
Collecting and Interpreting Soil Gas Samples from the Vadose Zone

A Practical Strategy for Assessing the
Subsurface Vapor-to-Indoor Air Migration
Pathway at Petroleum Hydrocarbon Sites

Regulatory Analysis and Scientific Affairs

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Executive Summary

This document focuses on the collection of soil gas samples for assessing the significance of the subsurface-vapor-to-indoor-air exposure pathway. While soil gas collection is not the only means of assessing this pathway, soil gas data play a prominent role in recent guidance published by the American Petroleum Institute (API 1998) and the United States Environmental Protection Agency (USEPA 2002a). For example, these data can be used to help make decisions concerning:

- Resource Conservation and Recovery Act (RCRA) corrective action environmental indicators (EI) for human health exposures
- Current exposure scenarios in existing buildings
- Future exposure scenarios in existing buildings
- Future exposure scenarios in future buildings.

This document is intended to complement API 1998 and USEPA 2002a. It provides more in-depth information on issues associated with soil gas sampling and data interpretation as applied to pathway assessment. This document is specifically focused on petroleum hydrocarbon impacted sites. However, much of the information presented is applicable to all soil gas sampling. Soil gas sampling has been used for many years for site assessment and remediation system monitoring purposes. The user, however, will find that the data quality objectives and acceptable methods of sampling for pathway assessment are different from those that are commonly acceptable for using soil gas data for delineation, site assessment, or monitoring remediation systems.

This document is unique in that it emphasizes conceptual models for vapor transport, describes how to choose sample locations and depths, explains how to check the data for inconsistencies and also provides checklists on each of these topics to assist field project managers. This document allows for flexibility in the selection and refinement of practicable and defensible sampling methods. The focus here is on identifying key issues associated with soil gas sampling and data interpretation.

Field project managers should find this document useful when developing scope-of-work requirements for site-specific work plans and bid requests. To support preparation of site-specific work plans, scope-of-work action items are included at the end of Sections 4.0 through 7.0.

Section 1.0 provides a brief introduction. Section 2.0 discusses soil gas transport, with emphasis on petroleum hydrocarbon vapors, and presents a brief synopsis of expected soil gas profiles based on empirical analysis of existing data. Section 3.0 discusses the conceptual vapor-migration model. Section 4.0 focuses on sampling locations, depths, and sampling frequency. Section 5.0 focuses on monitoring installations and sample collection procedures. Section 6.0 discusses methods of soil gas analysis. Section 7.0 discusses interpretation of soil gas data. Appendix A provides a site information checklist. Appendix B provides worksheets for three typical scenarios that can be used for planning sampling locations. Appendix C provides more details on sample collection. Appendix D gives supporting information on analytical methods, and Appendix E provides tools to be used in the data evaluation.

Recommendations presented here are based on the experience and professional judgment of the authors and are designed to be broadly applicable. This does not imply that the recommendations are universally applicable or that there are not situations for which other methods or procedures would be better suited. The user of this manual is cautioned to consider all of the site-specific information and to make decisions based on site-specific circumstances, experience, and professional judgment. In addition, some regulatory agencies have expressed preferences for sampling methods and techniques. The applicable regulatory preferences should be examined for each site.

This document does not address all potential strategies for assessing the vapor-to-indoor-air pathway. The user of this manual is directed to USEPA 2002a, and applicable state regulatory guidance for other methods to assess the vapor-to-indoor-air pathway (see PaDEP 2002; MaDEP 2002; WDHFS 2003; NJDEP 2004; CRWQCB 2003; CSDDEH 2003).

This document also does not address safety- and hazard-mitigation efforts to prevent fires or explosions resulting from the accumulation of hazardous vapors. It assumes that these situations have been controlled by emergency or immediate response actions before the planning of a soil-gas-sampling program is initiated. If the results of the soil-gas-sampling program indicate that there is an immediate concern for human exposures to vapor-phase chemicals of concern, then emergency response or interim actions should be implemented as required under state or federal regulations.

Contents

| | | |
|-------|--|----|
| 1.0 | Introduction | 1 |
| 2.0 | Soil Gas Transport and Soil Gas Profiles at Petroleum Hydrocarbon Impacted Sites..... | 3 |
| 2.1 | Expectations for Soil Gas Profiles at Petroleum Hydrocarbon Impacted Sites | 5 |
| 2.2 | Measured Soil Gas Profiles at Petroleum Hydrocarbon Impacted Sites..... | 7 |
| 3.0 | Conceptual Migration Model for Subsurface Vapor to Indoor Air..... | 14 |
| 4.0 | Development of a Strategy for Soil Gas Sampling | 17 |
| 4.1 | General Approach..... | 18 |
| 4.2 | Point Sampling | 18 |
| 4.3 | Transects and Vertical Profiles | 19 |
| 4.3.1 | Selection of Lateral Positions for Soil Gas Transects..... | 21 |
| 4.3.2 | Vertical Profiles..... | 22 |
| 4.4 | Summary of Sampling Depth and Location Selection Considerations..... | 24 |
| 4.5 | Some Comments on Sample Collection Adjacent to and Beneath Buildings..... | 29 |
| 4.6 | Sampling Frequency..... | 31 |
| 4.7 | Additional Considerations to Increase Confidence in Data Sets and the Interpretation of Soil-Gas-Sampling Results..... | 32 |
| 5.0 | Soil Gas Sample Collection..... | 35 |
| 5.1 | Basic Monitoring Installation Options..... | 35 |
| 5.1.1 | Permanent Probes | 36 |
| 5.1.2 | Temporary Driven Probes..... | 37 |
| 5.2 | Comparison of Monitoring Installations..... | 37 |
| 5.3 | Other Considerations for Sampling Probe Installations..... | 39 |
| 5.4 | Sample Collection Procedures..... | 39 |
| 5.4.1 | Soil Gas Equilibration | 39 |
| 5.4.2 | Sample Probe Purging | 40 |
| 5.4.3 | Sample Collection..... | 40 |
| 5.4.4 | Sample Collection Vacuum..... | 40 |
| 5.5 | Ways to Avoid Common Problems with Soil Gas Sampling | 41 |
| 5.6 | Alternatives to Soil Gas Sampling..... | 43 |
| 5.6.1 | Passive Implant Samplers | 43 |
| 5.6.2 | Flux Chambers..... | 44 |
| 6.0 | Analytical Methods | 46 |
| 6.1 | Analytical Method Selection | 46 |
| 6.1.1 | Field Analytical Methods | 48 |
| 6.1.2 | Common Analytical Methods..... | 48 |
| 6.2 | Data Quality..... | 48 |
| 7.0 | Analysis and Interpretation of Soil Gas Sampling Data | 50 |
| 7.1 | Data Organization..... | 52 |
| 7.2 | Data Analysis..... | 53 |
| 7.2.1 | Data Quality Analysis..... | 53 |
| 7.2.2 | Data Consistency Analysis | 54 |
| 7.3 | Exposure Pathway Assessment..... | 55 |
| 7.3.1 | Exposure Pathway Completeness | 55 |
| 7.3.2 | Exposure Pathway Significance..... | 56 |
| 7.4 | Further Evaluation | 56 |
| 8.0 | References | 58 |
| 9.0 | Additional Reading..... | 61 |
| 9.1 | Analytical Methods..... | 61 |
| 9.2 | Biodegradation | 61 |
| 9.3 | Data Analysis..... | 62 |
| 9.4 | General | 62 |
| 9.5 | Modeling | 63 |
| 9.6 | Sample Collection Methods..... | 64 |
| 9.7 | Site Characteristics and Conceptual Vapor-Migration Models | 65 |

| | |
|-------------|--|
| Appendix A. | Characteristics Checklist |
| Appendix B. | Selection of Soil Gas Sample Locations |
| Appendix C. | Soil Gas Sample Collection |
| Appendix D. | Analytical Methods |
| Appendix E. | Data Evaluation |

Figures

| | | |
|-------------|--|----|
| Figure 2-1. | Typical conventional conceptual model of soil gas migration..... | 3 |
| Figure 2-2. | Revised conceptual model of soil gas migration at petroleum hydrocarbon impacted sites. | 5 |
| Figure 2-3. | Soil gas profiles (Roggemans et al. 2002). | 9 |
| Figure 2-4. | Soil gas profile at a site with methane production in the source zone (Johnson et al. 2003). This figure shows the soil gas profiles for oxygen (circles) and methane (diamonds). | 10 |
| Figure 2-5. | Normalized soil gas concentration distribution for oxygen and hydrocarbon undergoing aerobic biodegradation with first-order rate $\lambda = 0.18 \text{ (h}^{-1}\text{)}$ and vapor source at concentrations of 20 mg/L, 100 mg/L and 200 mg/L located underneath a basement foundation at a depth of 8 m below ground surface. Hydrocarbon and oxygen contours are normalized to the source and the atmospheric concentrations, respectively. From Abreu (2005)..... | 12 |
| Figure 2-6. | Normalized soil gas concentration distributions for oxygen and hydrocarbon undergoing aerobic biodegradation with a first-order rate $\lambda = 0.18 \text{ (h}^{-1}\text{)}$ and a vapor source concentration of 200 mg/L located beneath a slab-on-grade foundation at depths of 1 m, 3 m, 5 m and 8 m below ground surface. Hydrocarbon and oxygen contours are normalized to the source and the atmospheric concentrations, respectively. From Abreu (2005)..... | 13 |
| Figure 4-1. | Considerations for vertical profiles at relatively flat sites (e.g., consistent distance between the ground surface and the vapor source depth) with consistent stratigraphy. | 23 |
| Figure 4-2. | Considerations for vertical profiles at sites with significant spatial variability in the distance between ground surface and the vapor source depth..... | 24 |
| Figure 4-3. | Sub-slab-to-indoor-air attenuation. | 31 |
| Figure 7-1. | Flowchart for data evaluation. | 51 |

Tables

| | | |
|------------|---|----|
| Table 4-1. | Considerations for Samples Collected Immediately above the Vapor Source | 25 |
| Table 4-2. | Considerations for Samples Collected Laterally Mid-Way between the Vapor Source and the Building Location | 26 |
| Table 4-3. | Considerations for Samples Collected Adjacent to the Base of an Existing Building Foundation or Basement | 27 |
| Table 4-4. | Considerations for Samples Collected Immediately below the Building Foundation or Basement | 28 |
| Table 4-5. | Considerations for Samples Collected within the Footprint of a Future Building Location | 29 |
| Table 6-1. | Common Analytical Methods | 48 |
| Table 7-1. | Example Comparisons of Biodegradation Stoichiometry and Fluxes | 55 |

1.0 Introduction

Topic:

This section provides general information about the subsurface-vapor-to-indoor-air exposure pathway.

Purpose:

To define the following activities for collecting and interpreting soil gas samples:

- Collecting information
- Identifying sample locations
- Determining sample collection methods
- Selecting sample analytical methods
- Interpreting results.

Significance:

Soil gas data can be used to assess for significant concentrations of petroleum hydrocarbon vapors in the subsurface, to determine if vapor migration to a building is occurring, to estimate possible indoor air concentrations, and to identify significant attenuation of vapor transport by natural processes.

Soil gas sampling has been conducted for many years as a tool for evaluating the distribution of chemicals of concern in soil and groundwater, for guiding site characterizations, and for monitoring remedial action progress. However, soil gas data collected for a site characterization are generally focused on developing an understanding of the location and distribution of chemicals of concern in environmental media (e.g., soil, groundwater) and not on determining the definitive concentrations of chemicals of concern in soil gas. As a result, the methodologies used for traditional site characterizations may not be appropriate for evaluating the subsurface-vapor-to-indoor-air exposure pathway.

When assessing the subsurface-vapor-to-indoor-air pathway, an initial screen is conducted to identify those sites where further site-specific investigation and assessment are warranted. As the sampling of indoor air poses many practical and technical challenges, the ensuing site-specific pathway assessment often focuses on soil gas collection and analysis (as described in API 1998). For the evaluation of the subsurface-vapor-to-indoor-air exposure pathway, soil gas samples are collected to:

- Establish a snapshot of the concentrations of chemicals of concern in soil gas at a location along the exposure pathway between the source and the building location
- Analyze the potential for human receptors to be exposed in indoor environments
- Predict the expected indoor air concentration based on the soil gas concentrations using an estimated attenuation factor

- Account for the fate and transport processes between a sampling location and the indoor environment.

In the case of petroleum hydrocarbons, aerobic biodegradation has the potential to attenuate concentrations of chemicals of concern in soil gas and fluxes significantly as the vapors move toward buildings from soils or groundwater containing concentrations of petroleum hydrocarbon chemicals of concern. Therefore, soil gas data collected for the subsurface-vapor-to-indoor-air exposure pathway need to be focused on the purpose and use of the data and be based on these specific data-quality objectives.

The collection and use of soil gas data to evaluate the subsurface-vapor-to-indoor-air exposure pathway is a relatively new approach for this exposure pathway, and limited information is available on the appropriate methodologies. To address this need, options for the collection, analysis, and interpretation of soil gas data are presented in this document. This document emphasizes conceptual models for vapor transport in the formulation of sampling plans and data analysis and presents information needed to support the selection of sample locations and depths. The overall process of collection and analysis of soil gas samples is supported through important reminders and checklists at the end of each section. A systematic process is provided in the data analysis section to check the collected data for inconsistencies and for determination of situations requiring further study.

Specifically, five basic activities have been identified for the collection and interpretation of soil gas samples. These activities include the following:

1. Collecting information to understand the characteristics of the site (Section 3.0, Appendix A)
2. Identifying the location or locations for soil gas sample collection (Section 4.0, Appendix B)
3. Determining the method or methods for collecting soil gas samples (Section 5.0, Appendix C)
4. Selecting the method or methods to analyze soil gas samples (Section 6.0, Appendix D)
5. Evaluating and interpreting the results (Section 7.0, Appendix E).

To present a basic understanding of the processes affecting the subsurface-vapor-to-indoor-air exposure pathway and a foundation for decisions on soil gas sampling, the user is first provided with a discussion of soil gas transport (Section 2.0). This is followed by a discussion of the five activities identified for the collection and interpretation of soil gas samples.

2.0 Soil Gas Transport and Soil Gas Profiles at Petroleum Hydrocarbon Impacted Sites

Topic:

The conceptual model for soil gas migration and expectations for soil gas profiles at petroleum hydrocarbon sites are discussed here.

Purpose:

To show how chemicals volatilize from impacted soil or groundwater and migrate to regions of lower chemical concentration (e.g., the atmosphere, conduits, basements).

Significance:

The migration of hydrocarbon vapors throughout most of the subsurface is thought to be primarily the result of diffusive transport processes. Other processes, such as advective soil gas flow, oxygen migration, and aerobic biodegradation, also can significantly affect the soil gas migration to buildings.

Soil gas migration is typically conceptualized as shown Figure 2-1. Chemicals volatilize from impacted soil or groundwater and migrate to regions of lower chemical concentration (e.g., the atmosphere, conduits, basements). Although Figure 2-1 schematically depicts houses, vapor intrusion to commercial buildings and other structures also can be of concern. This guidance is broadly applicable to all building scenarios.

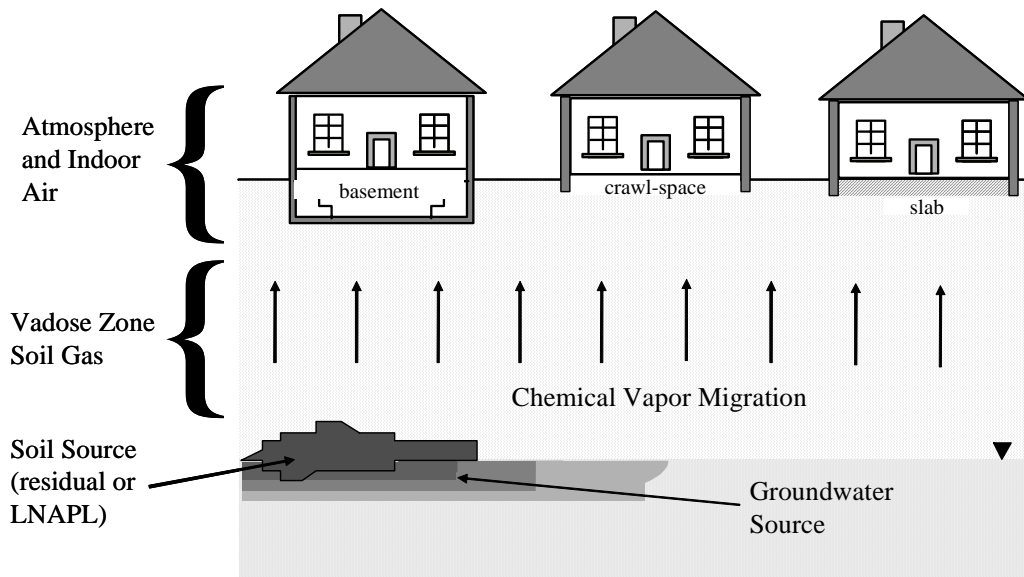


Figure 2-1. A typical conventional conceptual model of soil gas migration.

This migration of hydrocarbon vapors throughout most of the subsurface is thought to be primarily the result of diffusive transport processes. However, atmospheric pressure fluctuations also could contribute to vapor spreading, with the significance of the vapor spreading depending on the thickness and composition of the vadose zone. Near buildings or other enclosed spaces, significant advective soil gas flow fields may exist due to under- or over-

pressurization of a building (e.g., resulting from the operation of indoor appliances, such as a clothes dryer or the heating, ventilation, and air conditioning (HVAC) system; temperature differences; building-wind interactions).

Processes causing hydrocarbon vapor transport also can bring oxygen from the atmosphere to the subsurface. With petroleum hydrocarbon impacted soils, the soil gas composition and overall vapor migration also can be affected by aerobic and anaerobic biodegradation. For example:

- Oxygen moving down into the subsurface from the atmosphere and hydrocarbon vapors moving upward from the source will be consumed partially (or completely) in regions of active aerobic biodegradation, and carbon dioxide (CO₂) will be produced. This can result in the attenuation of hydrocarbon vapor fluxes (mass per total area per time) to the atmosphere and enclosed spaces. In some cases, this also can result in the creation of oxygen-depleted zones in the subsurface near and immediately above the source.
- Anaerobic decomposition of residual LNAPL in soils and dissolved chemicals of concern in groundwater may occur in the oxygen-depleted source zones, and methane (CH₄) may be generated. The methane gas then migrates upward in the direction of enclosed spaces and the atmosphere, and it can undergo aerobic biodegradation in the more oxygen-rich subsurface regions (as do the hydrocarbon vapors originating from the source as discussed above).

Thus, a more complex conceptual model is needed to adequately describe subsurface petroleum hydrocarbon vapor migration. One such conceptualization is shown in Figure 2-2.

Vapor Migration

Vapor migration results from the following processes:

Diffusion – the random kinetic energy of molecules results in a net movement of chemicals from areas of higher concentration to areas of lower concentration. The diffusive flux of chemicals is proportional to the concentration gradient (change in concentration divided by distance) and the effective porous medium diffusion coefficient (typical values are in the 0.001 - 0.01 cm²/s range for many chemicals and typical vadose zone conditions [see Figure 4 in Johnson 2002]).

Advection – the movement of chemicals with the bulk motion of the soil gas, where the flow of the bulk soil gas is the result of a soil gas pressure gradient caused by subsurface-building-pressure differences or atmospheric pressure fluctuations.

Diffusion is likely the dominant process far from a building and near the source, and advection is likely the dominant process near the building. The effect of atmospheric pressure fluctuations are not yet easily quantifiable, but it is likely that the resulting oscillatory movement of soil gas has a net effect on chemical migration that is small in shallow soils and of similar magnitude to diffusion in deeper soils (Massmann and Farrier 1992; Parker 2003).

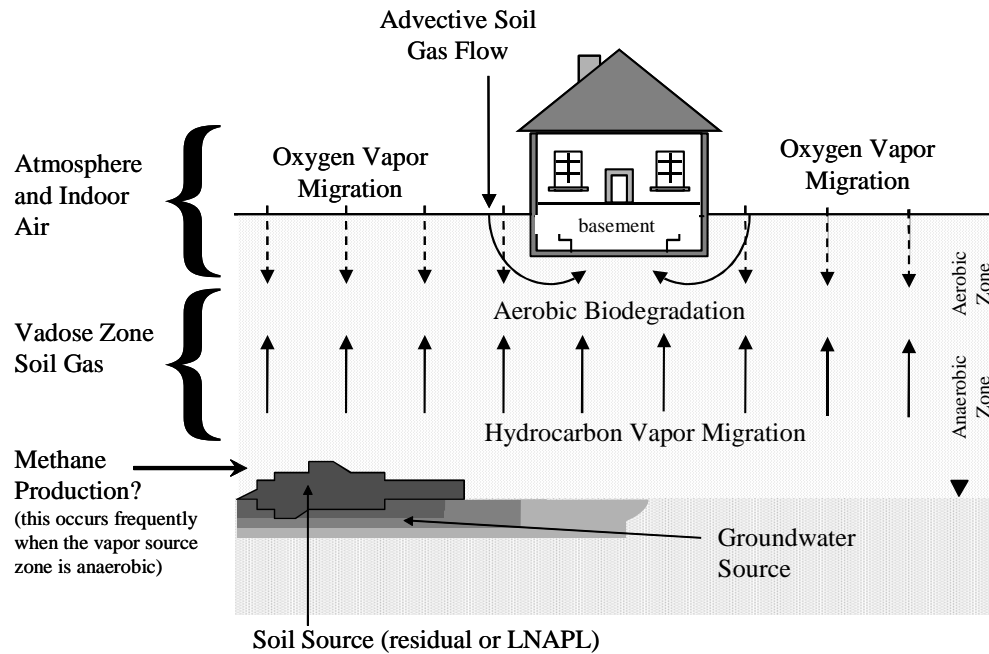


Figure 2-2. Revised conceptual model of soil gas migration at petroleum hydrocarbon impacted sites.

For further reading about soil gas migration processes as they relate to the vapor-to-indoor-air exposure pathway, see API 1998; Johnson 2002; Johnson et al. 1999; Little et al. 1992; and Roggemans et al. 2002.

2.1 Expectations for Soil Gas Profiles at Petroleum Hydrocarbon Impacted Sites

It is useful, when selecting appropriate soil-gas-sampling locations and depths, to be able to anticipate the qualitative nature of soil gas profiles. This information also is critical to assessing data quality after sampling and analyses are performed as discussed in Section 7.0. In this section, qualitative expectations for soil gas profiles are discussed, followed by the presentation of sample graphs of soil gas profiles in Section 2.2.

Based on the preceding discussion, the following observations are qualitatively expected at petroleum hydrocarbon impacted sites:

- The highest concentrations of chemicals of concern in soil gas will be found near the source.
- Concentrations of chemicals of concern in soil gas will decrease with distance away from the source zone absent advection and in the direction of the ground surface and enclosed spaces. Concentrations of chemicals of concern in soil gas also will decrease with distance laterally away from the source zone. However, it is possible for hydrocarbon vapors to become trapped below a layer of fine-grained soils or a moisture barrier. This would affect the concentration distribution.
- The composition of the hydrocarbon vapors at the source will reflect the composition of the petroleum liquid and the chemical properties of those components. Hydrocarbon

vapors at the source also may contain a significant fraction of methane if the soil gas in the vapor source zone is oxygen-depleted (anaerobic) and methanogenesis is occurring.

