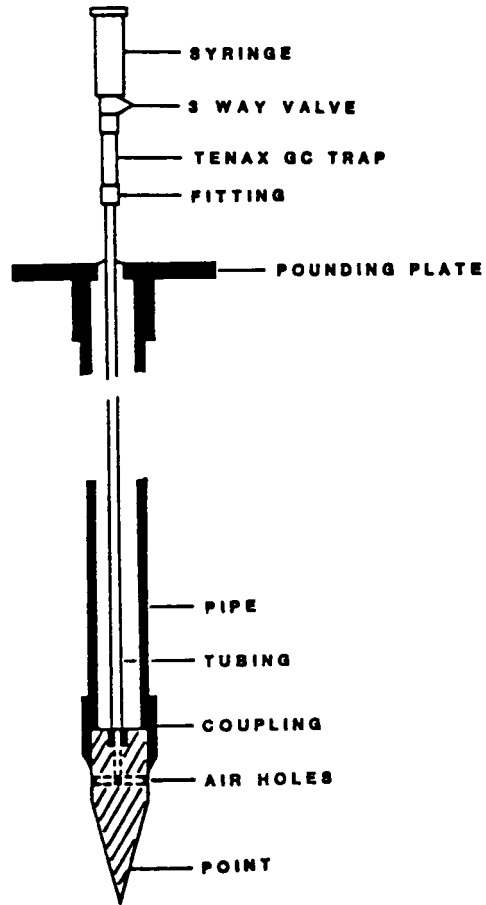


NOTE 1—Ground probe designed and used by Crow et al., 1985, from Ref (10).

FIG. X1.2 Example of Whole-Air Active Sampling System

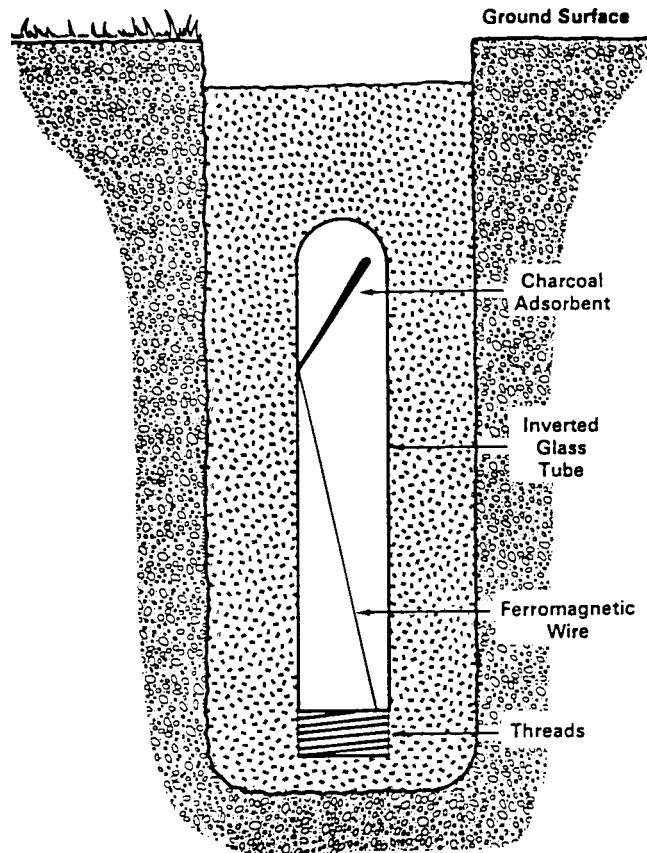


NOTE 1—Surface flux chamber and peripheral equipment after Eklund et al., 1984, from Ref (10).
FIG. X1.3 Example of Whole-Air Passive Sampling System

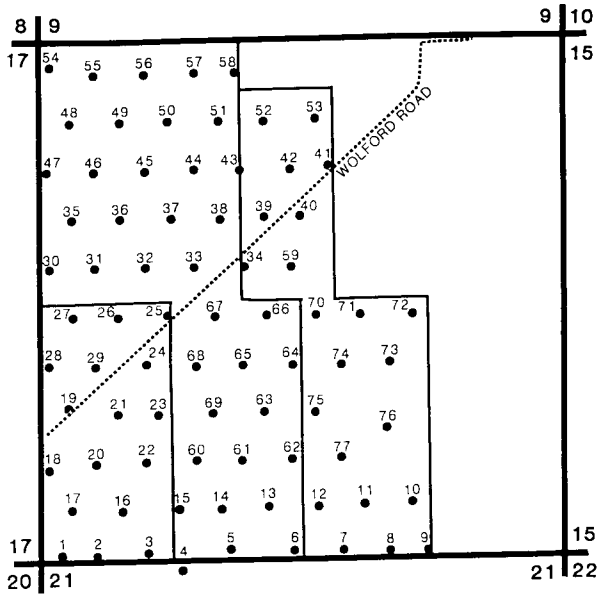


NOTE 1—Ground probe design used by Swallow and Gachwend, 1983, from Ref (10).

