

Ground Water Issue Paper: An Approach that Uses the Concentrations of Hydrocarbon Compounds in Soil Gas at the Source of Contamination to Evaluate the Potential for Intrusion of Petroleum Vapors into Buildings (PVI)

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1.0 INTRODUCTION

The federal underground storage tank program was originally created in 1984 (U.S. EPA, 2014a). It was designed to protect ground water used as drinking water from contamination by releases of motor fuel from underground storage tanks. In the early years, the focus was clearly on groundwater with little emphasis on human exposure to vapors of petroleum hydrocarbons that might enter buildings.

In 1983, the National Academy of Science published their report titled *Risk Assessment in the Federal Government: Managing the Process* (NRC, 1983). As one response to the NRC report, the U.S. EPA published its *Guidelines for Exposure Assessment* (U.S. EPA, 1992). The *Guidelines* emphasize a comprehensive evaluation of all possible routes of exposure. In the *Guidelines*, inhalation is as important a route of exposure as is ingestion. As a consequence, exposure to petroleum vapors that might intrude into a building became an exposure scenario of concern at sites where there was a release of motor fuel from an underground storage tank.

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1.1 Purpose of this Issue Paper

This Issue Paper offers an alternative approach to screening that could be applied before a decision is made to do sub-slab monitoring or indoor air monitoring. The approach in this Issue Paper is based on three factors: (1) the concentrations of hydrocarbons in soil gas at the source of the vapors, (2) the separation distance between the receptor and the source of the vapors, and (3) a presumption that aerobic biodegradation will reduce the concentrations of hydrocarbons in the unsaturated zone.

Results from monitoring indoor air can be influenced by ambient air quality and sources and sinks in the building; all of which are variable in time. Results from monitoring sub-slab air can be variable in both time and in location below the slab. This increases the chances that monitoring will fail to detect vapor intrusion. Concentrations in soil gas at the source of the hydrocarbons are much less variable. This approach can also be used in parallel with sub-slab monitoring or side-slab monitoring to support the findings of the near-slab monitoring.

The U.S. EPA Office of Underground Storage Tanks (OUST) is currently developing guidance to evaluate the risks from vapor intrusion of petroleum compounds from fuel spills at underground storage tank sites. This document, *Technical Guide For Addressing Petroleum Vapor Intrusion At Leaking Underground Storage Tank Sites*, focuses on evaluating the potential for petroleum vapor intrusion from underground storage tanks regulated under 40 CFR280 (see <http://www.epa.gov/oust/fedlaws/index.htm>).

The OUST guidance organizes site characterization at a fuel release site into a sequence of decision points. In the first tier, any building of concern is evaluated for immediate threats such as fires or explosions. If no immediate threats are present, the potential for petroleum vapor intrusion is evaluated in the second tier.

The location of any building of concern is compared to the location of known petroleum contamination in soil and sediment or in ground water. If it cannot be shown that the building is separated from known contamination by clean sediment or ground water (in the horizontal plane), the building is considered

to be in a lateral inclusion zone and the exposure to hydrocarbon contaminants must be characterized further. The next step is to compare the vertical separation of the building from hydrocarbons in soil and sediment or in ground water. If it cannot be shown that there is an adequate vertical extent of clean unsaturated sediment between the building and known contamination in sediment or ground water, the building is considered to be in a vertical inclusion zone and the exposure to hydrocarbon contaminants must be characterized further. Wilson et al. (2012a) provides technical recommendations to define lateral and vertical inclusion zones at a site.

If a building of concern is in the vertical inclusion zone, either remediation is necessary, further characterization is necessary, or both are necessary. This Issue Paper provides recommendations for additional characterization that might be conducted before samples are acquired below the slab of a building or from the indoor air of a building.

If it is necessary to remediate a site by active soil venting or some other remedy that removes or destroys hydrocarbons, the approach in this Issue Paper may be a useful technique to characterize the efficacy of the remedy and determine whether the remedy was adequate to manage the risk for PVI.

This Issue Paper provides technical recommendations. This Issue Paper is not guidance provided by U.S. EPA OSWER or U.S. EPA OUST.

1.2 Evolution of U.S. EPA Guidance and Recommendations on Petroleum Vapor Intrusion

In response to the 1983 National Academy of Science report (NRC, 1983), U.S. EPA has taken two distinct approaches to evaluate vapor intrusion: one based on shallow soil gas samples, and a second based on vertical separation distances.

1.2.1 Guidance based on shallow soil gas samples

The U.S. EPA's first approach to providing specific technical guidance for evaluation of vapor intrusion was the OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from

Groundwater and Soils [Subsurface Vapor Intrusion Guidance] (U.S. EPA, 2002). The guidance was built around generic attenuation factors (α) where the factor is the concentration in indoor air divided by the concentration in a soil gas sample. To evaluate risk, a sample of soil gas is acquired and analyzed; then the concentration of the compound of concern in the soil gas is multiplied by the attenuation factor to predict the concentration in indoor air. Examples are presented in Table 1.1. The values of the attenuation factor are based on professional judgment and on representative values of the attenuation factor that were measured in buildings in case studies.

The guidance provided in U.S. EPA (2002) has been updated. U.S. EPA now provides a *Vapor Intrusion Screening Level (VISL) Calculator* and associated *User's Guide* (U.S. EPA, 2014e, 2014f). Screening levels for benzene and hexane at 25°C are provided in Table 1.2.

The *OSWER Draft Guidance* and the *Vapor Intrusion Screening Level (VISL) Calculator* were developed to describe the intrusion of vapors of chlorinated solvents, in particular solvents such as trichloroethylene (TCE). The attenuation factors are most appropriate for chemicals that behave like TCE.

Table 1.1. Example Generic Screening Levels corresponding to a lifetime risk of 1×10^{-4} . Values are from pages 57 and 58 of U.S. EPA (2002).

Chemical	Target Indoor Air Concentration ¹ ($\mu\text{g}/\text{m}^3$)	Target Shallow Soil Gas Concentration ² ($\mu\text{g}/\text{m}^3$)	Target Deep Soil Gas Concentration ³ ($\mu\text{g}/\text{m}^3$)	Target Groundwater Concentration ⁴ ($\mu\text{g}/\text{L}$)
Benzene	31	310	3100	140
Hexane	200	2,000	20,000	2.9

¹ Target Indoor Air Concentration to Satisfy Both the Prescribed Risk Level and the Target Hazard Index [$R=10^{-4}$, $HI=1$]

² Target Shallow Soil Gas Concentration Corresponding to Target Indoor Air Concentration Where the Soil Gas to Indoor Air **Attenuation Factor=0.1**.

³ Target Deep Soil Gas Concentration Corresponding to Target Indoor Air Concentration Where the Soil Gas to Indoor Air **Attenuation Factor=0.01**.

⁴ Target Groundwater Concentration Corresponding to Target Indoor Air Concentration Where the Soil Gas to Indoor Air **Attenuation Factor = 0.001** and Partitioning Across the Water Table Obey's Henry's Law.

Table 1.2. Example Generic Screening Levels corresponding to a lifetime risk of 1×10^{-4} . Values are from the *Vapor Intrusion Screening Level (VISL) Calculator* (U.S. EPA, 2014e).

Chemical	Target Indoor Air Concentration ¹ ($\mu\text{g}/\text{m}^3$)	Target Sub-slab and Exterior Soil Gas Concentration ² ($\mu\text{g}/\text{m}^3$)	Target Groundwater Concentration ³ ($\mu\text{g}/\text{L}$)
Benzene	31	310	140
Hexane	730	7,300	9.9

¹ Target Indoor Air Concentration to Satisfy Both the Target Cancer Risk (TCR) and the Target Hazard Quotient (THQ) where $TCR=10^{-4}$, and $THQ=1$.

² Target Sub-slab and Exterior Soil Gas Concentration Corresponding to Target Indoor Air Concentration Where the Soil Gas to Indoor Air **Attenuation Factor=0.1**.

³ Target Groundwater Concentration Corresponding to Target Indoor Air Concentration Where the Soil Gas to Indoor Air **Attenuation Factor = 0.001** and Partitioning Across the Water Table Obey's Henry's Law.

1.2.2 Guidance Based on Vertical Separation Distances

The *OSWER Draft Guidance* opted to not address intrusion of petroleum vapors from releases of motor fuel from underground storage tanks. As stated on page 2 of the *OSWER Draft Guidance*:

The draft guidance is suggested for use at RCRA Corrective Action, CERCLA (National Priorities List and Superfund Alternative Sites), and Brownfields sites, but is not recommended for use at Subtitle I Underground Storage Tank (UST) sites at this time. The draft guidance recommends certain conservative assumptions that may not be appropriate at a majority of the current 145,000 petroleum releases from USTs. As such, the draft guidance is unlikely to provide an appropriate mechanism for screening the vapor pathway at UST sites.

As is described in the U.S. EPA publication *Petroleum Hydrocarbons And Chlorinated Solvents Differ In Their Potential For Vapor Intrusion* (U.S. EPA, 2011), there is a fundamental difference in the behavior of chlorinated solvents such as TCE and petroleum hydrocarbons such as benzene. Because TCE is not biologically degraded in the presence of molecular oxygen, it is usually not degraded in the unsaturated zone. As a consequence, the potential for vapor intrusion is most sensitive to the rate of diffusion of TCE along a vertical concentration gradient in the soil gas. In contrast, the potential for vapor intrusion of benzene and other petroleum hydrocarbons is most sensitive to biological degradation of the hydrocarbon as it diffuses along the concentration gradient. Over the same separation distance, the concentration of benzene that might enter a building is much lower than the concentration of TCE.

Robin V. Davis with the Utah Department of Environmental Quality had collected and collated data on the concentrations of petroleum hydrocarbons in ground water and in soil gas at sites with a release of motor fuel from an underground storage tank. In May 2011, Robin Davis provided her database to the U.S. EPA to provide a basis for establishing separation distances that can distinguish sites with a significant risk of petroleum vapor intrusion from sites with no

significant risk. Peter Eremita (Maine Department of Environmental Protection) and Jackie Wright (Environmental Risk Sciences Pty Ltd, Carlingford, New South Wales, Australia) also provided significant data.

U.S. EPA evaluated the empirical database on the distribution of petroleum hydrocarbons in soil gas above contaminated ground water or sediment (U.S. EPA, 2013a). The report identified vertical separation distances from contaminated ground water that were adequate to allow natural aerobic biodegradation to reduce the concentration of fuel hydrocarbons in soil gas to acceptable levels. The report also identified vertical separation distances from sediment contaminated with residual fuel hydrocarbons. See *Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds* (U.S. EPA, 2013a). See “PVI Database” at <http://www.epa.gov/oust/cat/pvi/index.htm>.

These empirically derived separation distances were used to support guidance on separation criteria in the OUST draft guidance (U.S. EPA, 2013b). The provisional recommended vertical separation distances are presented in Table 1.3.

The vertical separation distance represents the thickness of clean, biologically active soil between the source of petroleum hydrocarbon vapors and the lowest (deepest) point of a receptor (building foundation, basement, or slab). For this purpose, clean is defined as having a concentration of Total Petroleum Hydrocarbons (TPH) in soil or sediment ≤ 250 mg/kg for Diesel Fuel or Weathered Gasoline or ≤ 100 mg/kg for Fresh Gasoline. The source of vapors can be motor fuel present as a light nonaqueous-phase liquid (LNAPL), as residual LNAPL, or dissolved in ground water.

In 2010, a team of industry scientists, consultants, and a state regulator (McHugh et al., 2010) proposed that three meters (9.8 feet) was a sufficient vertical separation distance above hydrocarbon contamination in ground water and that ten meters (32.8 feet) was a sufficient distance above a LNAPL source. These distances are significantly greater than the provisional U.S. EPA recommended vertical separation distances in Table 1.3. This difference is because the McHugh

Table 1.3. Recommended vertical separation distance between contamination and building foundation, basement, or slab.

Media	Benzene	TPH	Indication of NAPL	Vertical Separation Distance (feet)
Soil (mg/kg)	≤ 10	≤ 250 for Diesel Fuel or Weathered Gasoline ≤ 100 for Fresh Gasoline	No	≥ 6
	> 10	> 250 for Diesel Fuel or Weathered Gasoline > 100 for Fresh Gasoline	Yes	≥ 15
Groundwater (mg/L)	≤ 5	≤ 30	No	≥ 6
	> 5	> 30	Yes	≥ 15

et al., (2010) analysis was not able to resolve some anomalies (Robin Davis, personal communication).

In 2013, a different team of industry scientists, consultants, and a state regulator (Lahvis et al., 2013) independently analyzed the data set used to extract the provisional U.S. EPA recommended vertical separation distances. From their analysis, they found that there is a >95% chance that the concentration of benzene in soil gas will be ≤30 µg/m³ whenever the separation distance from LNAPL was ≥13 feet. In their analysis, they found that there was a >95% chance that the concentration of benzene in soil gas will be ≤30 µg/m³ at any separation distance above benzene dissolved in ground water. Compared to Lahvis et al., (2013), the provisional U.S. EPA recommended vertical separation distances for contaminated groundwater are conservative. However, there is little practical difference in the separation distances for LNAPL.

Wilson et al. (2012a) provides technical recommendations to implement the provisional separation criteria in U.S. EPA (2013b). If application of the separation criteria determines that a building is in the vertical inclusion zone and further action is necessary, this Issue Paper provides one approach that could be used to further screen the vertical distribution of hydrocarbon contamination at the site and determine whether it is necessary to collect soil gas samples from beside or below the foundation of the building or samples of indoor air.

2.0 CONCEPTUAL MODEL OF AEROBIC BIODEGRADATION OF PETROLEUM VAPORS

The approach taken in this document is based on measurements of hydrocarbons in soil gas at the source of the vapors. It is built around a conceptual model for biodegradation of hydrocarbons in soil gas that is widely accepted (Abreu et al., 2009a,b; DeVaul, 2007; Lavis et al., 2013; Ostendorf and Kampbell, 1991; Roggemans et al., 2001; U.S. EPA, 2012; U.S. EPA, 2013a,b).

2.1 Interaction of Diffusion of Oxygen and Diffusion Petroleum Vapors

U.S. EPA (2011) provided a generalized conceptual model of the interaction of oxygen and petroleum vapors in the unsaturated zone (Figure 2.1). Hydrocarbons enter soil gas by either partitioning from dissolved hydrocarbons in ground water or by volatilization of residual hydrocarbons in the unsaturated zone and nonaqueous phase hydrocarbons floating on the ground water. The hydrocarbons diffuse upward from their source.

Aerobic biodegradation of petroleum hydrocarbons consumes oxygen which diffuses down from the surface. The rate of aerobic biodegradation is limited by the supply of oxygen. The bulk of biodegradation occurs at a front where the rate of diffusion of oxygen

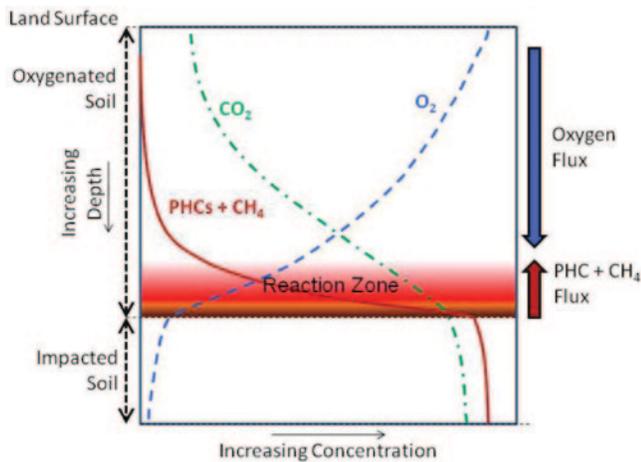


Figure 2.1. The vertical distribution of hydrocarbon and oxygen in soil (reprinted from Figure 3 of U.S. EPA, 2011).

from the surface matches the stoichiometric oxygen demand of the hydrocarbons diffusing upward from their source. However, as the residual hydrocarbon vapors continue to diffuse upward to the surface, they are further degraded.

Roggemans et al. (2001) compared the distribution of LNAPL and hydrocarbons and oxygen in soil gas at 28 sites. They were able to categorize the behavior of oxygen and hydrocarbons into four patterns as described in Table 2.1.

Roggemans et al. (2001) noted that pattern C can be explained by a failure to replace the oxygen that was consumed to degrade hydrocarbons with oxygen from the atmosphere. At the three sites that followed pattern D, the soil gas was isolated from the atmosphere by some restriction such as a layer of wet clay with negligible air-filled porosity, by the foundation of a building or by pavement. However, the presence of wet clay or the foundation of a building or pavement does not necessarily cause a site to follow pattern C.

At sites that fall into pattern C, there is no detectable biodegradation of hydrocarbon vapors, and the intrusion of hydrocarbons would be expected to follow the same pattern as chlorinated solvents.

Table 2.1. Four patterns for the distribution of oxygen and petroleum hydrocarbons in soil gas at gasoline spill sites as described by Roggemans et al. (2001).

Pattern	Number of Sites with Pattern	Distribution of Hydrocarbons	Distribution of Oxygen throughout the Vadose Zone	Consequences of Pattern
A	16 of 28	Hydrocarbons in soil gas.	Adequate concentrations of oxygen in shallow soil gas, but not enough oxygen in deep soil gas to support biodegradation of hydrocarbons.	Depth distribution of hydrocarbons matches Figure 2.1. Conceptual model of this approach is appropriate to site.
B	5 of 28	Hydrocarbons in soil gas.	Concentrations of oxygen are adequate to support degradation of hydrocarbons.	Conceptual model of this approach is appropriate to site.
C	3 of 28	Hydrocarbons in soil gas.	Concentrations of oxygen are not adequate to support degradation of hydrocarbons.	Conceptual model of this approach is not appropriate to site. The approach should not be used.
D	4 of 28	No hydrocarbons detected in soil gas.	Concentrations of oxygen are adequate to support degradation of hydrocarbons.	Not enough information to apply the approach. If detection limits are below screening levels, no reason to apply the approach.

If a site matches patterns A or B, the concentrations of a hydrocarbon of concern that leave the subsurface and can intrude into a building are controlled by a number of factors. The primary control is the rate constant for biodegradation of the hydrocarbon in the aerobic zone. The extent of biodegradation is a function of the rate constant and the residence time of the hydrocarbon in the aerobic zone. The residence time is controlled, in turn, by the length of the diffusion path in the aerobic zone. The length of the diffusion path is controlled by the depth of the reaction zone. The depth of the reaction zone is controlled by the balance between the flux of oxygen from the surface and the flux of oxygen demand associated with the hydrocarbons. As a result, the depth of the reaction zone is controlled by the separation distance between the source of the vapors and the upper boundary on the soil and by the strength of the oxygen demand. Finally, the strength of the oxygen demand is controlled by the concentrations of the hydrocarbons in soil gas at the source.

DeVaull (2007) developed algebraic equations that described the behavior of hydrocarbons as depicted in Figure 2.1. His equations locate an intermediate point between the source of vapors and the atmosphere (or the receptor), where the diffusion of oxygen to that point is balanced by the diffusion of oxygen demand from the source of hydrocarbon vapors. In soil gas above this intermediate point, the concentrations of oxygen should be adequate to support aerobic biodegradation of petroleum hydrocarbons.

The actual concentration of an individual hydrocarbon will be controlled by the interaction between diffusion of the hydrocarbon along a concentration gradient from the source to the receptor and degradation of the hydrocarbon at each point along the concentration gradient. This interaction leads to complexity. Degradation changes the concentration gradient. The gradient controls residence time along the diffusion flow path, which, in turn, controls the extent of degradation.

Figure 2.2 compares the distribution of concentrations of benzene in soil gas in aerobic sediment to the distribution that would be expected if there was no biodegradation and the distribution was only controlled by diffusion along the concentration gradient. Data are taken from the VW-10 location at the Hal's Chevron

Site in Green River, Utah (U.S. EPA, 2014b; Wilson et al., 2009). All the soil gas samples had adequate oxygen to support aerobic biodegradation.

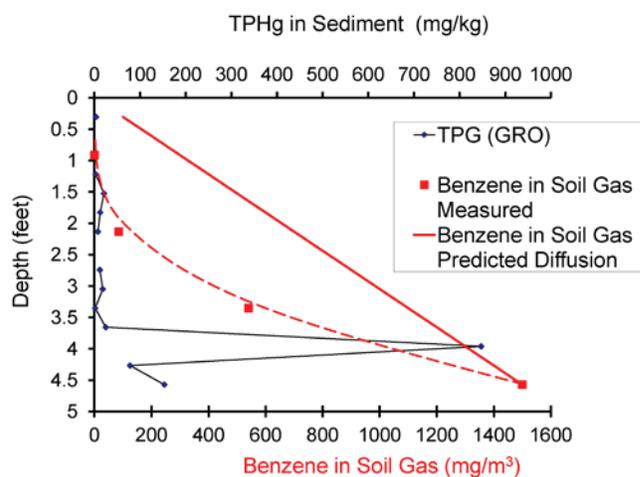


Figure 2.2. Comparison of benzene in soil gas to the distribution expected from diffusion along a concentration gradient.

The expected redistribution of benzene from diffusion follows a straight line. The actual concentrations of benzene were substantially lower and followed a curved distribution.

As a general observation, the distribution of concentrations of individual hydrocarbons along a diffusion path in aerobic soil or sediment follows a first order rate law of concentration on distance (Johnson, et al., 1999). This interaction is illustrated in Figure 2.3. Data are taken from the Coachella Site COA-2 as evaluated by Ririe et al. (2002).

The concentrations of oxygen declined as depth increased and the concentrations of oxygen followed a linear distribution with depth. In contrast, the concentrations of benzene increased as depth increased. The logarithm of the concentration of benzene followed a linear relationship with depth. As the benzene diffuses toward the surface, for a given length in the diffusion path, a constant fraction of the benzene vapors that are present at that depth are removed.

If Z_o is the concentration of benzene at the deepest depth interval where the concentrations of oxygen are adequate for biodegradation and Z is some shallower

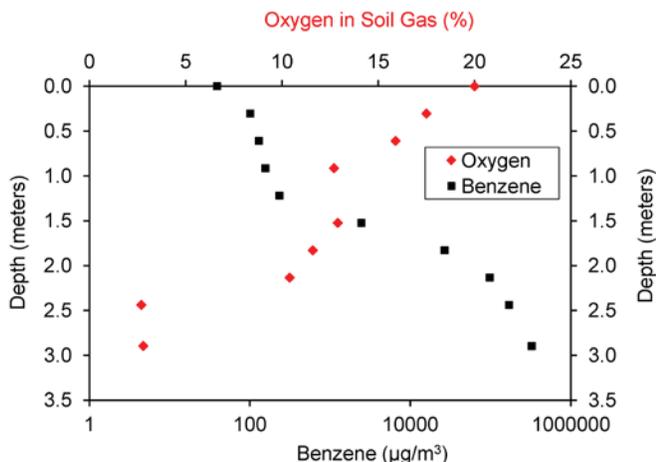


Figure 2.3. Inverse distribution of oxygen and benzene in soil gas (Coachella Site COA-2 in Ririe et al., 2002).

depth, then the length of the diffusion path in the aerobic zone is Z minus Z_0 . If the concentration of benzene in soil gas at depth Z_0 is C_0 and the concentration at depth Z is C , then the attenuation in concentration of benzene between Z_0 and Z is C/C_0 . If attenuation in concentration with depth follows a first order law, then:

$$(Z - Z_0) \text{ is proportional to } \ln\left(\frac{C}{C_0}\right).$$

Therefore,

$$L * \ln\left(\frac{C}{C_0}\right) = (Z - Z_0)$$

or

$$L = (Z - Z_0) / \ln\left(\frac{C}{C_0}\right)$$

where L is a proportionality constant (Johnson et al., 1998; Johnson et al., 1999; DeVaul, 2011).

The data in Figure 2.3 are re-plotted in Figure 2.4. Because there was adequate oxygen in the deepest sample, the deepest sample is Z_0 . The depth of the sample is expressed as the distance above Z_0 .

The value of L was estimated as the slope of a linear regression of the length of the diffusion path length on the natural logarithm of concentration of benzene in soil gas. In this case, the value of L is -0.29 meters. Because the value of L is negative, the concentration of benzene declines as the distance above Z_0 increases. For every increase in distance above Z_0 equal to L , the concentration of benzene declines by a factor of 2.7.

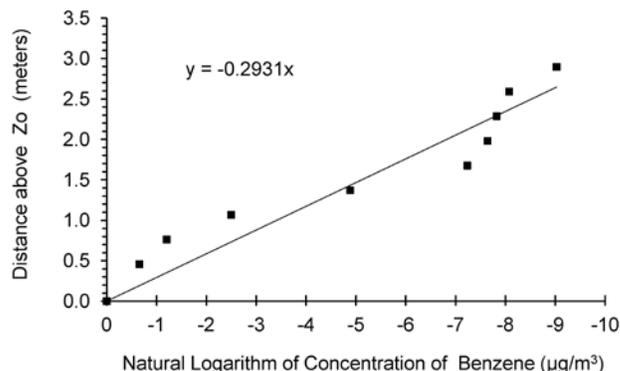


Figure 2.4. Relationship between the length of the diffusion path in the aerobic zone and the reduction in concentrations of benzene in soil gas (data from Coachella Site COA-2 in Ririe et al., 2002).

If data are available on the distribution of concentrations of hydrocarbons with depth, a fitted value for the proportionality constant L can be used to extrapolate a concentration that would be expected in soil gas in contact with the foundation of a building. However, such data are rarely available.

DeVaul (2007) defines the proportionality constant L as an aerobic diffusive reaction length (L_R). By making reasonable assumptions, DeVaul showed that:

$$L = L_R = \sqrt{\frac{D_{eff} * H}{k_w * \theta_w}} \quad \text{Equation 2.1}$$

where D_{eff} is the effective diffusion coefficient, H is the Henry's Law Constant (concentration in air divided by concentration in water), K_w is the first order rate constant for biodegradation of the hydrocarbon of interest in the water phase, and θ_w is the water filled porosity. DeVaul used the relationship of Jury et al. (1983) to estimate D_{eff} from the molecular diffusion coefficients in air and in water, the Henry's Law Constant and the total and water filled porosity.

Values for the aerobic diffusive reaction length (L_R) are particularly sensitive to the air filled porosity. As part of a sensitivity analysis, DeVaul (2007) compared values for aerobic diffusive reaction length (L_R) in

soil with high and low total porosity and high and low water content. See Table 2.2.

Values for L_R varied over an order of magnitude. A smaller value of L_R corresponds to more rapid attenuation. The upper range of the calculated L_R for benzene (26 cm) is in reasonable agreement with the value of L for benzene that was fit to the distribution of benzene in soil gas in Figure 2.4 (29 cm).

Although the alkylbenzenes and aliphatic hydrocarbons differ greatly in their physical properties and the rate constant for their biodegradation, the calculated values for L_R are similar. This can be explained by the off-setting influence of these properties.

The rate constant for biodegradation of the alkylbenzenes in the pore water of the sediment is one hundred fold slower than the rate constant for the aliphatic hydrocarbons. However, degradation can only happen to hydrocarbons that are dissolved in water and the Henry's Law constant for aliphatic hydrocarbons is approximately two hundred fold higher. If there were equivalent amounts of the compounds in the sediment, the concentrations of aliphatic hydrocarbons in water would be two

hundred fold lower. As a result, the estimated aerobic diffusive reaction lengths (L_R) for aliphatic hydrocarbons are only about 70% longer than for aromatic hydrocarbons. It is reasonable to expect the aromatic hydrocarbons and aliphatic hydrocarbons to be degraded concomitantly as they diffuse upward from the source of contamination.

This simple conceptual model makes it possible to estimate the concentration of a particular hydrocarbon that would leave the upper boundary of the soil and be available to intrude into a building knowing only (1) the separation distance between the source and the receptor at the upper boundary, (2) the concentration of the particular hydrocarbon of concern at the source, (3) the concentration of all of the other hydrocarbon vapors in the soil gas at the source, and (4) the rate constant for biodegradation of the particular hydrocarbon in the aerobic zone.

Table 2.2. Range of values expected for the aerobic diffusive reaction length (L_R). Data from DeVaul (2007).

Compound	D_{eff}	H	Mean K_w	L_R
	cm ² sec ⁻¹	dimensionless	hr ⁻¹	cm
Benzene	0.00097-0.026	0.23	0.79	2.1 - 26
Toluene	0.00097-0.026	0.28	0.79	2.3 - 29
Ethyl benzene	0.00083-0.022	0.33	0.79	2.4 - 29
Xylenes	0.00079-0.021	0.22	0.79	1.9 - 23
EC* > 5-6 aliphatic hydrocarbons	0.0011-0.029	51	71	3.6 - 44
EC > 6-7 aliphatic hydrocarbons	0.0011-0.029	54	71	3.7 - 45
EC > 7-8 aliphatic hydrocarbons	0.0011-0.029	56	71	3.8 - 46
EC > 8-9 aliphatic hydrocarbons	0.0019-0.051	59	71	3.9 - 47

*Equivalent Carbon number based on boiling point.

2.2 Rates of Biodegradation in Aerobic Geological Material

DeVaul (2007) collected and collated first order rate constants for biodegradation of fuel hydrocarbons in water. Recently, DeVaul (2011) provided an expanded collection of rate constants. See Figure 2.5. Notice the vertical orange bar. Most of the rate constants for aerobic biodegradation of aromatic hydrocarbons in groundwater are within an order of magnitude of each other. The rate constants for degradation of the alkanes were higher.

The average rates in the expanded data set in DeVaul (2011) are approximately two fold lower than the rates in DeVaul (2007). However, the general relationships hold. The first order rate constants for degradation of the aromatic hydrocarbons in water were consistent with each other. There was useful agreement between rates for degradation of benzene. The lowest rate constant of 41 rate constants was only an order of magnitude lower than the geometric mean and median of the rate constants. The rate constants for alkanes are one to two orders of magnitude higher than the rates of degradation of the aromatic hydrocarbons.