- Oxygen concentrations in the soil gas above impacted soils and groundwater will decrease with depth down through the soil, reaching zero directly above the source in most soils with shallow hydrocarbon impacts. Decreasing oxygen concentrations with depth also can be caused by background oxygen demand, especially in soils with high levels of natural organic matter. The contribution of background oxygen utilization can be assessed through soil gas monitoring in nearby un-impacted areas.
- In regions where oxygen concentrations decline with depth, increasing CO₂ concentrations with depth are generally observed through the aerobic region of the subsurface. CO₂ is produced during the aerobic biodegradation of petroleum hydrocarbons and the aerobic biodegradation of methane that might be produced under anaerobic conditions closer to some source zones. The decreases in oxygen with depth and the increases in CO₂ with depth should be consistent with each other as discussed later in Section 7.0.
- There will likely be some region of the subsurface in which aerobic biodegradation occurs. The significance of this process with respect to attenuation of concentrations of chemicals of concern in soil gas will depend primarily on:
 - Surface conditions (to the extent that they limit oxygen migration into or hydrocarbon vapor migration out of the subsurface)
 - Subsurface conditions (e.g., moisture content, lithology, nutrient availability)

Estimating the Time Necessary To Achieve Near-Steady-State Conditions

API (1998) and Johnson et al. (1999) discuss the importance of considering whether soil gas profiles have reached near-steady conditions, and they provide an equation for estimating the time necessary to achieve near-steady conditions, T_{ss} :

$$T_{ss} \approx \frac{R_v \theta_v L^2}{D_v^{eff}}$$

where D_v^{eff} is the effective diffusion coefficient discussed above (generally having values in the range 0.001 – 0.01 cm²/s), L is the distance from the source to ground surface (cm), θ_v is the vapor-filled void volume (often in the range 0.1 – 0.3 cm³-voids/cm³-soil), and R_v is the vapor-phase retardation factor (chemicals like the propanes, butanes, and pentanes, and oxygen will have R_v close to unity, while chemicals most often of concern because of health considerations [e.g., monoaromatic hydrocarbons, MTBE] will have vapor-phase retardation factors on the order of $10 < R_v < 100$). Using these values, one can estimate times to reach near-steady conditions of a few hours to a few days for shallow sites (< 1 m depth to the vapor source); a few months to a few years for intermediate-depth sites (up to 3 m depth to the vapor source); and as much as a year to decades for deeper vapor sources (> 10 m depth). Aerobic biodegradation, if significant, will aid in reducing those times to reach near-steady conditions because the path length over which concentrations reduce significantly will be shorter.

- Concentrations of chemicals of concern and the total hydrocarbon concentration in soil gas at the source
- Thickness of the aerobic region
- Rate of biodegradation reactions.
- Because oxygen transport and aerobic biodegradation play a significant role when soil gas profiles are established, the soil gas profiles measured near buildings may be quite different from those that would be measured beneath them, especially if the building foundation reduces the oxygen flux to the subsurface. In those cases, the effects of aerobic biodegradation on the soil gas profile will be minimal beneath the foundation.

The discussion of soil gas profiles assumes that the releases that have generated the vapor source have been in place for some period of time and that the concentrations of chemicals of concern in soil gas have reached a near-steady condition. Some data indicate that soil gas profiles are affected by seasonal changes; therefore, the near-steady conditions still exhibit some temporal variability.

2.2 Measured Soil Gas Profiles at Petroleum Hydrocarbon Impacted Sites

To better illustrate the connection between the conceptual model shown in Figure 2-2 and measured vertical soil gas profiles, sample soil gas profiles are shown in Figure 2-3 and Figure 2-4. Each of these profiles is consistent with the conceptual model, yet each is qualitatively different from the others. In these plots, normalized soil gas concentrations (actual values divided by the maximum concentration at that site) are plotted as a function of depth below ground surface (z/L = actual depth to soil gas sample/depth to the source at that site).

Roggemans et al. (2002) performed an empirical assessment of soil gas profiles from petroleum hydrocarbon impacted sites and classified the data in terms of generalized hydrocarbon-oxygen soil gas profiles. Figure 2-3 represents specific examples of these profiles; all data originate from sites impacted by gasoline or other petroleum products. Note that most of the profiles presented by Roggemans et al. (2002) were measured near buildings or beneath paved surfaces; few were measured beneath buildings.

The profiles in Figure 2-3 and Figure 2-4 show oxygen utilization (as evidenced by decreasing concentrations with depth below ground surface) and some level of hydrocarbon concentration reduction, although it is variable.

In profile A of Figure 2-3, the oxygen penetrates about half of the distance down to the vapor source, but then is consumed by aerobic biodegradation over a short distance. This aerobic biodegradation is also reflected in the hydrocarbon concentration profile that shows the hydrocarbon concentration decreasing several orders of magnitude over a short distance near the anaerobic/anoxic transition zone. Profile A was the most frequently observed by Roggemans et al. (2002).

In profile B, the oxygen is present throughout the vadose zone, except at the vapor source zone interface. The corresponding hydrocarbon profile reflects reduction in hydrocarbon concentration by aerobic biodegradation with distance above the vapor source. The effect of aerobic

biodegradation, however, is less dramatic than in profile A. Profile B might be observed at shallow sites where transport distances are short and biodegradation is slow relative to the oxygen diffusion time scale through the vadose zone, or where vapor source concentrations are relatively low with respect to atmospheric oxygen concentrations (as might be the case above dissolved hydrocarbon groundwater plumes).

Profile C was collected beneath a basement overlying a high concentration vapor source. It is distinguished from the other profiles by the lack of oxygen at the monitoring points and less attenuation of the hydrocarbon vapor concentration. Relative to profile A, which also corresponds to a high concentration vapor source (but one beneath an uncovered surface) data suggest that in this case the building affects the oxygen transport and significance of the resulting aerobic biodegradation.

Profile D has an oxygen profile similar to that in profile B, but the hydrocarbon attenuation with distance away from the source is much more significant (i.e., a four-order-of-magnitude decrease in concentration over a very short depth). This profile occurs when the source is located in a zone having lower diffusion rates than the overlying soils; for example, this data set corresponds to a case where the vapors originate from within, or below, the capillary fringe.

Figure 2-4 presents vapor concentration profiles from a site impacted by heavier hydrocarbons (the source is composed of hydrocarbons in the C_{12} to C_{24} range). Of interest in Figure 2-4 is the production of methane gas from hydrocarbon decomposition and the subsequent attenuation of the methane gas within a short distance by aerobic biodegradation processes. Qualitatively, Figure 2-4 is similar to profile A in Figure 2-3, with the exception that methane is the dominant component of the hydrocarbon vapor concentration.

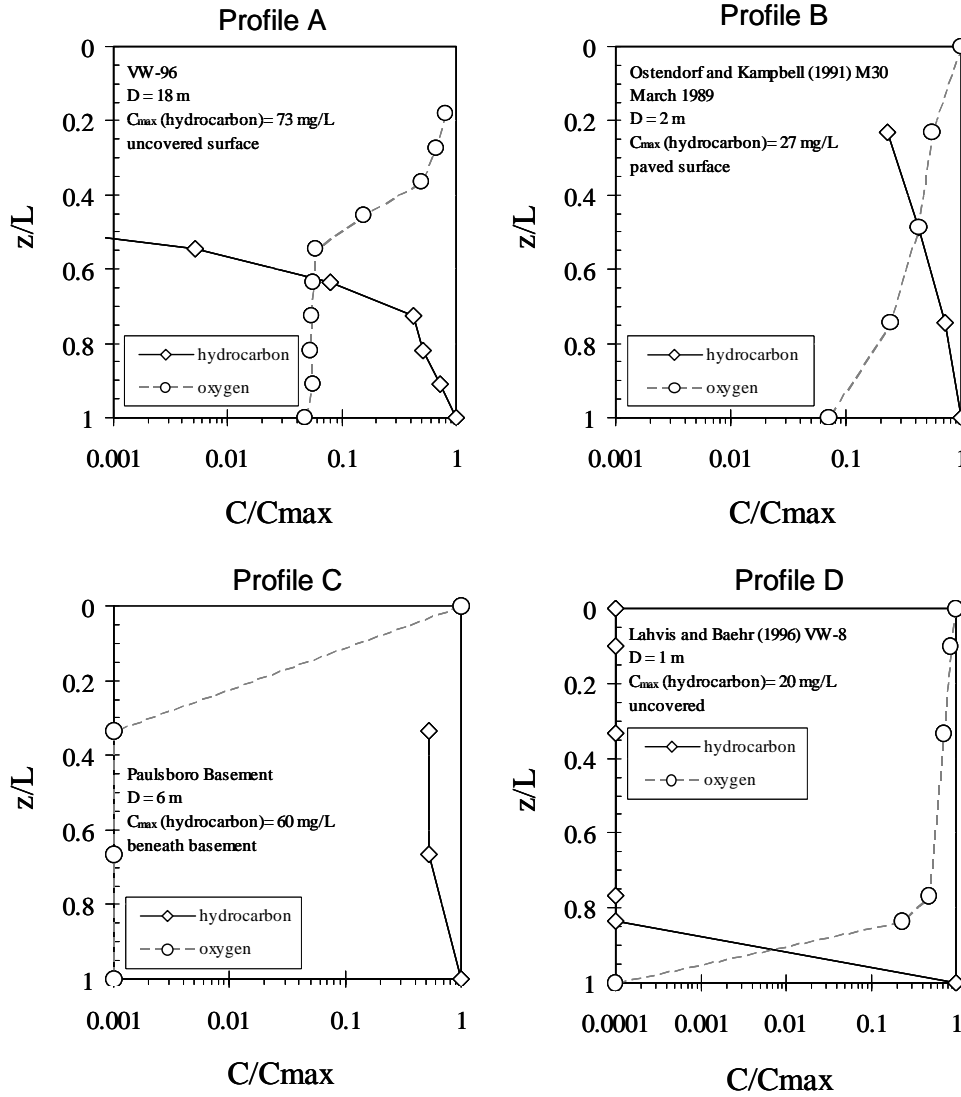


Figure 2-3. Soil gas profiles (Roggemans et al. 2002).

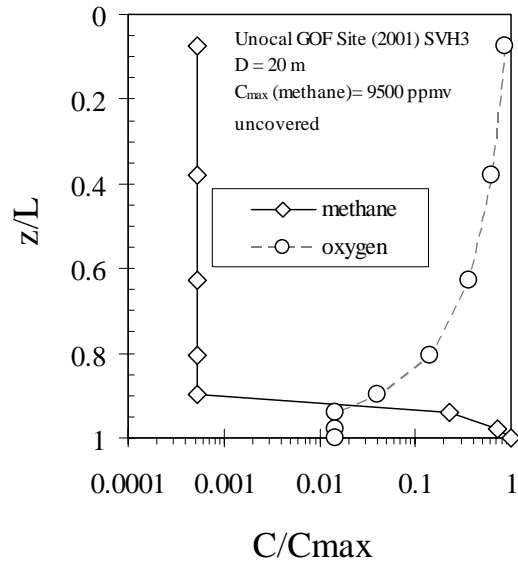


Figure 2-4. Soil gas profile at a site with methane production in the source zone (Johnson et al. 2003). This figure shows the soil gas profiles for oxygen (circles) and methane (diamonds).

Roggemans et al. (2002) attempted to correlate soil gas profiles with site characteristics and surface cover conditions, but were unable to find any obvious correlations (i.e., soil gas profiles below paved surfaces did not necessarily resemble those below buildings, and soil gas profiles beneath paved surfaces varied from site to site). Thus, the ability to anticipate the reduction in hydrocarbon vapor flux caused by biodegradation, based on site properties, is limited at this time. Soil-gas-profile data, therefore, are critical to understanding the subsurface processes and the net effect on hydrocarbon vapor migration to enclosed spaces.

To help visualize the impact that oxygen and aerobic biodegradation can have on vapor profiles at a site, **Figure 2-5** and **Figure 2-6** from Abreu (2005), show results from three-dimensional numerical simulations of vapor transport and aerobic biodegradation under homogeneous conditions near a building with a basement. **Figure 2-5** presents how significantly the chemical of concern and oxygen soil gas profiles and the attenuation factor can be affected by changes in the source concentration, for a progression of source concentrations from 20 mg/L to 200 mg/L. For reference, the Roggemans et al. (2002) report suggests that source vapor concentrations > 200 mg/L would be representative of gasoline source zones above the water table, while source soil vapor concentrations < 20 mg/L would be expected to occur near dissolved plumes down-gradient of source zones. In the 200 mg/L case, the effect of biodegradation is minimal relative to simulations without biodegradation, while the 2 mg/L source vapor concentration case corresponds to attenuation that is six orders of magnitude different from the 200 mg/L case ($\alpha=5.6 \times 10^{-11}$ versus 7.1×10^{-5}). The major difference between the figures is the oxygen penetration depth beneath the building. In the 20 mg/L case, oxygen is found at elevated levels beneath the building footprint, so that chemical vapors are subjected to aerobic biodegradation along most of the transport pathway. It should be noted that these results are presented here simply to visualize trends and that they are specific to this depth; the influence of concentration

on attenuation factors for aerobically biodegradable chemicals is expected to be more significant as the source depth is increased (Abreu 2005).

Figure 2-6 illustrates the effect of depth on soil gas profiles and vapor attenuation coefficients for aerobically biodegradable chemicals. Simulations are shown for slab-on-grade foundations and relatively high (200 mg/L) soil vapor source concentrations at depths ranging from 1 m to 8 m below ground surface (Abreu 2005). The effect of biodegradation relative to non-biodegradation simulations is minimal for the shallower depths, but is very significant for the source located 8 m below ground surface.

Overall, the simulations illustrate that the significance of the effect of aerobic biodegradation is expected to be linked to the presence of oxygen beneath a foundation, and that attenuation due to aerobic biodegradation will increase with increasing source depth and decreasing source concentration.

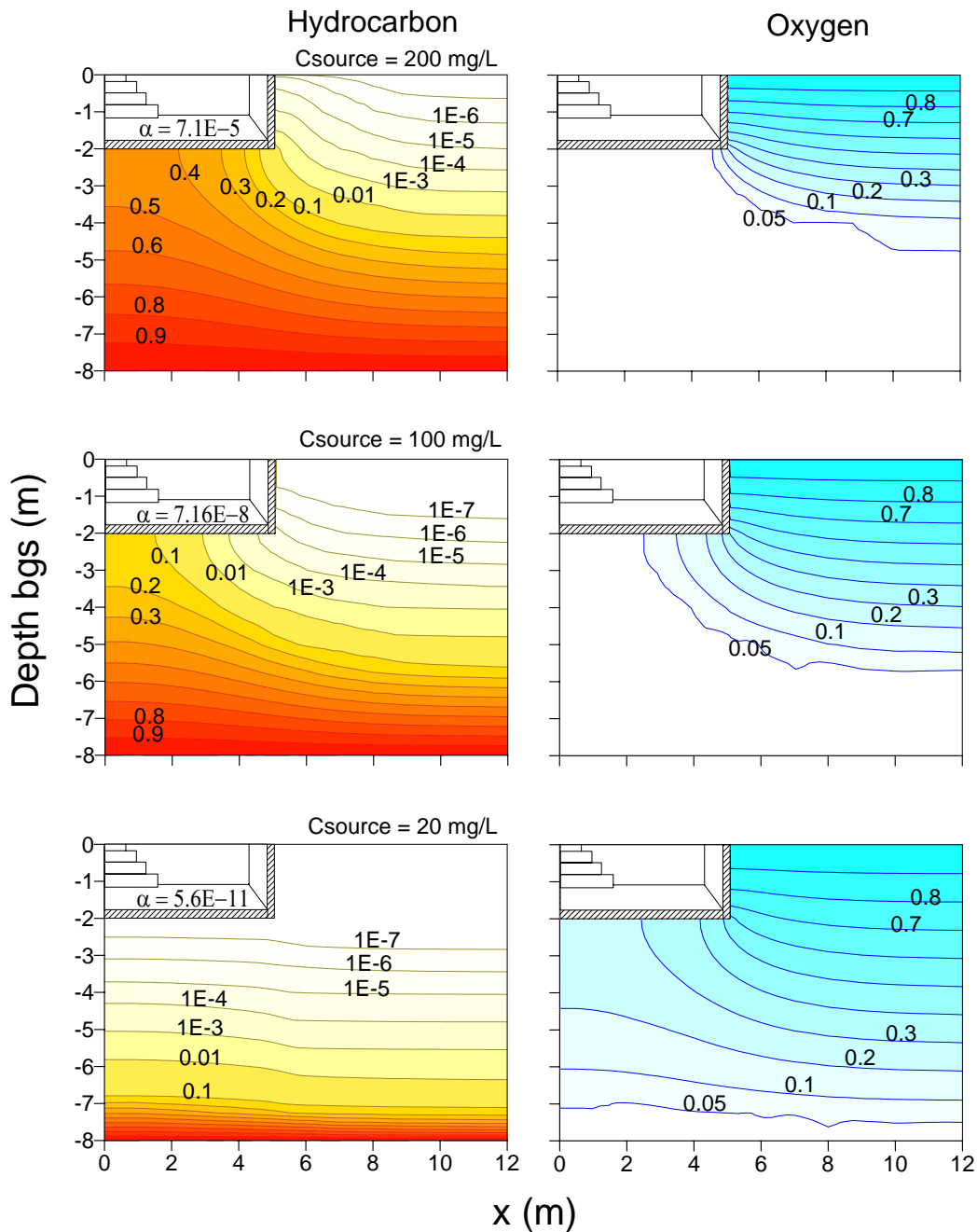


Figure 2-5. Normalized soil gas concentration distribution for oxygen and hydrocarbon undergoing aerobic biodegradation with first-order rate $\lambda = 0.18 \text{ (h}^{-1}\text{)}$ and vapor source at concentrations of 20 mg/L, 100 mg/L and 200 mg/L located underneath a basement foundation at a depth of 8 m below ground surface. Hydrocarbon and oxygen contours are normalized to the source and the atmospheric concentrations, respectively. (Abreu 2005).

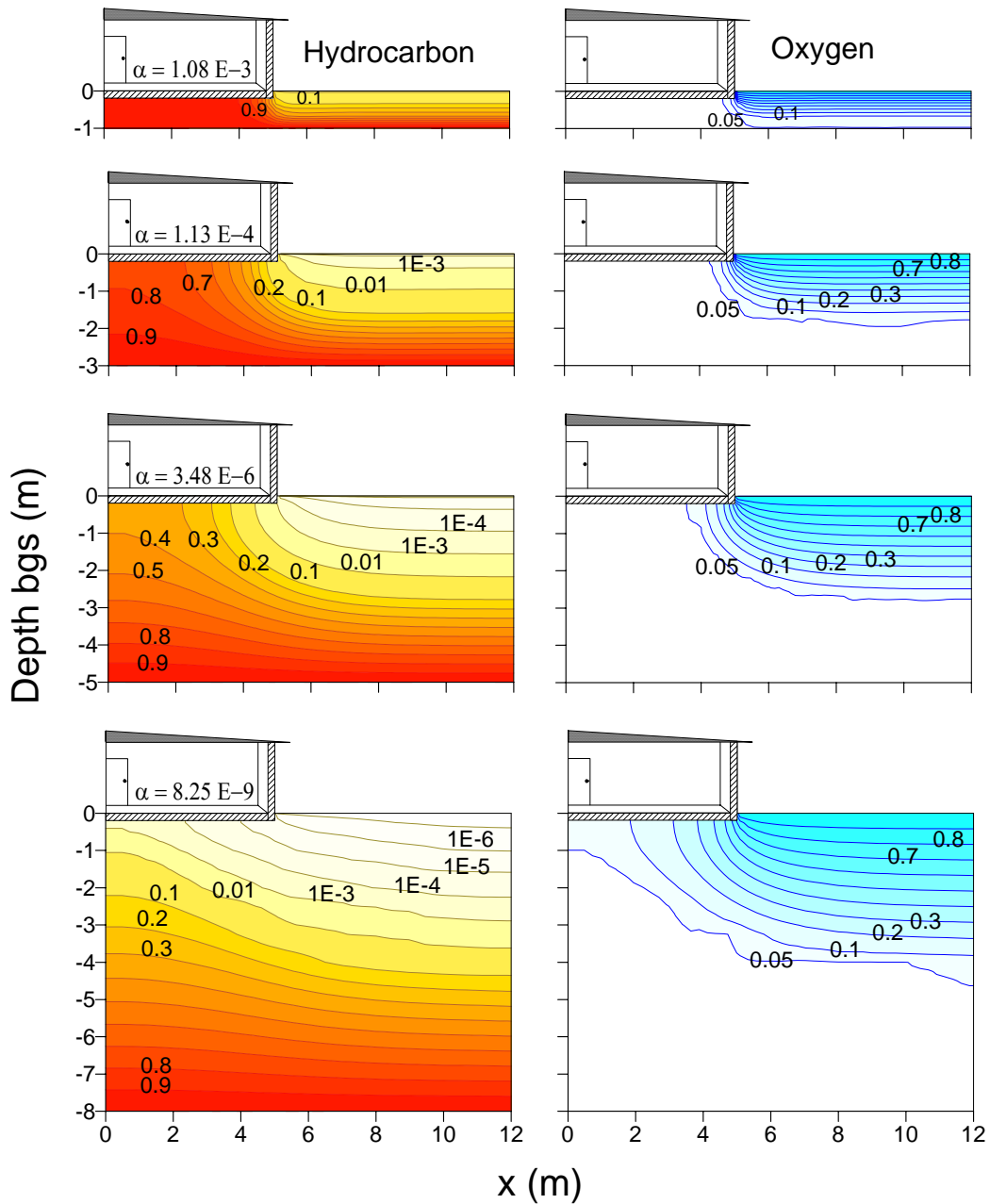


Figure 2-6. Normalized soil gas concentration distributions for oxygen and hydrocarbon undergoing aerobic biodegradation with a first-order rate $\lambda = 0.18 \text{ (h}^{-1}\text{)}$ and a vapor source concentration of 200 mg/L located beneath a slab-on-grade foundation at depths of 1 m, 3 m, 5 m and 8 m below ground surface. Hydrocarbon and oxygen contours are normalized to the source and the atmospheric concentrations, respectively. (Abreu 2005).

3.0 Conceptual Migration Model for Subsurface Vapor to Indoor Air

Topic:

This section provides background information to assist in developing a conceptual migration model for a specific site. The conceptual migration model is important for planning a soil-gas-sampling program.

Purpose:

To define a conceptual migration model for describing the vapor source characteristics, the current and future building locations and features, and the geologic profile of the subsurface. The model conveys a working hypothesis of the movement of vapor-phase chemicals of concern within the subsurface to a current or future building.

Significance:

The conceptual migration model should effectively communicate the important features of the site geology, hydrogeology, and petroleum hydrocarbon distribution and composition relevant to vapor migration. It is especially important that the site be reasonably well characterized for the purposes of planning soil gas sampling and laboratory analyses.

Prior to selecting sampling locations and depths, a site-specific conceptual migration model should be developed. The *conceptual migration model* describes the vapor source characteristics, including the vapor source location, size, environmental media, the concentrations of chemicals of concern and the potential for these to change with time. It also should include a description of the expected soil gas concentration distribution, and a discussion of:

- whether or not this distribution has reached near-steady conditions under current site conditions (e.g., present locations of buildings and surface cover),
- whether or not future site uses might alter the soil gas distribution (e.g., future building locations and surface features), and
- how the soil gas profile is expected to be influenced by geologic features.

