



Designation: D5314 – 92(Reapproved 2006)

Standard Guide for Soil Gas Monitoring in the Vadose Zone¹

This standard is issued under the fixed designation D5314; 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

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 Groundwater and Vadose Zone Investigations.

Current edition approved July 1, 2006. Published July 2006. Originally approved in 1992. Last previous edition approved in 2001 as D5314 – 92 (2001). DOI: 10.1520/D5314-92R06.

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.*

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, 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:²

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D1452 Practice for Soil Exploration and Sampling by Auger Borings

D1605 Practices for Sampling Atmospheres for Analysis of

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- Gases and Vapors (Withdrawn 1992)³
- D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres
- D2652 Terminology Relating to Activated Carbon
- D2820 Test Method for C Through C Hydrocarbons in the Atmosphere by Gas Chromatography (Withdrawn 1993)³
- D3249 Practice for General Ambient Air Analyzer Procedures
- D3416 Test Method for Total Hydrocarbons, Methane, and Carbon Monoxide (Gas Chromatographic Method) (Withdrawn 1992)³
- D3584 Practice for Indexing Papers and Reports on Soil and Rock for Engineering Purposes (Withdrawn 1996)³
- D3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions
- D3670 Guide for Determination of Precision and Bias of Methods of Committee D22
- D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)
- D3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method
- D4220 Practices for Preserving and Transporting Soil Samples
- D4490 Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes
- D4597 Practice for Sampling Workplace Atmospheres to Collect Gases or Vapors with Solid Sorbent Diffusive Samplers
- D4696 Guide for Pore-Liquid Sampling from the Vadose Zone
- D4700 Guide for Soil Sampling from the Vadose Zone
- D5088 Practice for Decontamination of Field Equipment Used at Waste Sites
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E260 Practice for Packed Column Gas Chromatography
- E355 Practice for Gas Chromatography Terms and Relationships
- E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
- E697 Practice for Use of Electron-Capture Detectors in Gas Chromatography

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 D653.

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 groundwater 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 groundwater contaminant compounds (1).⁴

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.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ The boldface numbers given in parentheses refer to a list of references at the end of the text.

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 on partitioning, migration, emplacement and degradation. Subsection 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:

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

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 groundwater 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 groundwater. 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.⁵ 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 distribution 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.

⁵ See 6.2 for a discussion of active soil gas sampling techniques.

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 groundwater. This can be retarded if the contaminants partition into other phases before reaching groundwater 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 groundwater accelerate the contact of contaminants with groundwater. When these contaminants do reach groundwater, 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 groundwater, become dissolved in groundwater 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 groundwater, 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 groundwater (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 recoverable 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 D1357). 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 E177). 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

TABLE 1 Suggested Quantitative Limits for Data Quality Objectives

QA/QC Objective	Measure	Formula	Limit
Accuracy Precision	Laboratory standard	Standard recovery	90 to 110 %
	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

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 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 groundwater 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 groundwater monitoring wells, contaminant product recovery wells or excavations to recover contaminated soil. Soil gas monitoring has made a significant contribution to groundwater 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.

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 (42, 43), 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 (44) 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 Terminology D2652). Some may be affected by high soil gas relative humidity. Humidity greater than 90% may

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 D3686). 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 D3687).

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 vapor 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 (43) and a sampler originally developed for detecting the presence of hydrocarbons in petroleum exploration (33, 45). 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 (45), 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 D4597). 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 D4700). 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 groundwater conditions, soil characteristics and the equipment used (see Practice D1452). Suitable procedures for some methods are described in the literature (46, 47). Current soil preservation practice may not apply (see Practices D4220).

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 (48). Recovery efficiency of contaminants in soil headspace can be greatly enhanced by pulverization of the soil (49) 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 (47), 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 D4696). 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 groundwater 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