Results: Aerobic Petroleum Biodegradation Rates in Soil

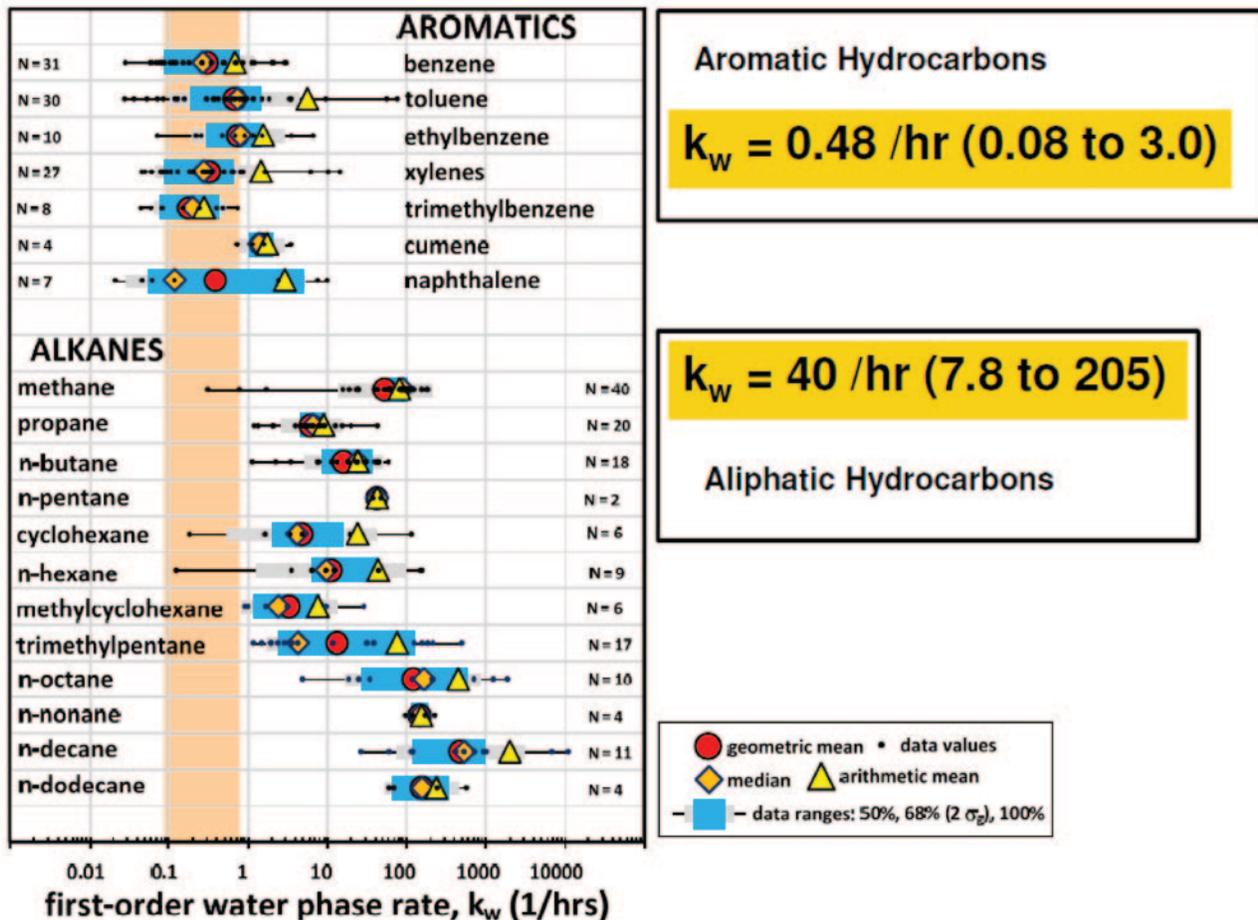


Figure 2.5. Range, median, geometric mean and arithmetic mean of rate constants for biodegradation of fuel hydrocarbons in soil and sediment.

2.3 Effect of Building Size on the Distribution of Oxygen in Unsaturated Zone

If a large building has a foundation that is slab-on-grade, the foundation may reduce the access of oxygen from the atmosphere to the unsaturated zone, and reduce aerobic biodegradation of hydrocarbon vapors in the unsaturated zone. Any area below the slab with concentrations of oxygen that are too low to support biodegradation is in an oxygen shadow of the slab. The restriction of the supply of oxygen would increase the possibility of petroleum vapor intrusion. Under a contract with U.S. EPA, Abreu et al. (2013) used a three dimensional computer model to evaluate the importance of the size of the slab on the vertical separation distance that was necessary adequate oxygen to support aerobic biodegradation of petroleum hydrocarbons. The following is from page 40 of their report.

At the highest vapor concentration modeled in this report (10,000,000 $\mu\text{g}/\text{m}^3$):

- *An oxygen shadow developed within one year beneath a small building 33 ft x 33 ft (10 m x 10 m) with a shallow 5 ft (1.6 m) vadose zone*
- *An oxygen shadow developed within one year beneath a medium size building 98 ft x 98 ft (30 m x 30 m) with a moderate thickness vadose zone 15 ft (4.6 m)*
- *An oxygen shadow did not develop under a building with dimensions of 66 ft x 66 ft (20 m x 20 m) with a moderate thickness vadose zone 15 ft (4.6 m) even after a simulated transport time of 20 years*

A vapor concentration of 10,000,000 $\mu\text{g}/\text{m}^3$ is high. This concentration of total hydrocarbons would only be expected in soil gas in contact with NAPL hydrocarbons or soil gas above ground water in contact with NAPL. The recommended vertical separation distance above NAPL in the [Draft] *Technical Guide For Addressing Petroleum Vapor Intrusion At Leaking Underground Storage Tank Sites* (U.S. EPA, 2013b) is 15 feet. Based on the modeling of Abreu et al. (2013), the recommended separation distance is appropriate for

a conventional residential house or a small commercial building with the same dimensions.

The approach taken in this Issue Paper assumes that oxygen will be available for aerobic biodegradation of hydrocarbons in the unsaturated zone below a building. The approach is intended for a building of the size of a typical residential house (66 ft x 66 ft or 20 m by 20 m). It is not intended for large commercial buildings.

The model results suggest a potential concern with large buildings. However, model results have not been verified against a reasonable number of case studies. The models may not adequately account for processes that allow oxygen transport across large foundations. Because there is little field data to evaluate how large buildings affect oxygen distribution, it would not be appropriate to apply the evaluation approach to large buildings at this time.

3.0 MODELS AVAILABLE TO EVALUATE PETROLEUM VAPOR INTRUSION

Environmental models are based on the application of mass conservation principles to transport and transformation of quantities in the environment. Generally, all environmental models are based on a two-part conceptualization: an empirically-determined principle relating chemical, physical and biological quantities, and empirical coefficients. Taken together, these two components have the potential for representing transport and transformation of petroleum vapors in the vadose zone below a building.

Although vapor intrusion models may represent important processes, the ability to determine definitively that there are no vapor impacts to buildings (“screen for PVI”) also depends on application-related factors. These factors include the degree to which the site conceptual model matches the structure of the mathematical model, the inherent limitations imposed by the assumptions in the mathematical model, the values chosen for input parameters, and the ability to calibrate the mathematical model to site conditions.

In the approach taken in this Issue Paper, the concentration of a chemical is measured in soil gas at

the source of contamination. Then a mathematical model is used to forecast a concentration of the chemical in air in a building. To complete the evaluation, the predicted concentration is compared to a regulatory standard.

The regulatory standard is a fixed number that is specified by the appropriate regulatory authority. However, there is uncertainty associated with the forecast of the model. There is uncertainty in the chemical analysis of the soil gas; however, this uncertainty is usually not important. There is uncertainty in whether the sample that was collected and analyzed was representative of the soil gas at the source of vapors. Section 4 discusses this contribution to uncertainty in some detail. Finally, there is uncertainty in the assumptions made in the mathematical model compared to the real, but unknown, situation. This is the greatest source of uncertainty. One way to deal with this uncertainty is to perform an uncertainty analysis on the assumptions in the model.

The most commonly used mathematical models for vapor intrusion are modifications of the Johnson and Ettinger model (Johnson and Ettinger, 1991). However, these models do not explicitly evaluate the contribution of aerobic biodegradation of compounds in soil gas. These models were not written around the conceptual model presented in Section 2. This section describes three mathematical models that were designed to predict the biodegradation of petroleum hydrocarbons in soil gas, and incorporate the contribution of biodegradation into a prediction of vapor intrusion. These models are the BioVapor model (API, 2012), the PVIScreen model (U.S. EPA, 2014g) and the Abreu Three Dimensional Model (Abreu et al., 2009a,b).

The BioVapor model is set up from default parameters. If the user has site specific data that is different from the default assumptions, the user can update the model. The user can also change the assumed value for parameters for which there are no data, and conduct a sensitivity analysis. The user must run each simulation in the sensitivity analysis separately.

The PVIScreen model shares a similar theoretical structure with BioVapor. However, instead of being set up with a discrete value for each parameter, it is set

up with a range of values or a frequency distribution of values for many of the parameters. Individual values for the parameters are selected at random in a Monte Carlo simulation. One thousand separate simulations are performed. The PVIScreen model automatically performs the sensitivity analysis and reports the most probable concentration of a chemical in indoor air and the percent of the simulations that exceed the regulatory standard that is specified by the user.

The BioVapor model and the PVIScreen model are publically available at no cost to the user. They are supported by a user's manual. A user can learn to run the models in a few hours to a day. Each model run takes at most a few seconds.

BioVapor or PVIScreen can only simulate the behavior of hydrocarbons in the vertical dimension. The Abreu Three Dimensional Model (Abreu et al., 2009a,b) simulates the effects and interactions in three dimensions. As a result, it can simulate the effect of a building on the access of oxygen from the atmosphere to the hydrocarbons in the subsurface below the building. Although the Abreu Three Dimensional Model is more capable than the BioVapor model or the PVIScreen model, it is more complex than BioVapor or PVIScreen. It is not intended for users other than its developers and it is not publically available.

Representative simulations made with the Abreu Three Dimensional Model are published in Abreu et al. (2009a) and U.S. EPA (2012). Figures and data tables provided in Abreu et al. (2009a) are provided in this Issue Paper as figures. A user can compare the figures to identify the particular simulation that most closely describes the conditions at the user's site. The figures allow the user to predict a value for the attenuation factor between soil gas and indoor air knowing only the separation distance between the building and the source of vapors and the concentration of hydrocarbon vapors in the soil gas at the source of contamination. To complete the exposure evaluation, the user multiplies the measured concentration of benzene or other chemical in soil gas by the attenuation factor to estimate the concentration in indoor air. It is not necessary to know anything about the model or the process of implementing the model to use the figures. However, there is no mechanism to evaluate the uncertainty in the model simulations.

3.1 BioVapor

BioVapor is a spreadsheet model that runs in EXCEL®. It is based on the conceptual model described in Section 2 and in particular the equations of DeVaul (2007). The model provides a simulation of a steady state one-dimensional distribution of hydrocarbons from the source of hydrocarbon vapors to indoor air in a building sited above the source of hydrocarbon vapors. BioVapor does not directly account for spatial or temporal variation in the input parameters. As a result, one run of the model with one set of input parameters should not be expected to provide an accurate prediction of the actual behavior of petroleum vapors at a site. The user is expected to perform a sensitivity analysis, to set up the model for a reasonable range of input parameters and compare the range of predicted indoor air concentrations to the appropriate regulatory standards.

The model has input screens for **Environmental Factors**, for **Chemicals**, for **Chemical Concentrations**, and for a **Chemical Database** (Figure 3.1).

Environmental Factors include assumptions about the supply of oxygen, exposure and risk factors, building parameters and vadose zone (unsaturated zone) parameters. The user can describe the supply of oxygen three ways. The user can specify (1) a concrete slab-on-grade foundation or a basement with a concrete slab in contact with the soil, or (2) specify bare soil as would be the case with a pier-and-beam foundation or a basement with an earthen floor, or (3) the depth of the aerobic zone below a building.

The user can accept defaults or input particular values for **Exposure and Risk Factors** for inhabitants of a building, including the target hazard quotient for

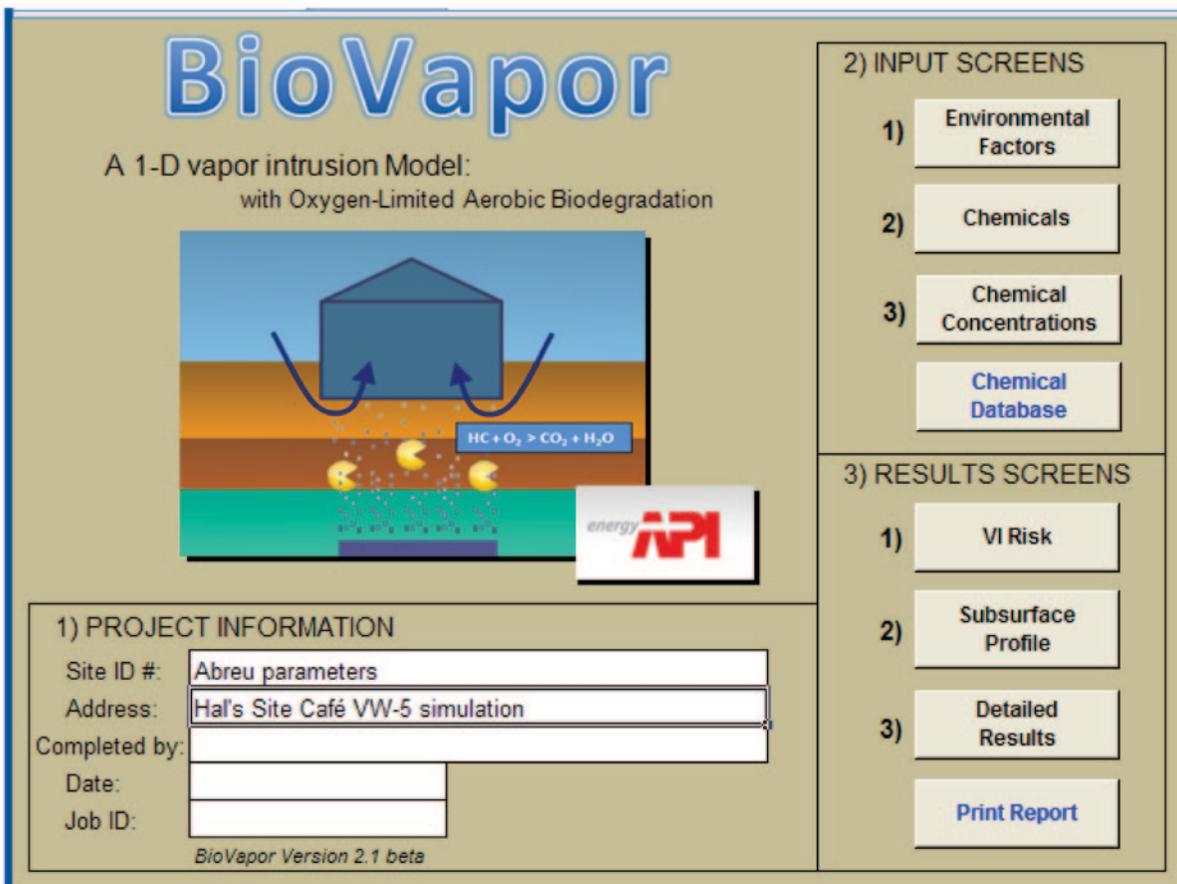


Figure 3.1. Screen capture of the opening screen of BioVapor.

individual chemicals, the target excess individual lifetime cancer risk, the carcinogen averaging time, the non-carcinogenic averaging time, the body weight of an adult, the exposure duration, the exposure frequency and the indoor inhalation rate exposure adjustment.

The user can accept default parameters or input particular values for **Building Parameters** that include the indoor mixing height, the air exchange rate, the foundation thickness, the foundation area, the foundation crack fraction, the total porosity of soil-filled cracks, the water-filled porosity of soil-filled cracks and the airflow through the basement foundation. These parameters are further described and defined in the User's Guide (API, 2012).

Finally, the user can accept default parameters or define values for **Vadose Zone Parameters** including soil porosity, soil water content, soil organic carbon fraction, soil bulk density, air flow under the foundation, depth of the aerobic zone under the foundation, oxygen concentration under the foundation, annual mean temperature, baseline rate of soil oxygen respiration, the depth to the source from the bottom of the foundation and the minimum oxygen concentration required for aerobic respiration. At other places in this Issue Paper, the depth of the source from the bottom of the foundation is termed the separation distance.

The input screen for **Chemicals** requires the user to identify the chemicals in ground water or chemicals in soil gas that act as the source of vapors. The user identifies the chemicals that are potential risk drivers, such as benzene, that will be compared to standards. The user also identifies other individual chemicals, such as pentane, that are not regulated compounds but which contribute to the oxygen demand of the chemicals in the soil gas. Finally, the user identifies classes of chemicals that might contribute to oxygen demand, such as, total petroleum hydrocarbons in the range of gasoline (TPH-GRO C6-C10).

The input screen for **Chemical Concentrations** requires the measured concentration of each individual chemical or class of chemicals that was specified in input screen **Chemicals**.

Calculations in BioVapor draw from a **Chemical Database**. The user can edit or modify individual properties for a chemical such as the first-order rate constant for biodegradation or the Henry's Law constant.

BioVapor has an output screen for Vapor Intrusion **VI Risk** (Figure 3.2). The output includes the **Source-to-Indoor Air Attenuation Factor**, the **Predicted Indoor Air Concentration**, the **Hazard Quotient**, and the **Risk Level** for exposure to indoor air containing the chemical of concern.

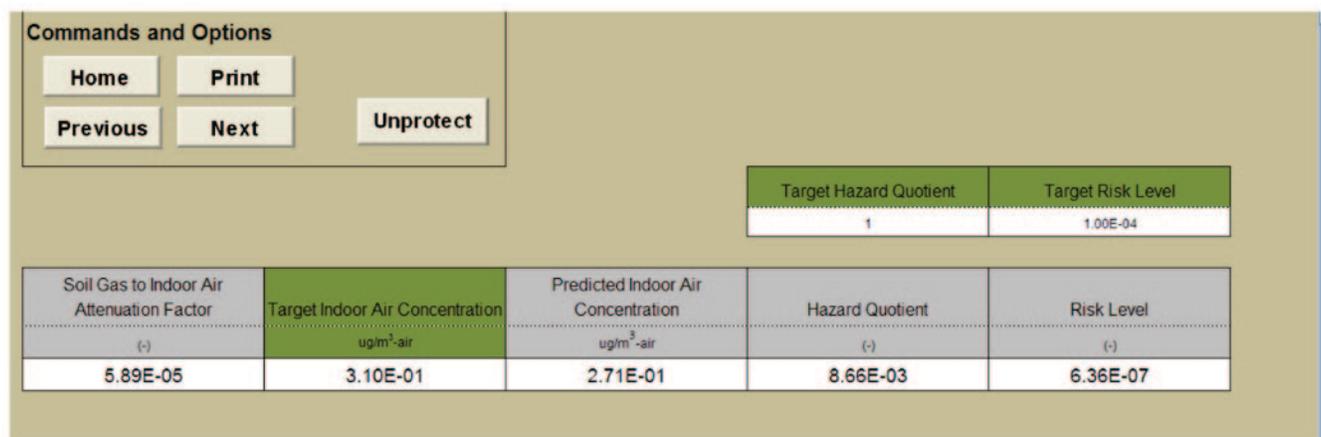


Figure 3.2. Screen capture of the VI Risk output screen of BioVapor.

There is also an output screen that provides a **Subsurface Profile** comparing the concentrations oxygen and the chemicals with depth (Figure 3.3).

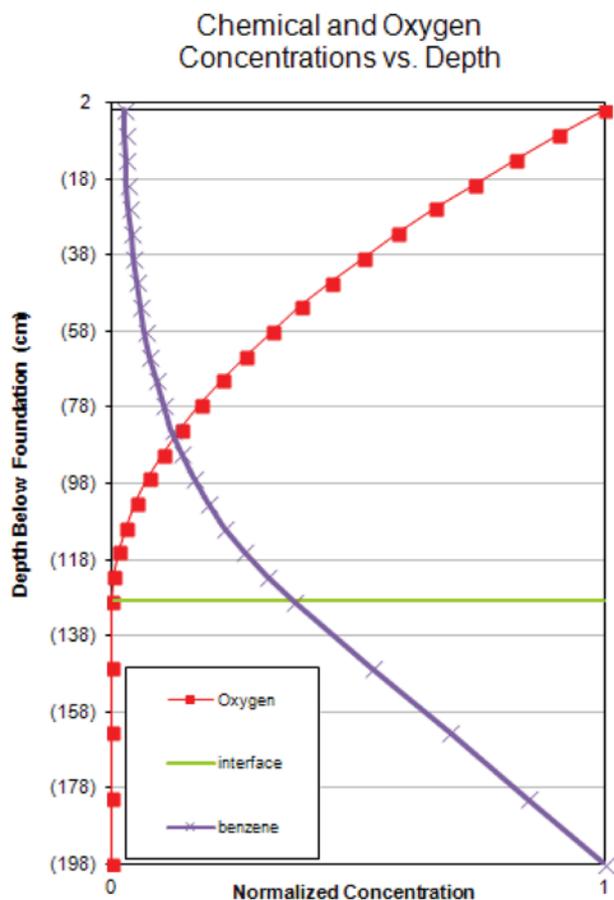


Figure 3.3. Screen capture of the **Subsurface Profile** output screen of BioVapor.

There is also a screen with **Detailed Results** including the depth of the aerobic zone, the indoor air attenuation factor to be expected when there is no biodegradation, and the flux of the chemical into the building.

As applied in this Issue Paper, BioVapor simulations were set up using the **Residential Default Values** on the **Environmental Factors** input screen with the following expectations. **Airflow under Foundation** (Q_f) was set to be equal to **Air Flow Through Basement Foundation** (Q_s). The value was 83 cm³ of air per second. The **Air Exchange Rate** was set to 12 per day. The default rate constant for biodegradation of benzene in BioVapor is 0.79 per hour. The rate

constant in the **Chemical Database** (row 14, column U) was changed to 0.079 per hour. These parameters were altered from the default values to produce simulations that were conservative forecasts of the expected concentrations of benzene in indoor air. Simulations made with these values for the parameters are called BioVapor Generic simulations. If the values for water content or content of soil organic matter in the **Environmental Factors** input screen were altered to reflect site specific knowledge, the simulations were termed BioVapor Site Specific.

The list of **Environmental Factors** illustrates both the strength and weakness of BioVapor or any other mathematical model that attempts to forecast the concentration of a vapor from soil gas in indoor air. The list of parameters is comprehensive and includes many factors that are known to influence PVI. However, site specific values for many of these parameters will not be available at any particular site. The models must be set up with a large number of assumed values.

3.2 PVIScreen

The PVIScreen model was created by staff of U.S. EPA/ORD to address uncertainty in model parameters. Because uncertainties in parameters are unavoidable, PVIScreen is designed to always perform an uncertainty analysis. The PVIScreen model incorporates the uncertainty in the output from a model into the process of comparing the output from a model to a regulatory standard.

As of this writing (March 2014), PVIScreen is in the process of peer review and clearance. When it is cleared for distribution, it will be available on an EPA website.

PVIScreen extends the concepts of BioVapor by

- implementing an automated uncertainty analysis,
- linking directly to a fuel leaching model,
- providing the capability to use a flexible unit conversion system,
- displaying key risk outputs directly with model results, and
- providing an automatically-generated model application report.

3.2.1 Uncertainty Analysis in PVIScreen

Uncertainty analysis, as used here, includes the impact of the inherent sensitivity of the model to changes in parameter values and the actual magnitude of those changes. The method used in PVIScreen is to presume that selected parameters of the model are uncertain and then use Monte Carlo simulation to combine different values for parameters in multiple runs of the model. To accomplish this task, the model is provided with ranges of values for each parameter or a frequency distribution of values for each parameter. For each set of inputs, PVIScreen runs 1,000 simulations and then builds frequency distributions of the model outputs.

Prime examples of unmeasured parameters are the biodegradation rates, the building air exchange rate, the flow of air from the soil into the building, the foundation crack width, and soil moisture. PVIScreen allows these parameters to be defined by a range (minimum and maximum) or a statistical distribution (Table 3.1). Parameters indicated as following a uniform distribution increase uniformly from the minimum value (cumulative frequency of 0) to the maximum value (cumulative frequency of 1). The moisture content for example ranges from 0.05 to 0.20 for these examples. Frequency distributions defined by more than two points are used for the biodegradation rates which were obtained from DeVaul (2007 and 2011).

The PVIScreen model was set up using a combination of site specific values for the examples that follow and ranges for parameters which would reasonably not be expected to be determined for the site (Table 3.1). In particular the values for the air exchange rate, crack width, and advective flow into the building (“Qsoil”) are taken from previous OSWER guides. The other parameters appearing in the table are based on site-specific measurements for the field cases.

The biodegradation rates are automatically considered to follow the distributions developed by DeVaul (2007 and 2011). Although the actual distributions used by PVIScreen consist of multiple points, the rate constants range from 0.028 per hour to 3.0 per hour for benzene, 7.1 per hour to 710 per hour for TPH by TO-15, and 0.31 per hour to 190 per hour for methane. The data on the rate constants for biodegradation of benzene, TPH and methane are presented in Figure 3.4.

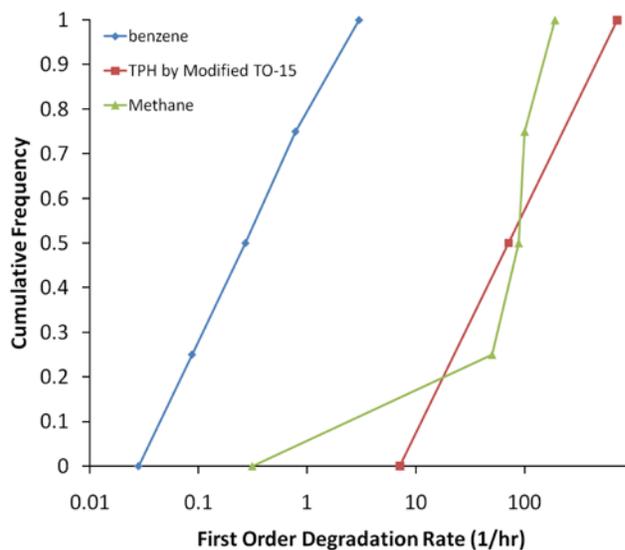


Figure 3.4. Cumulative frequency distributions for the first order degradation rate constants.

Table 3.1. Parameters in PVIScreen that are constants or are uniformly-distributed parameters.

Parameter	Distribution	Values	Unit
MoistureContent	Uniform	0.05	dimensionless
		0.2	dimensionless
Porosity	Uniform	0.3	dimensionless
		0.35	dimensionless
FractionOrganicCarbon	Uniform	0.005	dimensionless
		0.015	dimensionless
SoilTemperature	Uniform	10	c
		15	c
AirExchangeRate	Uniform	0.1	1/hr
		1.5	1/hr
CeilingHeight	Uniform	8	ft
		12	ft
Width	Constant	30	ft
Length	Constant	30	ft
FoundationDepthBelowGrade	Constant	8.5	ft
FoundationThickness	Uniform	6	in
		8	in
dirt floor	no		
CrackWidth	Uniform	0.5	mm
		5	mm
Qsoil	Uniform	1	L/min
		10	L/min
DiffusionInAir	Constant	0.175	cm ² /s
DiffusionInWater	Constant	1.70E-05	cm ² /s
SurfaceConcentration	Constant	2.89E+05	mg/m ³
MinimumBiodegradationConcentration	Constant	1.38E+04	mg/m ³

3.2.2 Running PVIScreen

In PVIScreen, the building, vadose zone and aquifer are defined in a layout which relates the bottom of the foundation to a zone of petroleum contamination. Typically, the source of contamination is a region that contains contaminated soil gas or a separate-phase hydrocarbon (NAPL- or non-aqueous phase liquid). Input parameters describe the size and characteristics of each component in the model and PVIScreen

adjusts and annotates the site schematic depending on the inputs (Figure 3.5).

The Opening Screen of PVIScreen (Figure 3.6) has buttons that direct the user to Select Input, View/Edit Input, Run PVIScreen, Schematic, Results, Report, About, and Exit. The buttons are enabled in sequence to direct the user through the necessary steps for running the model.

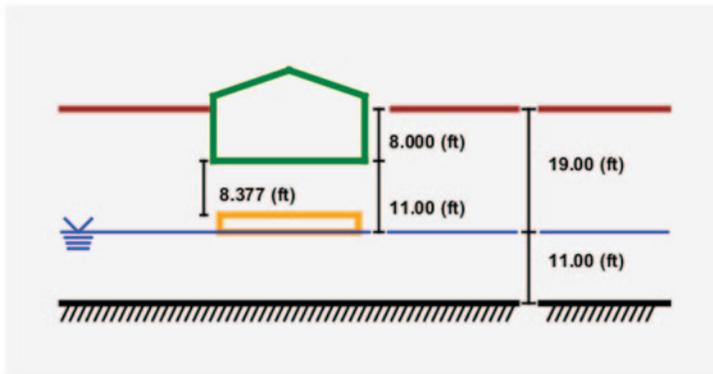


Figure 3.5. PVIScreen site schematic for a NAPL source directly beneath a building.