The conceptual model should identify the current and reasonably potential future subsurface-vapor-to-indoor-air exposure pathways that may be present. The exposure

Vapor Transport along Utility Conduits

If vapor transport from the source area to the building could occur along utility conduits, then vapor sampling inside the utility conduits, manholes, or sumps should be considered in addition to vadose-zone-soil-gas sampling. Specific guidance for utility sampling is beyond the scope of this document; however, consideration should be given to field instrument screening at utility access points as an initial step to determine if the utility is acting as a conduit for vapors. It is important to establish in the conceptual migration model whether it appears that vapor migration is taking place along the utility backfill or if there is actual vapor transport inside the utility itself. Any utility sampling program must include safety precautions to protect personnel (e.g., oxygen and combustible gas monitoring, confined-space entry requirements) and to avoid damage to utilities.

pathways should be defined by the vapor source (e.g., soil, groundwater, light non-aqueous phase liquids [LNAPL]) and locations where the subsurface-vapor-to-indoor-air exposure pathway is of concern (e.g., current or potential future building). Specific buildings and future building sites should be identified. A description of the existing or anticipated building construction type (e.g., slab on grade, basement, multiple stories), design (e.g., basement or floor-slab thickness), and use (e.g., residential, commercial, industrial) should also be identified.

As part of the development of the conceptual migration model, it is important to review available information for the site to determine the state of knowledge about subsurface conditions and to identify specific information that is necessary to evaluate the subsurface-vapor-to-indoor-air exposure pathways. The conceptual migration model should effectively communicate the important features of the site geology, hydrogeology, and petroleum hydrocarbon distribution and composition relevant to vapor migration. It is especially important that the site be reasonably well characterized for the purposes of planning soil gas sampling and laboratory analyses, including information related to the:

- Types of petroleum hydrocarbons with volatile chemicals of concern (e.g., gasoline, jet fuel, diesel) that are currently or previously stored or handled at the site
- Petroleum hydrocarbon chemicals of concern and their concentrations in soil and groundwater (e.g., benzene, toluene, ethylbenzene, xylenes, MTBE, naphthalene). The particular chemicals of concern for a site, the use of the data, and the regulatory requirements are used to determine the appropriate laboratory analytical methods.
- Potential sources and source areas of vapors (e.g., soil, groundwater, LNAPL)
 - Presence of LNAPL, which may represent an expanding vapor source
 - Presence of residual LNAPL, which may represent a stable or reducing vapor source
 - For groundwater sources of vapors, it is useful to know whether the groundwater plume is expanding, stable, or shrinking as this will give an indication of the temporal variability of concentrations of chemicals of concern in soil gas and whether future concentrations in soil gas at a specific location are likely to be higher or lower than current concentrations. In addition, groundwater table fluctuations should be evaluated when assessing the temporal variability of groundwater sources.
- Geology and hydrogeology in the area of the site
 - Distinct soil strata and qualitative contrasts between them (e.g., finer- or coarser-grained soils, higher or lower moisture content strata). Finer-grained soils are generally more moist and tend to be the zones where there are significant concentration gradients. The coarser-grained soils often represent preferential vapor-migration zones.

- It is also important to consider whether there are relatively thin, finer-grained soil layers that may have a significant impact on vapor migration but can be difficult to detect during drilling.
- Approximate location of vapor sources in the subsurface and distances (lateral and vertical) between the vapor sources and the building location. The distances are important in determining the number of and locations for soil-gas-sampling probes.
- Possible preferential vapor-migration conduits (e.g., utility conduits, sewers)
 - Of particular interest are the utilities that intersect a vapor source and also connect to a building
 - If there is significant vapor migration in preferential pathways, then the measurement of concentrations of chemicals of concern in soil gas may not be representative of vapor concentrations that would migrate into an indoor environment. Other investigative techniques (e.g., utility vapor screening, indoor air measurements) for the subsurface-vapor-to-indoor-air exposure pathway may provide better data to evaluate the pathway. The user of this manual is directed to USEPA 2002a, and applicable state regulatory guidance for other methods to assess the vapor-to-indoor-air pathway (see PaDEP 2002; MaDEP 2002; WDHFS 2003; NJDEP 2004; CRWQCB 2003; CSDDEH 2003).
- Construction features of existing or future buildings (e.g., size, age, presence of foundation cracks, entry points for utilities).

Appendix A provides a summary of the information that is useful for understanding the site.

4.0 Development of a Strategy for Soil Gas Sampling

Topic:

This section deals with articulating the questions to be answered by the soil gas sampling and developing a strategy for soil gas sampling.

Purpose:

To develop a strategy for soil gas sampling based on:

- The practicality of collecting soil gas samples at a particular site
- A conceptual migration model for subsurface vapor to indoor air
- Questions to be answered by the sampling
- Regulatory requirements
- Technical issues.

Significance:

The development of a conceptual migration model, a discussion of the sampling options, a list of key considerations, and an exploration of reasonable sampling scenarios for petroleum hydrocarbon impacted sites are needed to establish an effective soil-gas-sampling program.

Section 3.0 discusses the development of the conceptual migration model for subsurface vapor to indoor air. This section discusses options for collecting soil gas samples. Because the strategy for soil gas sampling may vary from site to site, prescriptive guidance on sampling locations, depths, and frequencies is not provided. However, a discussion of the sampling options, a list of key considerations, and reasonable sampling scenarios for petroleum hydrocarbon impacted sites are discussed in this section. Local regulatory agencies may have sampling guidance that differs from that presented here. Appendix B provides worksheets for three typical scenarios that can be used for planning sampling locations.

The options for soil gas sample collection discussed in this section are based on consideration of:

- The practicality of collecting soil gas samples at a particular site
- A conceptual migration model for subsurface vapor to indoor air
- Questions to be answered by the sampling
- Regulatory requirements
- Technical issues.

Information about site considerations for sampling is included in Section 5.0 and in Appendix C.

In developing a soil-gas-sampling strategy, the questions to be answered by the soil gas sampling should be clearly articulated prior to designing the soil-gas-sampling plan. The questions to be answered by soil gas sampling at petroleum hydrocarbon impacted sites are often similar to one or more of the following:

1. Is the subsurface-vapor-to-indoor-air exposure pathway currently complete for individual chemicals of concern?

2. Are concentrations of chemicals of concern in soil gas currently above applicable regulatory action levels or other levels of concern?
3. Is biodegradation contributing to the attenuation of hydrocarbon vapors between the source and building at this site?
4. How might the answers to questions (1) to (3) change when considering plausible future activity and land-use scenarios?

The sampling approach selected for a site will depend on the site-specific conditions and the questions to be answered about the site. The selection of sampling locations and depths needs to consider the conceptual migration model (e.g., location of the vapor sources and the buildings of concern, the expected vapor distribution, and characteristics of the subsurface). It is likely that a phased program of soil gas sampling may be used at some sites, while at other sites the conditions may indicate that specific types of sampling and specific sampling locations are appropriate. The basic sampling approaches include:

- Point samples at specific depths in one or more lateral locations. These may be collected using temporary driven probes or by installing permanent soil-gas-sampling probes.
- Vertical profiles of samples at two or more depths. These can be installed at one or more lateral locations, called *transects*. These soil gas samples may be collected using temporary driven probes or by installing permanent soil-gas-sampling probes.

4.1 General Approach

Below are three basic steps in the selection of soil-gas-sampling locations.

1. Develop a conceptual migration model describing the current or potential future subsurface-vapor-to-indoor-air exposure pathways. The model may require modification as soil gas data are collected.
2. Identify the questions to be answered by the soil gas sampling and any regulatory requirements.
3. Select the sampling approach, the locations, and depths to provide information sufficient to assess the pathway and to answer the questions posed for the site.

Varied Sample Locations and Depths

It is a good idea to design the sampling program to collect soil gas samples at one or more locations or depths where concentrations are expected to be above the laboratory detection limits so that the field and laboratory methods can be verified. If all of the analytical results are below the laboratory detection limits, it is not easy to confirm that the field methods were implemented correctly (e.g., sample collection without dilution). In addition, there is increased confidence in the data when there are samples at two or more depths, given that the sample results are internally consistent and are consistent with the conceptual migration model.

4.2 Point Sampling

Point sampling is the collection of an individual soil gas sample from a specific depth at a single sample location. Often, soil gas sampling begins with point sampling. Consideration should be

given to how representative one sample will be of the concentrations of chemicals of concern in soil gas either spatially or temporally. It may be necessary to collect several point soil gas samples to develop an understanding of the distribution of concentrations of chemicals of concern in soil gas. A discussion of sampling frequency is given in Section 4.6.

Point sampling is often implemented when conducting an initial assessment of the subsurface-vapor-to-indoor-air exposure pathway. Point samples are collected at a specified depth, and the concentrations of chemicals of concern in soil gas are compared with chemical- and depth-specific target levels. The concentrations of chemicals of concern in soil gas also may be compared to measured concentrations of the chemicals of concern in ambient air samples. The most common locations for point sampling are immediately adjacent to, or beneath, a building foundation and at the vapor source. Use of the latter presumes that the location of the vapor source is known with confidence, and this may or may not be the case at a given site. If the concentration of a chemical of concern in soil gas is above the target level, then a more site-specific analysis should be conducted or remedial action should be implemented. Concentrations of chemicals of concern in soil gas below target levels indicate that the subsurface-vapor-to-indoor-air exposure pathway may not be significant. See Section 7.0 for more information about data analysis.

Another application of point sampling may be to evaluate the results of simple, conservative models of vapor transport in soil or from groundwater. Where modeling indicates that there may be concentrations of chemicals of concern above target levels at a building, it might be appropriate to collect several point soil gas samples to compare to the model results and further investigate if the pathway is actually complete.

Point samples may be collected using temporary driven probes or permanent probes as described in Section 5.1. It is important that the soil gas sample collected from a point sample is appropriate for the comparison. Therefore, the decision on the location and depth of the point sample should consider the vapor source (e.g., soil, groundwater, LNAPL), the mobility of the source (e.g., groundwater), and the impacts of heterogeneity in soil.

4.3 Transects and Vertical Profiles

Questions (1) and (2) at the beginning of this section arguably can be assessed with the collection of representative soil gas samples either at the vapor source or immediately adjacent to or beneath a foundation. In some situations, that information may be sufficient. In other circumstances, the added knowledge that comes from lateral transects and vertical profiles may be valuable for the following reasons:

- The assessment of the subsurface-vapor-to-indoor-air exposure pathway is typically triggered by the knowledge that a vapor source (e.g., petroleum hydrocarbon impacted soils or groundwater) is present in close proximity to a building (or future building location). If a single sample is collected near the building foundation and that sample results in non-detectable concentrations of chemicals of concern in soil gas, then there may be some question about the soil gas collection method or representativeness of that single soil gas sample. If a sample also were collected near the vapor source and this

sample were to have detectable concentrations of the expected magnitude, then the confidence in the validity of the near-foundation sample increases.

- The major difference between petroleum hydrocarbon impacted sites and sites impacted with other volatile chemicals of concern (e.g., chlorinated hydrocarbon impacted sites) is that aerobic biodegradation can be a significant contributor to the overall attenuation of petroleum hydrocarbon chemical of concern vapors as they migrate in soil from the source toward the building and ground surface. At some sites, very high total hydrocarbon vapor concentrations (e.g., within 10-percent of the lower explosive limits) will be detected near the source, and very low, or non-detectable, concentrations will be present near the buildings of concern. In this case, the collection of soil gas samples at points between the source and building, and review of the total hydrocarbon concentration, as well as chemical of concern concentration and oxygen-soil-gas profiles, will help to establish aerobic biodegradation as a key attenuation mechanism.
- Confidence in the overall understanding of vapor migration at a site is increased when consistency exists between the conceptual migration model and the soil gas profiles and transects.

Aerobic Biodegradation

Establishing the significance of aerobic biodegradation as it relates to hydrocarbon fluxes and indoor air concentrations requires a series of samples collected along the subsurface-vapor-migration pathway and analyzed for chemicals of concern and respiration gases. At many sites, the source is located directly beneath a building and vertical profiling is sufficient in those cases. At other sites where the source is displaced laterally from the building, a lateral series of vertical profiles between the source and building may be necessary.

This discussion has been included here to provide some insight to the underlying emphasis on vertical profiles and transects in this document. As stated above, point samples at key locations may be sufficient to determine whether the exposure pathway is complete or significant.

One of the unique features of petroleum hydrocarbon impacted sites is the potential for chemical of concern vapor fluxes and concentrations to be significantly attenuated by aerobic biodegradation. To establish the occurrence of aerobic biodegradation, a single sample might be sufficient—in particular, a sample showing depleted oxygen levels (and increased carbon dioxide); however, the estimation of attenuation rates resulting from aerobic biodegradation requires a soil gas profile or transect between the vapor source and the building.

Lateral Distance Threshold

Recently there has been discussion concerning the need for a threshold lateral distance criterion. For example, the USEPA (2002a) proposes that the pathway is not complete and sampling is not necessary if the distance between a known source and the building is greater than 100 feet. For reference, the USEPA criterion was based primarily on the authors' professional judgment and practical considerations. Based on theoretical considerations, it is known that this distance criterion should consider the depth to the vapor source, the vapor source strength, the indoor-air target levels, and local geology (Abreu and Johnson 2004; Lowell and Eklund 2004). Thus, the USEPA's 100-foot distance might, or might not, be protective at every site. For petroleum hydrocarbon impacted sites, the 100-foot distance is likely sufficient for most sites, provided that the vapor source edge is well defined, vertical migration of oxygen is not significantly impeded by surface or subsurface features, and conditions that could promote lateral migration are not present (e.g., landfill gas production, highly layered soils)

In addition, confidence in the conceptual migration model for a site and in quantifying the attenuation is increased when vertical profile or transect data are available. As discussed above, this confidence increases when there is consistency within the soil gas data set (e.g., concentrations decrease along the path between the source and building, decreasing oxygen concentrations with depth) and when there is consistency between the geologic profile developed under the conceptual migration model and the soil gas data (e.g., higher concentration gradients through finer-grained soils).

4.3.1 Selection of Lateral Positions for Soil Gas Transects

Soil gas transects can be used when the vapor source (e.g., soil, LNAPL, groundwater) is not located directly beneath the building or location of a future building. Soil gas transects consist of two or more sampling locations between the source and the building of concern. The purpose of collecting soil gas transects is to demonstrate and quantify the attenuation of concentrations of chemicals of concern in soil gas moving laterally from the source to the building.

A basic sampling program might involve three sampling locations. For example:

- One sampling location at the edge of the source zone closest to the building of concern
- One sampling location mid-way between the source and building
- One sampling location at the building.

While these three sampling locations are likely sufficient, based on the experience of the authors, users might consider additional intermediate points if the spacing between sampling probes is more than about 50 feet.

Transect samples may be collected using temporary driven probes or permanent probes as described in Section 5.1. The location and depth of the transect samples should consider the vapor source (e.g., soil, LNAPL groundwater), the mobility of the source medium (e.g., groundwater), and the impacts of heterogeneity in soil.

4.3.2 Vertical Profiles

A soil-gas vertical profile consists of two or more samples collected from a single location between the top of the source and the ground surface or building foundation. The purpose of collecting soil-gas vertical profiles is to demonstrate and quantify the attenuation of concentrations of chemicals of concern in soil gas vertically from the top of the source to the ground surface or building foundation. For sites where the vapor source is directly beneath the building, soil-gas vertical profiles are typically used to determine the potential for and magnitude of vapor migration into the building. The following should be considered in selecting vertical sampling depths:

- To estimate the maximum concentration of chemicals of concern in soil gas, a sample is needed immediately above the vapor source
- To estimate the concentration of chemicals of concern in soil gas near the foundation, samples should be collected immediately adjacent to, or beneath, the building foundation
- To establish the occurrence and significance of aerobic biodegradation, two or more soil gas samples should be collected between the vapor source and the building foundation
- The vertical distance between adjacent samples based on practical considerations is usually not less than about 2 feet, and at some sites, this practical constraint might limit the number of samples collected
- For deeper sources, where the distance between the source and the building foundation is greater than approximately 40 feet, profiles consisting of five or more sampling depths are often necessary to provide resolution of the soil gas profile
- Sampling locations also may be selected based on the lithology of the site (e.g., in more permeable soil zones, whether natural or artificial, or at locations where changes in concentration are expected)
- When assessing sites where impacted groundwater, LNAPL, or a smear zone is the vapor source, a closer spacing of samples should be considered, relative to the remainder of the profile (e.g., several samples spaced 2 feet apart) near the groundwater table/capillary fringe, as the concentration gradients are often greatest at that depth.

A vertical profile could be developed using only three sample depths. However, depending on site-specific circumstances (e.g., depth to top of source area, lithology) four or more sample depths may be appropriate. Some situations preclude the use of vertically-nested soil gas probes or vertical profiling. As a rule of thumb, when groundwater is within a few feet of a foundation, it is likely that only one soil-gas-sampling depth is practical. The site characteristics and physical constraints will factor into the number of vertical samples.

Vertical profile samples may be collected using temporary driven probes or permanent probes as described in Section 5.1. The decision on the number of vertical profile samples should consider the vapor source (e.g., soil, groundwater, LNAPL), the depth of the source (e.g., groundwater, LNAPL), and the impacts of heterogeneity in soil. The lithologic profile, surface topography, and

depth to the vapor source should be considered when installing vertical profile probes at multiple lateral positions. For relatively flat sites (e.g., consistent distance between the ground surface and the vapor source depth) and consistent stratigraphy (e.g., depths to distinct geologic units), use of consistent sampling depths is preferred so that sampling results can be compared more easily (see Figure 4-1). For cases with significant spatial variability in the distance between ground surface and the vapor source depth, it is preferable to collect all of the deepest samples at the elevation of the vapor source and all of the shallowest samples at the foundation or basement elevation. (see Figure 4-2) Given these constraints, the selection of depths for intermediate points should target depths where significant changes in concentration are expected (e.g., immediately above and below fine-grained soils, near the capillary fringe for groundwater sources).

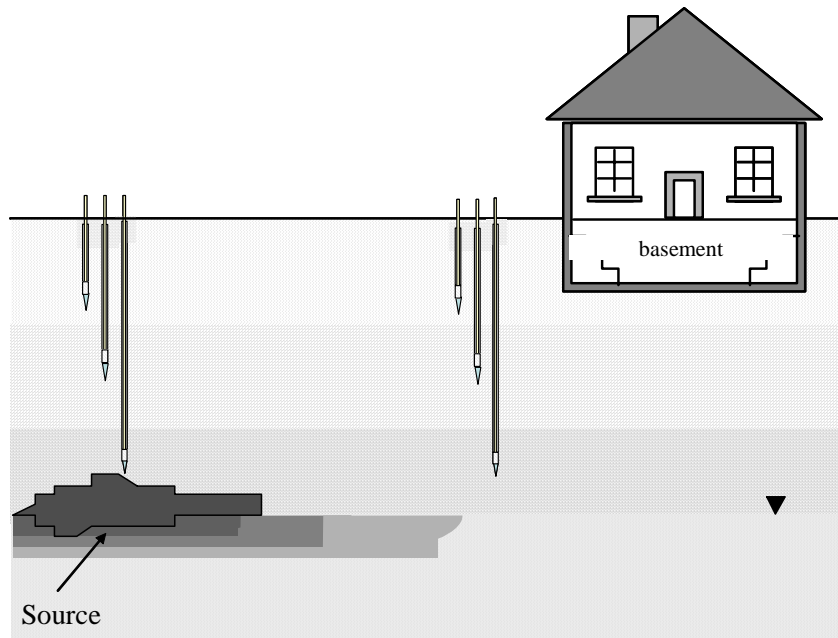


Figure 4-1. Considerations for vertical profiles at relatively flat sites (e.g., consistent distance between the ground surface and the vapor source depth) with consistent stratigraphy.

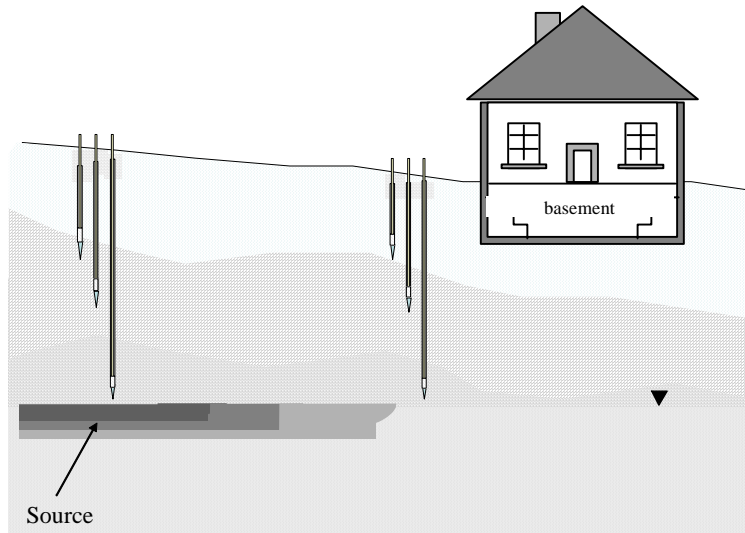


Figure 4-2. Considerations for vertical profiles at sites with significant spatial variability in the distance between ground surface and the vapor source depth.

4.4 Summary of Sampling Depth and Location Selection Considerations

Based on the discussions above, Table 4-1 through Table 4-5 have been prepared to summarize the use of data from the various sample depth locations and to offer some key comments and cautions for each. For each location, the user should consider whether the samples are representative of the concentrations of chemicals of concern at the location. For any site, the utility of the locations and depths will vary depending on the conceptual migration model and the questions of interest.