FIG. X1.4 Example of Sorbed Contaminant-Active System



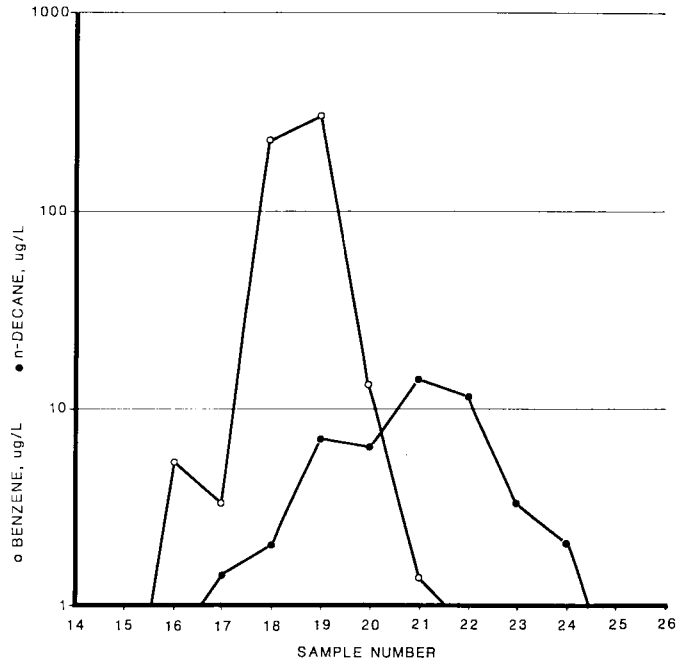
NOTE 1—Schematic diagram of emplacement of a sorbed contaminant-passive system (10).
FIG. X1.5 Example of Sorbed Contaminant-Passive System



MAP SCALE: 1" = 1,000'

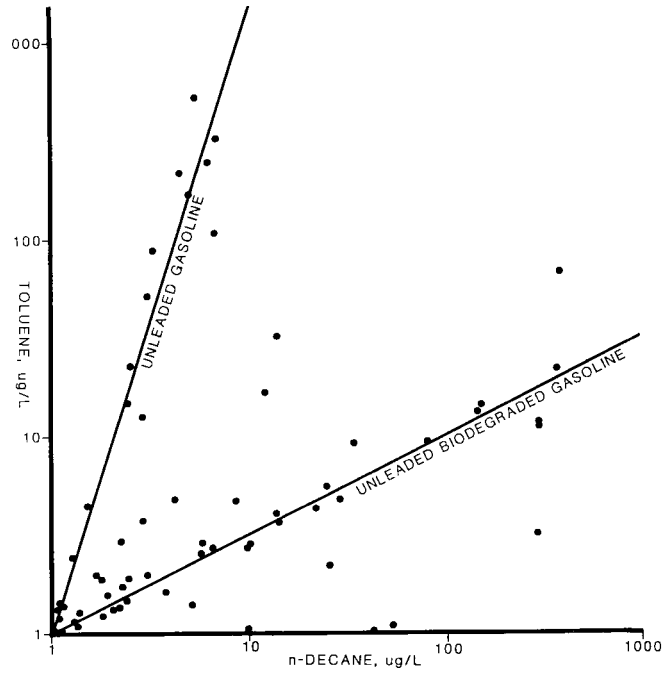
NOTE 1—In any application, soil gas monitoring can be performed over a wide range of spatial designs, including soil gas sampling in grid patterns at a single depth or multiple depths. This example illustrates a staggered grid pattern of samples recovered at a single depth.

FIG. X1.6 Typical Soil Gas Grid Array and Map Display



NOTE 1—Soil gas data from survey profiles displayed on an X – Y plot is an effective aid to data interpretation. This display is useful to examine the overall context for soil gas measurement data potentially indicating contamination. If the profile is displayed as a cross section through a grid pattern or as a linear array of sample points, the profile display can illustrate spatially significant groupings of data subpopulations.

FIG. X1.7 Typical Soil Gas Profile



NOTE 1—Bimodal populations of data that represent coincident contaminant occurrences (for example, soil gas contaminant vapors sourced from converging plumes of two different fuels or mixtures of gasoline and biodegraded gasoline) can be defined using compositional analyses. One technique of compositional analysis is cross-plotting as shown.