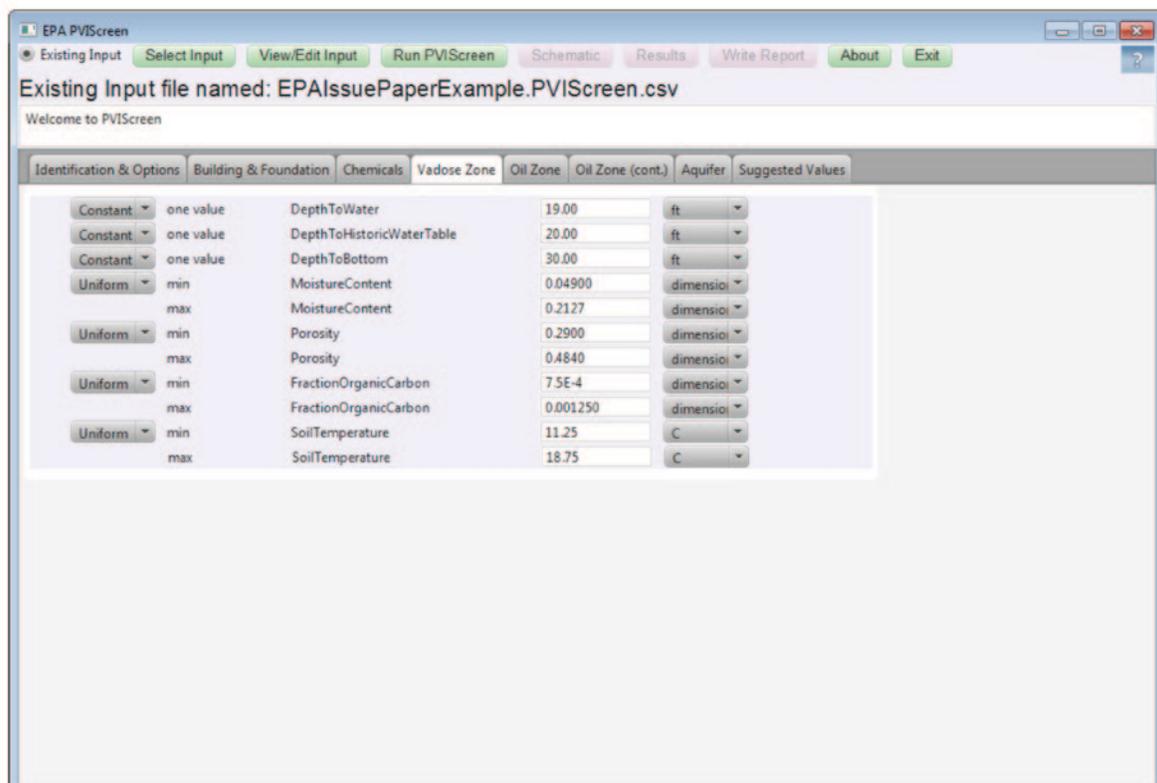


Figure 3.6. Screen capture of PVIScreen, showing the tabs that give the user access to set up the model and tabs to access the output of the model.

After completing all required runs of the model, the results are processed into output probability curves for each chemical specified to be in the soil gas. These output probability curves, along with risk levels, are the main outputs of the model. There is a tab for each chemical in the soil gas.

Figure 3.7 provides the output of the predicted concentrations of benzene in indoor air from an example PVIScreen simulation. The example simulation used concentrations of benzene and other hydrocarbons that would be expected to be in soil gas in contact with NAPL. The chart is in the tab that presents the output for benzene concentrations in indoor air. The x axis is the base-10 logarithm of the concentration of benzene in indoor air, where concentration is in $\mu\text{g}/\text{m}^3$. The y axis is the relative frequency of that concentration.

Notice the grey line at the bottom of the figure. This is the probability density function of the predicted concentrations of benzene. It is analogous to the

familiar bell curve that describes the normal or Gaussian distribution. The concentration that occurs at the highest frequency is the most probable concentration. This is the concentration at the top of the curve that is marked with the “M”. The value of that most probable result is $0.2371 \mu\text{g}/\text{m}^3$. The base-10 logarithm of 0.2371 is -0.625 , as is plotted on the x-axis in the figure. As the concentrations become progressively higher than $0.2371 \mu\text{g}/\text{m}^3$ or progressively lower than $0.2371 \mu\text{g}/\text{m}^3$, they are less frequent.

The multicolored line in Figure 3.7 is the cumulative frequency distribution. It is the frequency of all concentrations that are equal to or less than the concentration that is plotted on the x-axis. The cumulative frequency distribution starts low and increases as more values are added. PVIScreen truncates the curve below an indoor air concentration of $10^{-4} \mu\text{g}/\text{m}^3$. When all the values are included the frequency is 1.0 or 100%. The cumulative probability curve is color coded for the probability that the

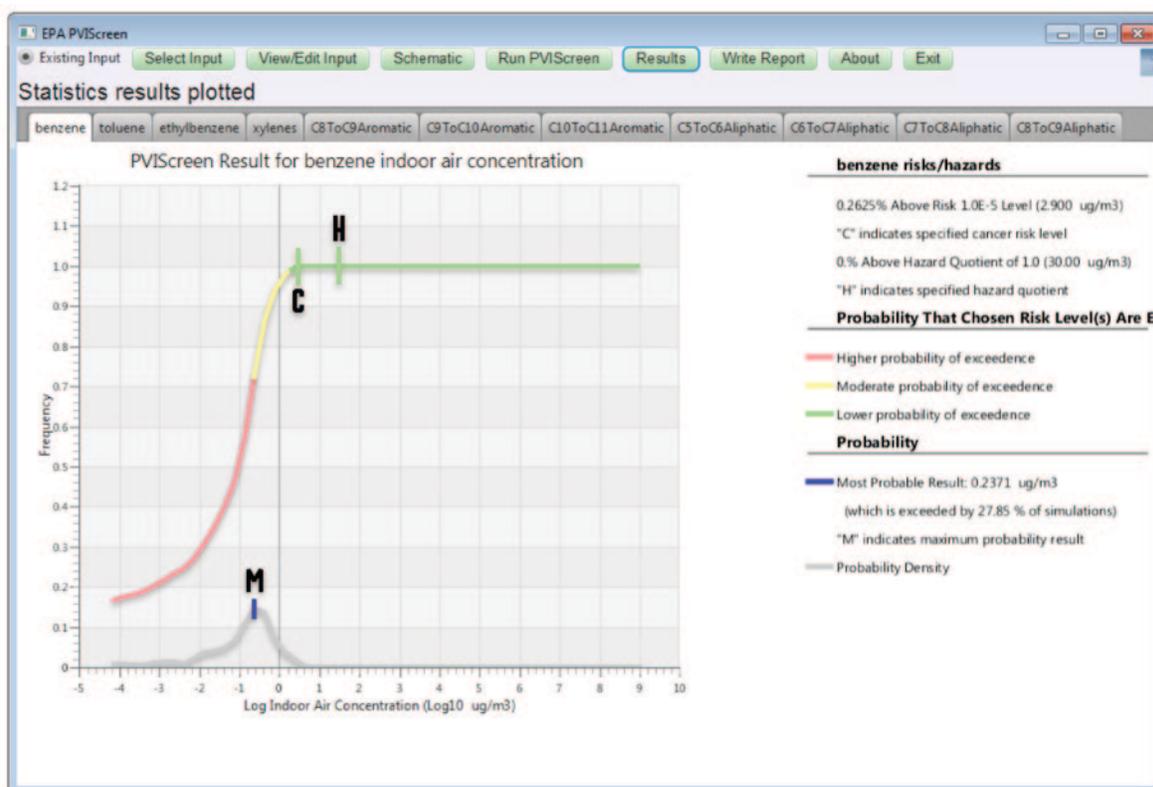


Figure 3.7. Screen capture of PVIScreen, showing results for benzene. “M” indicates the most probable PVIScreen result, “C” and “H” indicate the specified cancer risk and non-cancer hazard levels, respectively.

selected value of C or H will be exceeded in the cumulative distribution. The probability of exceeding the value of C or H is the probability of error in saying that there is no risk of death from cancer or acute disease. If C or H falls into the portion that is coded green, the probability of error is low. If C or H falls into the portion coded yellow, the probability is moderate, and if C or H falls into the red, the probability is high.

When this particular PVIScreen simulation was set up, the acceptable risk of dying from cancer due to exposure to benzene in indoor air was set at 1 in 100,000 (1.0E-05 or ten to the minus five risk level). This corresponds to a benzene concentration of $2.9 \mu\text{g}/\text{m}^3$, which is the mid-point of the inhalation exposure for carcinogenic risk specified in the EPA's Integrated Risk Information System (IRIS). This concentration is marked with a green vertical line segment on the cumulative frequency distribution. The segment is labeled C. Under the circumstances defined in the input to PVIScreen for this simulation, 0.2625% of the Monte Carlo runs exceeded $2.9 \mu\text{g}/\text{m}^3$. The uncertainty analysis indicates that there should not be a risk of cancer from benzene in indoor air (The Most Probable Result of $0.2371 \mu\text{g}/\text{m}^3$ is less than the acceptable risk level of $2.9 \mu\text{g}/\text{m}^3$). The chance of error in that determination is 0.3%.

The vertical green line labeled H is the concentration of benzene ($30 \mu\text{g}/\text{m}^3$) that corresponds to the Hazard Quotient that was specified in the input. As noted in the legend, none of the Monte Carlo simulations exceeded $30 \mu\text{g}/\text{m}^3$. The uncertainty analysis indicates that there should not be a risk of an acute hazard from benzene in indoor air. Because 1000 runs were included in the simulation, the chance of error in that determination is less than 0.1%. Because the most probable concentration (the vertical blue line mentioned above) is well below both the cancer and hazard levels, there is additional confidence in the determination that this case presents low risk.

PVIScreen automatically produces a report which

- describes the model,
- shows the physical layout for the simulation,
- ranks the input chemicals for cancer and non-cancer risks, and

- repeats the input data.

Figure 3.8 presents a screenshot of a portion of the report that is automatically generated for each simulation. In addition to the sections pictured in the figure on **PVIScreen Background and Run Identification**, the report also contains sections on **Site Description, Risk Results, Input Data, and Chemical Input Data**.

The report is written in standard hypertext markup language (HTML) and is displayed in a browser. PVIScreen displays the report if possible; otherwise it directs the user to the location of the report. Browser names and their directories can be loaded into an input file to assure PVIScreen can display the report.

3.3 Abreu Three-Dimensional Model

Lilian Abreu created a complex three-dimensional computer model of petroleum vapor intrusion that can be used to evaluate the role and contribution of the important properties of the building, as well as the behavior of the hydrocarbons in soil gas beneath and beside the building (Abreu and Johnson, 2005; Abreu and Johnson, 2006; Abreu et al., 2009a; Abreu et al., 2009b; Abreu et al., 2013). The model is not available to the public, and does not have a name. For convenience, it will be called the Abreu Three-Dimensional Model in this Issue Paper. Abreu et al. (2009b) is the most extensive presentation of simulations using the model.

The model is a numerical code that solves equations for transport and reaction of oxygen and hydrocarbons in three-dimensional space. It considers advective flow of air and diffusion in soil gas and soil water. The model considers the dimensions of the foundation of building, the depth of foundation below land surface, and the size and location of cracks in the foundation. It considers the volume of air in the building and the average turnover time of the air. It considers critical soil properties including the soil texture and the water-filled porosity of the soil. It also considers aerobic degradation of the hydrocarbons in soil gas and the oxygen consumption resulting from biodegradation of the hydrocarbons.

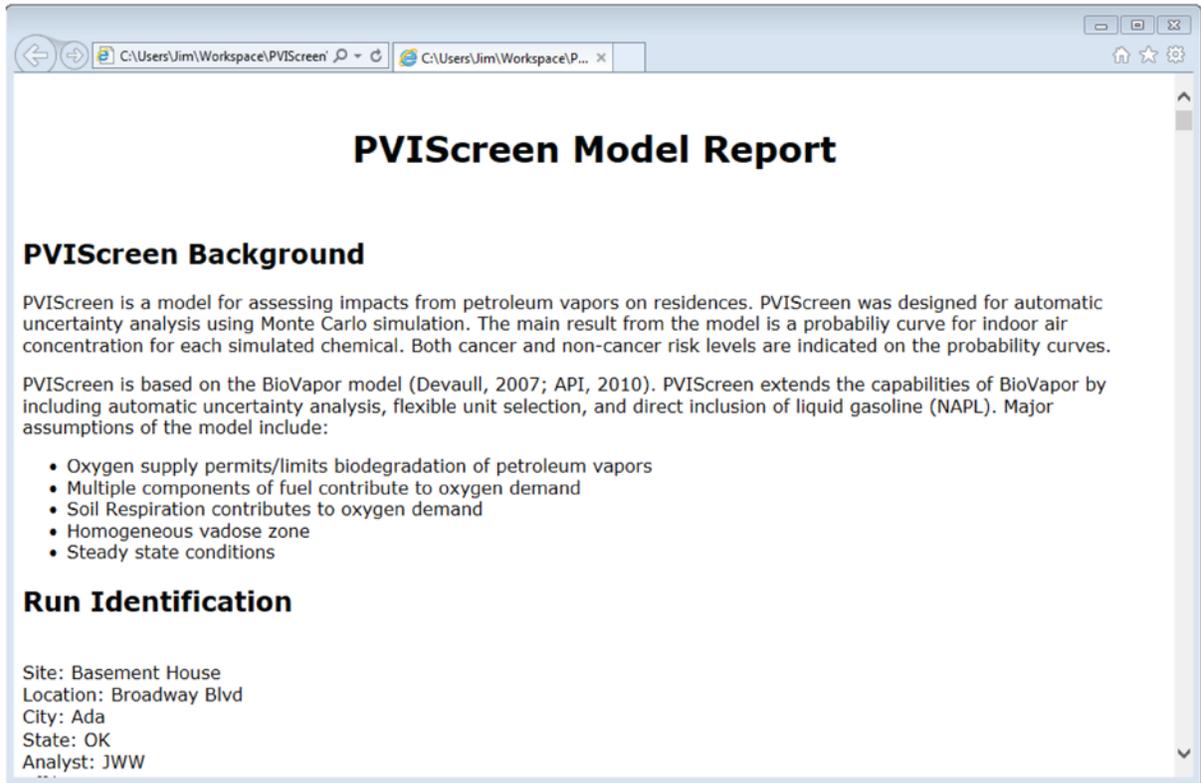


Figure 3.8. Screen capture of the first lines of a report generated with PVIScreen.

3.3.1 Effect of Depth of the Source of Hydrocarbon Vapors

Three simulations from the Abreu Three-Dimensional Model are depicted in Figure 3.9. The charts represent a cross section through the three-dimensional space simulated by the model. The charts start at the center of the building and extend past the building into open land.

The projections of the model are consistent with the conceptual model discussed in Section 2.0. The concentrations of oxygen decrease with depth until they can no longer sustain aerobic biodegradation.

Compare the lower left hand panel of Figure 3.9. The source of hydrocarbon vapors is 9 meters deep. Under open land, the concentrations of oxygen are not adequate for aerobic biodegradation at a depth near 6 meters below land surface. At depth intervals less than 6 meters, the concentration of hydrocarbons decline as a logarithmic function of decreasing depth.

For each meter of approach to the land surface, the concentration decreases approximately one-hundred fold.

Underneath the building, the relationship is more complex. The building tends to shield or shadow the soil from the atmosphere. As a result, the concentrations of oxygen are lower under the building, and the concentrations of hydrocarbons are higher. The highest concentrations are near the center of the building. In this situation, the vulnerability of a building to vapor intrusion would depend on the location of the cracks with respect to the dimensions of the building. Cracks in the center would produce more vapor intrusion than cracks at the periphery.

The Abreu Three-Dimensional Model is capable of integrating the different contribution from various locations into an overall estimate of the attenuation factor (α). This is an important feature that is not shared by the other screening models that are available.

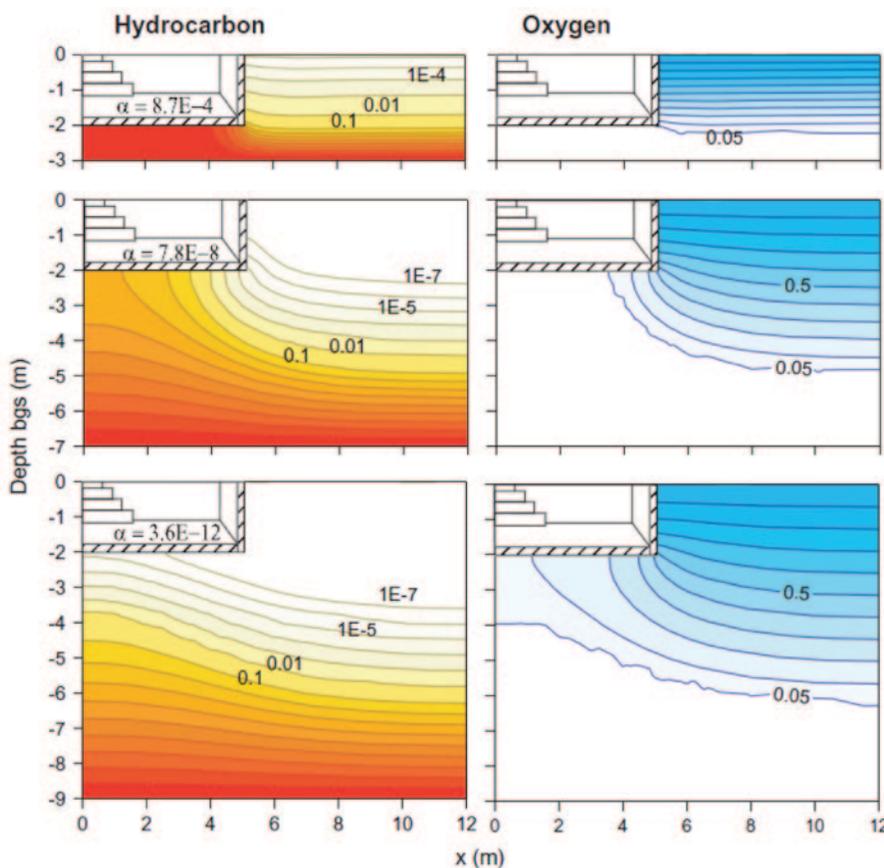


Figure 3.9. Simulations of the distribution of oxygen and hydrocarbon vapors near and beneath a building after transport and reaction processes come to a steady state. The total concentration of hydrocarbons in soil gas at the source was $1.14\text{E}+08 \mu\text{g}/\text{m}^3$. The rate constant for biodegradation of hydrocarbons in soil water was 0.79 per hour. The contours of concentrations of hydrocarbons are normalized to the source. The contours of oxygen are normalized to the atmosphere. Figure 5 in Abreu et al. (2009a). Reprinted from *Groundwater Monitoring & Remediation* with permission of the National Ground Water Association. Copyright 2009.

Compare the panels depicting hydrocarbons in Figure 3.9. Notice that the estimated values for the attenuation factor are a sensitive function of the separation distance between the source of vapors and the bottom of the receptor. If the separation distance is 7 meters, the estimated value of α is $3.6\text{E-}12$. If the separation distance is 5 meters, the estimated value of α is $7.8\text{E-}08$. If the separation distance is only 1 meter, the estimated value is almost ten thousand fold lower (α is $8.7\text{E-}04$). Changes of only a few meters will change the estimated value of α by ten-thousand fold.

3.3.2 Effect of a Basement Compared to Slab-on-Grade

The Abreu Three-Dimensional Model predicts a difference in the behavior of buildings that are constructed with a slab-on-grade foundation, or that have a basement (Figure 3.10). If the depth to the source of vapors from land surface is the same, the building with a basement is more at risk.

Because it is complex and because it is not publicly available, the Abreu Three-Dimensional Model may not be the most accessible or convenient model to screen a particular site. However, the forecasts of the model compare well to actual field data. Because it is so detailed, it should provide a robust estimate of the steady-state behavior of under specified conditions. The model is most sensitive to the concentration of hydrocarbons in soil gas at the source of the vapors, to the separation between the source of vapors and the building acting as a receptor and to the rate of biodegradation of the vapors. The model has been run over a realistic range of these three parameters (Abreu et al., 2009a). The conditions at a particular site can be matched to a preexisting model simulation to provide a convenient forecast of the value of the attenuation factor (α).

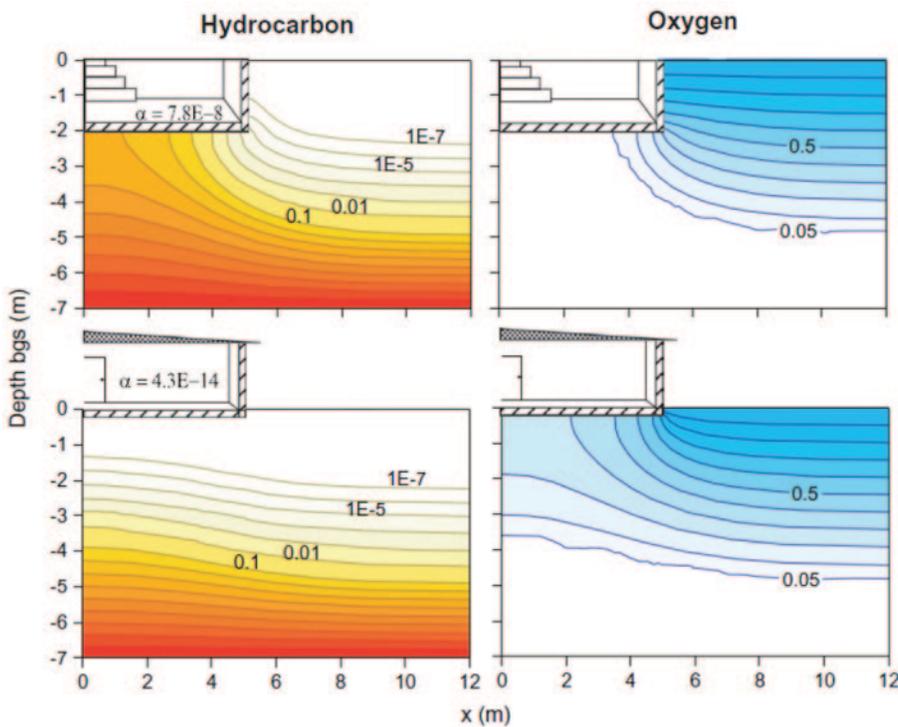


Figure 3.10. Comparison of the distribution of oxygen and hydrocarbon vapors in soil gas beneath or beside a building with a basement compared to a building that is constructed slab-on-grade. Reprinted from Figure 7 in Abreu et al. (2009a). Reprinted from *Groundwater Monitoring & Remediation* with permission of the National Ground Water Association. Copyright 2009.

3.4 Summary Figures of Abreu Three-Dimensional Modelling

Abreu et al. (2009a) ran multiple simulations for two buildings. One building had a basement with the bottom of the slab 2.0 meters below land surface. The other house was slab-on-grade with the slab 0.2 meters below land surface. The houses were 10 meters long and 10 meters wide. The thickness of the slab was 0.15 meters. The air mixed to a height of 2.4 m (ceilings were 8 feet high). As a result, the volume of indoor air was 244 m³. The air in the house was turned over every 0.5 hours. The only crack in the slab was along the perimeter of the foundation. The total crack length was 39 meters. The width of the crack was 0.1 cm.

The soil was a homogeneous sandy soil. The volume of total pore space in the soil was 37.5% of the total volume of the soil. The volume of water in the soil was 5.4% of the total volume. The water content of the simulation is relatively low. Because the bacteria that degrade the hydrocarbons inhabit the soil water, the rate of biodegradation as predicted by the model is directly proportional to the water content. To provide a conservative estimate, a soil type and water content were selected that are associated with less attenuation due to biodegradation.

3.4.1 Steps in an Exposure Evaluation of PVI for Benzene

For the convenience of the reader, Abreu et al. (2009a) organized some of their simulations into a simple figure that plots the simulated value of the attenuation factor (α) against the concentration of the hydrocarbons at the source for five different separation distances. See Figure 3.11. A semi-site specific estimate for the attenuation factor (α) is extracted from the figure by the following process. A sample of soil gas is acquired and analyzed for total hydrocarbons. This includes petroleum hydrocarbons and methane. The theoretical oxygen demand of the total hydrocarbons is expressed as the concentration of benzene with an equivalent demand. In their example, the concentration of total hydrocarbons was equivalent to 10 mg/L benzene. Then the separation distance between the depth of the gas sample and bottom of the receptor is determined. In the example, this distance is

2 meters. A line is projected up from the concentration of hydrocarbons to the separation distance and then across to the estimate of α . In this case, the estimate is 1.0E-07.

The concentration of benzene in indoor air is estimated by multiplying the measured concentration of benzene in the sample of soil gas by the estimate of α . The final step is to select an acceptable concentration of benzene and compare the estimated concentration of benzene in indoor air to the acceptable concentration.

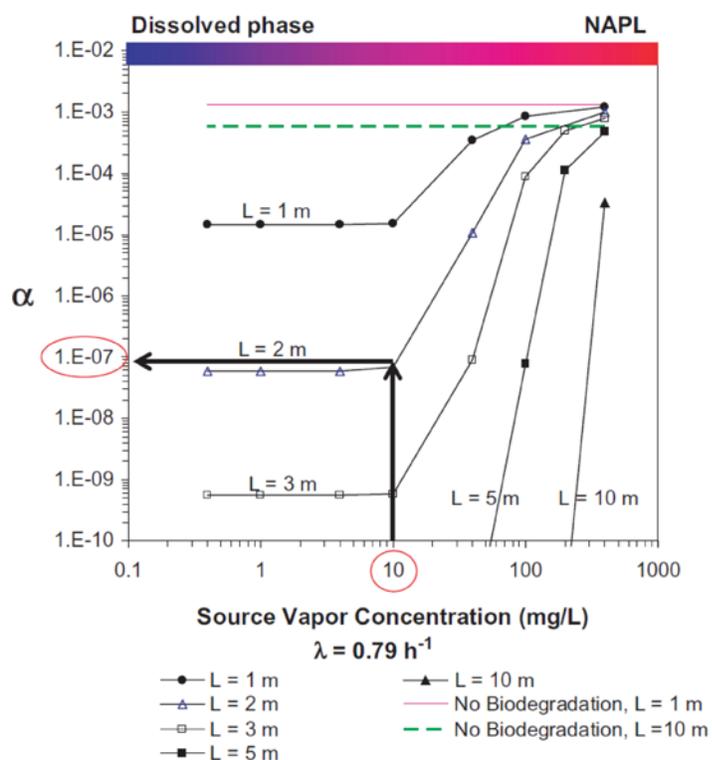


Figure 3.11. Simulated values of the attenuation factor as predicted from the concentration of hydrocarbon vapors at the source and the separation distance. Reprinted from Figure 10 in Abreu et al. (2009a). Reprinted from *Groundwater Monitoring & Remediation* with permission of the National Ground Water Association. Copyright 2009.

3.4.2 Figures to Estimate α to Screen for PVI of Benzene

Abreu et al. (2009a) provided additional estimates of the attenuation factor (α) as tables. Estimates were provided if there was no biodegradation, if the rate constant for aerobic biodegradation in soil water was 0.079 per hour, and if the rate constant was 0.79 per hour. A rate constant of 0.79 per hour was selected because it was the geometric mean of the rates of degradation of aromatic hydrocarbons as reported in DeVaul (2007). A rate constant of 0.079 was selected as a reasonable lower boundary on the rate constant.

DeVaul (2011) reported an updated collection of rate constants. The range of 31 rate constants for benzene biodegradation was 0.028 to 3 per hour. The geometric mean for benzene biodegradation was 0.3 per hour. The geometric mean divided by or multiplied by the geometric standard deviation was 0.079 to 1.2 per hour. A rate constant of 0.079 per hour would include the higher 84% of published rates. A rate constant of 0.79 would include the higher 24% of rates in DeVaul (2011).

Estimates were also provided in the tables for a building built slab-on-grade, as well as a building with a basement. Figures 3.12 through 3.17 present the estimates in the tables of Abreu et al. (2009a) as figures similar to Figure 3.11. Figures 3.13, 3.15 and 3.17 are for buildings with basements. Figures 3.12, 3.14 and 3.16 are for buildings built slab-on-grade. Figures 3.12 and 3.13 forecast an attenuation factor (α) where there is no biodegradation. Figures 3.14 and 3.15 make the forecast with a rate constant of 0.079 per hour, and Figures 3.16 and 3.17 make the forecast with a rate constant of 0.79 per hour.

The unit used in Figure 3.11 for the concentration of hydrocarbons in soil gas is not something that can be measured directly. It must be calculated from reported concentrations. When soil gas is analyzed for the concentration of total petroleum hydrocarbons (TPH_g), the conventional unit is $\mu\text{g}/\text{m}^3$ of a hydrocarbon with a molecular weight of 100 g/mole (C_7H_{16}). To facilitate direct comparison of analytical data to the figures, Figures 3.12 through 3.17 express the theoretical oxygen demand of the hydrocarbon vapors as the equivalent demand of C_7H_{16} in $\mu\text{g}/\text{m}^3$ and not the equivalent demand of benzene in mg/L.

The red and yellow regions in Figures 3.12 through 3.17 are projections of the values of the attenuation factor (α) that are necessary to attain the acceptable indoor air concentrations for benzene if the benzene content in the soil gas were the maximum concentration of benzene that could be expected in soil air above gasoline. If the soil temperature were 26 °C (summer in Florida), the vapor pressure of benzene would be 100 mm Hg or 0.13 atmospheres. Before the initiation of Reformulated Gasoline in 1995, the benzene content of gasoline could be as much as 2.5% (Kirchstetter et al., 1999). If the vapor pressure of benzene above gasoline is proportional to the mole fraction of benzene in gasoline, the concentration of benzene in soil gas would be 0.0042 atmospheres or $1.4\text{E}+07 \mu\text{g}/\text{m}^3$.