Table 4-1. Considerations for Samples Collected Immediately above the Vapor Source

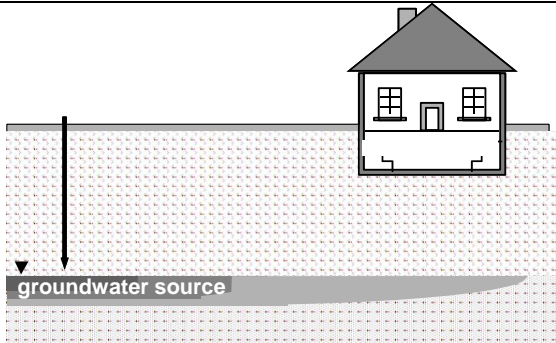
| Sample Depth or Location | |
|--|--|
| <p>Soil gas samples collected immediately above the vapor source (e.g., highest concentrations of chemicals of concern in soil or groundwater).</p> |  |
| Use of Data | Comments and Cautions |
| <p>These samples should represent the highest concentrations of chemicals of concern present in soil gas.</p> <p>In assessing if the pathway is complete or significant, these samples can be used to generate a conservative exposure concentration estimate for a present or future building scenario.</p> | <p>These concentrations are generally greater than concentrations of chemicals of concern in soil gas at the building.</p> <p>Understanding (through modeling or empirical data analysis) of the estimated soil-gas-vapor attenuation factor is needed to estimate concentrations of chemicals of concern in the building. In general, the models used with these concentrations are the more conservative screening models that do not consider biodegradation. As a result, the estimates of indoor air concentrations are likely to be biased towards values that are higher than what is likely to occur at the site.</p> <p>As the distance between the sample location and the building increases, the uncertainty in estimating concentrations of chemicals of concern in indoor air will likely increase.</p> <p>These concentrations reach near-steady conditions quickly and tend to be stable seasonally and are relatively unaffected by near-surface changes (e.g., surface cover, weather changes).</p> <p>If the concentrations in these samples are below target levels, then the vapor-to-indoor-air pathway is not likely to be significant (see Section 7.0).</p> |

Table 4-2. Considerations for Samples Collected Laterally Mid-Way between the Vapor Source and the Building Location

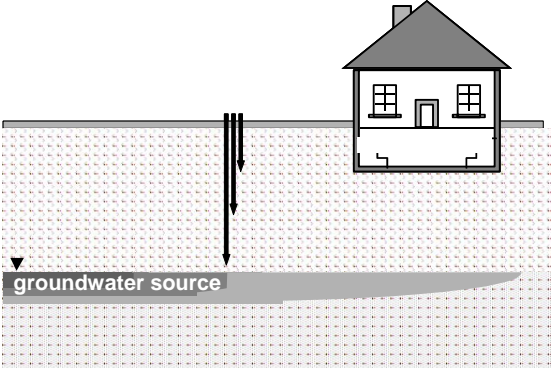
| Sample Depth or Location | |
|---|--|
| <p>Soil gas samples collected from a location laterally mid-way between the vapor source and the building location.</p> |  <p>The diagram illustrates a cross-section of the ground. On the right side, there is a simple line drawing of a house with a chimney, windows, and a door. To the left of the house, the ground is shown with a stippled texture. A horizontal line represents the ground surface. Below this surface, a darker shaded area represents a 'groundwater source'. A vertical line with a downward-pointing arrow indicates a sampling point located laterally between the groundwater source and the building.</p> |
| Use of Data | Comments and Cautions |
| <p>Used in conjunction with source vapor sampling, this sample may indicate site-specific attenuation along the subsurface-vapor-migration pathway.</p> | <p>Understanding (through modeling or empirical data analysis) of the estimated soil-gas-vapor attenuation factor is needed to estimate the concentrations of chemicals of concern in the building. In general, the models used with these concentrations are the more conservative screening models that do not consider biodegradation. As a result, the estimates of concentrations of chemicals of concern in indoor air are likely to be biased towards values that are higher than what is likely to occur at the site.</p> <p>These concentrations are difficult to interpret in the absence of concentrations of chemicals of concern in soil gas at the source zone and an accurate conceptual migration model.</p> |

Table 4-3. Considerations for Samples Collected Adjacent to the Base of an Existing Building Foundation or Basement

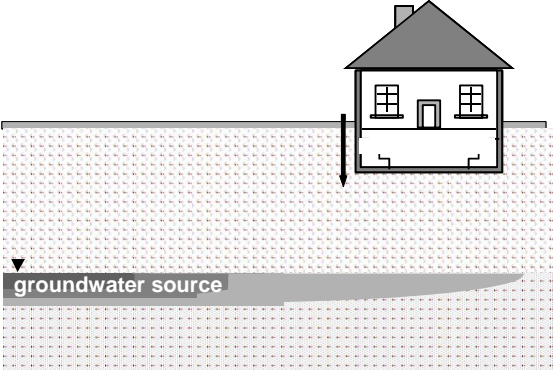
| Sample Depth or Location | |
|--|--|
| <p>Soil gas samples collected adjacent to the base of an existing building foundation or basement.</p> |  |
| Use of Data | Comments and Cautions |
| <p>Because these samples are collected close to the exposure location, they may be a useful predictor of concentrations of chemicals of concern in indoor air.</p> | <p>There is likely less attenuation of concentrations of chemicals of concern along the subsurface-vapor-to-indoor-air exposure pathway at this location than for more distant sample locations (e.g., Table 4-1 and Table 4-2).</p> <p>Depending on where subsurface vapors enter a building through the building foundation and on the oxygen distribution adjacent to and beneath the building, this sample location may or may not be representative of the actual concentrations of chemicals of concern in soil vapor that are entering a building.</p> <p>Depending on the distance from the source to the building, these concentrations may not reach near-steady conditions for some time after the release (see Section 2.1).</p> <p>These samples are more likely to be affected by changes in near-surface conditions (e.g., temperature, precipitation, barometric pressure fluctuations).</p> |

Table 4-4. Considerations for Samples Collected Immediately below the Building Foundation or Basement

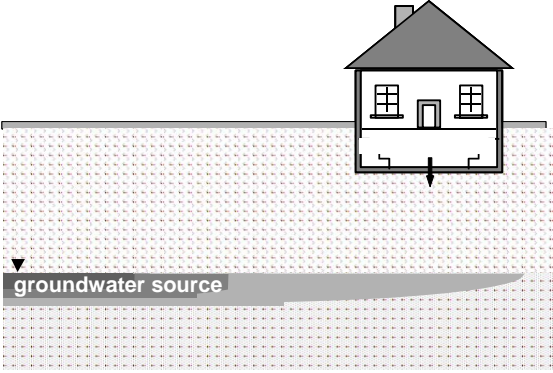
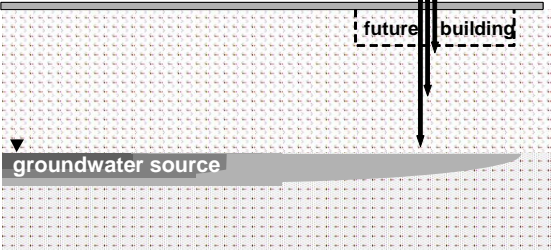
| Sample Depth or Location | |
|--|--|
| <p>Soil gas samples collected immediately below the building foundation or basement.</p> |  |
| Use of Data | Comments and Cautions |
| <p>Because these samples are collected close to the exposure location, they may be a useful predictor of concentrations of chemicals of concern in indoor air.</p> | <p>Logistical issues are associated with sample collection (e.g., building access, placing sampling probes, maintenance of sampling probes).</p> <p>These samples are more likely to be variable with time as they are affected by changes in near-surface conditions (e.g., temperature, precipitation, barometric pressure fluctuations, HVAC systems).</p> <p>The concentrations of chemicals of concern in soil gas under a building foundation may also be spatially variable. More than one sampling location may be required to develop a representative concentration.</p> <p>In general, empirical relationships are used with these concentration data to estimate concentrations of chemicals of concern in indoor air. Because the empirical relationships already reflect the effects of biodegradation between the vapor source and the building, the estimated indoor air concentrations are not inherently biased high or low.</p> <p>Depending on where subsurface vapors enter a building through the building foundation and the distribution of oxygen adjacent to and beneath the building, this sample location may or may not be representative of the actual concentrations of chemicals of concern in soil gas that are entering a building.</p> <p>Depending on the distance from the source to the building, these concentrations may not reach near-steady conditions for some time after the release (see Section 2.1).</p> |

Table 4-5. Considerations for Samples Collected within the Footprint of a Future Building Location

| Sample Depth or Location | |
|--|---|
| <p>Soil gas samples collected within the footprint of a future building location.</p> |  |
| Use of Data | Comments and Cautions |
| <p>In combination with modeling or empirical analysis, the concentrations of chemicals of concern in soil gas may provide an estimate of future subsurface-vapor-to-indoor-air exposure pathway impacts.</p> | <p>The samples collected at the source depth will likely be representative of future conditions (unless groundwater is very shallow).</p> <p>Intermediate depth and shallow samples may not be representative of future conditions, depending on the surface cover, as the building foundation and building HVAC system would have some effect on oxygen transport (and therefore on the significance of aerobic biodegradation).</p> |

4.5 Some Comments on Sample Collection Adjacent to and Beneath Buildings

Sampling directly through foundation slabs of existing buildings (i.e., through-slab sampling) presents significant logistical and practical issues, including:

- Access issues
- Disturbance of residents or building occupants
- Representativeness of the samples (depending on the actual vapor entry points to the building, these sample locations may or may not represent vapors that are entering the building)
- Ability to install permanent sampling installations that can be used for multiple sampling events
- Maintenance of permanent sampling locations
- Limitations on the types of sampling installations and depths that can be used.

For these reasons, sampling (and the placement of permanent soil-gas-sampling probes) adjacent to a building often is considered. To date, no well recognized study has been conducted to

defensibly address the representativeness of samples collected adjacent to a building, or beneath a building, for concentrations of chemicals of concern that may be entering the building. As a result, there isn't any consensus on which location consistently provides data that is more representative, but it is the case that some regulatory agencies recommend through-slab sampling.

The following should be considered for sampling locations near buildings:

- When the building overlies the vapor source, samples collected at the source zone depth are generally not affected by changes in surface conditions. Therefore, samples measured at source zone depth adjacent to and beneath a building should yield comparable concentrations. Thus, if the pathway assessment can be conducted using the deeper soil gas samples, then samples collected adjacent to a building should be sufficient.
- The construction of the building foundation, its size, age (particularly as it relates to the existence of cracks), and entry points of utilities all factor into the potential for migration of vapors from soils outside of the building into the indoor environment. These building attributes should be considered in the conceptual migration model and in the selection of sample locations.
- When it is important to demonstrate the significance of attenuation via aerobic biodegradation, the need to sample beneath the building becomes more critical. This is because oxygen transport to regions beneath the building footprint may be limited relative to areas outside the building footprint. As a result, oxygen may become depleted, and the effect of attenuation by aerobic biodegradation would be reduced.
- Differences between samples collected next to and beneath buildings will probably be most significant for shallow vapor sources (e.g., less than a 10-foot vertical separation between the basement or building foundation and the vapor source). There should be less difference for deeper vapor sources (e.g., greater than a 40-foot separation between the basement or building foundation and the vapor source).
- When committed to performing through-slab sampling, a site-specific sampling and data analysis plan should be developed prior to performing the fieldwork. The plan should include the number and location of samples to be collected, the analytical methods to be used, the required detection limits, and when appropriate, the selection and use of tracers. The plan should include a discussion of the rationale for each of the elements (e.g., sample locations) and specifications (e.g., assessment of variability) in the plan.
- Collection of tracer gas samples (e.g., radon) within the building and beneath the foundation may provide site-specific insight into the sub-slab attenuation factor (α) used to assess indoor impacts for the petroleum hydrocarbon chemicals of concern. If tracer gas samples are to be used to assess the site-specific, sub-slab attenuation factor, one should be working with measured tracer indoor air concentrations that are greater than ten-times the reasonably expected background concentrations or analytical detection limits. Radon may not be an appropriate tracer at some locations because of low concentrations in soil gas or because of indoor sources (e.g., building materials) of radon (Hartman, 2004a). The attenuation factor is defined as:

$$\alpha = \frac{C_{\text{indoor}}}{C_{\text{sub-slab}}}$$

and is represented in Figure 4-3.

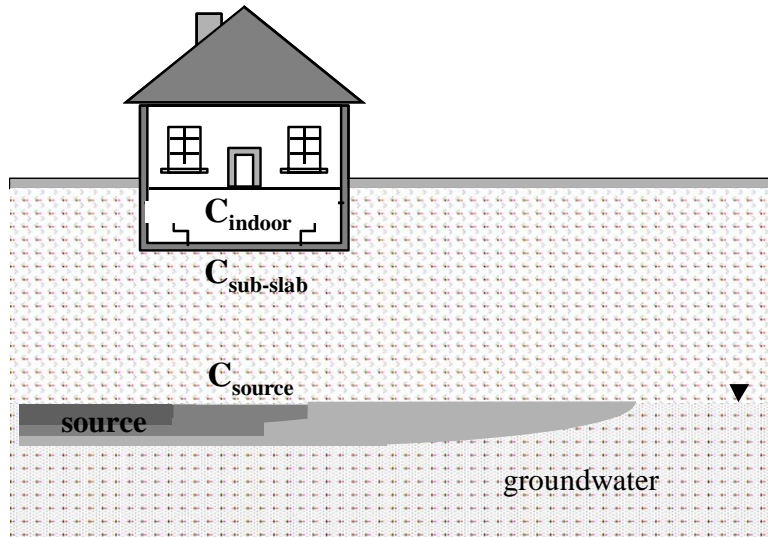


Figure 4-3. Sub-slab-to-indoor-air attenuation.

4.6 Sampling Frequency

Soil gas profiles tend to be relatively stable with time, unless the conditions near the vapor source change significantly, properties of the vadose zone change significantly, or conditions at the ground surface change. For example, rising or fluctuating groundwater levels will limit vapor migration from residual LNAPL in soil if the water level rises above the top of the residual LNAPL. Vapor profiles also might be affected by infiltration events, including lawn or landscape irrigation, if they significantly alter the air-filled porosity in the subsurface, submerge the source, or temporarily dilute the concentrations of chemicals of concern in shallow groundwater.

If multiple sampling events are desired, sampling frequencies should be selected to coincide with seasonal changes at the site. For example, samples should be collected during “wet” and “dry” seasons, or during seasonal “high” and “low” groundwater level periods.

It should be noted that one sampling event might be sufficient for a number of sites, especially those sites having concentrations of chemicals of concern in soil gas in the source area below target concentrations. In addition, at these sites:

- other data are consistent with the measured soil gas concentration (e.g., groundwater and soil data consistency as assessed through equilibrium partitioning calculations, see Section 4.7 and Appendix E), and
- all other lines of evidence gathered for the site support the conclusion that soil gas concentrations would not increase to concentrations of concern in the future.

Multiple sampling events are likely to be necessary at sites with higher concentrations of chemicals of concern in soil gas (e.g., concentrations greater than 1,000 times the indoor air target level), or where a demonstration of the stability of the vapor concentrations should be needed (e.g., if the time since the release is not long enough to feel confident that near-steady vapor profiles have developed, see Section 2.1).

4.7 Additional Considerations to Increase Confidence in Data Sets and the Interpretation of Soil-Gas-Sampling Results

As discussed in Section 4.2, point sampling may be sufficient to demonstrate pathway completeness at some sites; however, for other sites, the following options for increasing the confidence in the assessment of this pathway may be useful:

- Collection of soil gas vertical profiles and transects generally provides an added level of confidence in the data set. Confidence in the data set increases if the data set includes both low, or non-detect, concentrations of chemicals of concern near the ground surface and higher concentrations near the source.
- Confidence in the data set and interpretation increases when the soil gas profiles and transects are consistent with the conceptual migration model and the soil gas profiles (e.g., hydrocarbon, oxygen) observed at other sites (see Section 2.2 and Section 7.2).
- Confidence in the data set increases when the near-source concentrations of chemicals of concern are roughly equal to expected values. For example, for groundwater sources, a groundwater sample could be collected and groundwater elevation could be measured at the same time that the soil gas samples are collected. The groundwater samples can be collected from the same location as the soil gas samples or

Groundwater Concentrations

Calculation of a soil gas concentration based on a groundwater concentration provides an estimate of the expected soil gas concentration. However, a number of factors would result in the actual soil gas concentration being higher or lower than the estimated soil gas concentration. These factors include: a submerged LNAPL source, an LNAPL source in the vadose zone, groundwater well screens that are long, rapid biodegradation in the vadose zone, and, a soil gas sampling interval that is shallow relative to the groundwater table. In addition, it is not possible to collect vapor samples immediately above the water table (because of high water saturations in the capillary fringe). There is a decreasing concentration gradient moving up through the capillary fringe towards ground surface, so vapor concentrations in vapor samples collected above the capillary fringe are expected to be less than those predicted to be in equilibrium at the water table. The comparison of measured soil gas concentrations to the calculated expected concentrations is intended as a relative measure of the confidence in the data set and an indicator of the applicability of the conceptual migration model.

in the immediate vicinity. The groundwater sample can be used to calculate an expected soil gas concentration and this estimated value can be compared to the measured concentration as a check on the data that were collected. See Appendix E for additional discussion and a calculation worksheet. Groundwater elevation measurements also can be used to evaluate the potential for submerged sources to be present that would affect soil gas profiles based on changes in groundwater elevation.

- The collection of samples from more than one sampling event generally increases confidence in the data set, as this helps assess the temporal changes expected due to a fluctuating water table and other seasonal variations.

In addition, the following supplemental data, which may have already been generated during the site investigations, are beneficial in developing a better understanding of vapor migration at a given site:

- A photo log of a soil core accompanied by laboratory analysis of the following basic physical properties, as identified by Ririe et al. (2002), for each significant soil layer of the vadose zone:
 - Soil moisture
 - Bulk density
 - Air-filled porosity
 - Water-filled porosity
 - Total organic carbon
 - Hydraulic conductivity
 - Air permeability.
- Recent precipitation record for the area (easily obtained from weather-monitoring data)
- Surface cover (based on visual inspection)
- Groundwater elevation history (from groundwater elevation measurements at the site or from nearby sites).

These and other data needs are included in Appendix C.

Scope-of-Work Action Items:

- Develop the conceptual migration model to determine the applicable subsurface-vapor-to-indoor-air exposure pathways considering the following important site characteristics:
 - Source characteristics
 - Depth to groundwater
 - Distance from source to exposure location
 - Current building or future building
 - Locations of utilities and process piping
 - Soil types
 - Stratified vadose zone or homogeneous vadose zone.
- Define questions to be answered by the soil gas sampling
- Determine if there are any regulatory requirements for the sampling locations or frequencies
- Determine the applicable target levels and whether ambient air sampling will be conducted
- Develop the sampling plan:
 - Consider using the cross-sections in Appendix B or other visual representations to plan sampling locations and depths
 - Determine if a phased approach to sampling is appropriate
 - Select sampling locations, depths, and frequencies.

5.0 Soil Gas Sample Collection

Topic:

Collection methods for soil gas samples are described in this section.

Purpose:

To discuss common challenges associated with soil gas sampling and to present possible alternatives.

Significance:

Each soil-gas-monitoring method has advantages and limitations. Method selection should consider site-specific conditions, including the lithology of the vadose zone, the site configuration, the depth to the vapor source, and the projected sampling frequency.

This section provides an overview of the basic soil-gas-sample collection methods and the equipment used to collect those samples. More information is provided in Appendix C, including additional references and resources.

It will not be possible to use soil-gas-monitoring installations at all sites. For instance, with very fine-grained soils and high moisture contents, it may be difficult to collect representative soil gas samples in a reasonable time period using typical equipment and reasonable vacuum levels. The use of permanent probes for shallow vapor sources (< 3 feet below ground surface) also may be undesirable given the difficulties associated with collecting representative soil gas samples at those depths (e.g., increased potential of surface air leakage). In addition, site access restrictions and physical constraints may limit the locations available for installation and maintenance of any kind of soil gas probe, including temporary driven probes. Consider the practicality of each soil-gas-sampling method at a given site prior to proceeding through the tasks discussed in this section.

5.1 Basic Monitoring Installation Options

Soil-gas-monitoring installation options include:

- Permanent probes
- Temporary driven probes.

The monitoring installations are described in the following sections. The descriptions included in these sections are representative of typical installations; however, variations on these configurations are equally valid. Some regulatory agencies have developed guidance that specifies soil-gas-monitoring installation requirements. As for any monitoring installations, proper field procedures should be followed during drilling (e.g., decontamination of equipment and tools, health and safety measures, inspection of materials prior to use).

For further reading on sample collection methods, see ASTM 1992; CRWQCB 2003; CSDDEH 2003; DeVitt et al. 1987; Eklund 1985; Eklund 1992; Hartman 2002, 2003, 2004a; USEPA 1996.

5.1.1 *Permanent Probes*

Permanent probes, installed individually or as a nested group, are typically constructed in similar fashion to groundwater monitoring wells using augered soil borings or direct push techniques. For augered soil borings, a soil boring is augered to the depth of the lowest identified monitoring interval, and a sampling probe is set in sand-pack material (usually about a 1-foot interval) at the bottom of the boring. The sampling probe generally consists of small-diameter (e.g., < 1/4 inch inside diameter) tubing (e.g., copper, stainless steel, nylon) running from ground surface to the sampling depth. The end of this tubing may be covered with fine screen, or it may be connected to a short (e.g., 6- to 12-inch) perforated section of a 1-inch- or smaller-diameter pipe, or to a small-diameter metal mesh tube. The small-diameter tubing may be attached to a more rigid support, such as a 1-inch PVC pipe that extends from ground surface to the bottom of the borehole (CRWQCB 2003; Lahvis 2002; Hartman 2002, Hartman 2004a).

When three or more soil gas probes are set in one boring, the probes are generally placed at an interval just above the vapor source, at one or more intermediate depths, and at a shallow depth. The boring is sealed with bentonite above the sand-pack interval to the depth of the next deepest sampling interval, where another probe is set in sand-pack material. The boring is again sealed above the sand-pack interval with bentonite to the next sampling interval or the ground surface in the case of the shallowest probe. Typically, the surface seal (the seal above the last sampling interval) will be approximately 3 feet in thickness.

With direct-push techniques, a single sampling probe is installed by pushing it to the desired depth. These driven probes can be made of rigid tubing with disposable drive points; and in some cases, the rods are driven down and also left in place. Alternatively, probes can be installed via hollow, removable drive rods. In this case, the rods are driven down, the probe assembly is lowered into the drive rod, and the drive rod is removed while the probe assembly is held in place. Often, the installers rely on natural collapse of the formation around the probes, but on some occasions, a sand pack and a seal are installed through the drive rod as it is removed. The probe assemblies are

Sampling Probe Seals

It is important that any soil-gas-sampling probe be sealed to minimize the exchange of atmospheric air with the soil gas and to maximize the potential that the sample being retrieved is actually soil gas from the sampling depth. Leak testing is a challenge for soil-gas-sampling probes because air is being sampled; the leaks cannot be detected visually. In general, one relies on the results of the sampling volumes, pressures, and laboratory analytical results to determine if the soil-gas-sampling probes were sufficiently airtight. It is important to follow the field procedures (e.g., for permanent probes, seal above each sampling interval) and to install the soil-gas-sampling probes with care. It also is important to ensure that the sampling tubing is sealed at ground surface between sampling events (e.g., with stopcocks or other valves), as barometric pressure fluctuations will induce cyclical inhalation of ambient air and exhalation of soil gas, both of which can compromise the representativeness of the soil gas sample.

generally small-diameter, (e.g., 1/8- to 1/2-inch) 6-inch-long stainless steel mesh tubes connected to the ground surface by a length of small-diameter (e.g., 1/8- to 1/4-inch) flexible tubing. The sampling interval for the probes is generally short (e.g., 6 to 12 inches) (CRWQCB 2003; Hartman 2002; Lahvis 2002, BP 1998).

5.1.2 Temporary Driven Probes

Hollow metal rods (e.g., stainless steel) equipped with disposable or retrievable drive points may be driven into the soil by hand or with the aid of direct-push equipped vehicles. The probes are driven to the desired depth. Then, depending on the design, they are either sampled at that depth or pulled up a few inches to expose a sampling tip. Sampling is conducted through tubing connected directly to the exposed sampling tip or by extracting vapors through the drive rods (CRWQCB 2003; Hartman 2002). After sampling, the rods are removed, or the device is pushed deeper to the next sample depth. In some circumstances (e.g., finer-grained soils, deeper drilling depths), it can be difficult to remove the drive rods.

5.2 Comparison of Monitoring Installations

As discussed in the previous sections, the different sampling methods are applicable to different field conditions. The utility of each of the sampling methods is summarized here.

- *Permanent installations*
 - Permanent probes can be sampled over time to develop a temporal record of the concentrations of chemicals of concern in soil gas at a consistent set of locations and depths.
 - *Augered permanent soil-gas-sampling probes*
 - An advantage of the augered boring installation of vertically-nested probes is a smaller footprint of the soil-gas-monitoring installation.
 - Augered permanent probes provide the opportunity to carefully seal each sampling interval and install a sand pack around each sampling interval to ensure that adequate vapor volumes can be collected.
 - Augered probes can be installed in the vadose zone for most soil lithologies.
 - When groundwater occurs at a shallow depth (e.g., within a few feet of a foundation), it may not be possible to install vertically-nested probes.
 - *Direct push permanent probes*
 - Installation time for direct-push permanent probes may be shorter than for augered installations. In addition, the disruption to the subsurface will be minimized and the potential for generating soils that must be disposed of will be minimized.