FIG. X1.8 Soil Gas Compositional Analysis by Cross Plot

Project # _____ Sample # _____

Sampled by: _____

Date Sampled: _____, 199____ Time: _____ (AM/PM)

Sampling System (check one):

- Whole air-active approach
- Whole air-passive approach
- Sorbed contaminants-active approach
- Sorbed contaminants-passive approach
- Headspace or extraction approach
- Soil pore liquid headspace approach

Sample Type (check one):

- Direct field sample
- Field blank
- Travel blank
- Sample container blank
- Sample probe blank
- Sample replicate

Spiked? _____ with _____ cc of _____

Potential reaction products due to spiking: _____

System purge volume: _____ Volumes purged: _____ Sample volume: _____

Sorbent Device: Installed _____ (AM/PM), _____, 199____

Recovered _____ (AM/PM), _____, 199____

Sample container type: _____ Sample container # _____

Integral analyzer: _____ Detector: _____

Analyzer response: _____ (units) _____

Surface conditions (pavement, wet, frost, etc.) _____

Sample depth: _____ Sampling rate: _____

Sample horizon data-visual estimates:

Vadose zone make-up: Native soil+rock Fill Rock

Soil composition: Clay, _____%

Soil organic matter, _____%

Fine granular material, _____%

Coarse granular material, _____%

100 %

Moisture content of sampling horizon (qualitative):

- Dry
- Very Damp
- Slightly Moist
- Wet

Other characteristics of the sampling horizon:

- Free water present Probable connection to surface macropores
- Free product present
- Contaminant odors Indurated
- Poor perm. to vapor Soil discoloration
- Near slope or vent _____

Investigator Signature/Date _____

Investigator Affiliation _____

FIG. X1.9 Suggested Soil Gas Sample Data Sheet

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Appendix C

**NYSDOH Indoor Air Sampling and
Analysis Guidance, August 8, 2001**

INDOOR AIR SAMPLING & ANALYSIS GUIDANCE
August 8, 2001

SCOPE:

Air testing for specific chemical compounds can be performed to determine whether petroleum spills or other contaminant sources affect indoor air quality. This document provides guidance for preparing sites and collecting samples for laboratory analysis to ensure the integrity of the test results and allow for meaningful interpretation of the data.

Forms (attached) - Indoor Air Quality Questionnaire and Building Inventory Form
 - Product Inventory Form

OBJECTIVE:

The purpose of this document is to outline the recommended procedure for testing indoor air for volatile organic chemicals (VOCs). The procedure includes pre-sampling inspection and preparation of homes, product inventories, collection of samples, analytical method selection.

1. Pre-sampling inspection and preparation of homes:

A pre-sampling inspection should be performed 2 or 3 days prior to testing (if possible) to evaluate the type of structure, floor layout and physical conditions of the building(s) being studied and to identify and minimize conditions that may affect or interfere with the proposed testing. This information along with information on sources of potential indoor contamination should be identified on the building inventory form. Portable organic vapor monitoring equipment (i.e.: photoionization detectors (PIDs)) can be used to help evaluate potential interferences. Items to be included in the building inventory include use or storage of petroleum products including gasoline operated equipment, unvented kerosene heaters, recent use of petroleum based finishes or products containing petroleum distillates. Potential interferences should be corrected during the pre-sampling inspection. Removing the source from the indoor environment prior to testing is the most effective means of reducing the interference. Ensuring that containers are tightly sealed may be acceptable, but should be tested with a PID to demonstrate that the seal is tight. The inability to eliminate potential interference may be justification for not testing. Once these interfering conditions are corrected, aggressive ventilation may be needed prior to testing to eliminate residual contamination.

Any ventilation should be done twenty-four hours or more prior to the scheduled sampling time. If ventilation is deemed necessary, ventilate the house by opening windows and doors for at least 10 to 15 minutes. House ventilation should be avoided 24 hours prior to and during testing. During colder months, heating systems should be operating for at least twenty-four hours prior to the scheduled sampling time to maintain normal indoor temperatures above 65⁰ F before and during sampling.

FOR 24 HOURS PRIOR TO SAMPLING, DO NOT

- open any windows, fireplace dampers, openings or vents,
- operate ventilation fans unless special arrangements are made,
- smoke in the house,

- paint,
- use wood stove, fireplace or other auxiliary heating equipment, (e.g. kerosene heater),
- operate or store automobile in attached garage,
- allow containers of gasoline or oil to remain within the house or garage area, except for fuel oil tanks,
- clean, wax or polish furniture or floors with petroleum or oil-based products,
- use air fresheners or odor eliminators,
- engage in any hobbies which use materials containing volatile organic chemicals,
- use cosmetics: including hairspray, nail polish, nail polish removers, etc.
- apply pesticides.