This value of $1.4\text{E}+07 \mu\text{g}/\text{m}^3$ will be used as a plausible maximum value for benzene in soil gas in contact with NAPL. At most older spills, weathering processes will reduce the equilibrium concentration of benzene many fold. If the acceptable indoor air concentrations at the 10^{-6} , 10^{-5} and 10^{-4} risk levels are 0.3, 3 and $30 \mu\text{g}/\text{m}^3$, then the necessary attenuation factors (α) would be $2\text{E}-08$, $2\text{E}-07$ and $2\text{E}-06$, respectively.

The upper boundary on the red region in Figures 3.12 through 3.17 is the attenuation factor needed to reach the 10^{-4} risk level. The lower boundary of the red region is the attenuation needed to reach the 10^{-5} risk level. The lower boundary of the yellow region is the attenuation needed to reach the 10^{-6} risk level. At the right boundary of the red and yellow regions, benzene would be 2% of the hydrocarbons in soil gas. The regions make the very conservative assumption that the concentration of benzene in soil gas in contact with the source of hydrocarbon vapors does not change as the concentration of total hydrocarbons goes down. The regions assume that the concentration of benzene at the source only goes down when benzene is 100% of the total hydrocarbons. That is the reason for the break in the regions at a concentration of $1.4\text{E}+07 \mu\text{g}/\text{m}^3$.

If a particular separation distance and a particular value of total hydrocarbons plots above the colored region, the predicted value of α is not adequate to prevent PVI of benzene. If the predicted value is below the colored region, the value is adequate.

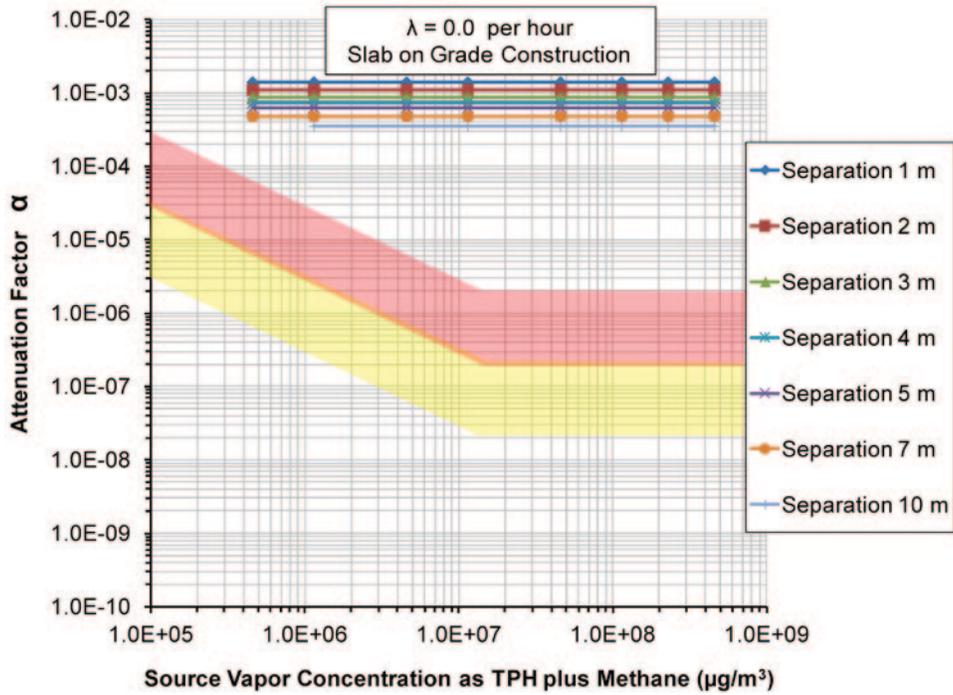


Figure 3.12. Forecasts of α assuming slab-on-grade construction and no biodegradation.

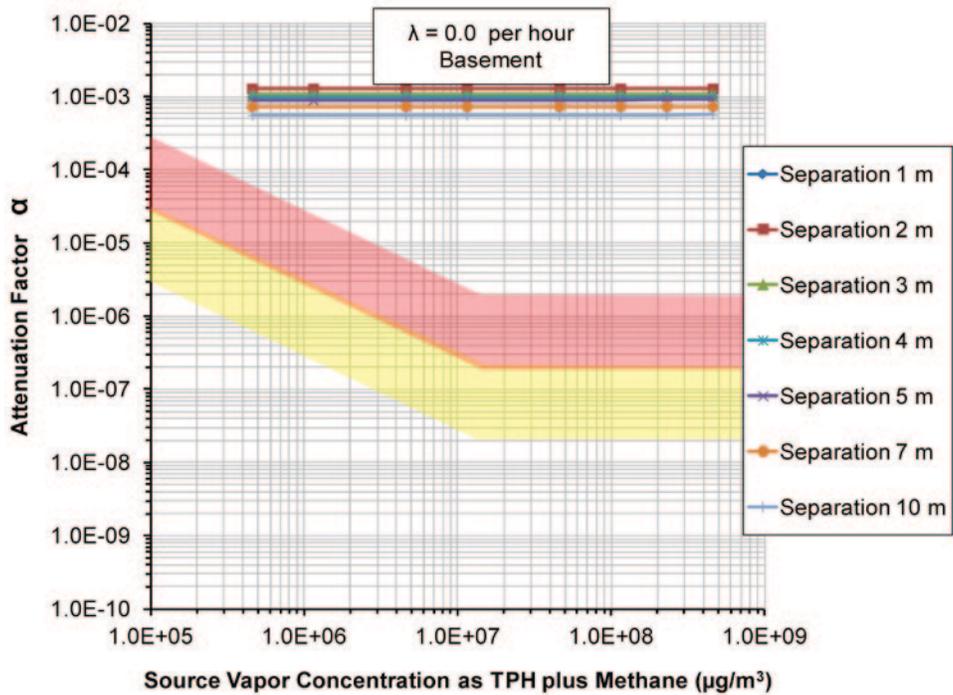


Figure 3.13. Forecasts of α assuming a basement and no biodegradation.

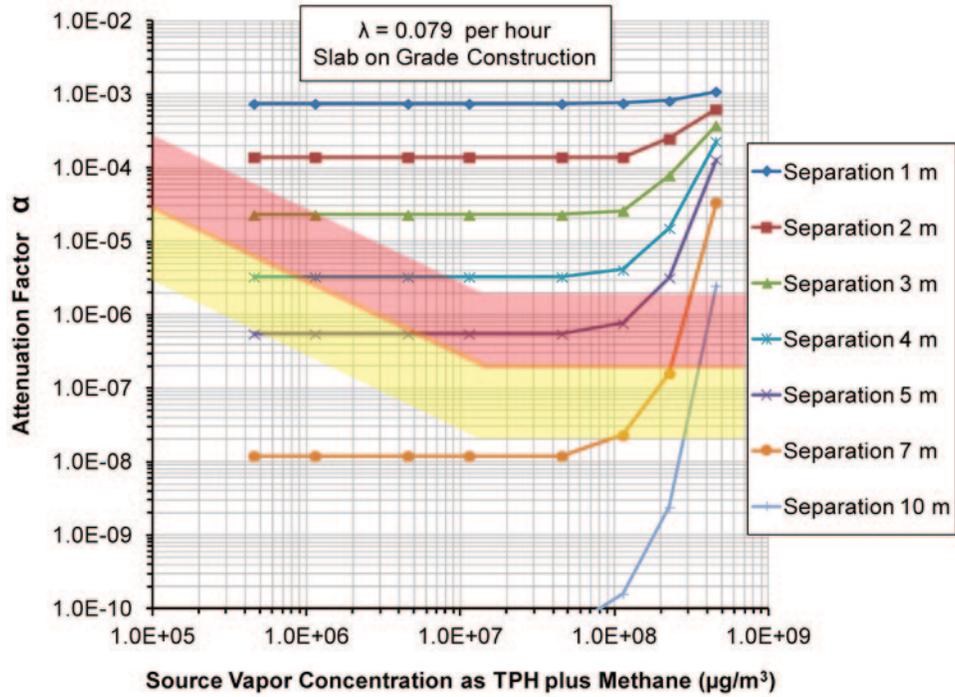


Figure 3.14. Forecasts of α assuming slab-on-grade construction and a low rate of biodegradation.

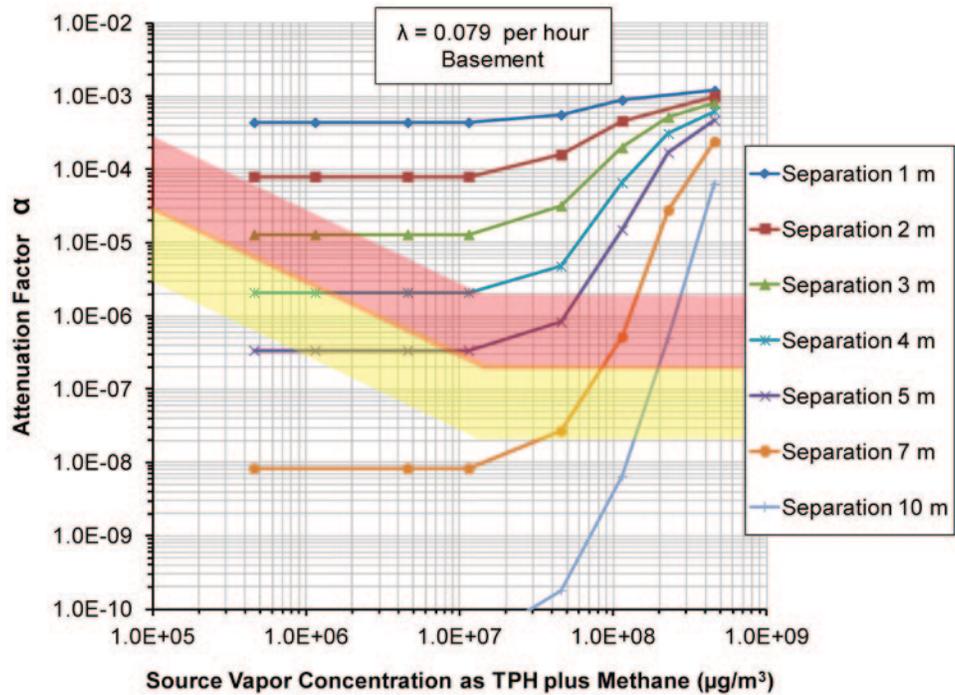


Figure 3.15. Forecasts of α assuming a basement and a low rate of biodegradation.

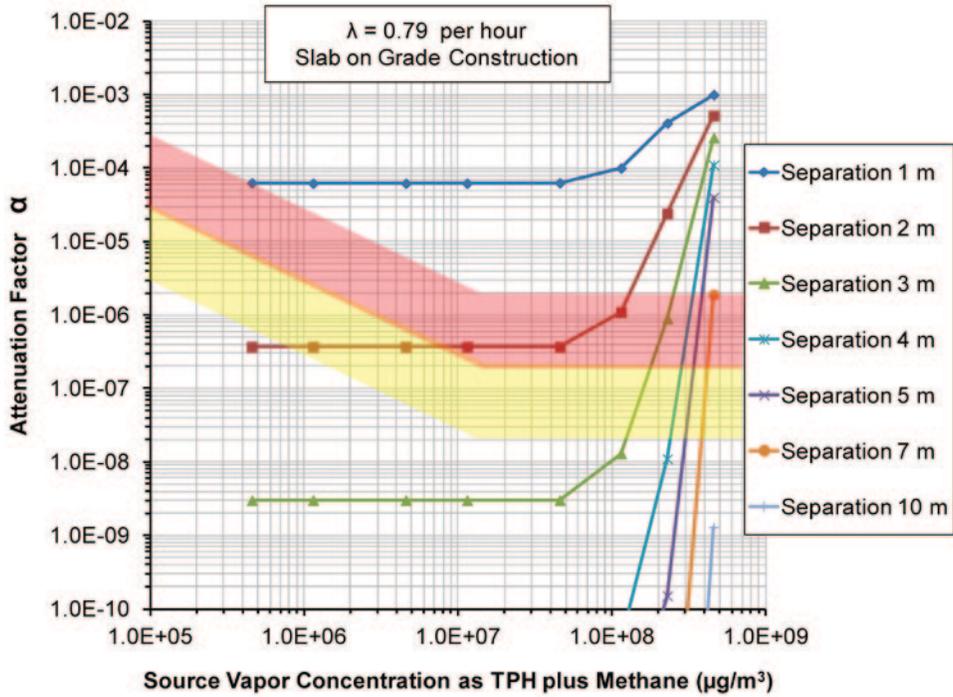


Figure 3.16. Forecasts of α assuming slab-on-grade construction and a medium rate of biodegradation.

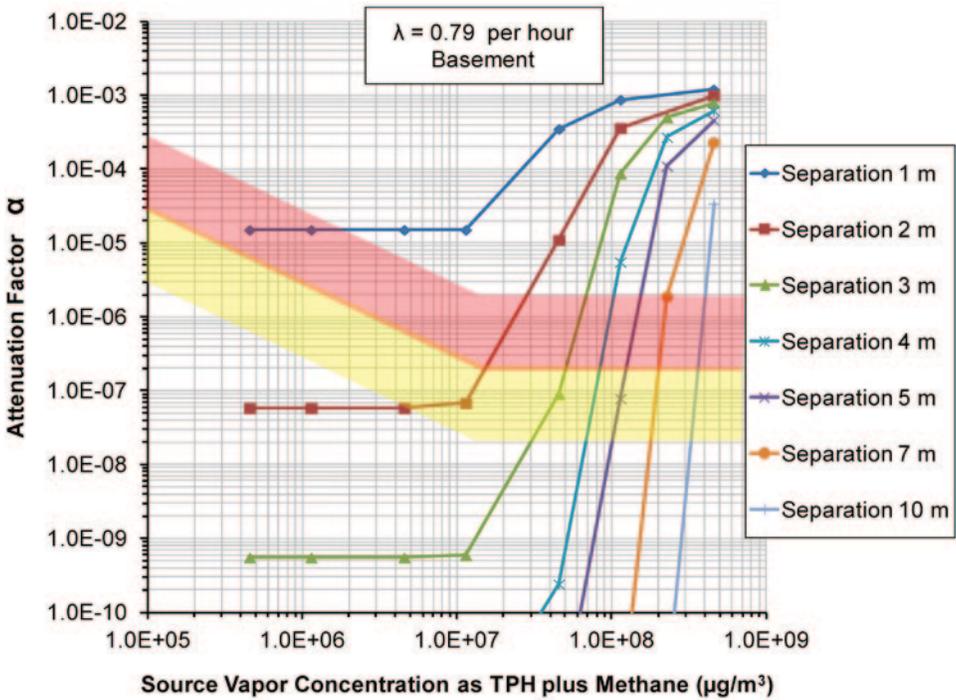


Figure 3.17. Forecasts of α assuming a basement and a medium rate of biodegradation.

Compare Figures 3.12 and 3.13. If the petroleum hydrocarbons do not degrade, there is little influence of separation distance or presence of a basement on the simulated values for the attenuation factors (α). In all cases, they cluster around 1.0E-03. The actual value of the attenuation factor would be largely controlled by properties of the building such as size and location of cracks, the volume of air in the building and the rate of exchange of air in the building. In every simulation, the values of α are not adequate to meet indoor air standards when the concentration of benzene in soil gas is the plausible maximum concentration.

Figures 3.14 and 3.15 present simulations with a relatively low contribution of biodegradation. In general, the lower the concentration of hydrocarbons in soil gas, the lower the attenuation factor (α). Below concentrations near 1E+07 $\mu\text{g}/\text{m}^3$, the curves flatten out. This is because the concentration of hydrocarbon is too low to bring the concentration of oxygen below the concentration needed for aerobic biodegradation. All of the soil profile is available for aerobic biodegradation. At high concentrations of total hydrocarbons in soil gas at the source, the predicted values of α converge on the values predicted in the absence of biodegradation. This is because the oxygen demand exerted by the hydrocarbons has made the concentration of oxygen too low to support aerobic biodegradation throughout most of the separation distance between the source of vapors and the building.

Even with a relatively low contribution of biodegradation, there are wide variations in the estimated value of the attenuation factor (α) for various values of the concentration of hydrocarbon in soil gas and various values for the separation distance. The risk of PVI is largely influenced by factors operating in the soil and sediment and less so by factors related to the building itself.

As mentioned previously, the predicted values of the attenuation factor (α) that fall above the colored shapes are not adequate to protect indoor air from PVI when the concentration of benzene in soil gas is the maximum concentration of benzene that could be expected in soil air above gasoline. If a prediction falls into this region of a chart, it is necessary to compare the actual measured concentration of

benzene in soil gas to predict α . The actual measured concentration of benzene will depend on the fuel that was spilled, on the age of the spill and on the extent of weathering of the fuel in the time since it was spilled.

Figures 3.14 and 3.15 will be used to screen sites in the case studies presented in Sections 5, 6 and 8.

Figure 3.18 compares the distribution of concentrations of benzene in all the samples of soil gas that were evaluated in U.S. EPA (2013a). The concentration in only a few percent of the samples approached 1.4E+07 $\mu\text{g}/\text{m}^3$, which is the plausible maximum value for benzene in soil gas in contact with NAPL. The predicted concentration of benzene in indoor air will be sensitive to both the predicted value of the attenuation factor (α) and the measured value of benzene in soil gas. Section 4 and Section 7 discuss methods to acquire samples of soil gas and determine the concentration of TPH and benzene.

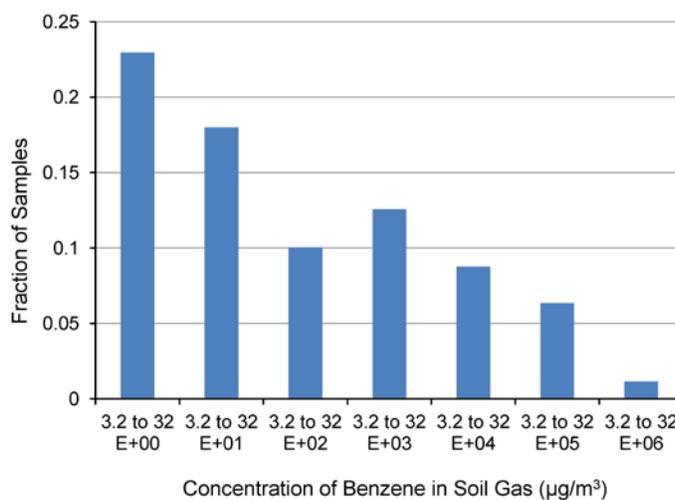


Figure 3.18. Distribution of Concentrations of Benzene in Soil Gas Samples that were evaluated in U.S.EPA (2013a).

3.4.3 Including Methane in Total Hydrocarbons

The screening approach using the simulations of Abreu et al. (2009a) requires that methane be included in the hydrocarbons. Usually, methane data are acquired by a different analysis. If the data are reported in ppb (volume/volume), multiply ppb by 0.662 to get $\mu\text{g}/\text{m}^3$. Methane has relatively more hydrogen than the higher alkanes and as a result it has a higher theoretical oxygen demand on a mass basis. To correct for the differences in theoretical oxygen demand, multiply the measured concentration of methane by 1.14 before adding the concentration of methane to the concentration of TPHg to calculate total hydrocarbons in soil gas.

3.4.4 Application of Exposure Evaluation of PVI to other Compounds

Abreu et al. (2009a,b) simulated the behavior of pure benzene in soil gas to the behavior of a mixture of hydrocarbons that represented a weathered gasoline. The Abreu Three-Dimensional Model predicts equivalent distributions of oxygen. The distribution of other TEX compounds was similar to the distribution of benzene; however, the distribution of aliphatic hydrocarbons differed from the distribution of benzene alone (Abreu et al., 2009b). One consequence is that Figures 3.14 through 3.17 can be used to estimate an attenuation factor (α) for other aromatic hydrocarbons, but they should not be used for aliphatic hydrocarbons such as hexane.

4.0 DATA REQUIREMENTS TO FORECAST PETROLEUM VAPOR INTRUSION

The Interstate Technology & Regulatory Council has produced a Guidance Document that describes a process for screening, investigating, and managing sites for PVI (ITRC, 2014). The ITRC Guidance Document has detailed specifications and recommendations on methods to sample and analyze soil gas.

To make a robust forecast of the contribution of petroleum vapor intrusion to concentrations of fuel

components in indoor air, it is necessary to have information on the properties of the building and the properties of the subsurface environment. If the approach uses the figures in Section 3.4, the exposure assessment assumes generic properties for the building. The exposure assessment is influenced by the properties of the soil gas at the source of the vapors, and the separation distance between the source of vapors and the building. These properties are described in this section.

If information on the properties of the building is available, the exposure assessment can be refined using either the BioVapor Model as described in Section 3.1 or the PVI Screen Model described in Section 3.2. Consult the user's guides of the models for instructions on the properties of the building being described. This Issue Paper does not consider the properties of the building.

4.1 Conversions of Concentrations from Units of ppb-v to $\mu\text{g}/\text{m}^3$

Data on concentrations of organic compounds in gas samples are conventionally reported on a volume basis in units of parts per million by volume (ppm-v) or parts per billion by volume (ppb-v). This is because the working standards used to calibrate the instruments are created by diluting standard gases. However, the oxygen demand of a hydrocarbon in gas is related to the chemical formula of the hydrocarbon, as well as its concentration on a volume basis. If concentrations of hydrocarbons are to be used to estimate their impact on oxygen demand, they should be expressed in units of $\mu\text{g}/\text{m}^3$. Standards for acceptable concentrations of individual organic compounds in soil gas are often expressed in units of $\mu\text{g}/\text{m}^3$.

Concentrations in ppb (v/v) can be converted to units of $\mu\text{g}/\text{m}^3$ using the following formula:

$$\mu\text{g}/\text{m}^3 = \text{ppb} * \text{molecular weight} * 0.0413$$

The formula applies for conditions at sea level and room temperature.

If you are interested, the formula is derived as follows. If you are not interested, skip to Section 4.2.

The ideal gas law states: $P_i * V = n_i * R * T$

where P_i is the absolute partial pressure of the individual hydrocarbon (i) in the gas, V is the volume of the sample of gas containing the hydrocarbon, n_i is the number of moles of the individual hydrocarbon in the sample, R is the universal gas constant, and T is the absolute temperature in degrees Kelvin[K].

The value of R is 0.08205 (L*atm)/(mole*T). The value of T [K] equals the temperature in degrees Celsius plus 273. At room temperature T is near 295 K. The molecular weight of a compound is defined as the number of grams (g) per mole (n), so $n = m / \text{molecular weight}$ where m is the mass in grams. Substituting $m / \text{molecular weight}$ for n and rearranging for concentration as m/V , then

$$\frac{m}{V} = P_i * \text{molecular weight} / (R * T)$$

At sea level, a gas present at a concentration of 1 ppb has a partial pressure of one billionth of the atmospheric pressure (P_{atm}). The equation above becomes:

$$\frac{m}{V} = \frac{\text{ppb} * \text{molecular weight} * P_{atm}}{R * T}$$

When P_{atm} is 1.0 atmosphere:

$$\frac{P_{atm}}{R * T} = \frac{1}{0.08205 * (273 + 22)} = 0.0413$$

4.2 Analysis of Compounds of Concern

To apply the approach to a particular building, it is necessary to know the concentration of compounds of concern (COCs) in the soil gas at the source of the vapors. The separation distance between the source of vapors and the building and the theoretical oxygen demand of all the hydrocarbons in the soil gas are used to estimate attenuation factors (α) for the concentrations of COCs between the source of vapors and indoor air in the building. To estimate the concentration of the COCs in indoor air, the estimate of α is multiplied by the measured concentration of the COC in the soil gas. To complete the exposure evaluation, the predicted indoor air concentration is compared to some reference standard concentration that is specified by the appropriate regulatory authority.

The most straightforward approach to determine the concentration of a COC in soil gas is to use an analytical procedure that would be used to measure the concentrations of the compound in indoor air. This

ensures that the analyses will meet all the requirements for data quality that are imposed by the regulatory authority.

4.2.1 Individual Petroleum Hydrocarbons

The U.S. EPA identifies four methods that are intended to determine the concentrations of individual petroleum hydrocarbons in samples of ambient air or indoor air. They are Method TO-15 (U.S. EPA, 1999a), Method TO-14A (U.S. EPA, 1999b), Method TO-3 (U.S. EPA, 1984) and Method TO-17 (U.S. EPA, 1999c). These methods can also be applied to soil gas. Because their maximum reporting concentration is near 10,000 $\mu\text{g}/\text{m}^3$, it is often necessary to dilute samples of soil gas before they can be analyzed.

Compendium Method TO-15 is widely used (U.S. EPA, 1999a). Gas samples can be collected into an evacuated stainless steel canister that has gone through a special process to make the interior of the canister chemically inert. After the gas sample is collected,

the canister is sealed and shipped to the laboratory for analysis by high resolution gas chromatography using a mass spectrometer as the detector.

Compendium Method TO-14A is an update of an older method and is similar to Method TO-15. The sample is collected into a stainless steel canister and it is analyzed using gas chromatography, but the method does not necessarily use a mass spectrometer as the detector. Detectors can include a flame ionization detector, an electron capture detector, or a photo-ionization detector. A gas chromatograph with a mass spectrometer detector is more expensive and requires more training to operate. As a result, the costs per sample for Compendium Method TO-15 may be greater than Method TO-14A. However, the mass spectrometer detector can distinguish between organic compounds that are not fully separated on the chromatography column. It is less likely to misidentify a compound.

Under routine conditions, Method TO-14A and TO-15 can detect individual petroleum hydrocarbons at concentrations above 0.5 ppb on a volume basis. This detection limit corresponds to a benzene concentration of 1.6 $\mu\text{g}/\text{m}^3$.

Method TO-3 uses a gas chromatograph with a flame ionization detector or an electron capture detector, or both detectors. The method does not specify a container for the gas sample. It can be used with a sample that is collected into a flexible plastic bag (such as a Tedlar[®] Gas Sampling Bag).

Method TO-17 requires that the gas sample be collected onto a special sorbent trap. The trap is then shipped to the laboratory for analysis. Methods TO-14A and TO-15 require approximately one liter or six liters of sample to fill the steel container. Method TO-17 requires as little as 50 mL. The smaller sample can be collected from a vapor point with a plastic syringe and loaded onto the trap in the field. This is a significant advantage when the pneumatic conductivity is low and it is difficult to acquire one or more liters of soil gas.

Method TO-17 using a Tenax TA trap allows for analysis of high molecular weight hydrocarbons as would be found in jet fuel or diesel fuel.

4.2.2 Fuel Oxygenates

Method TO-14A was developed for non-polar compounds such as hydrocarbons. However, Method TO-15 was developed to allow analysis of more polar compounds such as the fuel oxygenates. Analytes amendable to Method TO-15 include ethanol, methyl *tert*-butyl ether, ethyl *tert*-butyl ether, *tert*-amyl methyl ether and diisopropyl ether.

4.2.3 Lead Scavengers (EDB and 1,2-DCA)

Ethylene dibromide or EDB (1,2-dibromoethane) and 1,2-DCA (1,2-dichloroethane) can be analyzed using Method TO-15. However, the detection limit is high compared to acceptable concentrations in indoor air. A detection limit of 0.5 ppb on a volume basis corresponds to a concentration of 3.9 $\mu\text{g}/\text{m}^3$ for EDB and of 2.1 $\mu\text{g}/\text{m}^3$ for 1,2-DCA.

According to the EPA Integrated Risk Assessment Information System (U.S. EPA, 2014c), the acceptable concentration of EDB in indoor air at the 1 in 10,000 risk level is 0.2 $\mu\text{g}/\text{m}^3$. The acceptable concentration at the 1 in 1,000,000 risk level is 0.002 $\mu\text{g}/\text{m}^3$. Because an attenuation factor will be applied to concentrations in soil gas, Method TO-15 has adequate sensitivity to measure the lead scavengers in soil gas. However, to measure EDB in indoor air at adequate sensitivity, it will probably be necessary to use Method TO-14A with an electron capture detector.

4.2.4 Total Petroleum Hydrocarbons in Soil Gas

An analysis of Total Petroleum Hydrocarbons is generally represented as TPH. If the analysis only considers the range of hydrocarbons that form the bulk of gasoline, the analysis is termed TPH-g. Generally TPH-g includes compounds with six to ten carbon atoms. If the analysis only considers the range of hydrocarbons that form the bulk of diesel fuel, the analysis is termed TPH-d. Generally TPH-d includes compounds with ten to twenty-eight carbon atoms.

Computer models such as BioVapor, PVIScreen or the Abreu Three-Dimensional Model actually consider the composite oxygen demand of the hydrocarbons. This hypothetical parameter would be the equivalent of the

biological oxygen demand of waste water. Abreu et al. (2009a) expresses the composite oxygen demand as the concentration of benzene with an equivalent demand. Figures 3.4 through 3.9 express the composite demand as the concentration of C_7H_{16} with an equivalent demand. The molecular weight of C_7H_{16} (100 g/mole) is near the mean molecular weight of gasoline.

The computer models require a value for the composite oxygen demand. BioVapor and PVI-Screen will calculate this value internally if the concentrations of methane and all the individual petroleum hydrocarbons in soil gas are provided. The models can also be provided the Total Petroleum Hydrocarbons expressed as an equivalent hydrocarbon. Figures 3.14 through 3.17 also require a value for the composite oxygen demand expressed as the concentration of C_7H_{16} with the same oxygen demand.

Methods TO-3, TO-14A and TO-15 were designed for individual compounds. However, some vendors also offer an analysis of Total Petroleum Hydrocarbons in the range expected in gasoline (TPHg). One such vendor uses the following protocol:

TPH-g by EPA TO-15 is calibrated using a single point gasoline calibration standard analyzed with each analytical batch. The TPH-g is determined in each sample by summing the area of the total ion chromatogram of the GC/MS run and subtracting non-petroleum related components from the total area. This total area (approximately C3 to C12 range) and the response factor of gasoline are used to calculate the TPH result.