- Time for the soil gas to re-equilibrate after the drilling operation may be shorter for a direct-push installation than for an augered installation.
 - Driven probes may not be useful in all formations. For example, the presence of cobbles may hinder or preclude the use of direct-push technologies, direct-push installations may not offer any significant advantages over auger installations for deeper sampling depths (> 100 feet), and direct-push samplers sometimes have difficulty collecting soil gas samples in finer-grained soils (relative to augered installations with a more permeable sand pack of significant volume). There is also a potential for the driven probes to close off pore spaces along the borehole walls during installation in finer-grained soils, which can affect the representativeness of the soil gas samples.
 - Permanent installation provides the opportunity to carefully seal each sampling probe to minimize the introduction of atmospheric air. From a practical perspective, it is more difficult to install sand packs and seals through the inside of direct-push rods than to install sand pack in the larger diameter temporary casings of augered probes.
- *Temporary installations*
 - Temporary driven probes can be installed, sampled, and then removed with minimal surface disruption. Their use may be advantageous in situations where access restrictions preclude the installation of permanent probes and when samples will not be collected over time.
 - The use of temporary driven probes is often advantageous in situations where the groundwater or vapor source zone is relatively shallow (e.g., less than 6 feet below ground surface).
 - The use of temporary driven probes is beneficial when an on-site laboratory is used so that field decisions can be made to adjust or expand the sampling program (Hartman 2002).
 - Temporary driven probes also are useful for collecting data to identify suitable locations for permanent probes and in situations where concentrations of chemicals of concern in soil gas are not expected above target levels so that multiple sampling events are not needed.
 - Where temporary driven probes are used, additional mobilization and direct-push events are needed to develop temporal trends in the concentrations of chemicals of concern in soil gas. Soil gas samples collected within a few feet laterally of each other should produce similar results, so it is possible to develop a historic record using a sequence of temporary direct-push sampling events.
 - Temporary driven probes allow vertically-nested probes to be installed to provide a profile of the concentrations of chemicals of concern in soil gas in the subsurface.

However, the use of temporary driven probes to evaluate vertical profiles over time may be impractical because of additional mobilizations and the need for additional temporary driven probes to be installed in close proximity to previous temporary driven probes.

- The potential for cross-contamination of sampling depths should be considered when using the same push rod for multiple samples.

5.3 Other Considerations for Sampling Probe Installations

As noted at the beginning of this section, it is recommended that the practicality of soil gas sampling be assessed for any site before embarking on a soil-gas-sampling plan. However, it is even more of a concern at sites with finer-grained, very moist soils. At these sites, it is advisable to install one or two sample probes and evaluate the integrity of the soil gas samples from those first installations (i.e., using the data evaluation methods recommended in Section 7.0) prior to implementing an extensive sampling program. See Appendix C for suggestions for testing to determine if soil gas sampling is practicable.

5.4 Sample Collection Procedures

Procedures for collecting soil gas samples are discussed below. Some regulatory agencies have guidance for sample gas collection, and users should familiarize themselves with guidance specific to their site before designing a soil-gas-sample collection plan.

For further reading about soil gas collection methods, see ASTM 1992; CRWQCB 2003; CSDDEH 2003; Devitt et al. 1987; Hartman 2002, 2004a; USEPA 1996, 2001.

5.4.1 Soil Gas Equilibration

The subsurface soil gas profile should be allowed to re-equilibrate after any disturbance caused by installing the soil-gas-monitoring probes (or the operation of remediation systems). Based on experience, the following rules of thumb should be considered:

- Direct-push probes appear to have minimal disturbance on soil gas profiles, and samples can be collected immediately after reaching the driven depth
- The disturbance caused by the installation of permanent probes by drilling methods varies with the drilling method. (See Appendix C for more information about equilibration time for different drilling methods).
- If the sampling plan calls for multiple sampling events over several months, the data may be used to establish if the soil gas profile has equilibrated. Hartman (2004) suggests if the sampling plan only calls for one set of soil gas samples, several samples can be collected over a few days or weeks to determine the stabilized concentrations.

5.4.2 Sample Probe Purging

Following equilibration, the sampling equipment should be connected to the sampling probe. The sampling equipment should be checked for leaks prior to purging of the sampling probe. The sampling probe and equipment is purged to collect representative samples of soil gas at the sample interval. Based on experience, the purging and sampling should be conducted to minimize the purged volume (see Section 5.5 and Appendix C).

5.4.3 Sample Collection

Once the sampling probe has been purged, the soil gas sample and any replicates can be collected. Typically, soil gas is collected using small-diameter tubing and gas-tight valves and fittings. The sample may be drawn out of the ground by generating a vacuum using a pump, a syringe, or a sampling vessel that is under vacuum. The specific sample collection containers (e.g., SUMMA canisters, synthetic bags) are determined based on the analytical laboratory, or field analysis, requirements and the detection limits needed for the evaluation (see Section 6.0).

5.4.4 Sample Collection Vacuum

Some regulatory agencies specify upper limits on the vacuum that can be applied during sample collection, with the thought that higher vacuums will affect the concentrations or relative proportions of chemicals of concern in the sample. In other words, some scientists feel that increasing the vacuum enhances the volatilization of more volatile compounds from a mixture of chemicals of concern on soil, in residual LNAPL, or in groundwater. In addition, as the vacuum levels are increased, the chance for leakage in the soil-gas-sampling probes and aboveground equipment is increased. Because of these potential issues associated with increased vacuums on a soil gas sample, the following should be considered when evaluating the sample collection vacuum:

- Based on thermodynamic considerations, the application of typical vacuums (< 100 inches of water) should have a small effect on the concentration or composition of a soil gas sample. In theory, the application of a vacuum should not change the relative concentrations of chemicals of concern in a soil gas sample. Increasing vacuums, however, will increase the absolute concentrations of all chemicals of concern in the soil gas sample when those concentrations are expressed as a concentration under standard conditions of 1 atmosphere (atm)(as is typical for most laboratories). At most, this increase in concentration would be approximately $(P_{\text{atm}}/[P_{\text{atm}}-P_{\text{gauge}}])$, where P_{gauge} is the gauge vacuum and P_{atm} is 1 atm (=406 inches of water). For example, a 100-inch water vacuum might cause a 33-percent increase in concentrations.
- Based on experience, atmospheric gas short-circuiting and leakage during sampling is more likely when higher vacuums are applied.

5.5 Ways to Avoid Common Problems with Soil Gas Sampling

When planning a soil-gas-sampling program and developing a site-specific scope of work, the following issues should be considered. A list of issues is presented here, and possible solutions are included with each item.

- *Minimize leakage along sampling probes* — Leakage occurs because of improper installation of soil gas probes (e.g., when the tube or rod is not properly sealed in the ground), or because of the type of surface cover.
 - Vapor probes can be tested for surface leakage using a tracer gas (e.g., propane, butane, isopropanol) at the ground surface. The soil gas samples should be analyzed for the tracer. The tracer, however, should be a compound not present in the soil gas (propane and butane may be detectable as part of a gasoline release at a site) and one that can be detected with sufficient sensitivity (CRWQCB 2003; Hartman 2002).
 - Tracking oxygen concentrations at depth where vertically nested probes have been installed can be a means to determine if the sampling probes or equipment are leaking. If the oxygen concentrations do not decrease with depth and hydrocarbon vapor sources are present in that vicinity, then there is a potential for leakage along the sampling probes.
 - Sealing at the surface of shallow soil gas probes should be considered for temporary driven probes and should be installed for permanent probes. Probes can be sealed using bentonite. For temporary driven probes, sealing the surface with bentonite is difficult to work with when trying to maximize sampling efficiency (e.g., extra time to clean equipment, wet bentonite at the ground surface). Sealing might be also accomplished by wetting the ground surface around the probe. (See the sidebar “Sampling Probe Seals” in Section 5.1.1).
 - Based on experience, sampling intervals should be placed no closer to the ground surface than 3 feet. Shallower depths may be appropriate, but greater care is needed to limit short-circuiting and to ensure representative sample collection (e.g., competent surface seals, proper probe construction). Further, Hartman (2002) indicates that large purged volumes can increase the potential for short-circuiting, especially for shallow soil-gas-sampling probes.
 - In general, the probes, tubing, and fittings should be selected to minimize the overall internal volume of the equipment.
 - Careful installation procedures (e.g., proper placement of sand-pack and bentonite seals) should be used in the construction of permanent probes.
 - Avoid lateral movement of probes once they have been installed to minimize any separation between the soils and the outside of the probe.

- When pre-manufactured probe bundles are used for vertically-nested probes, they should be inspected at the surface prior to installation. The probe bundles should be inspected to be sure the connections are tight and there are no visible holes or defects.
- *Minimize the potential for short-circuiting due to utility lines or other conduits* — When the soil-gas-monitoring installation is placed too close to a utility, vapors are not being drawn from the vadose zone but instead are being drawn from within the utility.
 - A thorough understanding of the location of all utilities and process piping should be developed prior to any soil gas sampling. Soil-gas-sampling locations should be placed at a sufficient distance from utility or piping backfill areas to protect the utilities and process piping and to obtain representative samples.
 - Consideration should be given to using passive implant samplers (see Section 5.6) to investigate preferential flow pathways associated with utilities or process piping rather than drilled soil gas probes.
- *Minimize vertical sampling intervals* — Often, soil-gas-sampling probes are installed with sampling intervals that are too long. This increases the uncertainty in the interpretation of the measurements because the concentration is averaged over a larger area. At sites with heterogeneous stratigraphy, sampling intervals that overlap several different soil layers that may have significantly different properties will decrease the value of those data for pathway assessment.
 - Soil-gas-sampling probes with short (e.g., 6-inch) intervals are generally preferred.
 - Soil-gas-sampling probes with sampling intervals that are consistent with the site stratigraphy should be installed.
- *Avoid dilution of samples* — The sampling should minimize the potential for ambient air to be inadvertently pulled into the sample. Once the sampling equipment has been installed at a soil vapor probe, all of the fittings should be checked for leaks prior to collecting the soil gas sample (see Appendix C).
- *Provide consistent methods over time* — It is very important that the field procedures used in soil gas sampling are consistent within each sampling event and across multiple sampling events over time. Often, the results of soil gas sampling compared over time or across a site for the same sampling event do not correspond with other site information. Based on experience, this is often because of variations in field procedures.
 - All field procedures should be documented each time a sampling event is conducted (e.g., purged volumes, sampling equipment used, number of field blanks, duplicates).
 - The purged volume selected for a sampling event should be consistent and recorded for all of the sample locations across the site (Lahvis 2002, CSDDEH 2003).

- When planning each sampling event, the records from prior events should be thoroughly reviewed and consistent procedures followed.
- Sampling should be completed as quickly as is practical to produce an internally consistent data set (Lahvis 2002). For typical sites, all of the soil gas samples can be collected over the course of a day to a week.
- Consider collecting groundwater samples at the same time and in similar locations as soil gas samples.
- *Ensure adequate site characterization* — The proper placement of soil-gas-sampling probes and the associated sampling intervals is dependent on good site characterization.
 - Site characteristics discussed in Section 3.0 and Appendix A should be reviewed for the site. If there are deficiencies in the data, collection of additional information or site data should be considered prior to implementing the soil-gas-sampling program.

5.6 Alternatives to Soil Gas Sampling

As discussed previously, it will not be practicable at all sites to collect soil gas samples using the monitoring installations described in this section. Alternative sampling methods may be useful at some of these sites to assist in the evaluation of the subsurface-vapor-to-indoor-air exposure pathway. Two such methods, passive implant samplers and flux chambers, are briefly described here.

5.6.1 *Passive Implant Samplers*

Typically, passive implant samplers are an adsorbent material in a container that is placed in a small-diameter boring in the vadose zone soils. The passive implant samplers are commonly installed at shallow depths (e.g., less than 3 feet). The container permits the flow of soil gas, and the adsorbent collects the vapor-phase chemicals of concern. The samplers are placed in the ground for a period of time (e.g., 1 or 2 weeks) and then they are retrieved. The analysis of the adsorbent material estimates a total mass of chemicals that has been collected. It is difficult to accurately estimate the volume of soil gas that has contacted the sampler, and therefore, the mass cannot be converted easily to a vapor-phase concentration (CSDDEH 2003, Hartman 2002).

In general, the application of passive samplers is to determine the existence of vapor-phase chemicals of concern (e.g., locating sources, identifying preferential pathways) in the vadose zone and not to quantify the concentrations of vapor-phase chemicals of concern for exposure pathway assessment. Basic considerations for the use of passive implant samplers include the following:

- Passive implant samplers are not typically used to develop vertical profiles
- Passive implant samplers provide an alternative in very fine-grained soils where the practicality and integrity of samples from soil gas probes may be in question (CSDDEH 2003)

- Passive implant samplers would give an indication of whether the subsurface-vapor-to-indoor-air exposure pathway is incomplete if the masses detected in samplers located at various distances away from a vapor source were decreasing at an acceptable rate
- Passive implant samplers may be useful for identifying preferential pathways associated with utility conduits.

5.6.2 Flux Chambers

Flux chambers are containers that are typically dome- or rectangular-shaped and are placed on the ground surface or over a suspected foundation intrusion area. A sweep gas flow is induced across the flux chamber, and the effluent passes through a sorbent trap or into a large sample collection container (e.g., synthetic bag, SUMMA canister). Some flux chamber measurements are conducted without a sweep gas flow. This is a static test. The flux chamber is left in place to collect effluent vapors on a sorbent trap or in a large-volume sample container, or to allow build-up of vapor concentrations in a static flux chamber. The time for a flux chamber test depends on a number of factors, including whether a sweep gas flow is used, the expected vapor concentrations, and the type of sample containers used. At the end of the test, or at multiple times during the test, the concentration is determined. Using the time period for each measurement, the footprint area of the flux chamber, and the concentration and volume of the effluent vapors, the mass flux emission from the subsurface can be calculated (CSDDEH 2003; Eklund 1992; Hartman 2002, 2003).

Care should be taken when extrapolating the results from a small footprint flux chamber to the footprint of a residence or commercial building. Use of flux chambers requires knowledge of the soil-gas entry points for a given building, and these are often difficult to identify even when conducting a thorough survey of the potential localized vapor intrusion points. Entry point concerns are less important if the flux chamber is used in a crawl space of a building.

Scope-of-Work Action Items:

- Determine if soil gas sampling is practicable
- Determine if there are regulatory requirements for the sample collection
- Locate utilities and process piping
- Use the conceptual vapor migration model to determine whether:
 - Point samples or vertical profiles are to be collected
 - Temporary or permanent probes are to be installed.
- Define detailed field procedures and a method to document actual field procedures
- Consider what additional field procedures might be needed based on observations during installations and sampling (e.g., installation of additional probes).

6.0 Analytical Methods

Topic:

Analytical methods typically used in soil-gas-sampling programs at petroleum hydrocarbon sites and the data quality considerations that arise are examined in this section.

Purpose:

To determine the appropriate methods for analyzing soil gas samples from a specific petroleum hydrocarbon site.

Significance:

Different analytical methods can be used to quantify concentrations of vapor-phase petroleum hydrocarbons in soil gas samples, and the particular methods selected will need to be consistent with the data quality objectives for that site.

The analytical methods appropriate for analyzing soil gas samples will depend on the sampling methods and the data quality objectives for the site. More than one different level of analytical precision may be required; for example, the analysis of specific chemicals of concern may require a more stringent level of quantification than the analysis of fixed and respiration gases (e.g., N₂, O₂, CO₂, CH₄). It is important, however, that the analytical methods used are consistent within each sampling event. In addition, the stringent analytical requirements for specific chemicals of concern may preclude the use of many field-monitoring devices commonly used to evaluate soil gas (e.g., hand-held photo-ionization detector [PID], flame-ionization detector [FID], and explosimeter) as these do not provide the necessary accuracy or specificity.

6.1 Analytical Method Selection

Analytical methods are generally defined by the USEPA under the air toxic program (USEPA 1999), solid waste program (USEPA 1998b), or other promulgated methods (USEPA 1996a, 2002a). A number of different analytical methods can be applied to quantify concentrations of chemicals of concern in soil gas samples. However, the particular method selected will depend on the use of the data and any regulatory requirements. Therefore, prior to selecting a method for analyzing soil gas samples, the following questions should be answered:

- *What are the specific chemicals of concern or other analytes (e.g., natural attenuation parameters) that need to be identified by the analysis?* The specific analytes (e.g., benzene, naphthalene) for the subsurface-vapor-to-indoor-air exposure pathway should be identified. Generally, these will be the volatile and semi-volatile chemicals of concern identified during the overall investigation at a site. Many regulatory agencies have identified specific chemicals of concern that should be included in the analyte list. However, if specific chemicals of concern are not identified, an analytical method should be selected based on its ability to detect the range of analytes (e.g., volatile organic compounds [VOC], semi-volatile organic compounds [SVOC]) that may be present at a site.

Even though risk-based pathway assessment is based on concentrations of chemicals of concern, it is important also to measure the total petroleum hydrocarbon concentration in soil gas samples at petroleum hydrocarbon impacted sites. This is necessary to understand adequately the subsurface processes, especially as they relate to biodegradation. For example, the attenuation by biodegradation of any single chemical is influenced by the presence of all hydrocarbons in the soil gas, as they determine the total oxygen demand and oxygen-penetration depth. The total petroleum hydrocarbon measurement should be of the full range of detectable hydrocarbons, not of a specific product range of carbon numbers (e.g., as in a soil or water analysis that quantifies “gasoline range organics”).

- *What analytical method reporting limits are required to evaluate adequately the potential exposures?* It is important to determine the smallest concentrations of chemicals of concern in soil gas or other analytes that are expected to be required for purposes of evaluating the subsurface-vapor-to-indoor-air exposure pathway. For evaluation of this exposure pathway, indoor air target levels for chemicals of concern or other analytes should be identified. These indoor air target levels can be used to identify the necessary detection limits for the soil gas analyses. Generally, the detection limits for concentrations of chemicals of concern in soil gas should be no more than 100 times the target indoor air concentration so that non-detect concentrations can be conclusively evaluated. Appendix D includes additional information on reporting limits and a worksheet for defining detection limits.
- *Do soil or groundwater analytical results, or other field data, indicate that concentrations of chemicals of concern in soil gas will be high?* If concentrations of chemicals of concern or other analytes in soil gas are anticipated to be high, then the analytical method selected should be designed to address high concentrations. In cases where high concentrations are anticipated, solid waste program methods (USEPA 1998b) may be appropriate. There is some concern that the solid waste program methods may be biased low for some chemicals of concern. Hartman (2004a) indicates that for benzene, toluene, ethylbenzene, xylenes and chlorinated hydrocarbons the solid waste program methods and air toxics methods produce similar results.
- *How are the samples to be collected?* The analytical method selected, in many cases, will define the collection method (e.g., SUMMA canister) that should be used and typically the sample preparation that is required to analyze a sample.
- *Do the regulatory agencies require certification of the laboratory or that specific analytical methods be used?* Many state regulatory agencies require that samples be analyzed by specific methods. They may also require the laboratory that is conducting the analysis to be certified under a state program. In some cases, this may limit the use of field analytical methods.
- *Are there short turnaround times required for analytical results?* Turnaround times will be influenced by shipping requirements, holding times, laboratory backlog, and analytical method. Depending on the priorities of the subsurface-vapor-to-indoor-air exposure

pathway evaluation, field analysis may be preferable to shipment to a laboratory. Field analysis can provide nearly real-time results.

- *Are the analytical methods appropriate for the soil gas samples?* The analytical methods often are updated with newer techniques. It is suggested that the user consult with the regulatory agency and a qualified analytical laboratory to identify analytical methods appropriate for the specific site. Appendix D provides a summary of typical analytical methods appropriate for soil gas samples.

6.1.1 Field Analytical Methods

Portable gas chromatographs (GC) can achieve sensitivities and specificity similar to a fixed laboratory GC. In addition, recent developments in portable mass spectrometers (MS) now permit GC/MS analysis in the field. However, for a field GC to provide equivalent results to a fixed laboratory, it should follow the same analytical procedures (e.g., sample pre-concentration on a sorbent trap followed by desorption to concentrate very dilute samples) and implement comparable quality-control measures to the fixed laboratory.

Respiration gas analyses (e.g., oxygen, carbon dioxide) also can be conducted in the field using instruments specific for those analyses.

6.1.2 Common Analytical Methods

Table 6-1 identifies common analytical methods used for soil gas samples at petroleum hydrocarbon sites. A more detailed list of analytical methods is provided in Appendix D.

Table 6-1. Common Analytical Methods

| Analyte | Field Method | Fixed Laboratory Method |
|---|---|---------------------------|
| Benzene, Toluene, Ethylbenzene, Xylenes, MTBE | GC by Method 8260 | GC by Method TO15 or 8260 |
| Total Petroleum Hydrocarbons | GC by Method 8015 | GC by Method 8015 |
| Oxygen | Field meter w/ electrochemical cell (BP 1998) | GC/TCD by Method 3C |
| Carbon Dioxide | Field meter w/ infrared analyzer (BP 1998) | GC/TCD by Method 3C |
| Methane | Field meter (CRWQCB 2003) | GC/TCD by Method 3C |
| Nitrogen | Field meter | GC/TCD by Method 3C |

6.2 Data Quality

The accuracy of an analytical method is dependent on the handling and preparation of the sample and the maintenance of the analytical equipment. Most analytical methods prescribe minimum quality-control measures that are designed to monitor the performance of the analytical procedures. However, additional quality-control measures can be implemented by the laboratory or the analyst. At a minimum, the quality-control measures should include calibration of the instruments and an assessment of the analytical accuracy and precision (USEPA 2001). Details of

the analytical method quality-control measures are included in the documentation for the selected analytical method (USEPA 1998b, 1999, 2002).

Scope-of-Work Action Items:

- Determine target analyte list, including any desired tracer compounds
- Determine required detection limits
- Consult analytical laboratory to determine suitable analytical methods, required sample containers, constraints on holding times, and necessary shipping procedures
- Define numbers of samples, replicates, blanks, and any standards that are needed for the field program.

7.0 Analysis and Interpretation of Soil Gas Sampling Data

Topic:

In this section, guidance is provided on analyzing soil-gas-sampling data for the evaluation of the subsurface-vapor-to-indoor-air exposure pathway.

Purpose:

To evaluate the completeness of the exposure pathway and to provide guidance for presenting data and for assessing data quality and consistency.

Significance:

If the exposure pathway is potentially complete and likely to be important, then further evaluation (e.g., vapor-migration transport models) or other actions should be considered.

This section addresses the use of soil gas data for assessing the significance of the subsurface-vapor-to-indoor-air exposure pathway. It is assumed that the sampling locations, sampling methods, and chemical analyses are consistent with the recommendations given in previous sections of this document. It is important to note that the discussion below is specific to the assessment of petroleum hydrocarbon impacted sites.

A suggested step-by-step process for evaluating the subsurface-vapor-to-indoor-air exposure pathway is described below and graphically presented in Figure 7-1. In this step-by-step process, the data are organized and analyzed for quality and consistency. If the data quality and consistency are sufficient to assess the subsurface-vapor-to-indoor-air exposure pathway, compare the data set to indoor air target levels for the chemicals of concern established for the site to determine if the exposure pathway is potentially complete. If the exposure pathway is determined to be potentially complete, then an attenuation factor is applied to the indoor air target levels to determine subsurface soil gas target levels. The data set is then compared to the subsurface soil gas target levels to determine if the exposure pathway is likely to be of significance. If the exposure pathway is potentially complete and likely to be of significance, then further evaluation (e.g., vapor-migration transport models) or other actions should be considered.