2. Product Inventories:

Some household products contain volatile organic chemicals (VOCs) which can contribute to levels of VOCs in air. Products in buildings should be inventoried every time air is tested to provide an accurate assessment of the potential contribution of VOCs. Each room in the building should be inspected and products that contain VOCs should be listed on the Products Inventory Form along with PID readings obtained near the container. If available, the volatile ingredients should be recorded for each product. If the ingredients are not listed on the label, record the manufacturer's name and address or phone number if available.

3. Collection of Samples

To characterize contaminant concentration trends and potential exposures, air samples should be collected from the basement, first floor living space, and from outdoors. In settings with diurnal occupancy patterns such as schools and office buildings, samples should be collected during normally occupied periods to be representative of typical exposure. Sample collection intakes should be approximately three feet above the floor level to represent breathing zones. To ensure that air is representative of the locations sampled and to avoid undue influence from sampling personnel, samples should be collected for 2 to 8 hours, but at least a one-hour period and personnel should avoid lingering in the immediate area of the sampling device while samples are being collected. Sample collection techniques vary depending on the analytical method(s) being used and sample flow rates must conform to the specifications in the sample collection method. Some methods require collecting samples in duplicate. Sampling personnel should be completely familiar with the sampling protocol for the particular method being used.

a. Quality Assurance/Quality Control

Extreme care should be taken during all aspects of sample collection to ensure that high quality data are obtained. The laboratory should use only certified clean sample collection devices. The sampling team members should avoid actions which cause sample interference such as pumping gas prior to testing or using permanent marking pens in the field. Once samples are collected, they should be stored according to the method protocol and delivered to the analytical laboratory as soon as possible. Samples should not exceed recommended holding times prior to being processed by the laboratory. Blanks should be submitted and analyzed with the samples to provide a quality check. Laboratory procedures for sample accession and chain of custody should be followed.

b. Sampling Information

Detailed information must be gathered at the time of sampling to document conditions during sampling to aid in interpretation of the test results. The information should be recorded on the building inventory form. Floor plan sketches should be drawn for each floor and should include the floor layout

with sample locations, any chemical storage areas, garages, doorways, stairways, location of basement sumps and any other pertinent information including compass orientation (north). Outdoor plot sketches should include the building site, area streets, outdoor sample location, the location of potential interferences (such as gas stations, factories, lawn mowers), wind direction and magnetic orientation (north). In addition, any pertinent observations such as odors and PID readings should be recorded on the building inventory form and on associated sample accession forms.

The products inventory shall include those items discussed in Section 2.

c. Sample Analysis

New York State Law requires laboratories analyzing environmental samples from New York State to have current Environmental Laboratory Approval Program (ELAP) certification for certain contaminant categories and media (air, water, solid waste).

The goal of indoor air sampling is to evaluate exposure to VOCs by measuring levels low enough to compare to background indoor air levels. Therefore, the samples must be analyzed by methods that can achieve minimum detection limits of at least one part per billion (ppb) (1 to 7 micrograms per cubic meter (mcg/m^3) depending on the molecular weight for each compound). Several analytical methods for VOCs in air are capable of achieving these detection limits including Environmental Protection Agency (EPA) Method TO-14A/TO-15 and EPA Method TO-1/TO-2. Prior to choosing an analytical method, the laboratory should verify they are capable of detecting target compounds.

Petroleum is a mixture of many individual compounds. Various petroleum products (i.e. gasoline, diesel, fuel oil) have different chemical constituents and specific aromatic and aliphatic compounds can be good indicators for individual petroleum products. Analytical methods using a mass spectrometer detector allow for the identification of aromatic and aliphatic hydrocarbons, and oxygenated compounds such as ethanol, acetone and methyl tertiary butyl ether (MTBE).

Target compounds for gasoline may include the aromatics: benzene, toluene, ethylbenzene and xylenes; C-4 to C-8 straight and branched aliphatics; and the oxygenate additive MTBE.

Target compounds for fuel oil may include the aromatics: benzene, toluene, ethylbenzene, xylenes, naphthalene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, n-butylbenzene, sec-butylbenzene and tert-butylbenzene; and C-9 to C-12 straight and branched aliphatic hydrocarbons.

Sampling for other potential contaminants may involve different target compound(s) and different analytical methodology.

For additional information contact Mr. Gerry McDonald or Mr. Michael Hughes of the Bureau of Toxic Substance Assessment (518) 402-7810.