The TPH-g is expressed as the equivalent of a hydrocarbon with a molecular weight of 100 Daltons. The value of TPH-g can be entered in BioVapor or PVI-Screen as the concentration of heptane. If a sample is analyzed by Method TO-15, one sample of soil gas can be used to determine both TPH-g and the compounds of concern.

Methods TO-3, TO-14A, TO-15 and TO-17 were designed to determine the concentrations of Toxic

Organic compounds of regulatory concern. They are not calibrated for many of the compounds in petroleum motor fuel that are relatively benign. These compounds that are not included in Methods TO-3, TO-14A, TO-15 and TO-17 include propane, the butanes, the pentanes, and several heavier hydrocarbons that are important components of soil gas in contact with motor gasoline. As a result, it is not possible to estimate TPH-g by adding up the concentrations of the individual compounds in a TO-3, TO-14A, TO-15 or TO-17 analysis.

4.2.5 Methane, Oxygen, Carbon Dioxide, Nitrogen

Methods TO-3, TO-14A, TO-15 or TO-17 do not provide an analysis for methane. It is necessary to have an analysis for methane to correctly describe the composite oxygen demand of the hydrocarbons in soil gas (Abreu et al., 2009a; DeVauil, 2007; Jewell and Wilson, 2011). Methane can be determined by EPA Method 3C (U.S. EPA, 2014d) or by ASTM D-1945 (ASTM, 2010). The methods also determine the concentrations of oxygen, carbon dioxide and nitrogen.

If a modification of ASTM D-1945 is used to determine the concentrations of ethane, ethylene, acetylene, propane, n-butane, *iso*-butane, n-pentane, *iso*-pentane, and a composite of C_6 to C_7 hydrocarbons, it is possible to determine the concentrations of the petroleum hydrocarbons and the concentrations of methane, oxygen, carbon dioxide, and nitrogen in the same analytical run.

As will be described in Section 4.5, the concentration of oxygen in a sample of soil gas can be used to correct for dilution or leakage as the sample was acquired. The concentration of carbon dioxide can be used to distinguish a sample of soil gas from a sample of the atmosphere. The concentration of nitrogen can be used to calculate the mass balance of all the permanent gases in the sample and determine the accuracy of the analyses for the other permanent gases.

4.3 Correcting Concentrations of Contaminants for Leakage or Dilution

Figure 4.1 depicts two monitoring tools that can be used to collect soil gas from the source of hydrocarbon contamination. The device on the left is a typical probe built for the purpose of collecting soil gas. The device on the right is a conventional ground water monitoring well. Many of the ground water wells at fuel release sites were also designed to detect NAPL. As a result, they have a portion of the screen above the water table. In many respects, both the vapor probe and ground water well are similar. They are installed in a borehole. The sampling point is surrounded with a sand pack. The sand pack and sampling point are protected from contamination from the surface with a seal of grout or bentonite clay. The point of extraction of the sample is protected by a vault or cap.

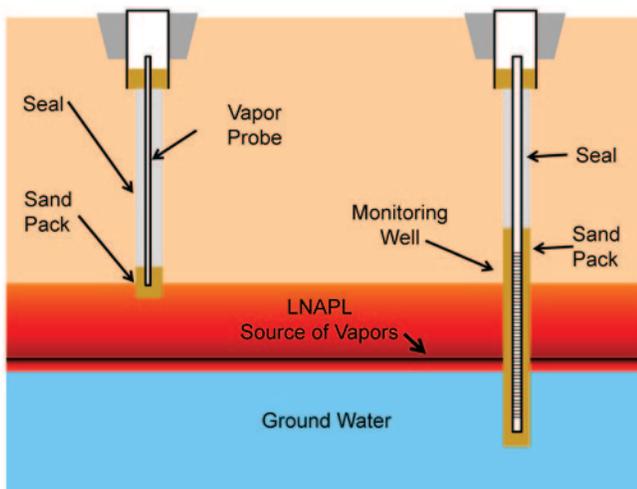


Figure 4.1. Depiction of a vapor probe set near the LNAPL source of vapors and a monitoring well screened across the water table.

If the water table is within the screened interval, a conventional monitoring well resembles a large vapor probe. There are only three important differences. The vapor probe has a much smaller diameter and much less void volume than the screen and riser of the ground water well, the vapor probe terminates above the water table, and the vapor probe is generally constructed of stainless steel or nylon tubing instead of PVC plastic. Jewell and Wilson (2011) were able to use ground water monitoring wells to sample soil gas at a number of UST fuel spill sites in Oklahoma.

Any real sample is subject to dilution of the analytes by leaks of air into the sampling train, and mixing of the soil gas in the unsaturated zone. When soil gas is sampled for chlorinated solvents, the general approach to control for leaks is to use tracer compounds to document any contribution of air from atmosphere above the sampling point to the sample. If the tracer compound is found in the sample above a certain concentration, the sample is compromised by the leaks.

In addition to leaks, there is another process that can dilute the sample. If the transition from oxygenated soil gas to anoxic soil gas occurs in the screened interval of the monitoring well, then the source vapors will be diluted with air that has much lower concentrations of benzene and TPH (Figure 4.2). The flow paths with less contaminated soil gas will dilute the gas in flow paths that are directly in contact with the source of petroleum hydrocarbons. Leak testing at the surface can only reveal the contribution of leaks in the sampling train. It cannot evaluate the effect of mixing in the soil profile.

If the casing of adjacent monitoring wells or vapor probes are not properly sealed with a well cap, air can enter through the screen of an adjacent monitoring well or vapor probe, and dilute the soil gas in the vicinity of the well or vapor probe that is being sampled.

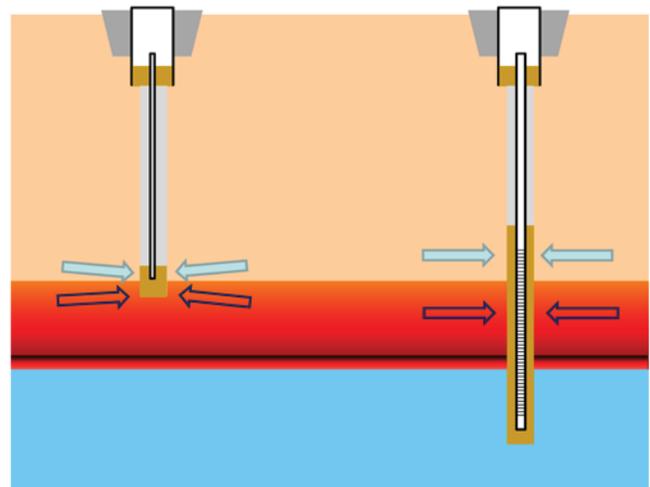


Figure 4.2. Dilution of soil gas samples by dilution with cleaner soil gas.

The approach taken in this Issue Paper is a screening level evaluation. If screening indicates that there is a reasonable possibility for PVI, then further characterization or site remediation is required. As a result, it is not necessary to know the exact concentrations of benzene or TPH in soil gas at the source. An upper boundary on the concentration is useful for the evaluation.

Air in contact with LNAPL is often devoid of oxygen. Davis et al. (2009) compared the concentrations of hydrocarbons and oxygen in soil gas from seven field sites in Australia. With very few exceptions, when oxygen was present, hydrocarbons were absent and oxygen was absent when hydrocarbons were present. The conceptual models discussed in Section 2 assume that the air at the source is devoid of oxygen. To put a conservative boundary on the true concentration of benzene, TPH and methane at the source of contamination, we will assume that all the

benzene, TPH or methane came from the source of contaminated vapors, which did not have oxygen. We will assume that all the oxygen in the sample came from a leak or came from clean air in the unsaturated zone.

A simple factor can correct for the effects of leaks as a sample is collected or dilution of the sample in the soil gas. The correction factor is the concentration of oxygen in the atmosphere divided by the difference in the concentration oxygen between the atmosphere and the sample of soil gas. If you are interested in a derivation of the correction factor, the derivation is provided below. If you are not interested, skip to Figure 4.3. This figure plots the correction factor for concentrations of benzene, TPH or methane from the measured concentration of oxygen, assuming the measured concentration of oxygen in the atmosphere is 21%.

The correction factor is derived as follows. The mass of benzene, TPH or methane in the sample of gas that was analyzed is the same mass of benzene, TPH or methane that was extracted from the soil gas in contact with the NAPL. The concentration of benzene, TPH or methane in the source gas collected into the sample and the concentration in the gas actually analyzed are related as follows:

$$\begin{aligned} \text{Conc. Source Gas} * \text{Vol. Source Gas} &= \\ & \text{Conc. Gas Analyzed} * \text{Vol. Gas Analyzed} \\ \frac{\text{Conc. Source Gas}}{\text{Conc. Sample Analyzed}} &= \frac{\text{Volume Gas Analyzed}}{\text{Volume Source Gas}} \end{aligned}$$

The fraction of the sample that was analyzed that is represented by the air from the vapor source is:

$$\frac{\text{Volume Source Gas}}{\text{Volume Gas Sampled}} = \frac{\text{O}_2 \text{ in Atmosphere} - \text{O}_2 \text{ in Soil Gas}}{\text{O}_2 \text{ in Atmosphere}}$$

Rearranging, and solving for the concentration in the source gas:

$$\begin{aligned} \text{Conc. Source Gas} &= \\ \text{Conc. Sample Analyzed} & \left(\frac{\text{O}_2 \text{ in Atm.}}{\text{O}_2 \text{ in Atm.} - \text{O}_2 \text{ in Soil Gas}} \right) \end{aligned}$$

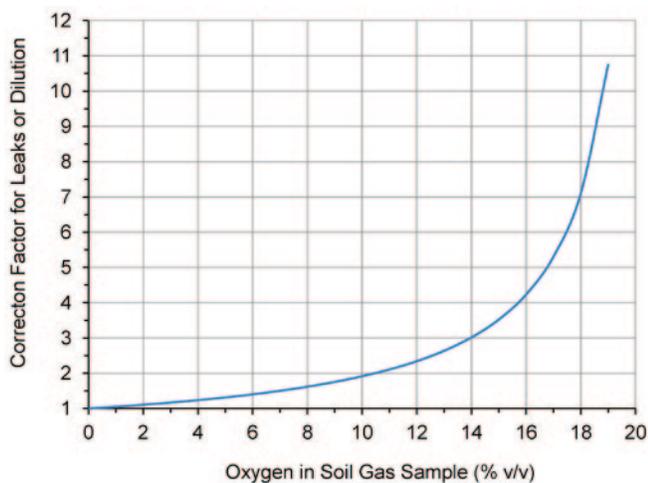


Figure 4.3. A correction factor for concentrations of hydrocarbons in soil gas near the source of hydrocarbons based on the concentration of oxygen.

When the concentration of oxygen is above 19% (v/v), the correction based on oxygen becomes uncertain. Do not apply the correction factor for concentrations of oxygen above 19%. The correction factor can be calculated for oxygen measured by ASTM D-1945 (ASTM, 2010), or it can be measured with a meter in the field. If it is measured with a meter in the field, determine the concentration of oxygen in the atmosphere immediately before and immediately after determining the concentration in the soil gas sample. If the concentration of oxygen is measured in the laboratory, collect a sample of the atmosphere and include it for analysis.

Wilson et al. (2012b) reported the concentration of the major components of soil gas from three wells at a fuel spill site in Antlers, Oklahoma (Table 4.1). See Section 6 for details of the site.

Table 4.1. Major components of soil gas at a motor fuel spill site.

		Concentration (Atmospheres)	MW-2B	MW-9	GMW-1B
Nitrogen	% (v/v)	78.0	6.6	19.9	24.1
Methane	% (v/v)	0.0002	71.0	61.2	60.1
Carbon Dioxide	% (v/v)	0.04	19.6	18.4	11.7
Oxygen	% (v/v)	21.0	1.23	1.02	3.92
Gasoline Hydrocarbons	% (v/v)	NA	1.90	0.16	0.59
Hydrogen	% (v/v)	0.00006	< 0.001	< 0.001	< 0.001
Sum	% (v/v)	99.04	100.33	100.68	100.41
Ratio of Oxygen to Nitrogen		0.27	0.19	0.05	0.16

As described in Wilson et al. (2012b), the concentrations of nitrogen, methane, carbon dioxide, oxygen, gasoline hydrocarbons and hydrogen were determined using an Agilent Micro 3000 gas chromatograph (GC). The instrument is configured with four miniaturized GC systems in a modular format. All four modules contain a micro-Wheatstone bridge thermal conductivity detector.

The concentrations of methane and carbon dioxide were high compared to the atmosphere, and the concentrations of nitrogen and oxygen were low. At this site, much of the methane and carbon dioxide was produced by fermentation of ethanol in the gasoline that was spilled. Methane and carbon dioxide in the ground water became super saturated, bubbled out of the ground water, and displaced the nitrogen in the soil gas. In monitoring wells MW-2B and GMW-1B, the ratio of oxygen to nitrogen in the gas sample was similar to the ratio in the atmosphere. This indicates that most of the nitrogen and oxygen in the sample came from a leak in the sampling process. In well MW-9, oxygen was depleted with respect to nitrogen. This indicates that most of the nitrogen in the sample actually came from soil gas, and much of the oxygen in the sample came from a leak.

Notice that the mass balance on the sum of the gases was within a percent. Some vendors will measure the other permanent gases and estimate nitrogen by difference. If nitrogen is actually measured, then the mass balance provides a check on the data quality of the analyses.

If the concentration of oxygen in a sample is high, this may indicate that a leak had a major impact on the concentrations of hydrocarbons in the soil gas. It may also indicate that the rate of biodegradation of the hydrocarbons may have been too slow to consume much of the oxygen in the soil gas. The concentration of carbon dioxide can distinguish between these two possibilities. The background concentration of carbon dioxide in the atmosphere is near 0.04%. The background concentration of carbon dioxide in normal soil gas is near 3% and the concentration in contaminated soil gas can be even higher.

4.4 Field Screening of Vapor Samples to Determine When to Sample

Chemical analyses are a significant cost of site characterization. The U.S. EPA data quality process requires that a sample be representative of the environmental medium being sampled. This issue is particularly important when the volume of the sample submitted for analysis is small with respect to the internal volume in the sampling instrument. This is the reason that ground water monitoring wells are often purged before water samples are taken for analysis. There are two approaches for collecting a representative groundwater sample from a well. The well can be purged for some specified volume, such as three casing volumes, or the well can be purged until sensitive parameters, such as the concentration of dissolved oxygen or the oxidation/reduction potential, come to equilibrium.

Jewell and Wilson (2011) sampled soil gas from conventional ground water monitoring wells. They purged the gas from the well at a flow rate of 10 liters per minute for a minimum of twenty minutes before they took a sample. This portion of the Issue Paper discusses the second approach: monitoring concentrations of hydrocarbons, oxygen and carbon dioxide in soil gas until they come to equilibrium.

This discussion does not apply to vapor probes, which usually have a small internal volume. The internal volume of a vapor probe may be 0.1 liter, while the volume of the sample is 1.0 or 6.0 liter. McAlary et al. (2009) offer useful suggestions for collecting samples from vapor probes, particularly when the pneumatic conductivity of the geological material is low. They recommend purging one internal volume, and then collecting the sample using conditions that impose a vacuum of no more than 100 inches of water on the soil gas.

4.4.1 Oxygen and Carbon Dioxide to Monitor Stabilization of Samples

A variety of field instruments are available to determine the concentrations of oxygen and carbon dioxide in gas. Field meters typically report concentrations of oxygen and carbon dioxide with increments of 0.1%. The concentration of carbon dioxide in the atmosphere (0.04%) is below the typical reporting limit of the meter.

The oxygen detectors sense an electrical current that is produced by a chemical reaction between the hydrocarbon and oxygen in the gas. The current is proportional to the concentration of hydrocarbon. Material in the detector is consumed as they operate. As a result, the detectors have a shelf life. When the detectors are no longer within specifications, they must be replaced. The carbon dioxide detector uses a spectrophotometer to measure the infrared absorbance of the gas at a wavelength characteristic of carbon dioxide. The carbon dioxide detectors do not degrade over time.

Generally, the oxygen detectors and the carbon dioxide detectors are not subject to interference from other compounds. To our knowledge, there are no compounds that might reasonably be expected in soil gas at gasoline spill sites that may produce a false reading for oxygen or carbon dioxide, or that might degrade the performance of the detector. However, it is always good to check the user's guide and the manufacturer's literature for potential interferences.

4.4.2 Stabilization of Oxygen and Carbon Dioxide in Soil Gas Samples from Water Monitoring Wells

Soil gas samples that are acquired from groundwater monitoring wells behave much like ground water samples. The concentrations can change as the soil gas is sampled. These concerns do not apply to small samples of soil gas taken from vapor probes. The following discussion applies only to soil gas samples that are acquired from groundwater monitoring wells.

During the course of sampling, the concentrations of oxygen typically decrease over time and the concentrations of carbon dioxide typically increase. The time taken for concentrations of oxygen and

carbon dioxide to equilibrate depends on the rate of extraction of air from the monitoring well and the internal volume of the well, and other factors that have not been defined.

Figure 4.4 and Figure 4.5 are examples of a well that equilibrated quickly and a well that equilibrated more slowly, relative to the total purge volume. To allow direct comparisons, the volume of air that was extracted was normalized to the total internal gas volume in the well. The total volume includes the sampling train and an estimate of the gas filled volume of the sand pack. Extraction of air is reported in purge volumes removed. Data for an additional eight sites are provided in Appendix A.

The data used in these case studies are provided as an illustration. They do not necessarily reflect current conditions at the site, and have no bearing on past or current regulatory action taken by the Oklahoma Corporation Commission or the Montana Department of Environmental Quality.

The concentrations of oxygen and carbon dioxide in Well M-2 at a site in Antlers, OK (Figure 4.4) equilibrated in as little as 1.4 purge volumes. In contrast, oxygen and carbon dioxide in Well MW-4 at a site in Helena, MT (Figure 4.5) required 14 purge volumes to equilibrate. This order of magnitude discrepancy in the kinetics of equilibration is a good argument for the use of field meters to recognize stable conditions before samples are taken for laboratory analysis.

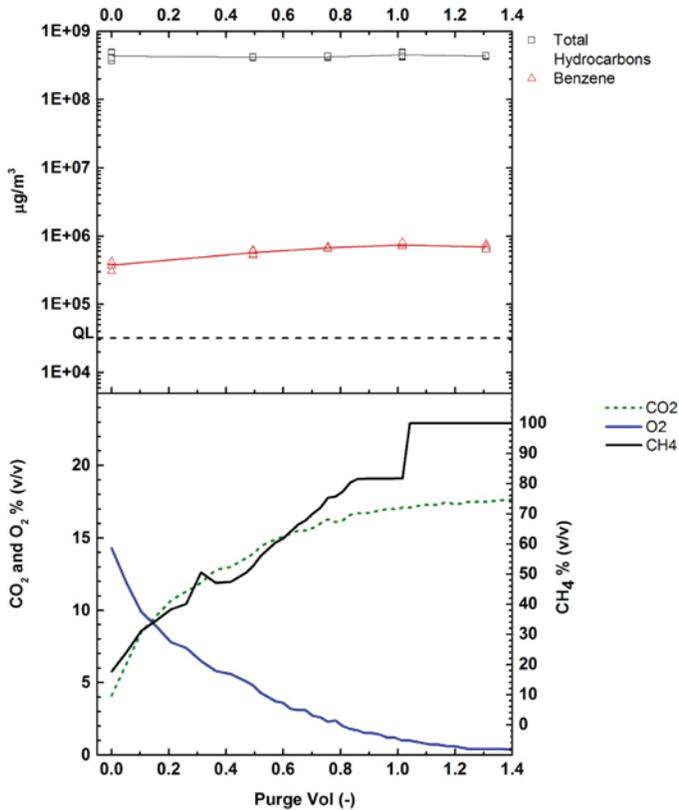


Figure 4.4. Kinetics of equilibration of oxygen, carbon dioxide, methane and benzene in soil gas from well MW-2 at the EZ Go service station in Antlers, Oklahoma.

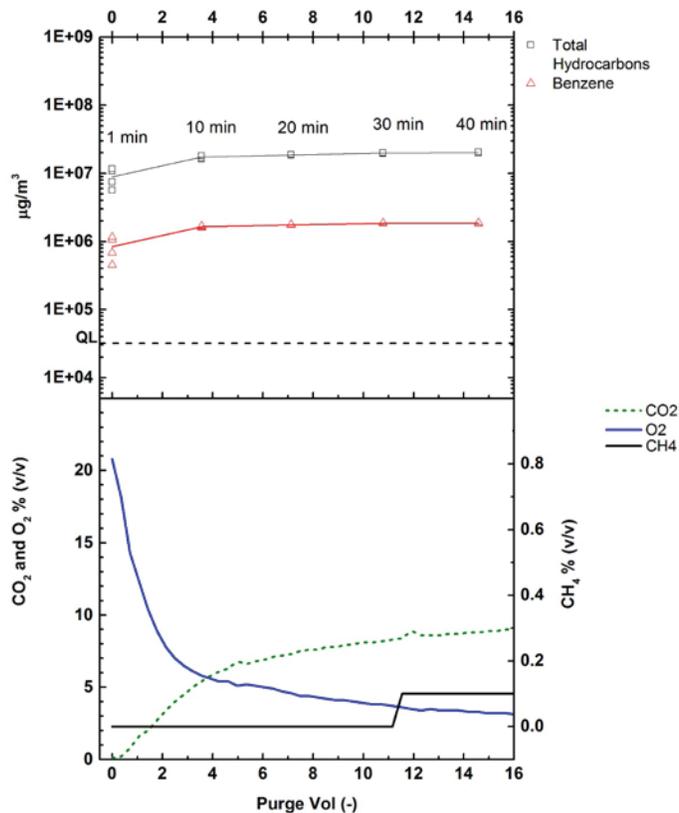


Figure 4.5. Kinetics of equilibration of oxygen, carbon dioxide, methane and benzene in soil gas from well MW-4 at the Kev's Auto site in Helena, Montana.

4.4.3 Stabilization of Methane and Petroleum Hydrocarbons in Soil Gas Samples from Water Monitoring Wells

In the field studies described in Figures 4.4 and 4.5 and Appendix A, the true equilibration of the wells was determined by measuring the concentrations of total hydrocarbons and the concentrations of benzene over time in the soil gas pumped from the well. Samples were collected after 1, 10, 20, 30 and 40 minutes of pumping. Petroleum hydrocarbons and methane were determined using a modification of ASTM D-1945 as described by Jewell and Wilson (2011). Total hydrocarbons concentration was calculated from the concentrations of all the individual gasoline hydrocarbons and methane. The concentrations of benzene and total hydrocarbons stabilized as the concentrations of oxygen and carbon dioxide stabilized (Figure 4.4 and 4.5). Data for an additional eight sites are provided in Appendix A.

At five of the ten sites, the concentrations of benzene and total hydrocarbons increased as the well stabilized. At four of the ten sites, the concentrations decreased as the well stabilized. At one site there was no significant change in the concentrations of benzene or total hydrocarbons as the well stabilized.

At many of the wells, the kinetics of stabilization of concentrations of benzene or total hydrocarbons in air samples was more rapid than the kinetics of stabilization of the meter readings for oxygen or carbon dioxide. The air samples were collected from a common outlet from the sampling train that also served as the inlet to the field meter. The difference in the rate of equilibration of the field meter and the air samples can only be explained as hysteresis in the readings from the field meter. If field meters for oxygen and carbon dioxide have stabilized, it is reasonable to conclude that the concentrations of benzene and petroleum hydrocarbons have stabilized.

4.5 Vertical Separation Distance between Source and Receptor

Figure 4.6 depicts the relationship between the bottom of a building that is the receptor of hydrocarbon vapors and the source of the vapors in the subsurface (taken from Figure 6 in U.S. EPA, 2013b).

U.S. EPA recommends a minimum separation distance from LNAPL in the unsaturated zone of 15 feet and a minimum separation distance from contamination dissolved in ground water of six feet.

The depth of the unsaturated zone changes with the elevation of the water table. Examine the center panel of Figure 4.6. When the water table is lower than the top of the LNAPL and the NAPL is exposed to the soil gas, the concentrations of hydrocarbons in soil gas will be the concentrations that would be expected for soil gas in contact with NAPL.

If the concentration of NAPL has reached residual saturation, the NAPL will not rise in elevation with a rise in the water table. Examine the bottom panel of Figure 4.6. Occasionally, the water table at a site may be high enough to inundate the residual NAPL. When that is the case, the soil gas will not be in direct contact with LNAPL. There will be less transfer of hydrocarbons to soil gas and the measured concentrations of hydrocarbons and compounds of concern in soil gas will be typical of the much lower concentrations that are seen above contaminated ground water. When the water table is high, it is also likely that NAPL would not accumulate in a monitoring well. When the water table drops and again exposes the NAPL to the soil gas, the concentrations of hydrocarbons in soil gas return to the higher concentrations expected for soil gas in contact with NAPL.

If the site characterization is done when the water table has inundated the NAPL, there is a danger of applying the criterion for separation from contaminated ground water, when the criterion for separation from NAPL is more appropriate.

To appropriately apply the U.S. EPA minimum screening distance for NAPL, it is necessary to know the distribution of NAPL to a depth of 15 feet below the bottom of the receptor, regardless of the position of the water table. Do not apply a minimum separation distance of six feet above contaminated ground water unless core samples have been acquired that extend at least 15 feet below the bottom of the receptor. If NAPL is present in the first 15 feet of core samples, then the vertical separation distance to hydrocarbon contamination is less than the recommended vertical

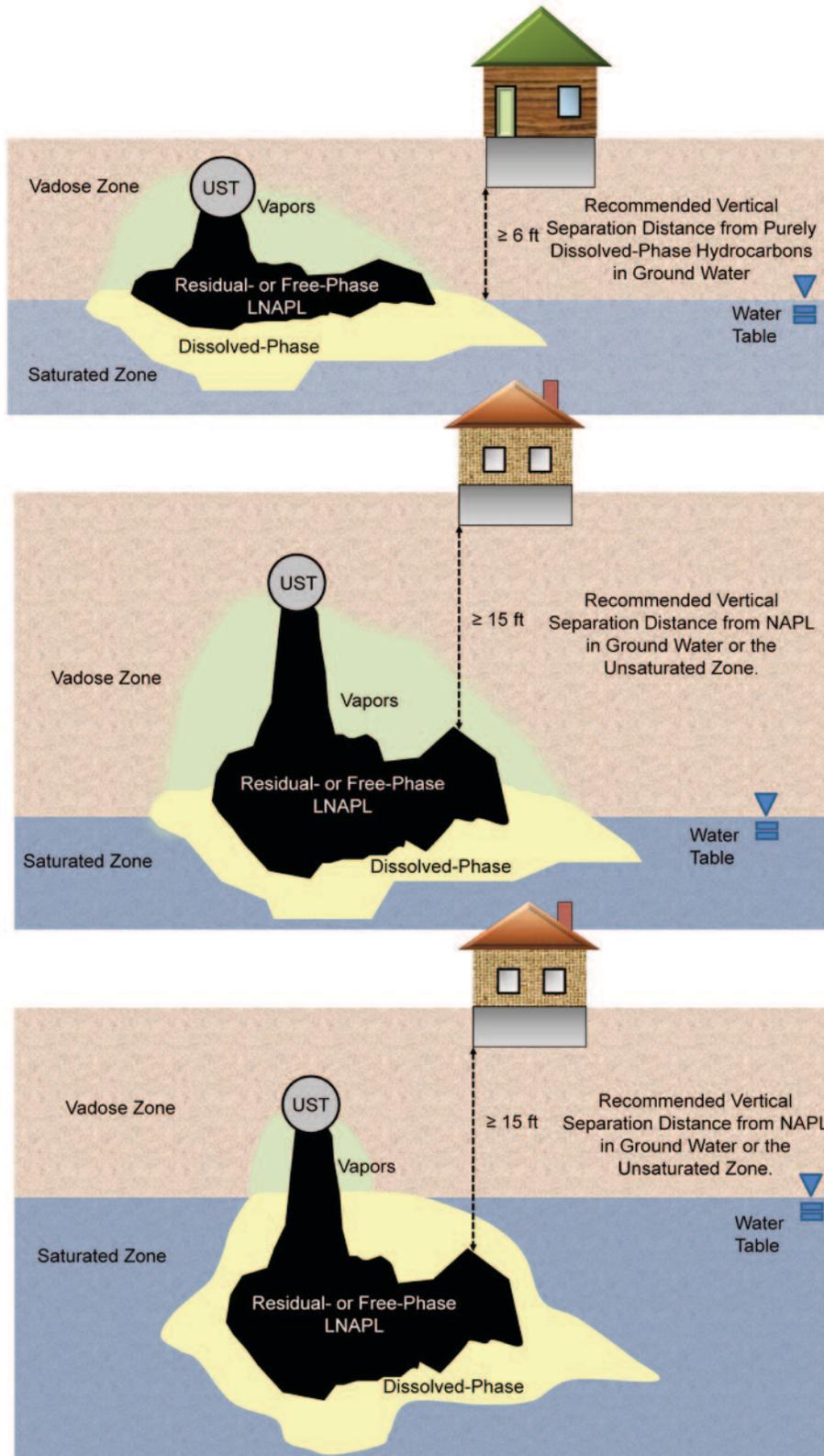


Figure 4.6. Recommended vertical separation between sources of hydrocarbon vapors and a building.

separation distance. See Wilson et al. (2012a) for recommendations on collecting and analyzing core samples to determine the vertical separation distance.

The driller's log for a vapor probe or ground water monitoring well is often a useful source of information to infer a separation distance. Most logs provide data on field screening of core samples for NAPL. Subsamples of the cores are enclosed in a plastic bag, and the air inside the bag is allowed to come to equilibrium with the NAPL in the core sample. Then the concentration of hydrocarbons in the air is determined with a field organic vapor analysis (OVA) meter. The meters can use a photoionization detector (PID), a flame ionization detector (FID) or a catalytic combustion cell (explosimeter). Meters that use a PID detector are sometimes called an organic vapor meter (OVM).