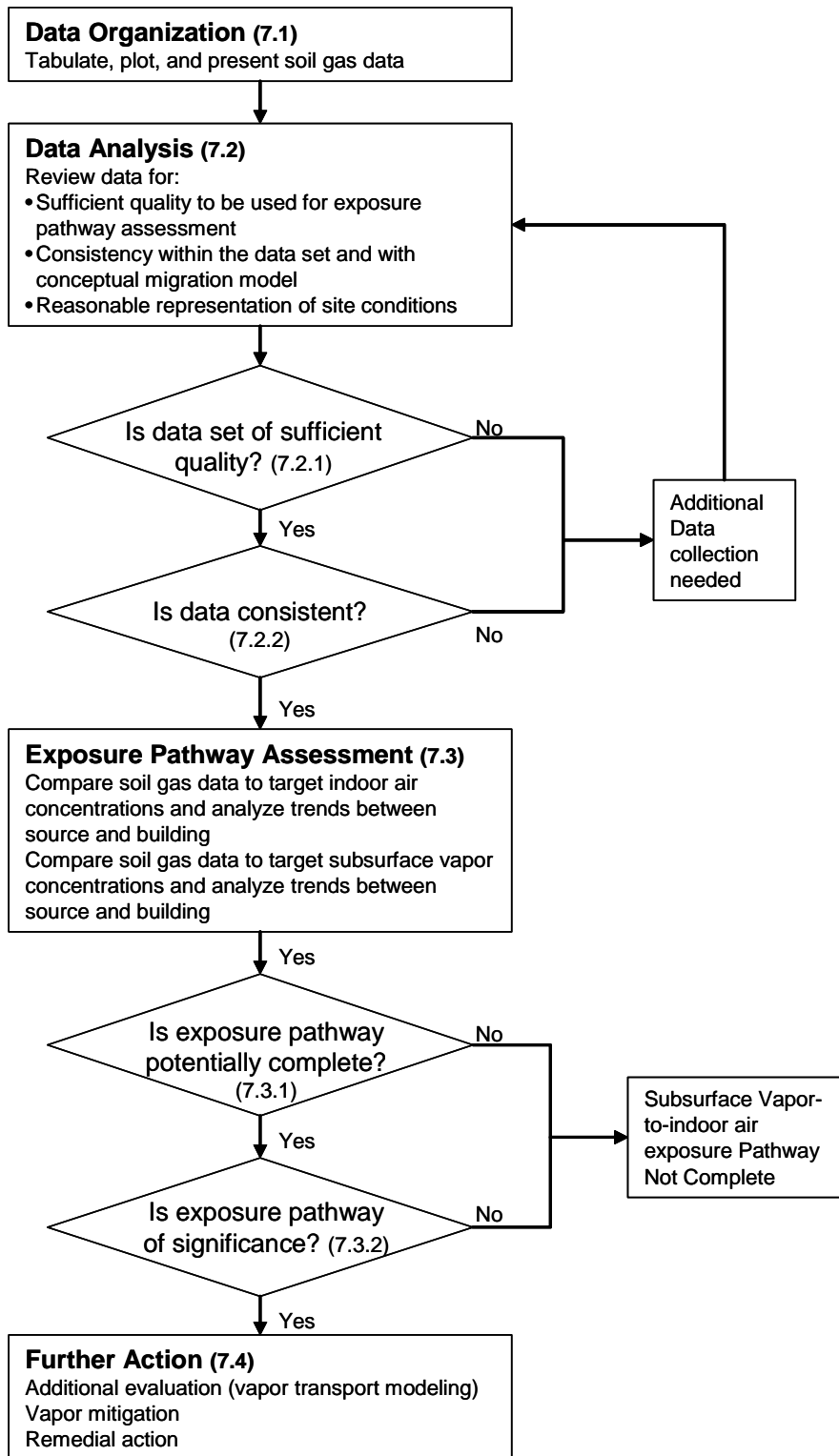


Figure 7-1. Flowchart for data evaluation.

7.1 Data Organization

Tabulate, plot, and present soil gas data in a manner that facilitates review and quick determination of spatial and temporal trends, relationships between the various data points, and data consistency. The following data organization and presentation formats are suggested:

- A table of all data listing sample location identifier, sample depth, sample date, sampling methods, chemical analysis methods, laboratory detection limits, and results of chemical analyses
- Plan view maps displaying the spatial locations of sampling probes, physical structures, utilities and process piping, and any information related to the extent and magnitude of chemicals of concern in other media (e.g., groundwater, soil, indoor air)
- Cross-section figures showing the vertical position of sample locations, geologic descriptions of the subsurface, and any information related to the extent and magnitude of chemicals of concern in other media (e.g., groundwater, soil, indoor air)
- For each vertical sampling location, plots showing concentrations of analytes in soil gas (e.g., oxygen, total petroleum hydrocarbons, methane, individual chemicals of concern, carbon dioxide) as a function of depth (e.g., see Figure 2-3).
- For sources displaced laterally from the building or location of a future building, two-dimensional plots showing concentrations of analytes in soil gas (e.g., oxygen, total petroleum hydrocarbons, methane, individual chemicals of concern, carbon dioxide) as a function of depth and distance
- Identify indoor-air target levels, soil-gas target levels, ambient outdoor-air concentrations, and background indoor-air concentrations of chemicals of concern
 - Soil-gas target levels may be determined by dividing the indoor air target levels by an accepted conservative vapor attenuation factor (e.g., 0.01 and 0.001 are vapor attenuation, or “alpha,” factors appearing in USEPA [2002a]). In some cases, regulatory agencies may have defined soil gas target levels. There also may be more than one soil gas target level; for example, one that applies near the building and one that applies near the source.
 - Concentrations of chemicals of concern in ambient outdoor air may be measured at the site, or may be from ranges of reference values (MaDEP 2002; Wallace 1989; Won and Corsi 1998).
 - Typical background concentrations of specific chemicals of concern in indoor air from sites not affected by subsurface petroleum hydrocarbons releases can be identified from the literature or the regulatory agency (MaDEP 2002; PaDEP 2002; Wallace 1989; Won and Corsi 1998; USEPA 1998a).

7.2 Data Analysis

Review the soil gas data to ensure that the quality and consistency of the data are sufficient to assess the significance of the subsurface-vapor-to-indoor-air exposure pathway. This review should first address the quality of the data for use in the exposure pathway assessment and then the consistency of the data within the data set and with the conceptual migration model. The following questions should be answered during the data analysis:

- Is the data set of sufficient quality to be used for exposure pathway assessment?
- Is the data set reasonably self-consistent?
- Is the data set consistent with the conceptual migration model?
- Is the data set reasonably representative of site conditions?

The users should answer the questions listed above and decide if they have sufficient confidence in the data and the conceptual migration model to proceed with the next step. The quality and consistency analyses are discussed in more detail in the following two sections.

7.2.1 Data Quality Analysis

The data quality analysis addresses the question of whether the data are sufficient to be used for exposure pathway assessment. Data should be reviewed for consistency with published or demonstrated limits of the analysis methods by conducting the following activities:

- Compare analytical results to detection limits to identify the measured concentrations of chemicals of concern. Note any qualifiers that the laboratory has placed on any of the concentration values.
- Compare analytical results to quantitation limits to understand the confidence in the concentration values. If the quantitation limit is close to the concentration of interest (e.g., concentration < 5 times the quantitation limit), then there may be more uncertainty in the results.
- Compare replicate results to assess variability in the sampling methods and laboratory analytical procedures
- Review laboratory analytical detection limits to verify consistency with the detection limits selected for the site (See Section 6.1)
- Evaluate uncertainty in analytical results by comparing duplicate and replicate samples and by identifying the frequency of anomalous data (e.g., 20-percent oxygen concentrations at the vapor source, or vapor profiles that do not exhibit the expected concentration trends discussed in Section 2.0)
- Review analytical results for the blank samples (e.g., field blanks, laboratory blanks, and trip blanks) to determine if there are any issues with the laboratory or field procedures that may have affected the results.

7.2.2 Data Consistency Analysis

The data consistency analysis addresses the question of consistency within the data set and with the conceptual migration model. In addition, the data consistency analysis addresses the question of whether the data set is reasonably representative of site conditions. The entire data set should be reviewed for internal consistency and for consistency with the site conceptual model. For example:

- The spatial distribution of concentrations of chemicals of concern in soil gas should be qualitatively and semi-quantitatively consistent with the spatial distribution of groundwater concentration and soil concentration data. For example, the highest concentrations of chemicals of concern in soil gas should be observed in areas with the highest concentrations of chemicals of concern in soil and groundwater. Within a set of samples across a site, higher concentrations of chemicals of concern and lower oxygen concentrations might be observed beneath buildings relative to unpaved areas of the site. Concentrations of chemicals of concern in soil gas should be consistent with the expected concentrations of chemicals of concern in soil gas given the vapor source (See Section 4.7 and Appendix E).
- The vertical distribution of concentrations of chemicals of concern in soil gas should be qualitatively and quantitatively consistent with the conceptual migration model for the site (see Section 3.0) and should be consistent with published soil gas profiles from petroleum hydrocarbon impacted sites (e.g., Figure 2-3). For example, oxygen concentrations should not increase with depth, and concentrations of chemicals of concern in soil gas should decrease with distance away from the source areas.
- Vertical gradients of oxygen, methane, carbon dioxide, and chemicals of concern should be semi-quantitatively consistent with each other (i.e., oxygen, carbon dioxide, methane, and hydrocarbon gradients should be self-consistent according to known aerobic biodegradation stoichiometry). Table 7-1 illustrates some examples for the comparison of oxygen (O₂) and total hydrocarbon fluxes. In the table, the mass flux values are based on the molecular weights of the molecules and the stoichiometry of the reaction equation (e.g., 5 oxygen molecules: $5 \times 2 \times 16 = 160$). Fluxes are calculated as the change in soil gas concentration (expressed in mass per volume units) divided by the change in distance, multiplied by the estimated effective diffusion coefficient. See Appendix E for information about concentration unit conversions.

Table 7-1. Example Comparisons of Biodegradation Stoichiometry and Fluxes

| <i>Aerobic Biodegradation Reaction</i> | <i>Expected Hydrocarbon to O₂ Ratio of Mass Fluxes When this is the Dominant Aerobic Reaction</i> |
|---|---|
| $C_4H_{10} + 5O_2 \rightarrow 4CO_2 + 2H_2O$ | 58:160 |
| $C_6H_6 + 15/2O_2 \rightarrow 6CO_2 + 3H_2O$ | 78:240 |
| $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ | 16:64 |

- Temporal trends should be evaluated. For example, if the vapor pathway assessment is predicated on near-steady vapor concentrations, multiple lines of evidence (e.g., temporal trends in soil gas data and estimates of the time-to-near-steady conditions—Section 2.1) should support the conceptualization. If there are significant temporal variations with time, one should assess if these are consistent with temporal trends in the factors that might influence vapor concentration profiles (e.g., changes in vapor concentrations with rising or lowering groundwater levels, changes in precipitation).

When data inconsistencies are identified, the sampling plans and protocols should be reviewed to identify any inherent biases or reasons for the data inconsistencies. A decision should then be made concerning the necessity of collecting additional data, or revising the sampling protocols or conceptual migration model. These issues should be resolved prior to further evaluation of the subsurface-vapor-to-indoor-air exposure pathway.

7.3 Exposure Pathway Assessment

Once the data quality and consistency has been determined as sufficient to assess the subsurface-vapor-to-indoor-air exposure pathway, evaluate the data to determine if the subsurface-vapor-to-indoor-air exposure pathway is complete (or likely to be complete for future-use scenarios). If the exposure pathway is complete or likely to be complete, evaluate the data to determine if the exposure pathway is likely to be significant.

Approaches for determining if the exposure pathway is complete based on soil gas data are discussed in the following sections.

7.3.1 Exposure Pathway Completeness

To determine if the subsurface-vapor-to-indoor-air exposure pathway is complete (or likely to be complete), the soil gas data review should include the following comparisons:

- If the concentrations of chemicals of concern in soil gas everywhere in the subsurface are below the indoor air target levels established for the site, then the exposure pathway is not complete

- If the concentrations of chemicals of concern in soil gas are above the indoor air target levels at one or more sample locations, determine if the concentrations decline (either laterally or vertically) to less than indoor air target levels between the vapor source and the building. If concentrations of chemicals of concern do not decline to less than the indoor air target levels, then the exposure pathway is potentially complete and further evaluation should be conducted to determine if the subsurface-vapor-to-indoor-air exposure pathway is likely to be significant.

In both cases, the determinations are based on existing data and current conditions. Users should decide if future-use scenarios are likely to affect the soil gas profiles. For petroleum hydrocarbon impacted sites, future changes in surface cover are typically of most concern, as increased low-permeability surface cover (e.g., pavement, foundations) could inhibit oxygen supply to the subsurface, which in turn can result in lessening the effect of attenuation due to aerobic biodegradation, and also can lead to methane production when petroleum hydrocarbon impacted soils are present. Migration of chemicals of concern in groundwater could cause changes in concentrations of chemicals of concern in soil gas. Installation of utility conduits through or near petroleum hydrocarbon impacted soils also could affect soil gas profiles and vapor transport locally.

In making the above determinations, the discussion in Section 4.0 concerning confidence in shallow versus deep soil gas samples, as well as the influence of surface cover on soil gas profiles at petroleum hydrocarbon impacted sites, should be considered.

7.3.2 Exposure Pathway Significance

To determine if a potentially complete subsurface-vapor-to-indoor-air exposure pathway is likely to be significant, the soil gas data review should include the following comparisons:

- If the concentrations of chemicals of concern in soil gas everywhere in the subsurface are below soil gas target levels established for the site then the exposure pathway is not likely to be significant.
- If concentrations of chemicals of concern in soil gas are above soil gas target levels at one or more sample locations, determine if concentrations decline (either laterally or vertically) to less than soil gas target levels between the vapor source and the building. If concentrations of chemicals of concern do not decline to less than soil gas target levels between the vapor source and the building, then the pathway is likely to be significant.

In each case, the determinations are based on existing data and current conditions, and the cautions discussed in Section 7.3.1 are applicable.

7.4 Further Evaluation

If concentrations of chemicals of concern in soil gas are above the soil gas target levels and do not decline (either laterally or vertically) to less than the soil gas target levels between the vapor source and the building, then further actions should be implemented. These further actions may include:

- Using the existing soil gas data in conjunction with vapor-migration transport models. Johnson et al. (1999) discuss a number of analytical approaches appropriate for

petroleum hydrocarbon impacted sites. One approach models the subsurface as one or more specific geologic layers specifying different soil properties for each. Another approach uses empirical matching of soil gas data with modifications to the Johnson and Ettinger (1991) algorithm to account for biodegradation. While it will not happen at all sites, it is not unreasonable to expect concentrations of chemicals of concern in soil gas to attenuate by factors of 10,000 to 100,000 between a hydrocarbon vapor source and indoor air.

- Considering the discussion in Section 4.0 concerning confidence in shallow versus deep soil gas samples when validating a vapor transport model with soil gas profiles.
- Conducting additional soil gas sampling to develop a more complete understanding of the profiles of concentrations of chemicals of concern in soil gas and potential for biodegradation of vapor-phase hydrocarbons in the subsurface and any temporal trends.
- Implementing indoor air sampling and analysis, and analysis of indoor background concentrations, to correlate concentrations of chemicals of concern in soil gas with concentrations of chemicals of concern in indoor air and to evaluate the subsurface-vapor-to-indoor-air exposure pathway.
- Comparing concentrations of chemicals of concern in soil gas to ambient outdoor air concentrations to correlate concentrations of chemicals of concern in soil gas with concentrations of chemicals of concern in outdoor air and to evaluate the subsurface-vapor-to-indoor-air exposure pathway.
- Implementing remedial actions to reduce the concentrations of chemicals of concern, along the subsurface-vapor-to-indoor-air exposure pathway, or other analytes in soil gas (e.g., methane) through source reduction or vapor mitigation at the building.

Important Reminders for Interpretation of Soil Gas Data:

- Organize the soil gas data in tables, graphs, and maps so that trends and inconsistencies can be identified.
- Compare the data with the conceptual migration model to determine if the data reasonably represent the site, or if the conceptual migration model should be revised.
- Identify applicable indoor air target levels, soil gas target levels, indoor background concentrations, and ambient air concentrations for comparison to measured data.
- Identify if additional data should be collected.

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Collecting and Interpreting Soil Gas Samples from the Vadose Zone

A Practical Strategy for Assessing the
Subsurface Vapor-to-Indoor Air Migration Pathway
at Petroleum Hydrocarbon Sites

APPENDIXES

Appendix A. Characteristics Checklist

Topic:

The information included in this checklist should be useful for developing the site-specific conceptual migration model and planning the soil gas sampling. The user should consider copying this checklist and compiling the information for each site.

Utilities and Process Piping

- Locate and map out all underground utilities near the soil or groundwater impacts; pay particular attention to utilities that connect impacted areas to occupied buildings.
- Locate and map out all underground process piping near the soil or groundwater impacts.

Buildings

- Locate and map out identified existing and potential future buildings.
- Identify the occupancy and use of the identified buildings (e.g., residential, commercial).
- Describe the construction of the building, including materials (e.g., wood frame, block,), openings (e.g., windows, doors), and height (e.g., one-story, two-story, multiple-story); identify any elevator shafts in the building.
- Describe the foundation construction, including:
 - Type (e.g., basement, crawl space, slab on grade)
 - Floor construction (e.g., concrete, dirt)
 - Depth below grade.
- Describe the HVAC system in the building, including:
 - Furnace/air conditioning type (e.g., forced air, radiant)
 - Furnace/air conditioning location (e.g., basement, crawl space, utility closet, attic, roof)
 - Source of return air (e.g., inside air, outside air, combination)
 - System design considerations relating to indoor air pressure (e.g., positive pressure is often the case for commercial buildings).
- Describe sub-slab ventilation systems or moisture barriers present on existing buildings, or identify building- and fire-code requirements for sub-slab ventilation systems (e.g., for methane) or moisture barriers below foundations for future buildings.

Source Area

- Locate and map out the source area for the vapor-phase petroleum hydrocarbons related to the subsurface-vapor-to-indoor-air exposure pathway.
- Describe the presence, distribution, and composition of any LNAPL at the site.

- Identify the vapor-phase petroleum hydrocarbons that are to be considered for the subsurface-vapor-to-indoor-air exposure pathway.
- Describe the status and results for the delineation of petroleum hydrocarbons in environmental media, specifically soil and groundwater, between the source area and the potentially impacted buildings.
- Describe the environmental media (e.g., soil, groundwater, both) containing petroleum hydrocarbons.
- Describe the depth to source area.
- Describe the potential migration characteristics (e.g., stable, increasing, decreasing) for the groundwater distribution of petroleum hydrocarbons.

Geology/Hydrogeology

- Review all boring logs and soil sampling data to understand the locations of:
 - Sources
 - Finer-grained soil layers
 - Higher-permeability layers that may facilitate vapor migration.
- Describe distinct strata (soil type and moisture content – e.g., “moist,” “wet,” “dry”) and the depth intervals between the vapor source and ground surface.
- Describe the depth to groundwater.
- Describe groundwater characteristics (e.g., seasonal fluctuation, hydraulic gradient).

Site Characteristics

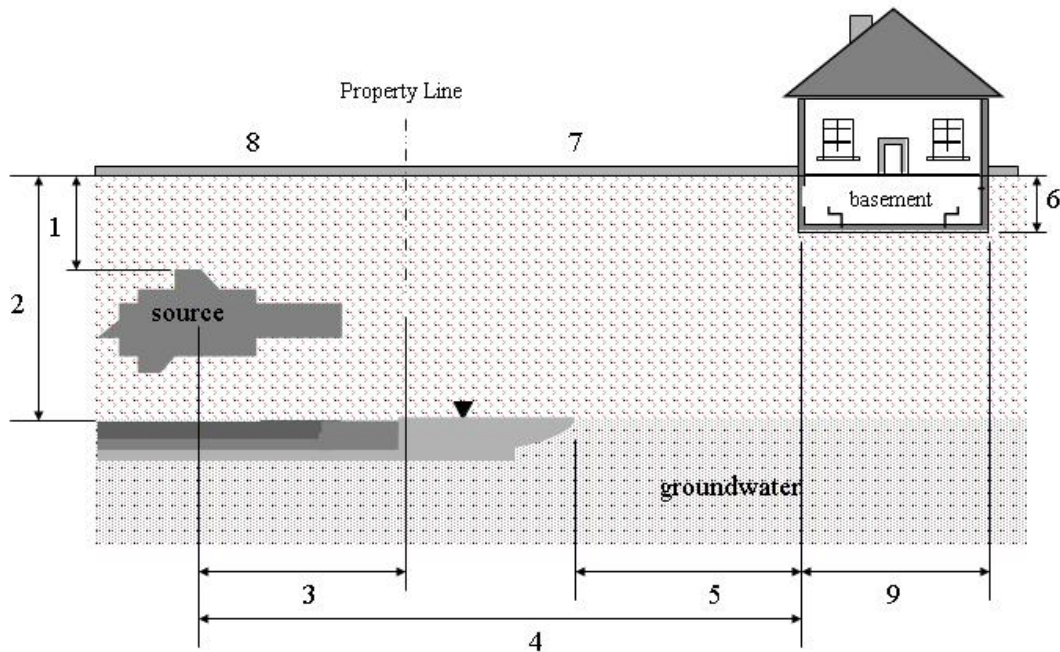
- Estimate the distance from edge of groundwater plume to building.
- Estimate the distance from vapor source area to building.
- Describe the surface cover between the vapor source area and the potentially impacted building.

Appendix B. Selection of Soil Gas Sample Locations

Topic:

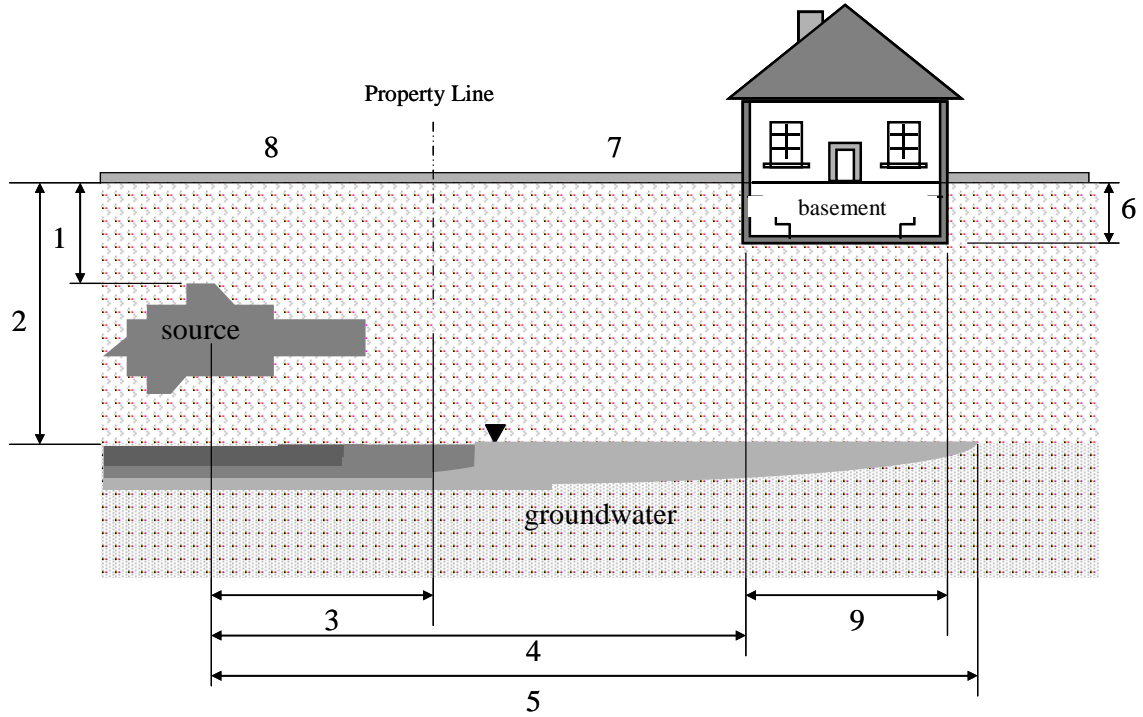
The scenario diagrams included in this appendix may be helpful in planning soil-gas-sampling locations and depths. The user should consider copying the scenario diagram that most-closely matches the site conditions and using it to record the site-specific dimensions. Once the diagram has been customized for the site, the locations and depths for soil gas samples can be identified.