Figure 4.7 provides example data from a spill of motor gasoline into a sandy aquifer at a site near Madison, Wisconsin. The field screening was conducted with

a Scott TLV Sniffer OVA meter that was calibrated to hexane (Scott Instruments, Exton, PA). U.S. EPA (2013b), as referenced in Wilson et al. (2012a), defines clean sediment for the purposes of screening for PVI as having less than 250 mg/kg TPH. Wilson et al. (2012a) recommends that any core sample that screens with more than 100 ppm organic vapors be analyzed for TPH. In the sediment depicted in Figure 4.7, whenever the OVA readings were less than 100 ppm, the TPH was less than 250 mg/kg.

The data used in this case study are provided as an illustration. They do not necessarily reflect current conditions at the site, and have no bearing on past or current regulatory action taken by the Wisconsin Department of Natural Resources.

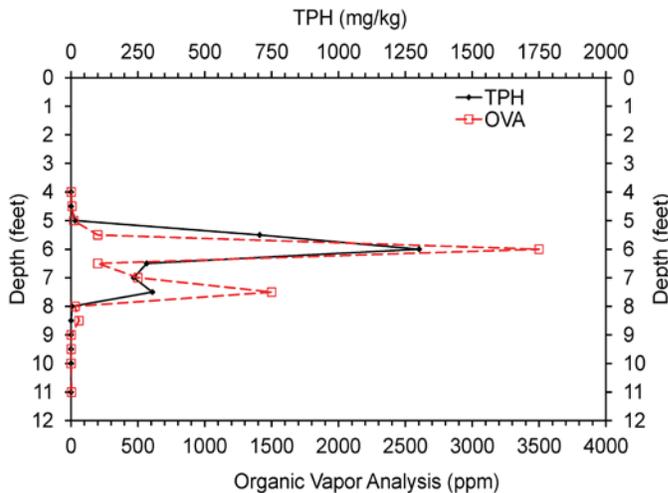


Figure 4.7. Relationship between the vertical distribution of TPH and field screening of core samples with an organic vapor analyzer (OVA).

Another, even more conservative criterion, is the concentration of TPH in soil gas where the TPH increases conspicuously above the background concentration. The depth interval where there is sharp increase in the OVA meter readings can be considered the first depth interval that has evidence of NAPL. The sample just above the increase is the deepest depth interval where there is no evidence of NAPL. The separation distance extends from the bottom of the foundation of the building to the deepest interval with no evidence of NAPL.

Compare Figure 4.8. This was a driller's log for vapor probes that were installed below the basement of the Oasis Hotel at the Former Hal's Chevron Site in Green River, Utah. Field screening revealed that OVA readings at depths of 3, 4, 5 and 6 feet below the

basement were 5.5, 6.7, 8.6, and 8.2 ppm using a PID detector. At a depth of 7 feet, the OVA reading was 191 ppm. The field log indicates "smear streaks at 7 feet". The true separation distance is greater than 6 feet and less than 7 feet. A separation distance of 6 feet would be appropriate for evaluation of PVI using BioVapor or PVIScreen or by using Figures 3.14 through 3.17 in this Issue Paper.

The data used in this case study are provided as an illustration. They do not necessarily reflect current conditions at the site, and have no bearing on past or current regulatory action taken by the Utah Department of Environmental Quality.



Project No.: 26CH.3430000
 Site: Hal's Chevron
 Address: Green River, Utah
 Drilling Contractor: EARTHPROBE
 Method/Equipment: Hand Auger
 Date Drilled: 10/08/03
 Well Completed: 10/08/03

Log of Borehole: VW-4
 Logged By: T. Clark
 Client: ChevronTexaco
 Top of Casing Elev.:
 Surface Elev.:
 Groundwater Elevation:
 Total Depth: 7.25'

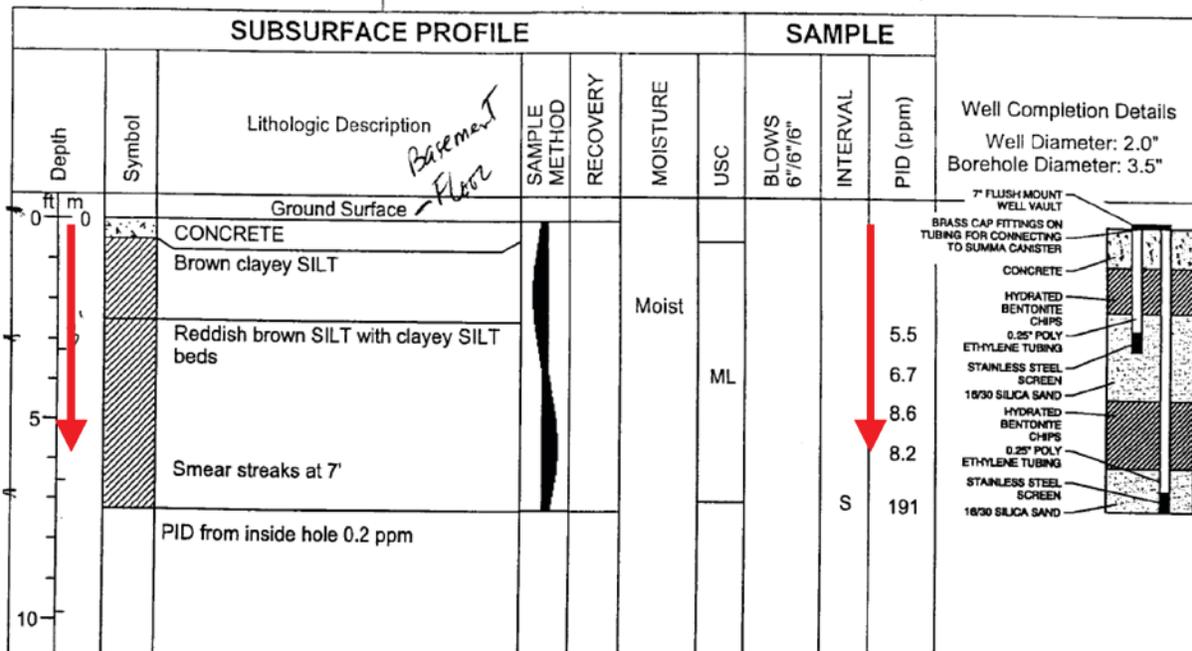


Figure 4.8. An example of a driller's log with information on the vertical extent of NAPL.

As a second line of evidence in an exposure assessment, the approach in this Issue Paper might be applied to a site that is not in the U.S. EPA vertical inclusion zone (U.S. EPA, 2013b; Wilson et al., 2012a). In this situation, the separation distance between NAPL hydrocarbons and the building will be greater than 15 feet. An example is provided in Figure 4.9. The site is the former Noon's Store in Helena, Montana. Core samples were screened every five feet to a total depth of 50 feet. To a depth of 30 feet, there is no evidence that the TPH would be expected to exceed 250 mg/kg. The reasonable lower boundary on the separation distance is 30 feet.

The data used in these case studies are provided as an illustration. They do not necessarily reflect current conditions at

the site, and have no bearing on past or current regulatory action taken by the Montana Department of Environmental Quality.

The driller's logs that are depicted in Figures 4.8 and 4.9 have three features in common. The driller attempted to collect a continuous core from the surface to several feet below the water table. Cores were acquired across the entire vertical interval, not just the material at the water table and five feet above the water table. Sub-cores were screened for NAPL across the entire vertical interval. Starting with the most shallow depth interval, several of the depth intervals that were screened had undetectable or trivial concentrations of hydrocarbons in air in equilibrium with the core samples.

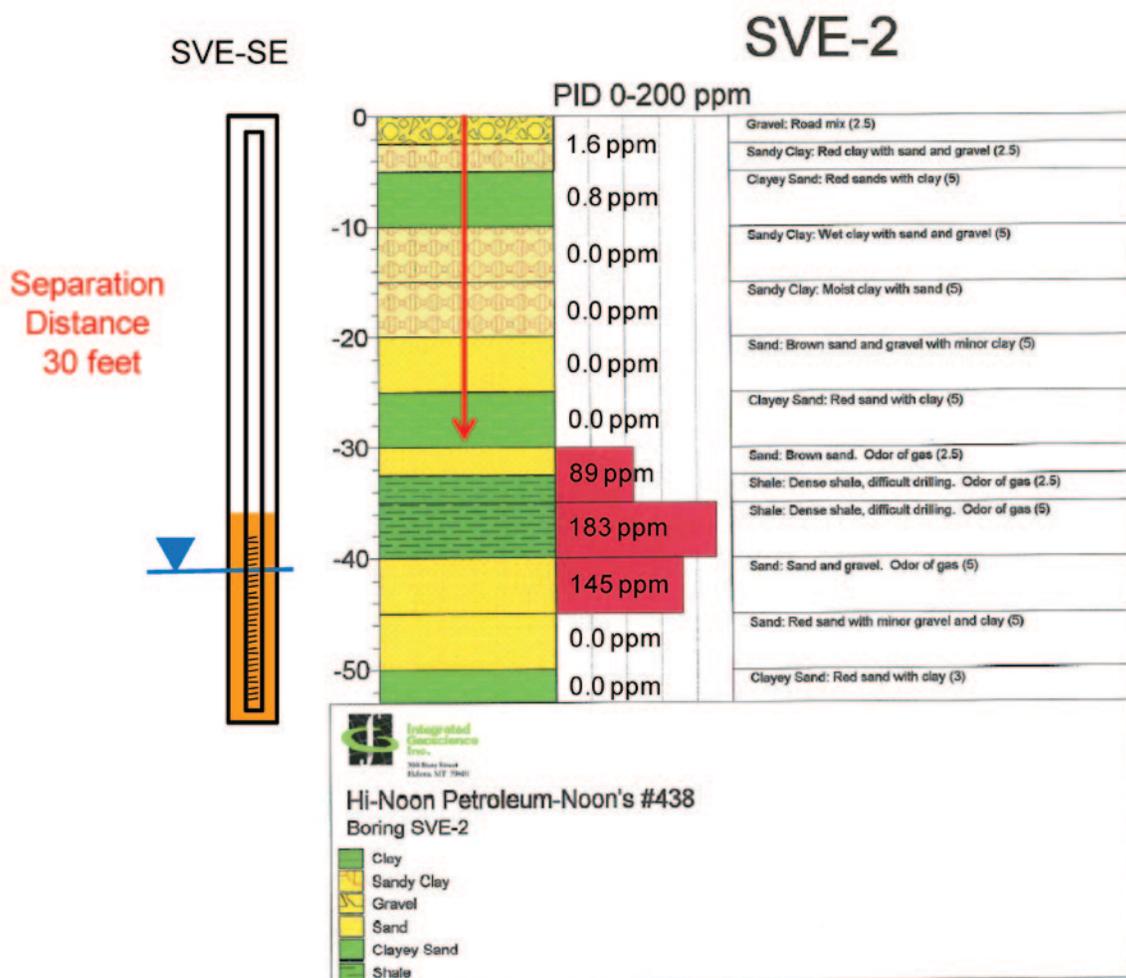


Figure 4.9. A second example of a driller's log with information on the vertical extent of NAPL.

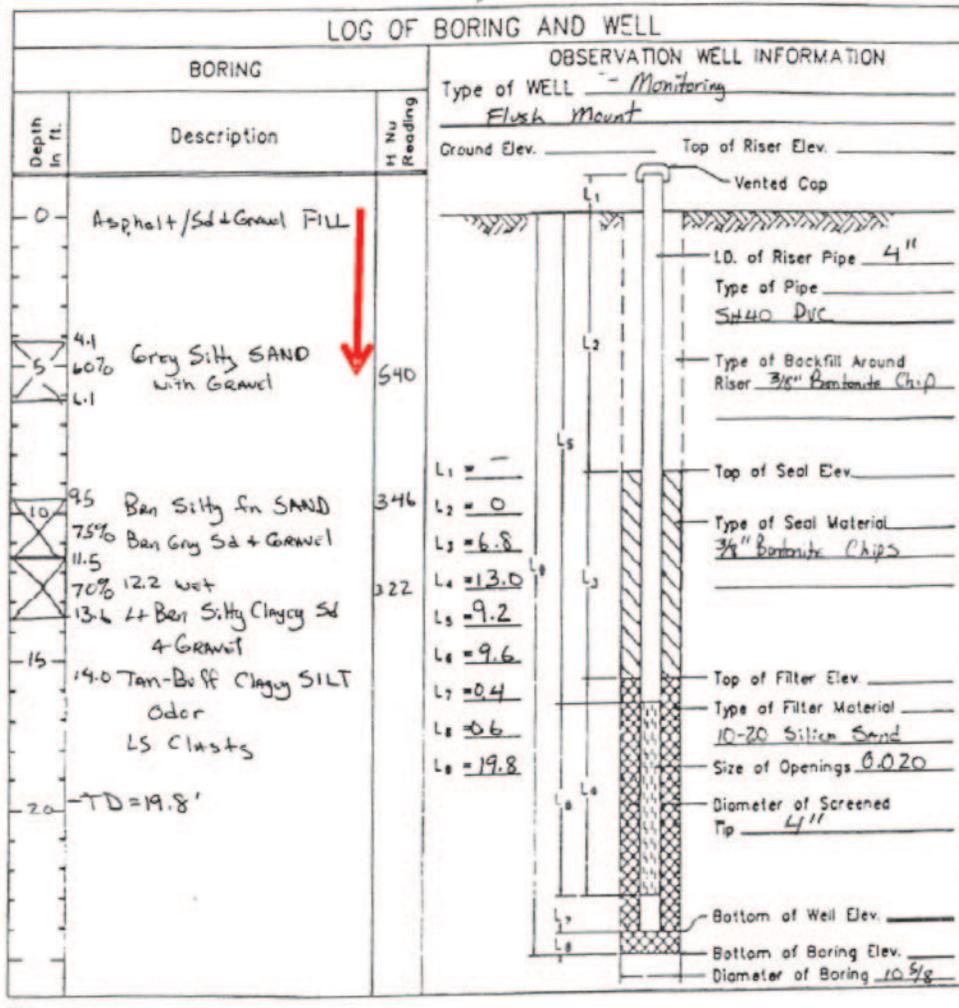
Compare Figure 4.10. This log was taken at a former Gasmat Site in Helena, Montana. The first sample for screening was taken at a depth of five feet. The screening indicated a potential for NAPL at this depth. The first depth interval that was screened had an unacceptable PID reading. There is no information that can be used to interpret a separation distance.

It would not be appropriate to apply the approach in this Issue Paper to soil gas data from this location. In situations where it is impossible to interpret a separation distance, it is more appropriate to apply the generic attenuation factor for shallow soil gas as is provided in guidance from the U.S. EPA or from the appropriate state regulatory agency.

GROUNDWATER WELL INSTALLATION REPORT

Well No. MW-6

Project GASMAT 563 Helena Location W of Tank Basin
 Project No. ECAM04 Installed By DIE/O'Keefe/Dalby Date 5/15/98 Time 0900
 Method of Installation Mobile B-61 Hollow Stem Auger



Separation Distance <5 feet

Top of Screen 6.8 feet

Figure 4.10. A third example of a driller's log with information on the vertical extent of NAPL.

5.0 APPLICATION OF THE APPROACH TO A SITE WITH BASEMENTS (GREEN RIVER, UT)

The data used in this case study are provided as an illustration. They do not necessarily reflect current conditions at the site, and have no bearing on past or current regulatory action taken by the Petroleum Storage Tank Trust Fund of the Utah Department of Environmental Quality.

A spill of motor fuel from underground storage tanks at the former Hal's Chevron in Green River, UT created a zone of LNAPL that extended underneath a motel and café that adjoined the service station. The motel has an office with a basement and the café has a basement. See Figure 5.1.

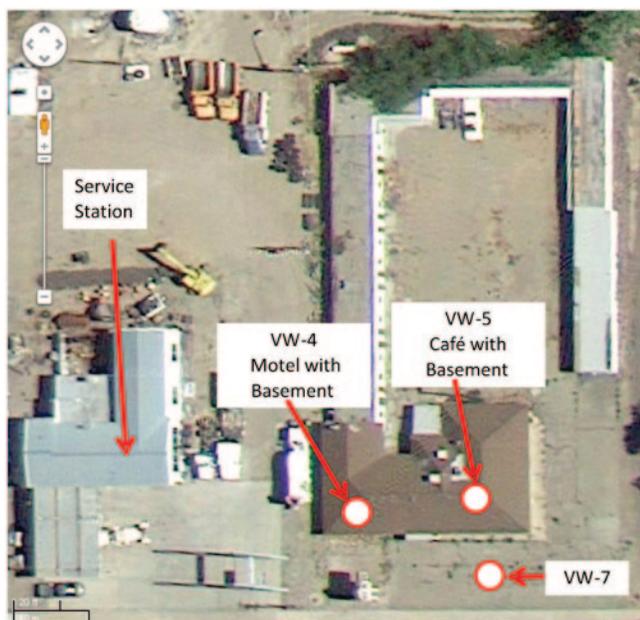


Figure 5.1. Aerial photograph of the Hal's Chevron Site in Green River, Utah. The photograph was downloaded from Google Maps®.

The Utah Department of Environmental Quality (DEQ) installed a series of monitoring wells to define the extent of contaminated ground water and the extent of LNAPL underneath the motel and café. They also installed sets of multi-depth vapor monitoring points. Figure 5.2 compares the location of the monitoring points and buildings to the known extent of NAPL at

the site. The extent of NAPL was defined by Robin Davis and other staff of the Utah DEQ. They used a large number of wells and core sampling points that are not depicted in Figure 5.2.

The Utah DEQ installed multi-depth vapor monitoring points in the basement of the motel office (VW-4 in Figure 5.2) and in the basement of the café (VW-5). All the other monitoring points were installed outside of the buildings. The vapor monitoring points had an inner diameter of 0.17 inch. The ground water wells had an inner diameter of 2 inches.

The release was in a series of silty fine sands, silts, clayey silts and silty clay (Figure 5.3). The monitoring wells were screened across the water table and the depth interval with NAPL. The deepest vapor monitoring point in each cluster was screened in the depth interval with NAPL.

5.1 Determining the Separation Distance from the Source to the Basement of the Café

Vapor point VW-7 is just south of the café (Figure 5.2). A series of core samples were acquired next to VW-7. A paste sampler was used to acquire a 10 cm³ sub sample at various depth intervals along the core samples. The sub samples were extracted into methanol and analyzed for TPH. The peak concentration of TPH was at a depth of 14 feet (Figure 5.3). From depths of three feet to 12 feet, TPH was <20 mg/kg. The floor of the basement in the café was eight feet below land surface. Based on the TPH in core samples, the separation distance was at least 12 - 8 = 4 feet, but not greater than 14 - 8 = 6 feet.

Figure 5.4 is the driller's log for the vapor monitoring points below the basement of the café. To a depth of seven feet below the basement floor or 15 feet below land surface, the PID screening did not indicate the presence of NAPL. Allowing 0.5 feet for the depth of the concrete in the floor, the separation distance is at least 7 - 0.5 = 6.5 feet.

The two estimates of the separation distance are in acceptable agreement. A separation distance of 6.5 feet will be used for purposes of screening. Because BioVapor and PVIScreen allow input of the separation

distance, a value equivalent to 6.5 feet was used in the models. The figures based on the Abreu Three-Dimensional Model plot the separation distance in

meters. A distance of 6.5 feet is 1.98 meters. The line corresponding to a separation distance of 2 meters will be used to estimate a value of the attenuation factor.

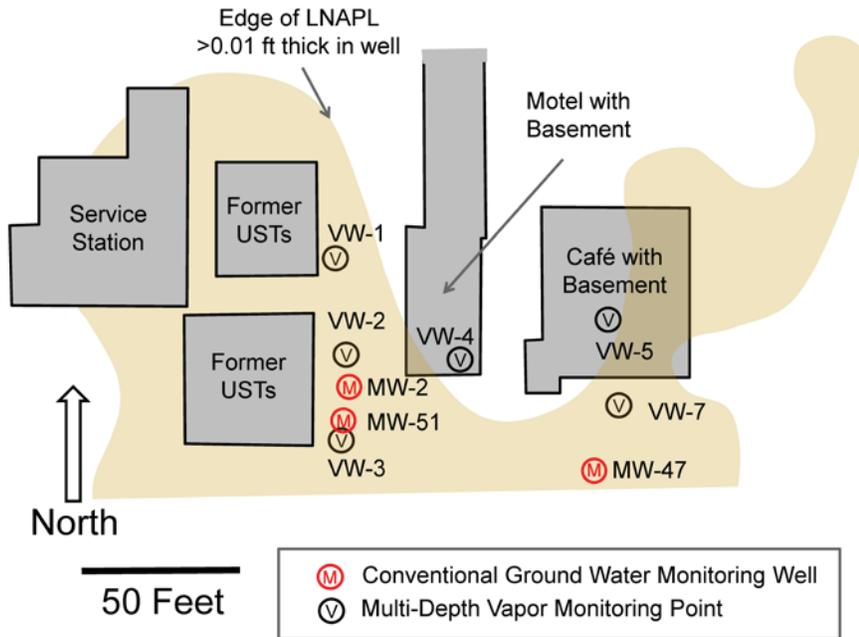


Figure 5.2. Relationship between the extent of NAPL, the location of receptors and the location of monitoring points at the Hal's Chevron Site.

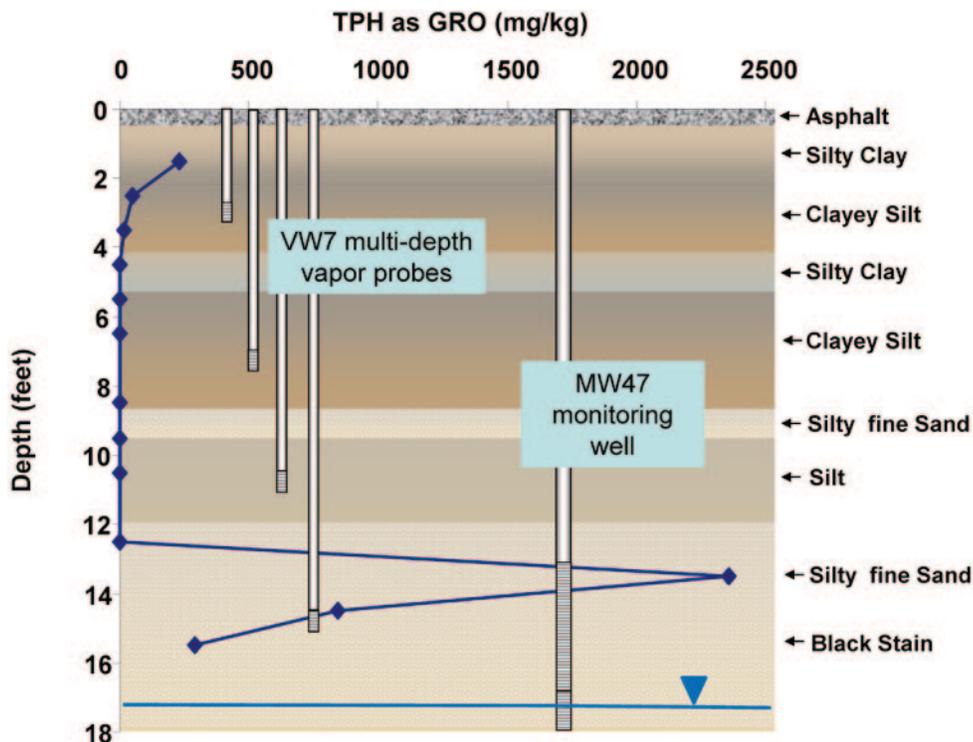


Figure 5.3. Relationship between the screened interval of a conventional ground water monitoring well and the screened intervals of a cluster of vapor monitoring points to the soil texture, the depth to ground water, and the vertical distribution of Total Petroleum Hydrocarbons (TPH) in core samples.

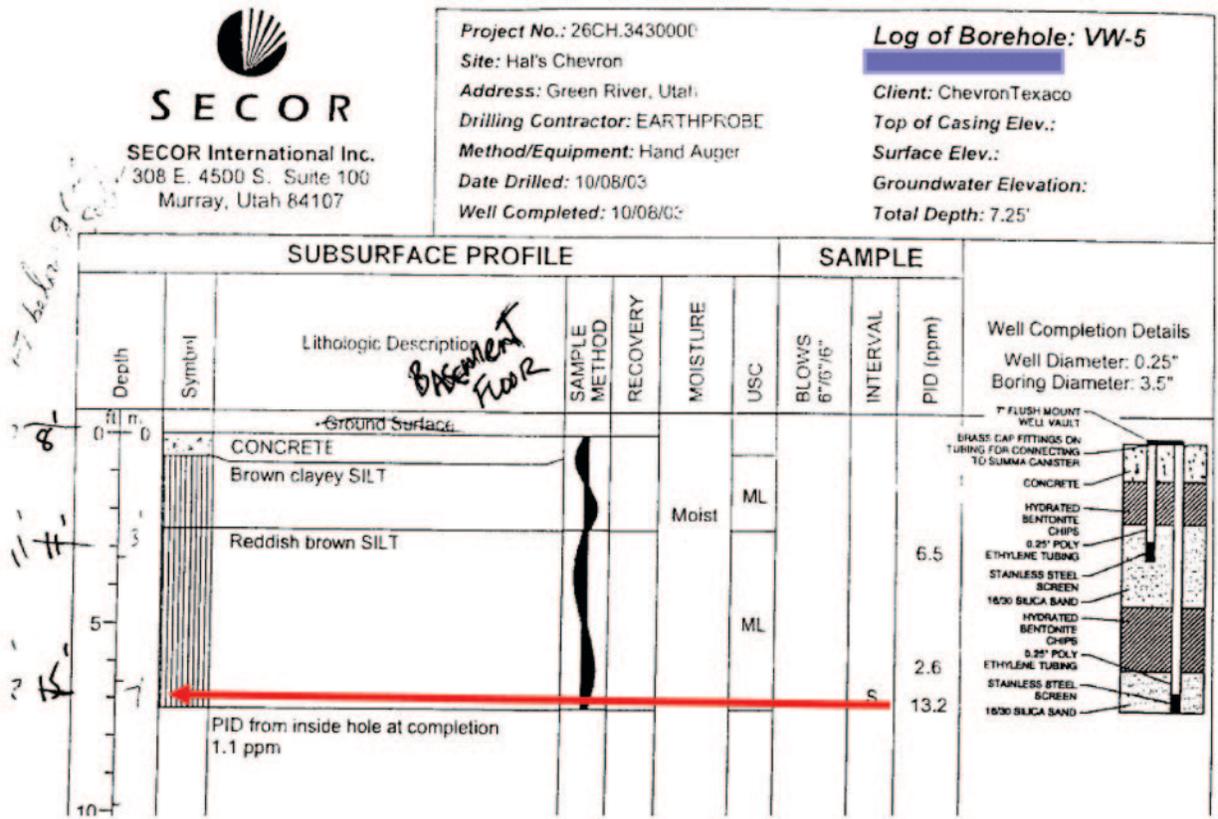


Figure 5.4. Driller's Log for vapor monitoring points at location VW-5 in the basement of the café.

5.2 Forecast of the Indoor Air Concentration in the Basement of the Café

Concentrations of benzene and petroleum hydrocarbons in the vapor monitoring points were determined by a modification of TO-15 (U.S. EPA, 1999a). Methane was determined by a modification of ASTM D-1945 (ASTM, 2010). Soil gas from the ground water monitoring wells was collected and analyzed as described in Jewell and Wilson (2011).

The primary data used to calculate the concentration of source vapors are presented in Table 5.1. At this site, the concentration of methane in soil gas was low, and methane made no appreciable contribution to the total hydrocarbons. The data from conventional monitoring wells in Table 5.1 and subsequent tables are corrected for leaks and dilution using the reported concentration of oxygen, as described in Section 4.3. The sample from the vapor probes comprised a little

more than one liter soil gas. Because the samples were so small, they can effectively be considered point samples. There should be no significant dilution of the sample as the sample is collected, and no correction was applied to the vapor probe samples.

When the correction for dilution was applied to the sample from the monitoring well, the concentrations were in reasonable agreement between monitoring points VW-7 and MW-47.

The total hydrocarbons in the vapor monitoring point and the soil gas from the ground water well are plotted as vertical red lines in Figure 5.5. Values are plotted for monitoring point VW-7 without correction and MW-47 with correction. Figure 5.5 reprints Figure 3.15 showing only the 2 meter line.

Source Vapor Concentrations are plotted to one significant figure. To be conservative, a figure was used that was based on a first order rate constant for biodegradation of 0.079 per hour.

Applying the correction made no difference in the prediction. The concentrations of total hydrocarbons in the two monitoring points predict a value of the attenuation factor (α) of 8E-05.

The concentration of benzene in indoor air was estimated by multiplying the attenuation factor (α) by the measured concentration of benzene in the soil gas in VW-7 and the corrected concentration of benzene in MW-47. Results are presented in Table 5.2.

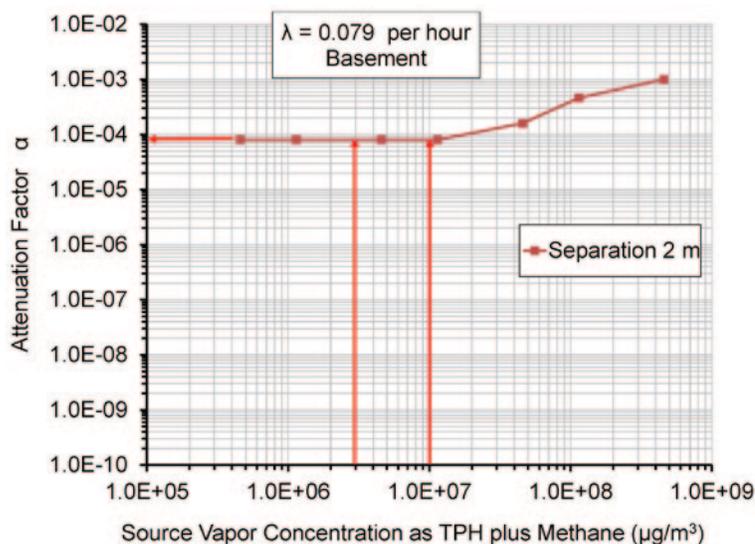


Figure 5.5. Estimates of the attenuation factor in soil gas below the café based on concentrations of vapor at the source.

Table 5.1. Concentrations of TPH-g and methane in soil gas near the café, and the calculated total concentrations of hydrocarbons in soil gas.

Monitoring Point	Oxygen	Correction Factor	TPH-g	Methane	Total Hydrocarbons
	%		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$ as C_7H_{16}
VW-7	Not Measured	No Correction	3.10E+06*	9.30E+03	3.1E+06
MW-47	17.2	5.65	1.02E+07	5.54E+03	1.0E+07

* Values are in scientific notation. The notation 3.10E+06 means 3.10×10^6 .

Table 5.2. Estimated concentration of benzene in indoor air in the basement of the café based on the Abreu Three-Dimensional Model, on BioVapor and on PVI Screen.

Location	Benzene	α	Estimated Concentration of Benzene in Indoor Air*			
			Abreu Figure	Generic BioVapor	Site Specific BioVapor	PVI Screen Most Probable Result
	$\mu\text{g}/\text{m}^3$		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
VW-7	4.6E+03	8E-05	4E-01	3E-01	8E-07	2E-04
MW-47	8.5E+04	8E-05	7E+00	7E+00	2E-05	4E-03

* The Utah Indoor Air Guidance (commercial) for benzene is $5\text{E}-01 \mu\text{g}/\text{m}^3$.

The concentration of benzene in indoor air was also predicted using the BioVapor model set up two different ways. The Generic BioVapor simulations were set up using the **Residential Default Values** on the **Environmental Factors** input screen with the following expectations. **Airflow under Foundation** (Q_f) was set to be equal to **Air Flow Through Basement Foundation** (Q_s). The value was 83 cm³ of air per second. To be consistent with the assumptions of the Abreu Three-Dimensional Model, the **Air Exchange Rate** was set to 12 per day. The default rate constant for biodegradation of benzene in BioVapor is 0.79 per hour.

The rate constant in the **Chemical Database** (row 14, column U) was changed to 0.079 per hour. These parameters were altered from the default values to produce simulations that were conservative forecasts of the expected concentrations of benzene in indoor air. Simulations made with these values for the parameters are called Generic Biovapor simulations.

See Figure 5.3. The water content of core samples in the interval from 2 feet to 10 feet below grade averaged 0.20 cm³ water/cm³ soil. This is the interval that supported aerobic biodegradation of the hydrocarbon vapors. This water content is four times higher than the default assumption. The average mass fraction of organic carbon in the interval from 2 feet to 10 feet below grade was 0.006 g organic carbon/ g soil. The Site specific Biovapor simulations used the average quantity of soil water and organic carbon in core samples from the site.

There was no practical difference in the estimated concentration of benzene in indoor air based on the Abreu Three-Dimensional Model and the estimate provided by the Generic BioVapor simulation (Table 5.2). Both of these estimates are conservative estimates. The true attenuation was most likely higher, which will produce lower concentrations of benzene in indoor air.

A higher content of water allows more living space for bacteria that degrade the hydrocarbons. The Site Specific BioVapor simulation had four times the quantity of water in the profile. At a given rate constant for biodegradation, the modeled rate of degradation is four times faster. At the same time,

the space available for diffusion of hydrocarbons is reduced 0.33 cm³/cm³ to 0.18 cm³/cm³. The reduction in concentrations in indoor air vary as the exponent of the first order rate constant for degradation. The estimate of the concentration of benzene in indoor air that was provided by Site Specific BioVapor simulation was five orders of magnitude lower than the Generic BioVapor simulation (Table 5.2).

The PVIScreen model was set up using one site specific value (Table 3.1 in Section 3). The moisture content was set at 0.20. The Most Probable Result from the PVIScreen simulations was intermediate between the predictions of the Site Specific BioVapor simulation and the Generic BioVapor simulation (Table 5.2).

The distribution of the PVIScreen simulations is presented in Table 5.3. For vapor well VW-7, the Most Probable Result was 2E-04 µg/m³, a concentration which was exceeded by 12.2% of the simulations. However, none of the 1000 simulations exceeded the acceptable cancer risk level of 0.52 µg/m³. Likewise, no simulations exceeded the hazard quotient of 1.0 (at 30 µg/m³). The indoor air results for monitoring well MW-47 were similar, but the Most Probable Result was an order of magnitude higher. Even so, no simulations exceeded either the cancer or non-cancer risk levels.

5.3 Validation of the Forecast for the Basement of the Café

The Utah Indoor Air Guidance (commercial) for benzene is 0.5 µg/m³. Because the estimates are near this value, it is necessary to further characterize the exposure. In the normal course of events, the next step would be to collect shallow soil gas near or below the foundation. The Utah DEQ anticipated the need for this data, and collected soil gas from the shallow and deep monitoring points on five dates extending from October 2003 to September 2009 (Figure 5.6). The samples described in Tables 5.1 and 5.2 were collected in September, 2011.

The soil gas had adequate concentrations of oxygen to support aerobic biodegradation. The concentrations of benzene steadily declined over time in the deep soil gas samples. The concentrations of benzene in the

Table 5.3. Distribution of the simulations in PVI-Screen of the concentration of benzene in indoor air in the café.

Location	PVI-Screen Most Probable Result $\mu\text{g}/\text{m}^3$	% Exceeding		
		Most Probable Result	Acceptable Cancer Risk ($0.52 \mu\text{g}/\text{m}^3$)	Acceptable Non-Cancer Hazard at Hazard Quotient = 1.0 ($30 \mu\text{g}/\text{m}^3$)
VW-7	2E-04	12.2	0.000	0.000
MW-47	4E-03	2.0	0.000	0.000

shallow soil gas samples also declined over time, but the variability was much greater.

The highest concentration of benzene at a depth of three feet below the basement was $140 \mu\text{g}/\text{m}^3$. Following the guidance in Table 1.2, and allowing for a generic attenuation factor from shallow soil gas into the indoor air of 0.1, this highest concentration would produce indoor air concentrations of $14 \mu\text{g}/\text{m}^3$. On the other sampling dates, the indoor air concentrations

would have been no more than $2.2 \mu\text{g}/\text{m}^3$. On the last sampling date, the predicted indoor air concentration would be $0.15 \mu\text{g}/\text{m}^3$.

The indoor air concentration predicted from shallow soil gas on the last sampling date ($0.15 \mu\text{g}/\text{m}^3$) was lower than the predictions from the simulations of the Abreu Three Dimensional Model or the Generic BioVapor Model ($7\text{E}+00 \mu\text{g}/\text{m}^3$, see Table 5.2).

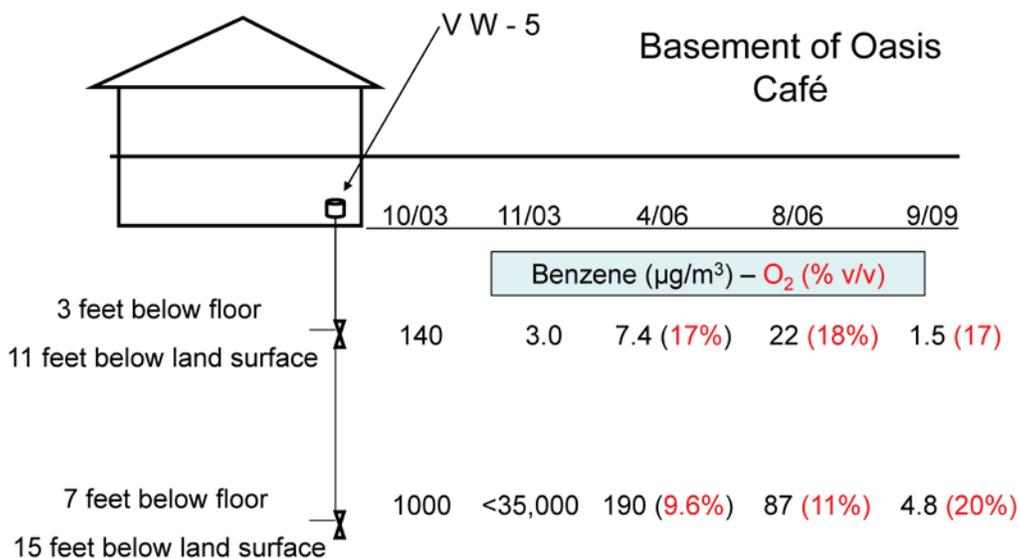


Figure 5.6. Concentrations of benzene and oxygen in soil gas beneath the café. Original graphic created by Robin Davis, Utah DEQ.

The prediction made from shallow soil gas (0.15 $\mu\text{g}/\text{m}^3$) was greater than the predictions from the Site Specific BioVapor model (2E-05 $\mu\text{g}/\text{m}^3$) or PVI Screen (4E-03 $\mu\text{g}/\text{m}^3$).

The simulations of the Abreu Three Dimensional Model or the Generic BioVapor Model were the best match to the prediction from shallow soil gas; however, they were roughly an order of magnitude higher than the prediction from shallow soil gas. The prediction based on shallow soil gas did not include any reduction in concentrations due to biodegradation. Compared to the prediction based on concentration in shallow soil gas and an attenuation factor of 0.10, the simulations of the Abreu Three Dimensional Model or the Generic BioVapor Model were conservative and over-predicted the concentration in indoor air.

5.4 Determining the Separation Distance from the Source to the Basement of the Office

The same approach will be applied to one other location at the Hal's Chevron site. The office of the motel was immediately adjacent to the tank pits for the underground storage tanks (Figure 5.2).

The concentrations of petroleum hydrocarbons and methane in the soil gas are provided in Table 5.4.

When the correction for dilution was applied to the ground water monitoring wells, the corrected concentrations were in reasonable agreement between monitoring points.

Examine Figure 5.7. Based on field screening with a PID detector, there is no evidence of petroleum NAPL contamination to a depth of six feet below the floor of the basement. Allowing 0.5 foot for the concrete floor, the separation distance is 5.5 feet. The closest equivalent in the figures based on Abreu et al. (2009a) is a separation distance of 2 meters.

Figure 5.8 reprints Figure 3.15 showing only the 2 meter line. The calculated total concentrations of hydrocarbons from Table 5.3 are plotted in Figure 5.8. They predict a value of the attenuation factor (α) of 4E-04 for MW-2; a factor of 6E-04 for VW-1 and MW-51; and a factor of 8E-04 for VW-2 and VW-3. These attenuation factors are multiplied by the measured concentration in soil gas to predict the measured concentration in indoor air (Table 5.5).

Table 5.4. Concentrations of TPH-g and methane in soil adjacent to the office of the motel, and the calculated total concentrations of hydrocarbons in soil gas.

Monitoring Point	Oxygen	Correction Factor	TPH-g	Methane	Total Hydrocarbons
	%		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$ as C_7H_{16}
VW-1	Not Measured	No Correction	2.2E+08	2.3E+06	2.2E+08
VW-2	Not Measured	No Correction	2.8E+08	1.9E+06	2.8E+08
MW-2	1.36	1.07	1.3E+08	2.0E+06	1.3E+08
MW-51	18.2	7.74	1.5E+08	1.4E+06	1.5E+08
VW-3	Not Measured	No Correction	2.8E+08	5.3E+06	2.9E+08

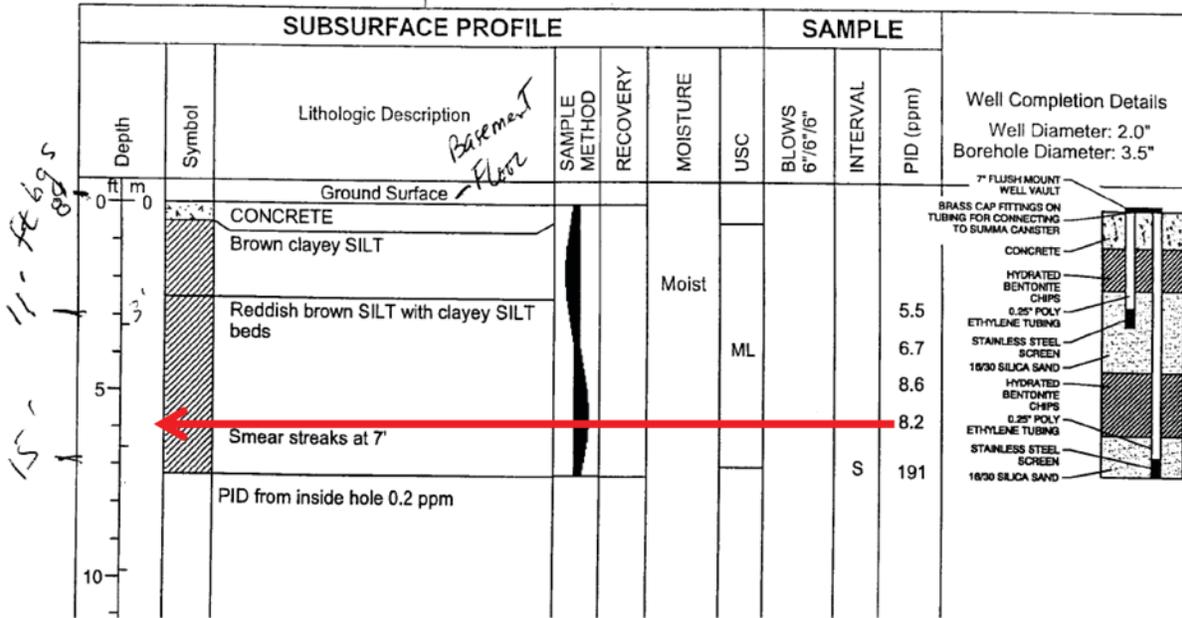


Figure 5.7. Driller's log for vapor monitoring points at location VW-4 in the basement of the office for the motel.

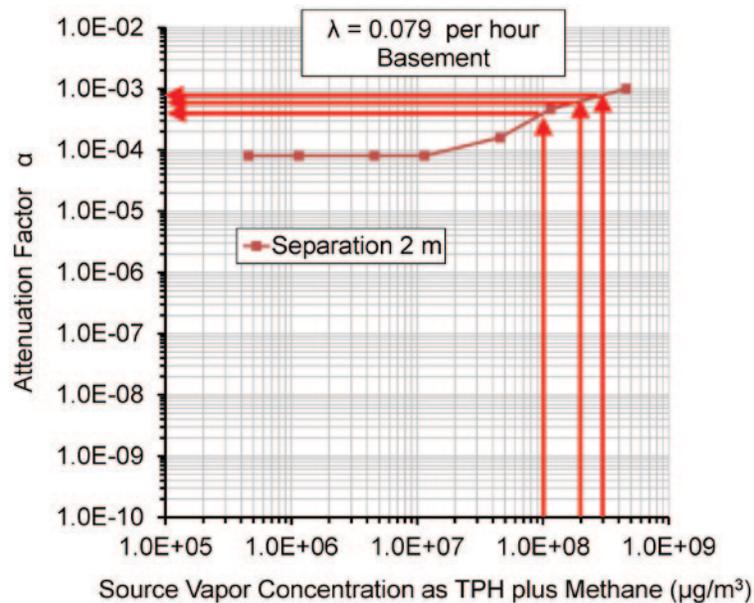


Figure 5.8. Estimates of the attenuation factor in soil gas below the office of the motel based on concentrations of vapor at the source.

5.5 Forecast of the Indoor Air Concentration in the Basement of the Office

Compared to the basement of the café, the concentrations of total hydrocarbons and benzene in soil gas adjacent to the basement of the office are ten to one-hundred fold higher (compare Tables 5.1 and 5.2 to Tables 5.3 and 5.4). It is not surprising that the forecasts of benzene concentrations in the basement of the office are from ten to one hundred fold higher (compare Table 5.2 to Table 5.5).

As was the case earlier, the estimated concentrations of benzene in indoor air based on Abreu et al. (2009a) are

in reasonable agreement with the estimates provided by the Generic BioVapor simulations. The estimates based on the Site Specific BioVapor simulation are approximately one-hundred fold lower.

The distribution of the PVIScreen simulations is presented in Table 5.6. The most probable concentrations ranged from $7E+01 \mu\text{g}/\text{m}^3$ to $7E+02 \mu\text{g}/\text{m}^3$. These concentrations were exceeded by between 10.6% and 25.3% of the simulations. The cancer screening level of $0.52 \mu\text{g}/\text{m}^3$ was exceeded by between 43.0% and 53.0% of the simulations. The exceedance for the non-cancer hazard was between 29.0% and 47.8% of the simulations.

Table 5.5. Estimated concentration of benzene in indoor air in the basement of the office of the motel based on the Abreu Three-Dimensional Model, on BioVapor and on PVIScreen.

Location	Benzene	α	Estimated Concentration of Benzene in Indoor Air			
			Abreu Figure	Generic BioVapor	Site Specific BioVapor	PVIScreen Most Probable Result
	$\mu\text{g}/\text{m}^3$		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
VW-1	1.1E+06	6E-04	7E+02	1E+03	4E-01	7E+01
VW-2	2.3E+06	8E-04	2E+03	3E+03	3E+00	4E+02
MW-2	4.4E+06	4E-04	2E+03	4E+03	1E-01	4E+02
MW-51	8.5E+06	4E-04	3E+02	9E+03	5E-01	7E+02
VW-3	3.6E+06	8E-04	3E+03	4E+03	5E+00	7E+02

Table 5.6. Distribution of the simulations in PVIScreen of the concentration of benzene in indoor air in the basement of the office of the motel.

Location	PVIScreen Most Probable Result $\mu\text{g}/\text{m}^3$	% Exceeding		
		Most Probable Result	Acceptable Cancer Risk ($0.52 \mu\text{g}/\text{m}^3$)	Acceptable Non-Cancer Hazard at Hazard Quotient = 1.0 ($30 \mu\text{g}/\text{m}^3$)
VW-1	7E+01	25.3	54.0	36.9
VW-2	4E+02	13.0	60.8	46.8
MW-2	4E+02	10.6	43.0	29.0
MW-51	7E+02	12.1	46.3	33.9
VW-3	7E+02	10.8	60.4	47.8

5.6 Validation of the Forecast for the Basement of the Office

As mentioned earlier, the Utah Indoor Air Guidance (commercial) for benzene is $0.5 \mu\text{g}/\text{m}^3$.

All of the estimates are near or are much higher than that guidance. Following U.S. EPA (2013b), it is necessary to further evaluate the exposure. The Utah DEQ had sampled shallow soil gas beneath the basement of the office. Data are provided in Figure 5.9. The shallow soil gas had adequate concentrations of oxygen to support aerobic biodegradation of the hydrocarbons. The concentrations of benzene are lower in the shallow soil gas. Applying a generic attenuation factor (α) of 0.1, the predicted indoor air concentration at the last sampling date would be $5\text{E}+00 \mu\text{g}/\text{m}^3$.

At this location, the estimates based on Abreu et al. (2009a), on the generic BioVapor model and on PVIScreen were higher than the estimates based on measured concentrations of benzene in shallow soil

gas. The estimates provided by the Site Specific BioVapor simulation were in reasonable agreement with the estimate from shallow soil gas based on a generic attenuation factor (α) of 0.1.

All the sampling locations for soil gas were located between the tank pits and the motel. This would have biased the screening models if the concentrations under the basement of the office were actually lower than the soil gas that was sampled for screening of PVI. The concentrations of benzene in soil gas adjacent to the office of the motel varied from $1\text{E}+06$ to $9\text{E}+06 \mu\text{g}/\text{m}^3$ (Table 5.4). The concentrations of benzene at an equivalent depth underneath the building were no more than $3\text{E}+03 \mu\text{g}/\text{m}^3$ (Figure 5.9).

It is probably impossible to avoid sample bias based on the location of the vapor points or monitoring wells. However, it is important to control for the bias. Select sampling points that are between the source and the receptor.

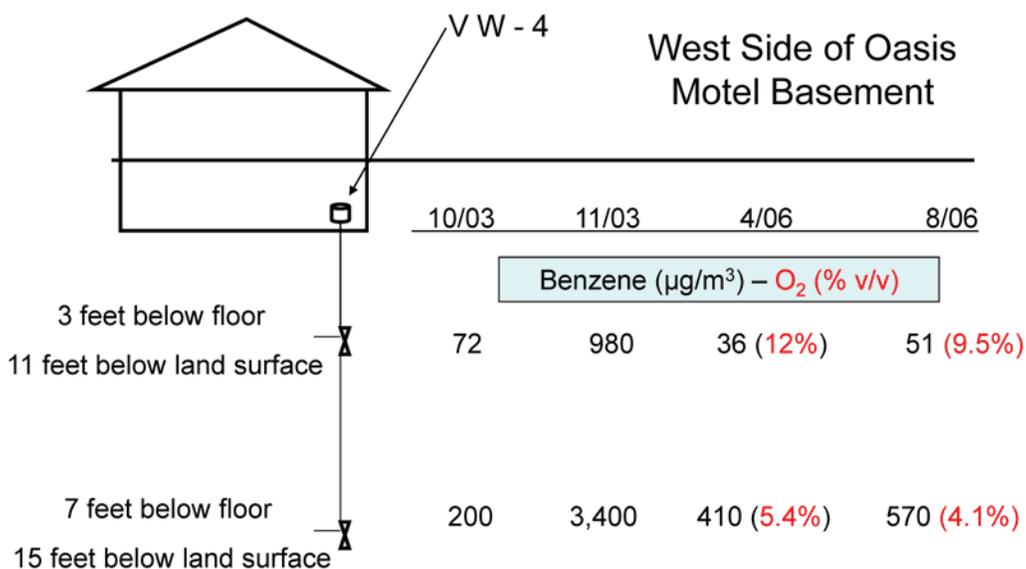


Figure 5.9. Concentrations of benzene and oxygen in soil gas beneath the office of the motel. Original graphic created by Robin Davis, Utah DEQ.

6.0 APPLICATION OF THE APPROACH TO A SITE WITH HIGH CONCENTRATIONS OF METHANE AND SLAB-ON-GRADE CONSTRUCTION (ANTLERS, OK)

The data used in these case studies are provided as an illustration. They do not necessarily reflect current conditions at the site and have no bearing on past or current regulatory action taken by the Oklahoma Corporation Commission.

This case study is a release of E10 gasoline at the EZ Go service station in Antlers, OK. The release was associated with underground storage tanks in a tank pit and associated distribution lines. Figure 6.1 depicts the relationship between the known extent of NAPL contamination and ground water monitoring wells, the convenience store that was the potential receptor, and sub-slab vapor probes installed near and beneath the slab of the convenience store.

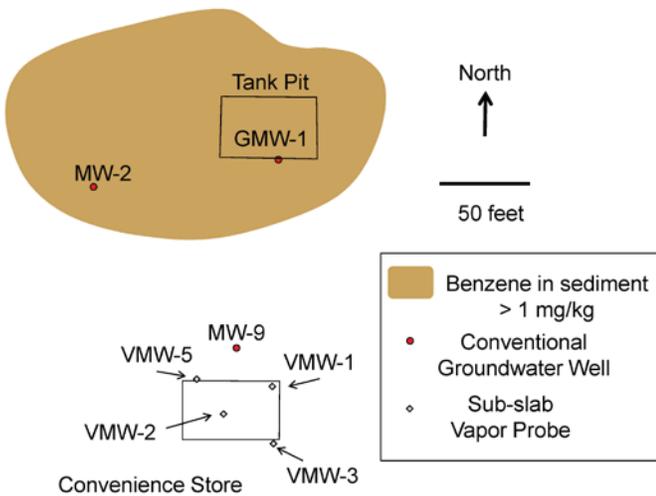


Figure 6.1. Relationship between location of the building that might act as a receptor, the known location of petroleum NAPL, the location of monitoring wells, and the location of vapor monitoring points.

Figure 6.2 describes the lithology of the unsaturated material and the top of the aquifer. The log for MW-2 indicated that the Sandy Silt Loam at 10 to 11 feet had tree roots and may represent the original land surface. There is a tendency at this site for water to perch at a level near ten feet below grade. The geological material was largely a combination of clay, sandy clay and clayey sand.

Figure 6.2 also depicts the depth intervals sampled by the wells. Both wells had long screened intervals in contact with the unsaturated zone.

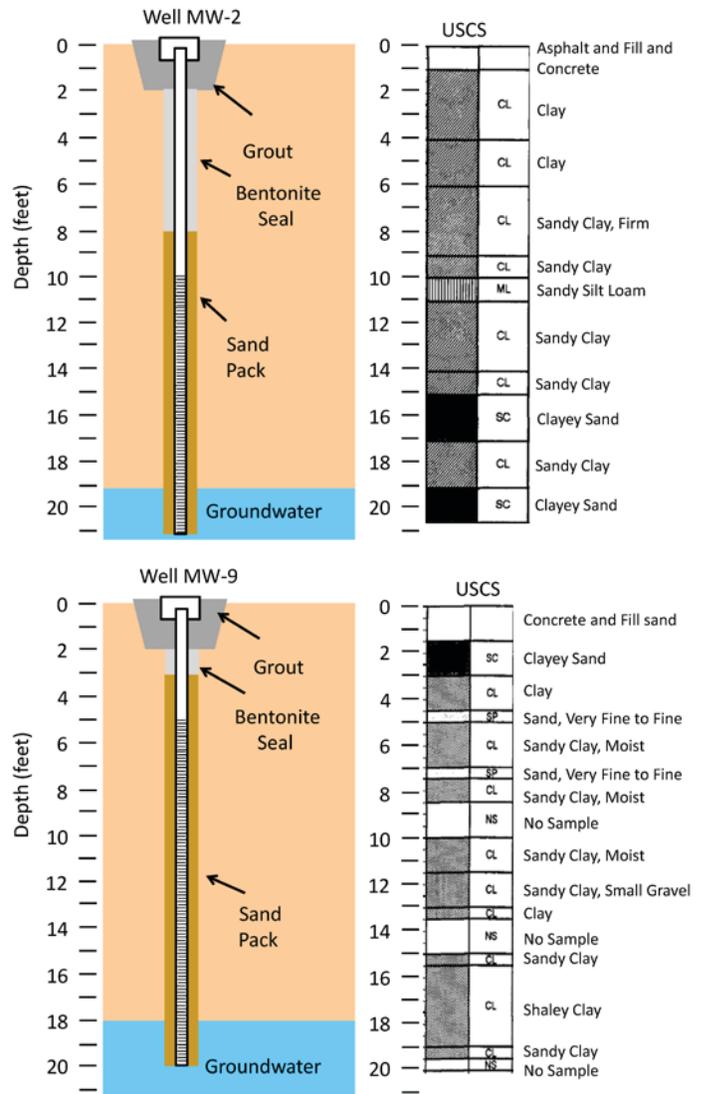


Figure 6.2. Comparison of the driller's logs to construction details of the ground water monitoring wells.

6.1 Determining the Separation Distance from the Source to the Slab of the Convenience Store

Figure 6.3 presents the results from the OVA screening of core samples to determine the vertical distribution of NAPL. Data are from the contractor's report to the Oklahoma Corporation Commission on the installation of the wells. At MW-2, in the center of the NAPL object, the OVA readings start to increase at depths below 10 feet and reach high levels. The OVA readings from samples at MW-9 are lower; however, their distribution is consistent with a separation distance of ten feet.

There was floating LNAPL in well MW-2. However, no floating LNAPL developed in MW-9. Core samples were sent for analysis of TPH and benzene in the sediment. At MW-2, samples from 15.5 feet and 21 feet had 388 and 855 mg/kg TPH-g and 8.4 and 16.5 mg/kg benzene. At MW-9, a sample at 20 feet had < 1 mg/kg TPH-g and < 5 µg/kg benzene.

6.2 Forecast of the Indoor Air Concentration in the Convenience Store

Gas samples were collected from well MW-9 and MW-2 following the protocol of Jewell and Wilson (2011). Gas samples were collected into 165 ml serum bottles and analyzed for fixed gases including oxygen and methane and for selected hydrocarbons including benzene and the light alkanes. The concentrations of individual hydrocarbons plus C6+ hydrocarbons were summed to calculate the total petroleum hydrocarbons in soil gas.

Results are presented in Table 6.1. Concentrations were reported by the analysts in ppm (v/v). The concentrations of oxygen and the formula in Section 4.3 were used to correct the reported concentrations for dilution or leakage and then the formula in Section 4.1 was used to convert the corrected concentrations to µg/m³.

The concentrations of TPH-g and benzene were very similar in the soil gas that was collected from MW-9 and MW-2 (Table 6.1). The concentrations of TPH in soil gas from MW-2 and MW-9 were consistent with soil gas in contact with weathered gasoline.

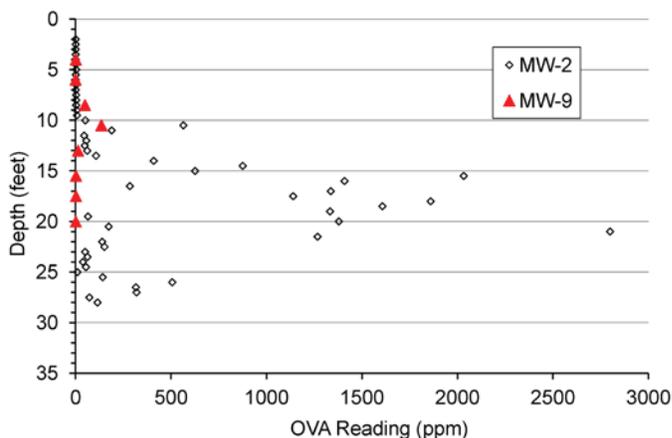


Figure 6.3. Results of field screening for NAPL in core samples from the two locations.