B.1 Scenario 1 – Building Not Over Source or Groundwater Distribution of Petroleum Hydrocarbons



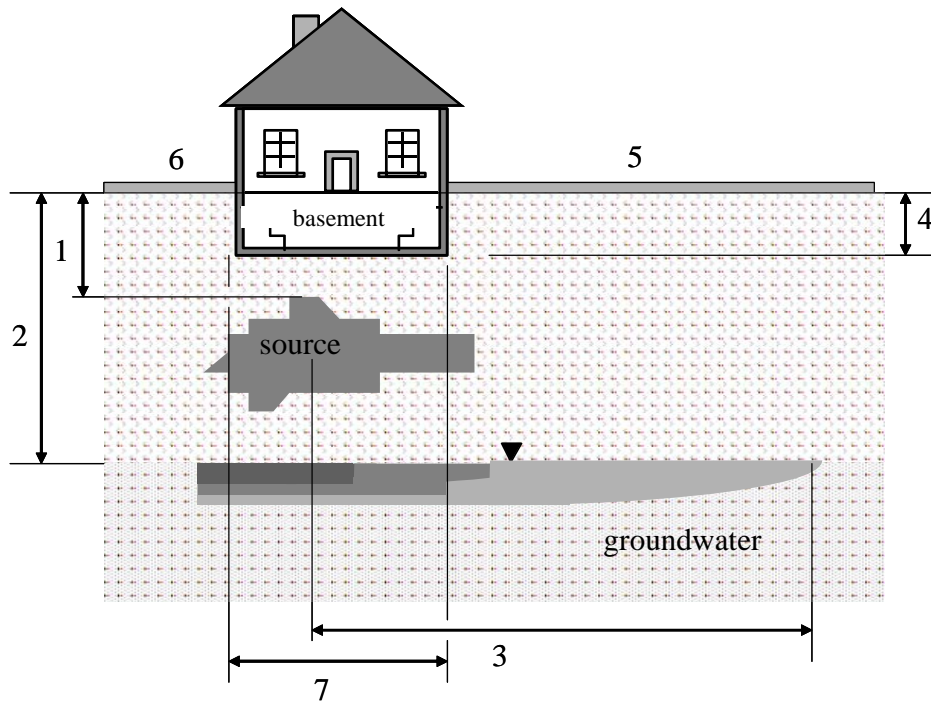
- | | | | |
|--|-------|--|-------|
| 1. Depth to top of source | _____ | 5. Distance from edge of groundwater plume to building | _____ |
| 2. Depth to top of groundwater | _____ | 6. Depth of foundation below ground surface | _____ |
| 3. Distance from source to property line | _____ | 7. Type of surface cover off site | _____ |
| 4. Distance from source to building | _____ | 8. Type of surface cover on site | _____ |
| | | 9. Width of building | _____ |

B.2 Scenario 2 - Building Over Groundwater Distribution of Petroleum Hydrocarbons



- | | | | |
|--|-------|--|-------|
| 1. Depth to top of source | _____ | 5. Distance from source to edge of groundwater plume | _____ |
| 2. Depth to top of groundwater | _____ | 6. Depth of foundation below ground surface | _____ |
| 3. Distance from source to property line | _____ | 7. Type of surface cover off site | _____ |
| 4. Distance from source to building | _____ | 8. Type of surface cover on site | _____ |
| | | 9. Width of building | _____ |

B.3 Scenario 3 - Building Over Source of Petroleum Hydrocarbons



- | | | | |
|--|-------|---|-------|
| 1. Depth to top of source | _____ | 4. Depth of foundation below ground surface | _____ |
| 2. Depth to top of groundwater | _____ | 5. Type of surface cover | _____ |
| 3. Distance from source to edge of groundwater plume | _____ | 6. Type of surface cover | _____ |
| | | 7. Width of building | _____ |

Appendix C. Soil Gas Sample Collection

Topic:

This appendix includes considerations for soil-gas-monitoring installations, soil-gas-collection procedures, and documentation of activities.

C.1 Basic Monitoring Installation Methods

This section provides useful construction information and details for the monitoring installation methods. Please note that the information is intended as general guidelines and not specific recommendations for all sites. Site-specific considerations, professional judgment, and regulatory requirements will dictate the methods and procedures used at any particular site.

C.1.1 *Permanent Probes*

- Based on experience, and as described in CRWQCB (2003), Lahvis (2002), Hartman (2002), and BP (1998), the following construction details should be considered for the installation of permanent probes:
 - Use short individual sampling intervals (e.g., 6 to 12 inches).
 - Color code or tag tubing or probes at the surface so that the sampling depth is easily identifiable for future sampling events.
 - Complete and seal permanent probes at the ground surface (e.g., road boxes, locked caps, vapor-tight valves).
 - If multiple sampling intervals are installed as vertically-nested probes, consider installing a groundwater sampling probe as part of the soil-gas-sampling cluster, especially if a groundwater plume is the vapor source.
 - When using augered borings for the installation of soil-gas-sampling probes, the following should be considered:
 - Install sampling probes with sand-pack intervals of about 1 foot.
 - Seal each sampling interval with bentonite or grout above and below the sand pack in the annulus of the boring.
 - If dry bentonite is placed in the boring, care should be taken to fully hydrate the bentonite. Placing the bentonite in small increments (e.g., < 6 inches) followed by water is helpful. Alternatively, the bentonite can be added using a combination of dry and hydrated bentonite, or in slurry form if the boring is of sufficient diameter.
 - Use down-hole support rods, which may offer practical benefits during installation, particularly for deeper probes (CRWQCB 2003).
 - See Figure C–5 for a schematic of augered permanent probes.

- When using direct-push borings for the installation of soil-gas-sampling probes, the following should be considered:
 - Avoid lateral movement of the probes once they are in the ground to prevent leakage of atmospheric air.
 - Installing sand-pack intervals and seals in small-diameter borings may be difficult.
 - See Figure C–6 for a schematic of direct-push permanent probes.

C.1.2 Temporary Driven Probes

- Based on experience, and as described in CRWQCB (2003) and Hartman (2002), the following construction details should be considered for the installation of temporary driven probes:
 - Seal probes at the surface with bentonite prior to sampling. **Warning:** sealing temporary probes at the ground surface can make the field operations difficult and a bit messy due to the exposed, wet clay.
 - If a sampling tube is used inside the driven rods, seal it inside the rod to prevent short-circuiting.
 - Attach the soil-gas-sampling probe tip to the sampler tubing or to the driven rods, depending on the method used.
 - See Figure C–7 for a schematic of direct push temporary probes.

C.2 Field Activities during Soil Gas Sampling

This section provides information about related field activities that should be considered during the installation of soil-gas-sampling probes or during soil-gas-sampling events.

C.2.1 General Site Conditions

- Conduct a vapor survey with a field instrument (e.g., PID or FID) of all underground utilities to determine if the utilities are preferential vapor-migration pathways.
- Note the current weather conditions (e.g., temperature, barometric pressure, humidity, sunny/cloudy).
- Note the date of the last precipitation event and the approximate rainfall depth.

C.2.2 Soil Conditions

- If permanent probes are installed, make a photo record of the soil core, if collected, and collect several soil samples for moisture content analysis.
- If the vapor source, or soil source, is not well defined, then collect soil samples during the installation of the soil-gas-sampling probes at each sample interval for laboratory analyses of chemicals of concern.
- Field screening of the soil samples also should be conducted, and other more qualitative indicators of impacts should be noted (e.g., odors and staining).

C.2.3 Groundwater Conditions

- Collect groundwater samples for laboratory analyses of chemicals of concern at the same time and in similar locations as the soil-gas-sampling locations. See note about groundwater sampling under Section C.1.1.

C.3 Sample Collection Procedures

This section provides information about sample collection procedures that should be considered when planning the soil-gas-sampling program. As an example, photos from one site showing the sample collection equipment are included at the end of this appendix.

C.3.1 Testing to Determine if Soil Gas Sampling is Practicable

- As a qualitative test, a 20-cubic-centimeter (cc) syringe could be connected to the soil-gas-sampling tubing to determine if a sample can be withdrawn (Hartman 2004). If the soil-gas-sampling tubing has a greater volume than 20 cc, the test will be inconclusive because vapors will not be drawn from the subsurface.
- Another example of a test that can be performed to determine if soil gas sampling is practicable at a site is the following:
 - 1) Install a T-connection at the end of the soil-gas-sampling tubing.
 - 2) Connect a vacuum gauge to one branch of the T-connection.
 - 3) Connect a syringe fitting (e.g., a Luer-lok® fitting) and a 60-mL or larger syringe to the remaining branch of the T-connector. (See Figure C-1)
 - 4) With the syringe connected, pull the plunger back to the full-scale reading and hold in that position.
 - 5) Monitor the vacuum created and its relaxation.
 - 6) If it does not relax within a few minutes to an hour, it is unlikely that soil gas sampling is practicable at the site.

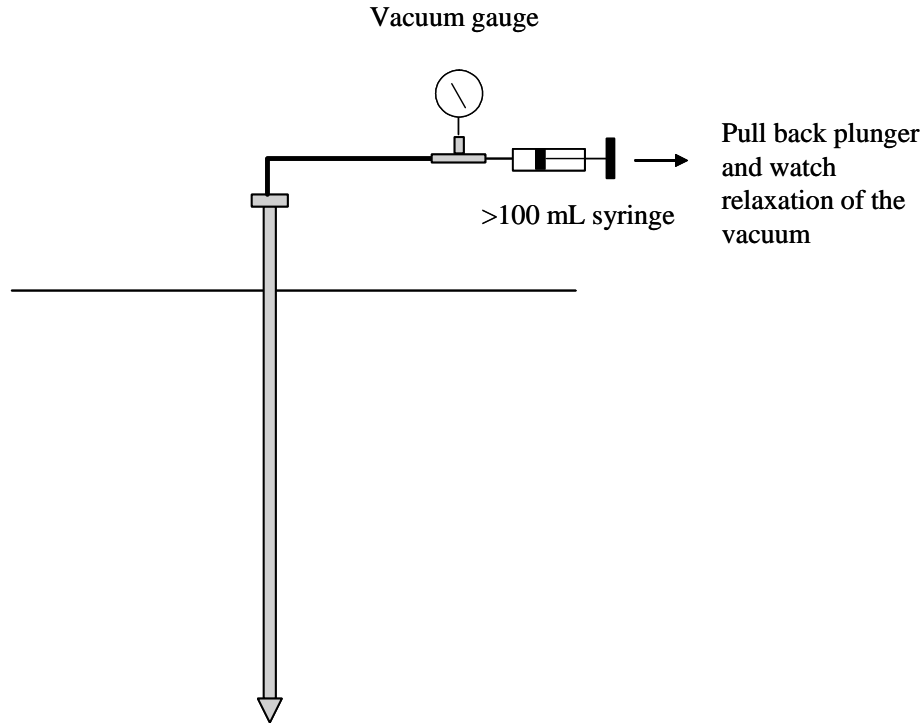


Figure C-1. Example test apparatus to determine if soil gas sampling is practicable.

C.3.2 Purging

- Calculate the dead volume based on the length and inner diameter of the sampling probe and the connected sampling tubing and equipment (i.e., it is assumed that the sampler and borehole sand-pack vapor space is equilibrated with surrounding vapors [as it should be if the probe has been well sealed]) so that the boring vapor space is not included in the dead volume.
- Purge sampling probe and equipment in order to collect representative samples of soil gas at the sample interval.
- The number of purged volumes is generally between one and five dead volumes (CSDDEH 2003, Hartman 2002, Lahvis 2002). Based on experience, minimizing the purged volumes is appropriate. In addition, Hartman (2004) indicates that minimizing the purged volume may reduce the uncertainty about where in the subsurface soil vapors are being drawn. The number of dead volumes purged may be based on a fixed value (e.g., three dead volumes), or other procedures such as:
 - Analyzing the purged gas with a field vapor analyzer (e.g., PID or FID) until the concentrations of total hydrocarbons stabilize (BP 1998), or using field instruments to measure respiration gases (e.g., O₂, CO₂) and assessing consistency across sequential purged volume samples.
 - Conducting a purged volume test to determine the number of dead volumes to remove that corresponds to the highest recovered vapor concentrations (CRWQCB 2003).

- The purged volume selected should be consistent at all of the sample locations across the site and should be recorded (CSDDEH 2003; Lahvis 2002).

C.3.3 Testing Monitoring Installations for Short-Circuiting

- During soil gas sampling, consider conducting a leak test at some proportion of, or all, soil-gas-sampling locations using tracer compounds. For example:
 - Use oxygen as a high-end indicator of short-circuiting. Elevated oxygen measurements in soil gas analytical results may indicate significant short-circuiting.
 - CRWQCB (2003) recommends leak tests be conducted for the below ground equipment using tracer compounds (e.g., butane, propane, isopropanol), some of which are ingredients in consumer products such as shaving cream. For example, the shaving cream is applied at the surface where air could enter the soil gas probes. The soil gas sample is analyzed for the tracer compound using a method that can achieve less than 10 ug/L detection limit. Butane and propane may be detectable as part of a release of gasoline at a site, so judgment should be used about whether this leak testing method can be used at a specific site.
 - Hartman (2002) recommends that leak tests be conducted at sites where leakage may be a concern (e.g., shallow sample intervals, large sample volumes).

C.3.4 Checking Aboveground Sampling Equipment for Leaks

- One method for checking the sampling equipment for leaks is described below:
 - 1) Connect all aboveground sampling equipment (everything that is to be connected to the in-the-ground soil gas probe tubing) to a 10-L Tedlar® bag containing a tracer gas of a known concentration (e.g., diluted helium).
 - 2) Place a valve between the tracer gas bag and the aboveground sampling equipment, and a vacuum gauge down-stream of this valve.
 - 3) Begin to draw tracer gas through the aboveground sampling equipment and adjust the valve to create a vacuum similar to what will be used when withdrawing soil gas from the in-the-ground soil gas probe tubing.
 - 4) Analyze the tracer gas that is collected to see if it has the same concentration as the original Tedlar® bag from which the sample was withdrawn. If not, then the aboveground sampling equipment is leaking.

C.3.5 Decontaminating Equipment

- Clean aboveground sampling equipment should be used for all parts of the soil gas sample collection. This can be implemented by using disposable parts or using proper procedures to clean reusable equipment.
 - If reusable sample containers are used (e.g., Summa® canisters), the supplier should be able to provide analytical results demonstrating the containers are clean.

- External sampling equipment parts may be washed in the field. If tubing is not disposable, then five or more volumes should be purged between samples (CSDDEH 2003).
- Tubing should not be re-used for shallower samples (lower concentrations expected) once it has been used to collect deeper samples (higher concentrations expected).

C.3.6 Sample Collection Flow Rates

- Select a flow rate that does not bias the sample. Minimize the flow rate, and therefore, the vacuum, to practical levels during sampling. For example, flow rates should not exceed about 1 L/min, and flow rates as slow as about 1L/h do not create significant logistical issues for sampling plans. Lahvis (2002) recommends a vacuum of less than 10 inches of water, although vacuums as high as 50 to 100 inches of water should not adversely bias samples, provided that the sampling equipment does not leak at those vacuums (see Section 5.4.4). Based on experience, sampling rates in the 1 L/min to 1 L/h range are practicable.
- For shallow groundwater situations, minimize the sample collection flow rate to prevent groundwater from entering the sample container.
- Measure and record the vacuum at which the samples were collected for each sampling probe.
- Monitor the vacuum during sampling with an in-line gauge (Lahvis 2002).

C.3.7 Sample Containers

- The sample containers chosen for a specific site will depend on the sampling equipment and analytical requirements.
- Examples of different sample containers include:
 - Specially-treated canisters, including Summa® polished or glass-lined canisters
 - These are available in volumes ranging from approximately 400 mL to 6 L.
 - They are under vacuum, and the vacuum should be verified before sampling in case the valve has been leaking in shipment.
 - The solid surfaces of the containers mean the samples are likely to be more stable in shipping.
 - Typically, sampling is conducted using a flow regulator on the canister (CRWQCB 2003).
 - Tedlar® bags
 - These are available in volumes ranging from approximately 1 to 100 L.
 - For shipping, the bags need to remain at standard pressure (Hartman 2002).
 - Cali-5-Bond® bags (information from www.calibrated.com)
 - These are available in volumes up to approximately 200L.

- They are five-layer bags designed to limit gas diffusion into or out of bags.
- Syringes
 - These are available in volumes ranging from approximately 0.5 mL to 10 mL.
 - Recovery of heavier VOCs may be biased low.
 - They are typically used for on-site analysis only.
- Sorbent sampling tubes
 - These are used to concentrate samples (e.g., Tenax® sorbent).
 - They can be single or multi-layer sorbent tubes.
 - The sorbents are specialized materials based on the chemicals of concern.
 - They are used for EPA TO-17 analyses (USEPA 1999).

C.3.8 Equilibration Time

- After the installation of soil-gas-sampling probes, allow sufficient time for the soil gases to equilibrate with the air inside of the sampling probes prior to conducting purging and sampling activities.
- CRWQCB (2003) recommends an equilibration time of 20 to 30 minutes for temporary driven probes, and 48 hours for probes installed using augered borings.
- The disturbance caused by the installation of permanent probes by drilling methods varies with the drilling method. Traditional auger-based drilling will introduce air throughout the soil column, but that disturbance may be limited to the immediate vicinity of the borehole and within the sand packs. If that is the case, thoughtful use of sampler purging may be sufficient to collect representative samples soon after the seals are set (within a few days of installation). Other more invasive methods, such as air-rotary drilling, would be expected to significantly disturb the soil gas profile in a wide area around the soil-gas-sampling installation, and it could take weeks to months for the soil gas profile to re-equilibrate.
- More quantitative estimates of the time necessary for re-establishment of near-steady soil gas profiles can be generated using the equation discussed in the sidebar in Section 2, “Estimating the Time Necessary To Achieve Near Steady-State Conditions”. For this application, consider choosing the travel distance L to be the depth to the vapor source or the lateral distance to the undisturbed vapor profile, whichever is less.
- If the sampling plan calls for multiple sampling events over several months, the data may be used to establish if the soil gas profile has equilibrated. Hartman (2004) suggests if the sampling plan only calls for one set of soil gas samples, several samples can be collected over a few days or weeks to determine the stabilized concentrations.

C.3.9 Other Sample Collection Issues

- Soil gas samples can be collected by different methods:

- *Grab sample* – a one-time sample collected over a short period of time (e.g., less than 15 minutes). Grab samples are generally used in soil gas sampling.
- *Composited grab samples* – for finer-grained soils, multiple samples from the same depth at low flow rates can be collected over time in order to minimize sampling vacuum while collecting enough samples for laboratory analysis (Lahvis 2002).
- Collect field blanks and trip blanks for laboratory analyses.
- Collect duplicate samples for laboratory analyses from 10-percent of the sampling intervals (Lahvis 2002).
- Analyze samples as quickly as possible to prevent loss of volatiles or degradation of the analytes. The times may depend on the analytical method holding times, or regulatory guidance. For example:
 - Analyze Tedlar® bags and gas-tight vials within 48 hours (CSDDEH 2003), up to 72 hours, SW-846, method 0040 (USEPA 1998b).
 - Analyze Summa® canisters within 72 hours (CRWQCB 2003), up to 30 days, method TO-15 (USEPA 1999).
 - Analyze samples collected for field analysis within 30 minutes (CRWQCB 2003).
- Do not chill soil gas samples for shipping to a laboratory because the volatiles may condense out of the vapor phase at the lower temperature (Hartman 2002).
- Prior to collecting a soil gas sample, check the individual sampling probe to be sure that it is not blocked (e.g., measure the vacuum on the sampling probe, pull a vacuum on the sampling probe then release the vacuum. Be sure that the pressure returns to the initial value).

C.4 Documentation

- Consider the following documentation tasks:
 - Record the depth for each soil-gas-sampling interval
 - For permanent probes, prepare a sketch or table to record the dimensions for each soil-gas-sampling location.
- Maintain records of all field procedures, including any leak testing, purging, and sampling for each sampling location. Record the time to complete each activity.
- Maintain records of the field activities (e.g., general site conditions, soil and groundwater conditions) conducted as part of the soil-gas-sampling program.

C.5 Photos

All photos courtesy of P. Lundegard, Chevron Corporation, Brea, CA.



Figure C-2. Vertically-nested sampling probes with sealed Luer-lok® fittings and a sampling syringe.



Figure C-3. Vertically-nested soil-gas-sampling probes sealed at the ground surface with a concrete pad and a vertical surface casing.



Figure C-4. Sampling syringe connected to one sampling tube. Note that each sampling tube is labeled and that the syringe and the sampling tube each have sample valves.

C.6 Soil Gas Probe Schematics

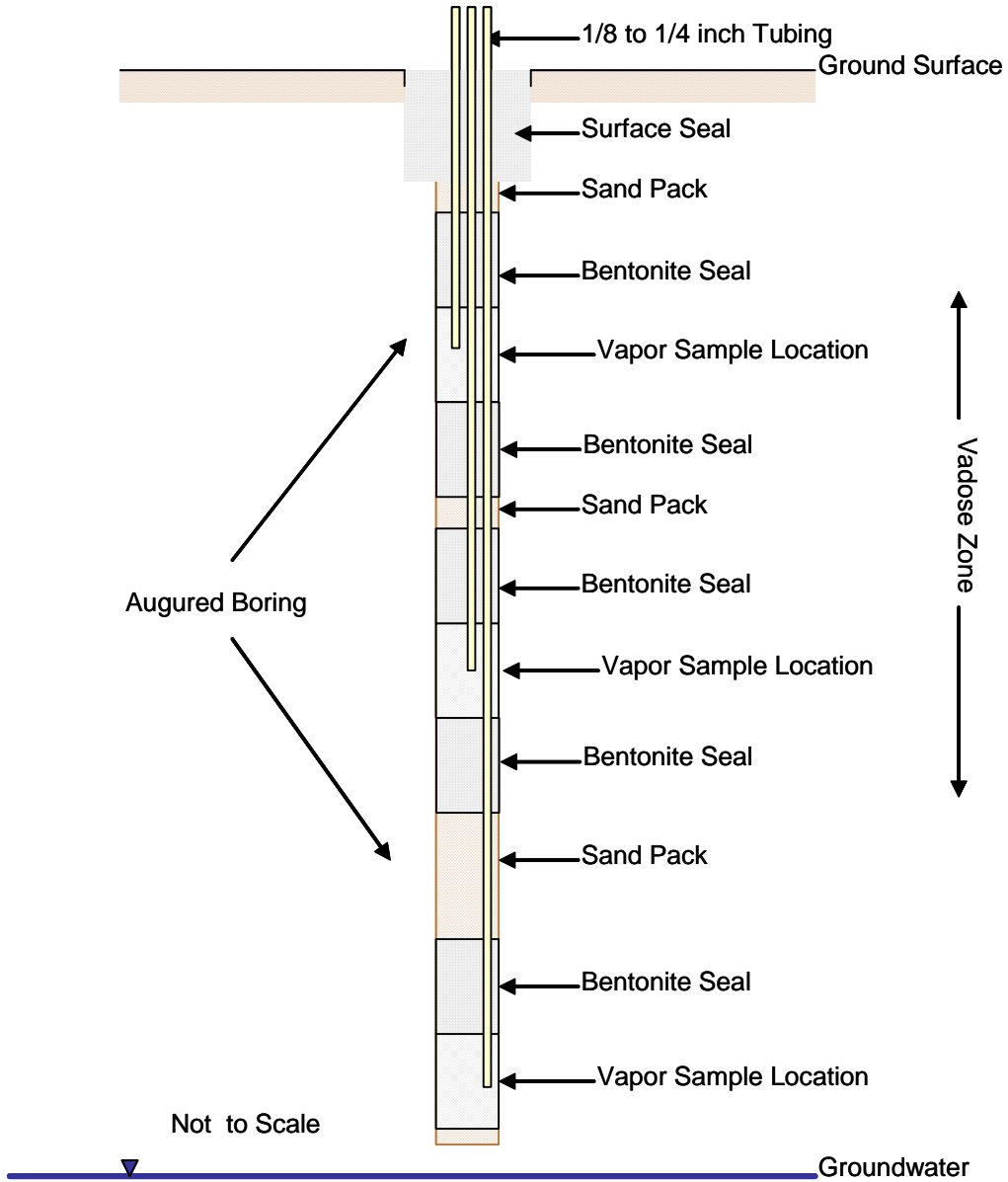


Figure C-5. Augered permanent soil-gas-probe installation.

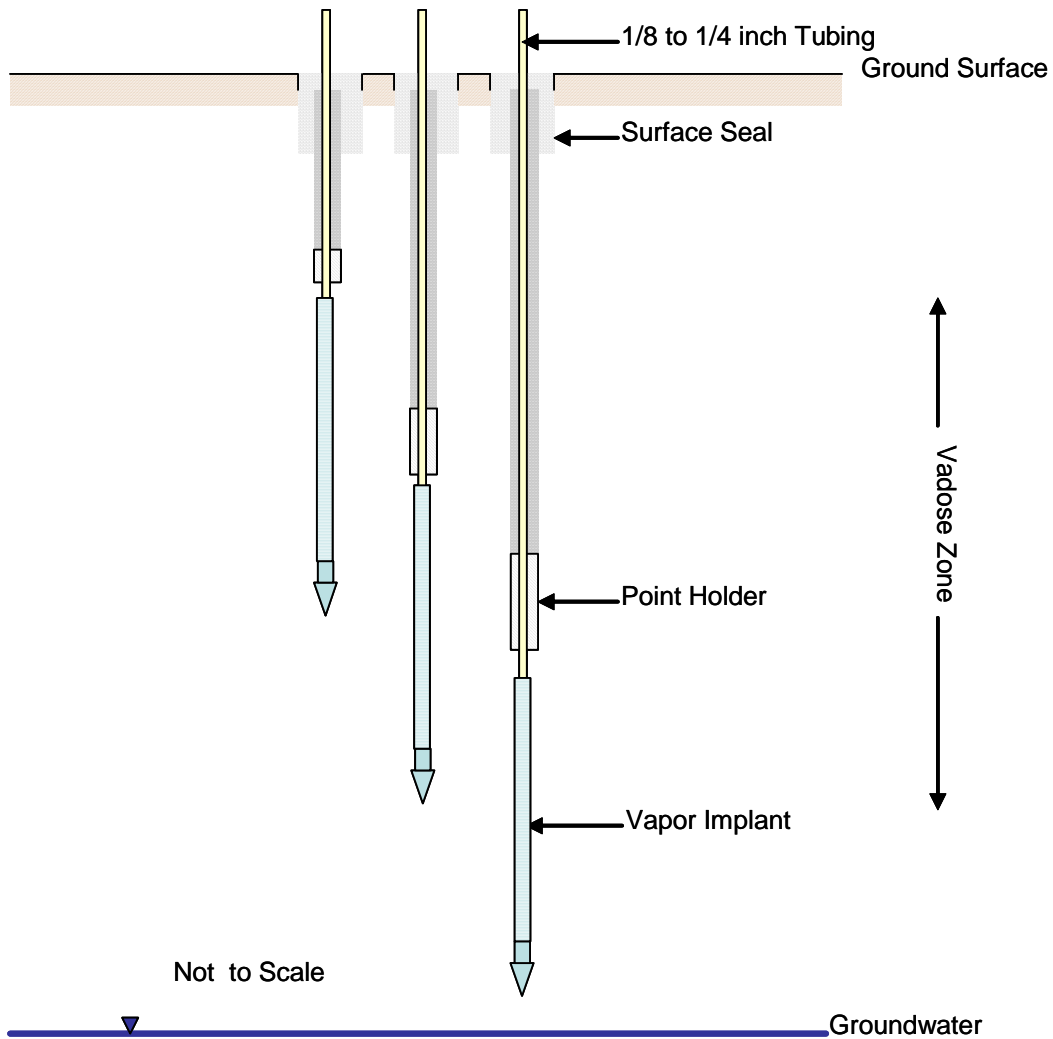


Figure C-6. Direct push permanent soil gas probe installation (developed based on illustration provided at www.geoprobe.com).

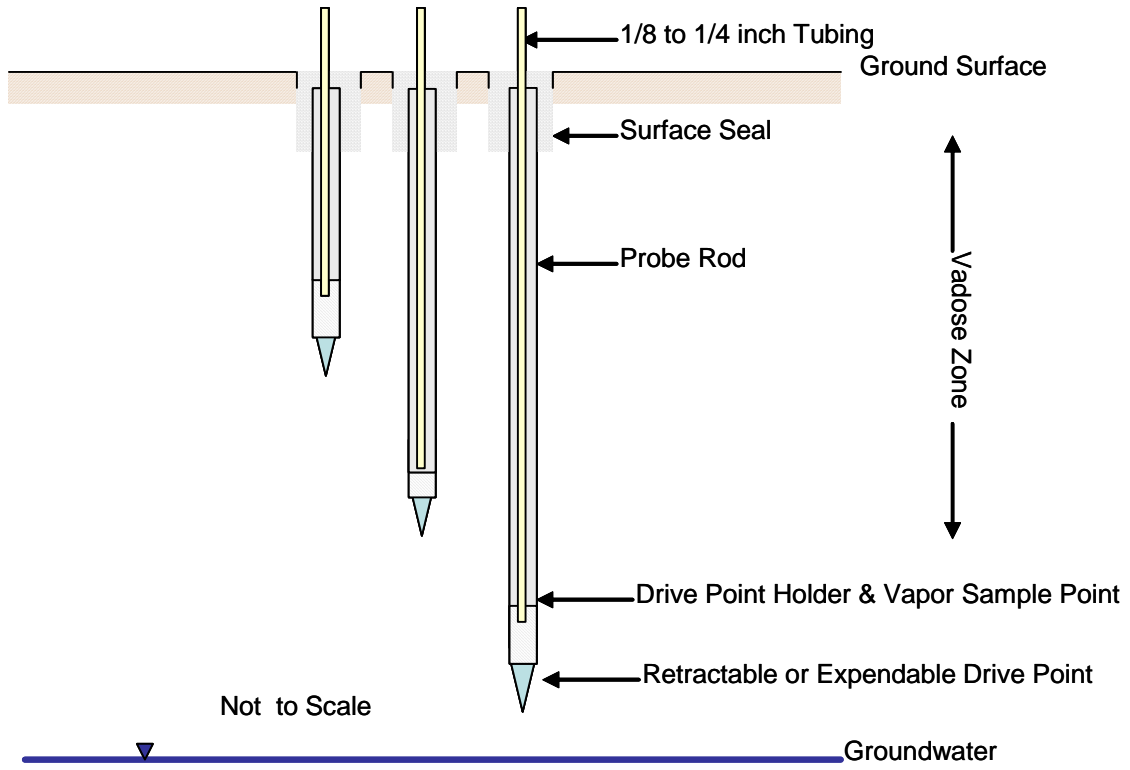


Figure C-7. Direct push temporary soil gas probe (developed based on illustration provided at www.geoprobe.com).

Appendix D. Analytical Methods

Topic:

This appendix provides information about analytical methods in greater detail.

The processing of a sample for analysis generally involves three steps:

1. Sample preparation
2. Analyte separation and detection
3. Data reporting.

D.1 Analytical Separation and Detection

Most available analytical methods for VOC and SVOC in soil gas use gas chromatography (GC) to separate analytes and then use a detector to identify individual compounds. Gas chromatography uses a variety of methods to separate closely related components of complex mixtures and a detector to identify the components or analytes. Detectors for GC include flame ionization detector (FID), flame photometric detector (FPD), photoionization detector (PID), electron capture detector (ECD), thermal conductivity detector (TCD), and mass spectrometer (MS). A mass spectrometer coupled with gas chromatograph (GC/MS) generally provides better identification of individual analytes in complex mixtures than other detectors that are commonly used in environmental analysis (e.g., PID and FID). The specific detector or a combination of detectors used is determined by the required specificity (e.g., analytes identified) and sensitivity (e.g., detection limit) of the application. Analytes that can be detected depend on the detector but include:

- Halogenated VOC (e.g., ethylene dibromide, 1,2-dichloroethane)
- Non-halogenated VOC (e.g., methyl tert butyl ether)
- Aromatic compounds (e.g., benzene, toluene, ethylbenzene, toluene)
- SVOC (e.g., naphthalene, acenaphthene)
- Natural attenuation parameters (e.g., nitrogen [N₂], oxygen [O₂], carbon dioxide [CO₂], methane [CH₄], and in some cases, hydrogen sulfide [H₂S]).

Table D-1 provides a summary of analytical methods that are generally appropriate for quantifying concentrations of chemicals of concern in soil gas. The specific method documentation or the analytical laboratory should be consulted to determine the appropriate sample collection, handling, and storage methods.

Table D-1. Summary of Analytical Methods¹

| Method No. | Type of Compounds | Collection Device | Methodology | Detection Limit ² | Reference |
|---------------------|---|------------------------------------|-----------------|--|-------------|
| TO-1 ³ | VOC | Tenax® solid sorbent | GC/MS or GC/FID | 0.02 – 200 ug/m ³ (0.01-100 ppbv) | USEPA 1999 |
| TO-2 ³ | VOC | Molecular sieve sorbent | GC/MS | 0.2 – 400 ug/m ³ (0.1-200 ppbv) | USEPA 1999 |
| TO-3 | VOC | Cryotrap | GC/FID | 0.2 – 400 ug/m ³ (0.1-200 ppbv) | USEPA 1999 |
| TO-12 | NMOC | Canister or on-line | FID | 200 – 400,000 ug/m ³ (100-200,000 ppbv) | USEPA 1999 |
| TO-13A ³ | PAH | Polyurethane foam | GC/MS | 0.5-500 ug/m ³ (0.6 – 600 ppbv) | USEPA 1999 |
| TO-14A | VOC (nonpolar) | Specially-treated canister | GC/MS | 0.4 – 20 ug/m ³ (0.2-2.5 ppbv) | USEPA 1999 |
| TO-15 | VOC (polar/nonpolar) | Specially-treated canister | GC/MS | 0.4 – 20 ug/m ³ (0.2-2.5 ppbv) | USEPA 1999 |
| TO-15A | VOC | Specially-treated canister | GC/MS | 0.005 ug/m ³ -0.02 ug/m ³ (0.002-0 .04 ppbv) | USEPA 2000b |
| TO-17 ³ | VOC | Single/multi-bed adsorbent | GC/MS, FID | 0.4 – 20 ug/m ³ (0.2-2.5 ppbv) | USEPA 1999 |
| Method 3C | N ₂ , O ₂ , CO ₂ , and CH ₄ | Canister | GC/TCD | 20,000 – 150,000 ug/m ³ (10,000 ppbv) | USEPA 2002a |
| Method 16 | H ₂ S | Tedlar® Bag, Canister | GC/FPD | 100 - 700 ug/m ³ (50 ppbv) | USEPA 2002a |
| 8015B/8015D | TPH/VOC | Tedlar® Bag, Canister, Glass vials | GC/FID | 300 – 3000 ug/m ³ (100 – 10,000 ppbv) | USEPA 1998 |
| 8021B | VOC | Tedlar® Bag, Canister, Glass vials | GC/PID | 4.0 – 60.0 ug/m ³ (0.3 -30 ppbv) | USEPA 1998 |
| 8260B | VOC | Tedlar® Bag, Canister, Glass vials | GC/MS | 10.0 – 50.0 ug/m ³ (0.6 -25 ppbv) | USEPA 1998 |
| 8270C | SVOC | Tedlar® Bag, Canister, Glass vials | GC/MS | 1,000 ug/m ³ (20,000 -100,000 ppbv) | USEPA 1998 |
| D1945-03 | natural gases and mixtures | Tedlar® Bag, Canister, Glass vials | GC/TCD | 800 – 29,000 ug/m ³ (10,000 ppbv) | ASTM 2003 |
| D1946-90(2000) | H ₂ , O ₂ , CO ₂ , CO, CH ₄ , C ₂ H ₆ , and C ₂ H ₄ | Tedlar® Bag, Canister, Glass vials | GC/TCD | 800 – 18,000 ug/m ³ (10,000 ppbv) | ASTM 1990 |

¹This is not an exhaustive list. Some methods may be more applicable in certain instances. Other proprietary or unpublished methods may also apply.

²Detection limits are compound specific and can depend on the sample collection and the nature of the sample. Detection limits shown are for the range of compounds reported by the analytical methods.

³To achieve high sensitivity, the indicated methods utilize a trapping-type sampling method and relation of results to air-borne concentrations may not be possible.

GC/MS = Gas chromatography/mass spectrometry

GC/FID = Gas chromatography/flame ionization detector

GC/FPD = Gas chromatography/flame photometric detector

GC/TCD = Gas chromatography/thermal conductivity detector

VOC = Volatile organic compounds

PAH = Polycyclic aromatic hydrocarbons

NMOC = Non-methane organic compounds

SVOC = Semi-volatile organic compounds

D.2 Detection Limits

It is important to determine the smallest soil gas concentration of chemicals of concern or other analytes that are expected to be required for purposes of evaluating the subsurface-vapor-to-indoor-air pathway. The indoor air target levels can be used to identify the necessary detection limits for the soil gas analyses. A low-end attenuation factor of 100 is used to relate the concentrations in soil gas relative to the indoor air target level to identify the detection limit. This worksheet is provided as an example for defining detection limits.

Table D-2. Detection Limit Determination Worksheet

| Chemicals of Concern | CAS Number (1) | Example Risk-Based Indoor Air Target Levels (ppbv) (2) | Example Detection Limits Based on 100 Times the Indoor Air Value (ppbv) |
|-----------------------------|-----------------------|---|--|
| Benzene | 71-43-2 | 9.8E-02 | 9.8E+00 |
| Toluene | 108-88-3 | 1.1E+02 | 1.1E+04 |
| Ethylbenzene | 100-41-4 | 5.1E-01 | 5.1E+01 |
| Xylenes | 1330-20-7 | 1.6E+03 | 1.6E+05 |
| MTBE | 1634-04-4 | 8.3E+02 | 8.3E+04 |
| Naphthalene | 91-20-3 | 5.7E-01 | 5.7E+01 |

(1) Lewis 2001

(2) USEPA 2002a – the cancer risk level used is 1E-06, and the hazard index used is 1.

D.3 Analytical Quality Control

As stated in USEPA (1998b, 1999, 2002), typical analytical method quality-control measures include:

- A calibration of the instrument to verify the response of the instrument compared to the initial calibration.
- Analysis of blank samples to look for laboratory-induced contamination (i.e., method blank) and to look for contamination from the instrument (i.e., instrument blank).
- Analysis of duplicate samples or blind duplicate samples to assess the precision of the method and variability of the sample (i.e., laboratory and field duplicates).
- Analysis of surrogate compounds (e.g., compounds similar to the target analytes) to evaluate the extraction efficiency on a per sample basis.
- Analysis of laboratory prepared samples spiked with known concentrations of analytes (i.e., spiked matrix sample) to verify the procedures of the analyst and to verify the extraction efficiency of the analytical system. These samples usually are not identified to the analyst.

Appendix E. Data Evaluation

Topic:

This appendix provides tools to support data evaluation.

E.1 Expected Maximum Vapor Concentrations

The following worksheets provide tools to estimate the maximum soil gas concentrations ($C_{\max,v}$) expected immediately above a groundwater source ($C_{\max,gw}$) and the maximum soil gas concentration immediately above an LNAPL source. These are developed using Henry's Law coefficients for groundwater sources and Raoult's Law for LNAPL sources for the petroleum hydrocarbon compounds. In the case of dissolved groundwater sources, it is not possible to collect vapor samples immediately above the water table (because of high water saturations in the capillary fringe). In addition, there is a decreasing concentration gradient in moving up through the capillary-fringe towards ground surface, so vapor concentrations in vapor samples collected above the capillary fringe are expected to be less than those predicted to be in equilibrium at the water table (or base of the capillary fringe).

If the measured soil vapor concentrations in deep soil gas are significantly greater than the calculated maximum vapor concentrations based on groundwater concentrations, then it is likely that residual LNAPL is present in the vadose zone (assuming that there is confidence in the field data). In theory, if the LNAPL, groundwater, and soil vapor are in intimate contact, and if samples of the equilibrated water and vapor are collected, then vapor concentrations predicted using the groundwater concentration should equal those predicted by LNAPL-vapor partitioning presented below. However, discrete water sampling is rarely performed, and the region of intimate contact may be small relative to sampling intervals of the monitoring installations (if there is contact at all).

The equation for estimating soil gas concentrations in equilibrium with groundwater is:

$$C_{\max,v} \left(\frac{ug}{m^3} \right) = H \times C_{\max,gw} \left(\frac{ug}{L} \right) \times CF_1 \quad (\text{Charbeneau 2000}) \quad \text{Equation E.1}$$

where:

H [L-water/L-vapor] = Henry's Law Constant

CF_1 = conversion factor for ug/L to ug/m³ = 1000

Table E-1. Worksheet for Maximum Soil Vapor Concentration (Using Equation E.1)

| Petroleum Hydrocarbons | CAS Number (1) | Henry's Law Constant (<i>H</i>) (L-water/L-vapor) (2) | Maximum Site Groundwater Concentration (<i>C</i> _{max,gw}) (ug/L-water) | Conversion Factor (<i>CF</i> ₁) (ug/L to ug/m ³) | Maximum Soil Vapor Concentration (<i>C</i> _{max,v}) (ug/m ³ -vapor) |
|------------------------|----------------|---|--|---|---|
| Benzene | 71-43-2 | 2.28E-01 | | 1000 | |
| Toluene | 108-88-3 | 2.72E-01 | | 1000 | |
| Ethylbenzene | 100-41-4 | 3.23E-01 | | 1000 | |
| Xylenes | 1330-20-7 | 2.90E-01 | | 1000 | |
| MTBE | 1634-04-4 | 2.04E-01 | | 1000 | |
| Naphthalene | 91-20-3 | 1.98E-02 | | 1000 | |

(1) Lewis 2001

(2) USEPA 2002

The equation for estimating vapor concentrations in equilibrium with LNAPL is:

$$C_{\max,v} \left(\frac{ug}{m^3} \right) = NMF \times \frac{P_v \times MW \times CF_2}{RT} \times CF_3 \quad \text{Equation E.2}$$

where:

MW [g/mole] = molecular weight of the chemical of concern

P_v [atm] = pure component vapor pressure of the chemical of concern

R [L-atm/mol-K] = universal gas constant = 0.0821

T [K] = the absolute temperature

*CF*₂ = conversion factor for g to mg = 1000

*CF*₃ = conversion factor for mg/L to ug/m³ = 1E+06

The LNAPL mole fraction (NMF) should be estimated for the site based on analytical data, product release information and professional judgment. The worksheet in Table E-2 uses equation E.2.

Table E-2. Worksheet for Maximum Soil Vapor Concentration Given an LNAPL Source (Using Equation E.2)

| Petroleum Hydrocarbons | CAS Number (1) | Estimated Mole Fraction (NMF) Of Analyte in the LNAPL | Molecular Weight (1) | Vapor Pressure (P _v) (atm) (2) | Conversion Factor [(CF ₂ *CF ₃)/RT] (g/L to ug/m ³)/RT at T= 298K | Maximum Soil Vapor Concentration (C _{max,v}) (ug/m ³ -vapor) |
|------------------------|----------------|---|----------------------|--|--|---|
| Benzene | 71-43-2 | | 78.1 | 1.2E-01 | 4E+07 | |
| Toluene | 108-88-3 | | 92 | 3.7E-02 | 4E+07 | |
| Ethylbenzene | 100-41-4 | | 106 | 9E-03 | 4E+07 | |
| Xylenes | 1330-20-7 | | 106 | 9E-03 | 4E+07 | |
| MTBE | 1634-04-4 | | 88 | 3.2E-01 | 4E+07 | |
| Naphthalene | 91-20-3 | | 128.2 | 3E-04 | 4E+07 | |

(1) Lewis 2001

(2) Charbeneau 2000

If the Henry's constant is not available for use in Equation E.1 or Equation E.4, solubility, vapor pressure and molecular weight values may be used to estimate the Henry's constant. Similarly, if the vapor pressure needed in Equation E.2 is not available, it can be estimated using solubility, Henry's constant and molecular weight values. In either case, the relation give in Equation E.3 would be used.

$$H \left(\frac{L - \text{water}}{L - \text{vapor}} \right) = \frac{P_v \times MW \times CF_2}{Sol \times RT} \quad \text{Equation E.3}$$

$$C_{\max,v} \left(\frac{ug}{m^3} \right) = NMF \times \left[\frac{\left(\frac{P_v \times MW \times CF_2}{RT} \right)}{Sol} \right] \times Sol \times CF_3 \quad \text{Equation E.4}$$

$$= NMF \times H \times Sol \frac{mg}{L} \times CF_3$$

where:

Sol [mg/L] = pure component solubility of the chemical of concern.

E.2 Conversion Table for Soil Gas Analytical Results

Soil gas analytical results are typically reported in two different sets of units. These units are volume per volume (e.g., parts per billion volume [ppbv]) and mass per volume (e.g., micrograms per cubic meter [$\mu\text{g}/\text{m}^3$]). Unlike aqueous samples, these two sets of units are not equivalent. The conversion of a gas concentration from ppbv to $\mu\text{g}/\text{m}^3$ is accomplished by assuming that the gas is an ideal gas:

$$PV = nRT \quad \text{Equation E.5}$$

where:

P [atm] = atmospheric pressure (1 atm)

V [L] = volume

n = moles of air

R [L-atm/mol-K] = universal gas constant = 0.0821

T [K] = standard temperature (273 K)

At standard temperature and pressure (i.e., 273 K and 1 atm), one mole of air occupies 22.4 L in volume. The ppbv concentration is moles of chemical of concern per 10^9 moles of air. The conversion equation is then:

$$\left(C \frac{\mu\text{g}}{\text{m}^3} \right) = (C \text{ ppbv}) \times \frac{1 \text{ mol COC}}{10^9 \text{ mol air - ppbv}} \times \frac{1 \text{ mol air}}{22.4 \text{ L}} \times \frac{273 \text{ K}}{298 \text{ K}} \times \frac{10^3 \text{ L}}{1 \text{ m}^3} \times MW \frac{\text{g}}{\text{mol COC}} \times \frac{10^6 \mu\text{g}}{\text{g}}$$

$$\left(C \frac{\mu\text{g}}{\text{m}^3} \right) = (C \text{ ppbv}) \times \frac{1}{22.4} \times \frac{273}{298} \times MW$$

$$\left(C \frac{\mu\text{g}}{\text{m}^3} \right) = (C \text{ ppbv}) \times 0.04 \times MW$$

where:

MW [g/mol] = molecular weight of the individual chemical of concern.

Table E-3. Conversion Worksheet

| Petroleum Hydrocarbons | CAS Number (1) | Vapor Concentration in ppbv | Molecular Weight (1) | Conversion Factor (CF_d) At 298K | Vapor Concentration in $\mu\text{g}/\text{m}^3$ |
|------------------------|----------------|-----------------------------|----------------------|--------------------------------------|---|
| Benzene | 71-43-2 | | 78.1 | 0.04 | |
| Toluene | 108-88-3 | | 92 | 0.04 | |
| Ethylbenzene | 100-41-4 | | 106 | 0.04 | |
| Xylenes | 1330-20-7 | | 106 | 0.04 | |
| MTBE | 1634-04-4 | | 88 | 0.04 | |
| Naphthalene | 91-20-3 | | 128.2 | 0.04 | |

(1) Lewis 2001

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