This is reasonable for soil gas from MW-2. The OVA meter readings on core samples were high and the concentrations of TPH-g and benzene in core samples were within the range that would be expected with NAPL hydrocarbons.

This is not what would be expected from soil gas from MW-2. The OVA meter readings on core samples were much lower and TPH-g and benzene were not detected in the core samples. The concentrations of benzene in ground water were also very low (data not shown). It is likely that the soil gas that was sampled from well MW-9 originated from the NAPL that is associated with well MW-2 and the tank pit.

The concentration of methane that was corrected for dilution and leakage was corrected again as discussed in Section 3.4.3 to express the concentration in units of THP-g with an equivalent oxygen demand (Table 6.2). The corrected concentration of methane and the concentration of TPH-g were added to calculate the concentrations of total hydrocarbons. The concentrations of total hydrocarbons were used in Figure 6.4 to estimate a value for the attenuation factor (α).

Table 6.1. Measured concentrations of oxygen, methane, and benzene in soil gas; calculated concentrations of total petroleum hydrocarbons; and corrections of measured concentrations for dilution and leakage during sampling. Samples were collected January 4, 2011.

Sample	Oxygen	Methane		Benzene		Total Petroleum Hydrocarbons	
	%	%	$\mu\text{g}/\text{m}^3$	ppm-v	$\mu\text{g}/\text{m}^3$	ppm-v	$\mu\text{g}/\text{m}^3$
Near the Convenience Store, TPH and Benzene Not Detected in Soil							
Well MW-9	2.3	40		43		7.8E+03	
Well MW-9 Corrected		45	2.6E+08	48	1.5E+05	8.7E+03	3.0E+07
High TPH and Benzene in Soil							
Well MW-2	1.9	63		180		1.3E+04	
Well MW-2 Corrected		69	4.1E+08	190	6.3E+05	1.5E+04	4.6E+08

Table 6.2. Concentrations of TPH-g and methane in soil gas near the convenience store, and the calculated total concentrations of hydrocarbons in soil gas.

Sample	Methane	Methane-Corrected	TPH-g	Total Hydrocarbons
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$ as C_7H_{16}
Well MW-9	2.6E+08	3.0E+08	3.0E+07	3.3E+08

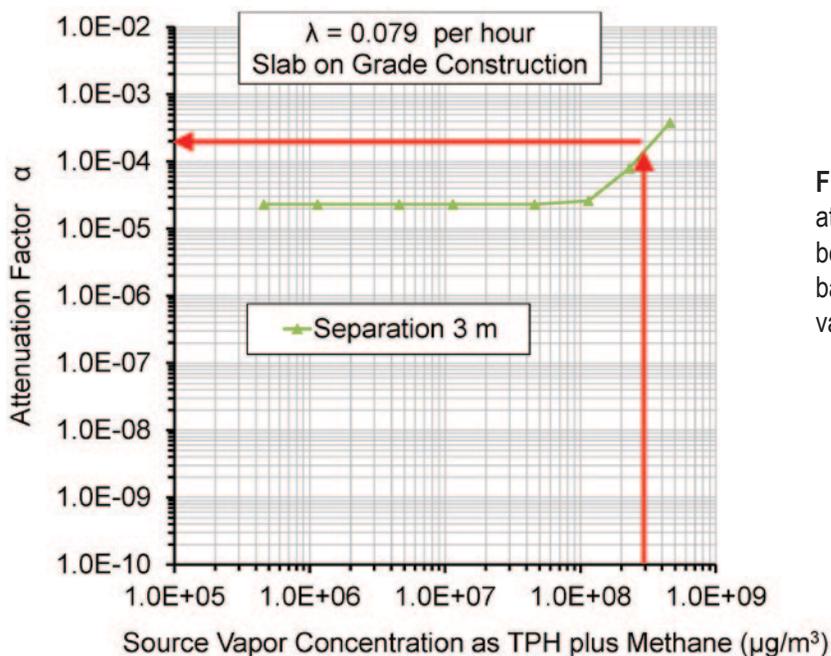


Figure 6.4. Estimates of the attenuation factor in soil gas below the convenience store based on concentrations of vapor at the source.

A concentration of $3E+08\mu\text{g}/\text{m}^3$ total hydrocarbons (as C_7H_{16}) in soil gas from Well MW-9 predicted an attenuation factor (α) of $2E-04$. The concentration of benzene in soil gas (corrected for dilution and leakage) was multiplied by the attenuation factor (α) to predict the concentration of benzene in indoor air of the convenience store (Table 6.3).

The concentration of benzene in indoor air was also predicted using the BioVapor model. The model was set up using the **Residential Default Values** on the **Environmental Factors** input screen with the following expectations. **Airflow Under Foundation** (Q_f) was set to be equal to **Air Flow Through Basement Foundation** (Q_s). The value was 83 cm^3 of air per second. To be consistent with the assumptions of the Abreu Three-Dimensional Model, the air exchange rate was set to 12 per day. Core samples were moist clay and sandy clay. The water content was set to $0.19\text{ cm}^3\text{ water}/\text{cm}^3\text{ soil}$. This is four times higher than the default assumption. The default first order rate constant for biodegradation of benzene was 0.79 per day. To allow comparisons to Figures 3.6 and 3.7, which are based on the Abreu Three-Dimensional Model with a first order rate constant of 0.079 per day, the rate constant for biodegradation of benzene in BioVapor was changed to 0.079 per day. This will provide higher estimates of the concentration

of benzene in indoor air from the simulation provided by the BioVapor model. Predictions are provided in Table 6.3.

In the Risk Information System (IRIS), the 10^{-5} risk level for exposure to benzene in air is 1.3 to $4.5\mu\text{g}/\text{m}^3$ (U.S. EPA 2014c). A contractor for the Oklahoma Corporation Commission used parameters from the Oklahoma Risk Based Corrective Action model and the U.S. EPA modification of the Johnson and Ettinger model to generate a site specific Target Indoor Air Concentration for benzene at a commercial facility. The site specific target was $0.5\mu\text{g}/\text{m}^3$. The predicted concentrations of the Abreu Three-Dimensional Model, the Generic BioVapor simulation, the Site Specific BioVapor Simulation and the Most Probable Result from the PVI-Screen simulations are near the 10^{-5} risk level and exceed the site specific Target Indoor Air Concentration.

Table 6.4 presents the distribution of the PVI-Screen simulations; 94.4% of the simulations exceeded the cancer risk level, and 23.95% of the simulations exceeded a Hazard Quotient of 1.

Following the draft guidance in U.S. EPA (2013) it is necessary to further characterize the exposure.

Table 6.3. Estimated concentration of benzene in indoor air in the convenience store based on the Abreu Three-Dimensional Model, on BioVapor and on PVI-Screen.

Location	Benzene	α	Estimated Concentration of Benzene in Indoor Air			
			Abreu Figure	Generic BioVapor	Site Specific BioVapor	PVI-Screen Most Probable Result
	$\mu\text{g}/\text{m}^3$		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
MW-9	$1.5E+05$	$2E-04$	30	100	9	20

Table 6.4. Distribution of the simulations in PVI-Screen of the concentration of benzene in indoor air in the convenience store.

Location	PVI-Screen Most Probable Result $\mu\text{g}/\text{m}^3$	% Exceeding		
		Most Probable Result	Acceptable Cancer Risk ($0.52\mu\text{g}/\text{m}^3$)	Acceptable Non-Cancer Hazard at Hazard Quotient = 1.0 ($30\mu\text{g}/\text{m}^3$)
MW-9	20	30.3	94.4	23.9

6.3 Validation of the Forecast for the Convenience Store

Well MW-9 was sampled during a survey of gasoline spill sites in Oklahoma (Jewell and Wilson, 2011). Based on the high concentration of benzene in soil gas from MW-9 near the convenience store, the Petroleum Storage Tank Division of the Oklahoma Corporation Commission tasked a contractor to install and sample shallow soil gas probes at the perimeter of the convenience store and sub-slab vapor probes through the slab-on-grade foundation. Their data are presented in Table 6.5.

The contractor in their report had the following observation:

VMW-1 and VMW-2 yielded the highest COC [compound of concern] and LCC [leak check compound] concentrations. The high COC concentrations could be due to the sandy fill below the foundation of the building. It is likely that sandy fill has a higher porosity than the surrounding soils resulting in the potential for greater vapor migration and accumulation of vapors in the fill below the foundation. The exterior vapor monitoring ports yielded lower COC concentrations which could be due to the clay layer observed in the exterior boreholes. The clay layer has a very low permeability

and likely minimizes the potential for vapor accumulation at the deeper depths. As an aside, given the nature of the facility and the very low detection limits, should outside ambient air have infiltrated the samples, it is also reasonable to conclude that it would likely increase COC concentrations in the samples.

The highest concentration of benzene in any of the shallow soil gas sample was in sub-slab monitoring point VMW-2 (10 $\mu\text{g}/\text{m}^3$). The indoor air concentrations that were predicted by applying a generic attenuation factor (α) of 0.1 to the concentration in sub-slab monitoring point VMW-2 was 1.0 $\mu\text{g}/\text{m}^3$. This was lower than the estimate provided by the Abreu simulations (30 $\mu\text{g}/\text{m}^3$), the estimate provided by the generic BioVapor simulation (100 $\mu\text{g}/\text{m}^3$), the estimate provided by the site specific BioVapor simulation (9 $\mu\text{g}/\text{m}^3$) or the PVIScreen most probable result (20 $\mu\text{g}/\text{m}^3$). At this location at this site, the models predicted higher concentrations of benzene in indoor air, compared to the estimate based on the maximum concentration of benzene in shallow soil gas.

There was only one round of soil gas sampling from the shallow monitoring points. The contractor recommended to the Petroleum Storage Tank Division of the Oklahoma Corporation Commission that they sample the shallow monitoring points a second time.

Table 6.5. Concentrations of benzene in shallow soil gas beneath and beside the foundation of the convenience store.

Sample	Depth	Benzene in Sample	Predicted Benzene in Indoor Air $\alpha = 0.1$
		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
VMW-1	2 inches below slab	9.4	0.94
VMW-2	2 inches below slab	10	1.0
VMW-3	4 to 5 feet below sidewalk	0.74	0.074
VMW-5	4 to 5 feet below sidewalk	1.9	0.19

6.4 Caveat with Respect to High Concentrations of Methane

The soil gas at the Antlers site had very high concentrations of methane. The high concentrations suggested that methane production was displacing other gases from the soil gas (Wilson et al., 2013, see also Wilson et al., 2012b; Ma et al., 2014). This situation is not considered in the structure of the Abreu Three-Dimensional Model or BioVapor or PVI Screen. If methane concentrations at the source of hydrocarbon vapors are above 10% (after correction for dilution and leakage), evaluate the concentrations of the compound of concern shallow soil gas, regardless of the predictions of the simple screening models discussed in this Issue Paper. If shallow monitoring points are not available, install a shallow monitoring point immediately adjacent to building. Sample the soil gas once and at least one additional time.

7.0 IMPLEMENTING THE APPROACH

This section describes in detail the sequence of activities that are involved in implementing the approach. This section provides a synopsis of material that is discussed at greater depth in Sections 2, 3 and 4, and summarizes data presented in the detailed case studies in Sections 5 and 6.

7.1 Sites that Are Appropriate for the Approach

This approach is designed for sites that have been previously screened to determine if they are within the lateral inclusion zone and the vertical inclusion zone (U.S. EPA, 2013b; Wilson et al., 2012a). In the most direct application, the approach is only applied to sites that are within both the lateral and the vertical inclusion zone. The approach can also be applied as a second line of evidence for sites that may or may not be in the vertical inclusion zone. The approach is intended for a building of the size of a typical residential house (up to 66 ft x 66 ft or 20 m by 20 m). The approach includes biodegradation of petroleum vapors in the unsaturated soil in the assessment of vapor intrusion. As a result, the approach is only appropriate for structures that are built on soil or

sediment that can support the activity of bacteria that degrade hydrocarbons using oxygen. This issue is discussed in more detail in Section 7.4.7.

The approach is intended for sites that do not have preferential pathways that are conduits for flow of hydrocarbon vapors. See U.S. EPA (2011) for further discussion.

7.2 Number and Position of Sampling Locations

The number and position of sampling locations is at the discretion of the individual case worker who is responsible for the site. At least one sampling location should be on the side of the building that faces a source of contamination. Presumably, the extent of contamination will decrease with distance from the source. If this is the case, there should be less contamination under the building being evaluated than there is at the sampling location.

The sampling location should be near the building being evaluated, but it is not necessary for the location to be immediately adjacent to the building. If these criteria are met, a single sampling location should be adequate for many sites.

7.3 Frequency of Sampling

The number and frequency of sampling events should be at the discretion of the individual case worker who is responsible for the site. Data from the first round of samples should be evaluated to determine if it is necessary to start immediately to remediate the site. If the forecast from the first round of samples indicates that concentrations of the compound of concern in indoor air should be acceptable, the location should be sampled at a minimum one additional time to confirm that the risk of PVI is managed.

7.4 Information Needed to Implement the Approach

The approach was created to make the maximum possible use of site characterization data that is already available for a site. The first step is to review the case files and collect the information necessary to

implement the approach. If any of the necessary information is not available from the case file, then the missing information must be acquired before the approach can be implemented.

As described in Sections 2, 3 and 4, the approach requires the following information for each particular location that is being screened for petroleum vapor intrusion:

- 1) The vertical separation distance between the bottom of the receptor and the primary source of the vapors.
- 2) The concentration of the particular hydrocarbons of concern in soil gas at the source of the vapors.
- 3) The concentration of the fuel hydrocarbons (TPG) in soil gas at the source of the vapors.
- 4) The concentration of methane in soil gas at the source of the vapors.
- 5) The concentrations of oxygen, carbon dioxide and nitrogen in the soil gas sample.
- 6) The appropriate regulatory standard for concentrations of the particular hydrocarbon of concern in indoor air.
- 7) Knowledge that conditions are appropriate to support growth of bacteria that degrade hydrocarbons.

7.4.1 The Separation Distance between the Receptor and the Source of the Vapors

To know the separation distance, it is necessary to know the important source of the vapors. If the source is the ground water, the separation distance is the distance to water table. This should be determined from the highest elevation of the water table in the monitoring record.

If the source is residual non-aqueous phase liquid hydrocarbons (NAPL) in the unsaturated zone, NAPL on the water table or NAPL below the water table, the separation distance is the extent of soil or sediment

that does not contain enough NAPL to influence degradation of vapors in soil gas, as defined below.

Do not assume the separation is defined by the top of smear zone that would be produced by variations in the depth to ground water. The separation distance must be determined by collecting and evaluating core samples.

The separation distance to NAPL is not related to the depth to ground water at the time the core samples were collected. When the water table is high the NAPL may be inundated, but the NAPL may be exposed to soil gas when the water table is lower. Determine that the well log extends to a depth of 15 feet below the bottom of the building. If core samples have not extended to 15 feet below the bottom of the building, it is necessary to acquire and screen additional core samples. Recommendations are provided in Wilson et al. (2012a).

There are two common techniques to estimate NAPL in the subsurface. First, core samples can be extracted and analyzed for TPH in the laboratory. If the concentration of TPH is less than 100 mg/kg for fresh gasoline, or less than 250 mg/kg for weathered gasoline or diesel, then the NAPL should not be expected to influence biodegradation.

Second, core samples can be screened in the field by sealing a plug sample from a core into a plastic bag, allowing hydrocarbons in the plug sample to equilibrate with the air in the bag, and then determining the concentration of TPH in the air in the bag with a field meter. The readings are often labelled as PID or OVA on a driller's well log. If the concentration of TPH in air that is equilibrated with the plug sample is below 100 ppm-v, then the NAPL should not influence biodegradation.

The resolution in determining the separation distance is controlled by the spacing of the core samples. If a good well log is available, and the log provides information on PID readings or OVA readings on core samples, the log should be used as the first line of evidence to determine the separation distance.

Soil or sediment that has been contaminated by a release of fuel will often be dark grey or black, and will smell of gasoline or hydrogen sulfide. Consult

the driller's log for any notes on the color or odor of the core samples. This can provide a second line of evidence.

The separation distance is the distance between the receptor and the deepest core sample that has less than 100 mg/kg of TPH as gasoline or less than 250 mg/kg of TPH as diesel fuel or weathered gasoline. It is not the distance between the receptor and the first sample that has more than 100 or 250 mg/kg of TPH.

Similarly, the separation distance is the distance between the receptor and the deepest core sample that produces less than 100 ppm-v of TPH in air when a sub-sample of the core is equilibrated with air. It is not the distance between the receptor and the first sample that produces more than 100 ppm-v of TPH in air.

If there is a significant distance between the deepest sample that has less than 100 mg/kg TPH [or 250 mg/kg TPH] or produces less than 100 ppm-v of TPH in air and the shallowest sample has more than 100 mg/kg TPH [or 250 mg/kg TPH] or produces less than 100 ppm-v of TPH in air, it may be worthwhile to acquire additional core samples and better define the separation distance.

7.4.2 The concentration of the particular hydrocarbons of concern in soil gas at the source of the vapors

The U.S. EPA identifies four methods that are intended to determine the concentrations of individual petroleum hydrocarbons in samples of indoor air or soil gas. They are Method TO-15 (U.S. EPA, 1999a), Method TO-14A (U.S. EPA, 1999b), Method TO-3 (U.S. EPA, 1984), and Method TO-17 (U.S. EPA, 1999c).

Compendium Method TO-15 is widely used. Gas samples are collected into an evacuated stainless steel canister that has gone through a special process to make the interior of the canister chemically inert. After the gas sample is collected, the canister is sealed and shipped to the laboratory for analysis by high resolution gas chromatography using a mass spectrometer as the detector.

The case file should contain records of the analysis

of soil gas for the particular hydrocarbons of concern using methods that are approved by the appropriate regulatory authority.

If records are not available, then soil gas samples should be acquired and analyzed. If vapor monitoring probes are available, they should be used. If they are not available, consider using groundwater monitoring wells to acquire the gas samples. Do not use temporary push wells to acquire the soil gas samples.

7.4.3 The concentration of the fuel hydrocarbons in soil gas at the source of the vapors

The case file may contain an analysis of TPH-g by EPA TO-15. The TPH-g is expressed as the equivalent of a hydrocarbon with a molecular weight of 100 Daltons, which is the weight of heptane. If this analysis is not available, it is necessary to sample the soil gas again and determine TPH-g by EPA TO-15. On the same sample also determine the concentrations of the compounds of concern.

7.4.4 The concentration of methane in soil gas at the source of the vapors

The case file may contain an analysis of methane in soil gas. If this analysis is not available, it is necessary to sample the soil gas again and determine methane by EPA Method 3C (U.S. EPA, 2014d) or by ASTM D-1945 (ASTM, 2010). This analysis can be performed on the same sample used to determine the concentrations of compounds of concern or the concentration of TPH.

Do not rely on the reading for methane provided by an infra-red detector in a field meter. The detector cannot distinguish methane from petroleum hydrocarbons.

7.4.5 The concentrations of oxygen, carbon dioxide and nitrogen in the soil gas sample

The concentration of oxygen can be used to correct a field sample for leaks in the sampling train and for dilution of the soil gas in the vapor probe or monitoring well (see section 7.5.3). This information is useful and the determination of oxygen in the soil gas sample is strongly recommended. The concentration of carbon dioxide can be used in a

qualitative way to distinguish a sample of atmospheric air from a sample of soil gas where petroleum hydrocarbons have been extensively biodegraded. The concentration of nitrogen can be used along with concentrations of oxygen and carbon dioxide to calculate a mass balance as a quality control check on the analyses. The analysis of carbon dioxide and nitrogen is useful but they are not necessary.

EPA Method 3C (U.S. EPA, 2014d) or ASTM D-1945 (ASTM, 2010) can determine methane, oxygen, carbon dioxide and nitrogen on the same sample in the same analytical run. Oxygen and carbon dioxide can also be determined using field meters.

7.4.6 The appropriate regulatory standard for concentrations of the particular hydrocarbon of concern in indoor air

The approach in this Issue Paper is used to make an exposure evaluation. That exposure evaluation at some point will be reviewed by the government agency with regulatory authority for the site. Check with the agency to insure that the approach is implemented with the current standards that are appropriate for the site.

7.4.7 Knowledge that conditions are appropriate to support growth of bacteria that degrade hydrocarbons

There are three circumstances where conditions may not be appropriate to degrade hydrocarbons.

The separation distance must be in soil or sediment that has a significant holding capacity for water, and provides adequate surface area for the growth of bacteria. Exclude from the separation distance any interval that is consolidated rock or is dominated by coarse sand or gravel without any fine materials.

The soil or sediment may be too dry to allow growth of bacteria. The soil water potential (Ψ) may be so low as to inhibit the growth of bacteria. Orchard and Cook (1983) showed that at a soil water potential of -1.0 megapascals (MPa), the rate of soil respiration was reduced to approximately one-third of the optimal rate. At a potential of -0.3 MPa, the rate was approximately one-half of the optimal rate. After water has been distributed through soil and reached equilibrium, the soil water potential is related to the depth to the water

table. At a potential of -0.3 MPa, the depth to the water table should be 112 feet. Soil water potential may be a problem if the depth to the water table is more than 100 feet. If the source of vapors is NAPL that occurs more than 100 feet above the water table, do not apply the approach.

The third condition is a building, pavement, or a layer of soil that prevents the transfer of oxygen from the atmosphere to soil gas. This Issue Paper is designed to screen a building that is used as a private residence. For a building with the footprint of a conventional private building, the transfer of oxygen should not be a problem. The approach in this Issue Paper should not be used for a larger building unless it can be shown that the concentration of oxygen is adequate in air immediately underneath the building foundation or adjacent paving.

On first examination, it would seem that a layer of soil that prevents the transfer of oxygen should be a problem. The most usual circumstance will be a layer of wet clay with little secondary porosity. The clay will inhibit the transport of oxygen to the source of hydrocarbon vapors, but it will also inhibit the transport of the hydrocarbon vapors to the receptor. Under most circumstances, a layer of wet soil will not cause an appreciable increase in the concentration of petroleum hydrocarbons in indoor air (U.S. EPA, 2013a).

7.5 Evaluate the Exposure

Once all the necessary information has been gathered, the next step is to forecast the indoor air concentration of the compound of concern.

7.5.1 Convert Units

Convert all the concentration data for compounds of concern, for total TPH and for methane into units of $\mu\text{g}/\text{m}^3$. If data are reported in ppm, multiply by 1000 to convert to ppb. If data are reported in percent, multiply by 10,000 to convert to ppb. Data in ppb can be converted to $\mu\text{g}/\text{m}^3$ with the following formula.

$$\mu\text{g}/\text{m}^3 = \text{ppb} * \text{molecular weight} * 0.0413$$

7.5.2 Calculate Total Hydrocarbons

Add the concentration of methane and the concentration of TPH to get the concentration of total hydrocarbons in the soil gas. To correct for the difference in the theoretical oxygen demand of methane and TPH, multiply the concentration of methane by 1.14 before adding the corrected concentration to the concentration of TPH. See Section 3.4.3 for details.

7.5.3 Correct for Dilution or Leakage

Use the concentration of oxygen in the sample of soil gas to calculate a correction factor for dilution and leakage in the sample. The correction factor can be calculated with the formula below, or it can be extracted from Figure 4.3.

Concentration in Source Gas =

$$\text{Concentration in the Sample Analyzed} \left(\frac{\text{O}_2 \text{ in Atm.}}{\text{O}_2 \text{ in Atm.} - \text{O}_2 \text{ in Soil Gas}} \right)$$

Multiply the measured concentration by the correction factor to calculate the concentration at the source of the hydrocarbons.

7.5.4 Forecast the Concentration of Compound of Concern in Indoor Air

This Issue Paper offers two approaches to forecast the concentration of benzene or other compound of concern in indoor air in a building. One approach uses the simulations of Abreu et al. (2009a, 2009b). The other approach uses the computer applications BioVapor (API, 2012) or PVIScreen (U.S. EPA, 2014g).

7.5.4.1 Approach Using Simulations of Abreu et al.

Abreu et al. (2009a, 2009b) modeled a large number of representative scenarios and combined the results of the simulations in simple figures. Figure 3.14 combines their simulations for a typical residential building that is built slab-on-grade, and Figure 3.15 combines simulations for a building with a basement. To use the figures, multiply the separation distance in feet by 0.3048 to calculate the separation distance

in meters. Find the largest separation distance that is plotted in the figure that is smaller than the separation distance at the site. Plot the concentration of total hydrocarbons on the X axis. Extend the concentration up to intersect the line representing the separation distance, then extend a line to the left to the Y axis to estimate the attenuation factor (α). To complete the evaluation, multiply the attenuation factor (α) by the corrected concentration of benzene in soil gas. This calculated value is the forecast of the concentration of benzene in indoor air in the building.

7.5.4.2 Approach Using BioVapor or PVIScreen

The concentration of total petroleum hydrocarbons, methane and the separation distance are input values for BioVapor and PVIScreen. Consult the User's Manual to learn how to use the applications. The computer applications allow the user to input site-specific parameters such as the water content of the vadose zone soil or the content of organic carbon. The parameters were used in the simulations of Abreu et al. (2009a, 2009b); however, they were held constant for all the simulations. BioVapor and PVIScreen allow a forecast that is based on the conditions that are most applicable to a particular site.

As is the case with approach of Abreu et al. (2009a, 2009b), BioVapor provides a single value for the forecast of indoor air concentrations. In contrast, PVIScreen performs a Monte Carlo simulation and provides a "most probable result" for the forecast of indoor air concentration, as well as, the fraction of the simulations that were above a pre-specified cancer risk level, and the fraction of simulations that were above a hazard quotient of 1.0.

7.5.4.3 Comparison of the Screening Approaches

In the case studies discussed in Sections 5 and 6, four separate forecasts were made of the concentration of benzene in indoor air of a building at the site. A forecast was made by comparing conditions at the site to the simulations of Abreu et al. (2009a, 2009b). A second forecast was made using the BioVapor model without modification of the generic input values for water content or for the concentration of soil organic matter (generic BioVapor). A third forecast was made using the BioVapor Model with site specific values

for water content or organic matter (site specific BioVapor). A fourth forecast was made using the PVIScreen model with site specific values.

The screening approaches were based on the analysis of soil gas from a deep monitoring point that collected gas at the source of the hydrocarbon vapors. In Sections 5 and 6, the forecasts of the screening approaches were validated by comparing them to a prediction made by applying a generic attenuation factor (α) to the measured concentration of benzene in soil gas from a second shallow vapor probe or sub-slab monitoring point. Guidance provided by U.S. EPA (2014e) sets the value of the generic attenuation factor (α) at 0.1.

The screening approaches can be evaluated by comparing to the forecast of the screening approach to the prediction that was provided by applying the generic attenuation factor. Table 7.1 identifies the four pairs of monitoring points where the comparison can be made.

Figure 7.1 compiles data from the four comparisons that are described in Table 7.1.

The solid blue line in Figure 7.1 is a line of equivalent concentrations. If the data point plots above the solid blue line, the concentration of benzene in indoor air that was predicted from the screening approach was greater than the concentration that was predicted based

on the generic attenuation factor. If the data plots below the line, the concentration of benzene predicted from the screening approach was less than the concentration predicted from the generic attenuation factor.

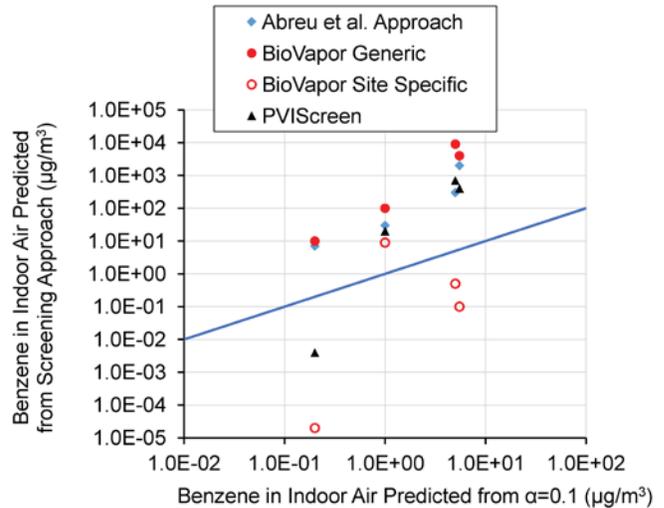


Figure 7.1. Relationship between the concentrations of benzene in indoor air that are predicted from a generic attenuation factor and the concentrations of benzene in indoor air that are predicted from a screening approach that includes aerobic biodegradation of benzene.

Table 7.1. Locations of monitoring points that allow a comparison of the prediction made by applying a generic attenuation factor to prediction made by applying screening models that include aerobic biodegradation of benzene.

Section of Issue Paper Site	Location	Shallow Monitoring Point Used to Sample Soil Gas to Apply a Generic Attenuation Factor of 0.1	Deep Monitoring Point Used to Sample Soil Gas to Implement the Screening Approach
Section 5 Green River, Utah	Café	VW-5	MW-47
Section 5 Green River, Utah	Office of Hotel	VW-4	MW-51
Section 5 Green River, Utah	Office of Hotel	VW-4	MW-2
Section 6 Antlers, Oklahoma	Convenience Store	VMW-2	MW-9

The forecasts that were provided using the simulations of Abreu et al. (2009a) or the Generic BioVapor model were very conservative. The concentrations were consistently from thirty fold to a thousand fold higher than the predictions based on a generic attenuation factor (α) of 0.1.

The forecasts provided by the simulations of Abreu et al. (2009a) or the Generic BioVapor model were even more conservative than the predictions made using the generic attenuation factor. If a forecast made from the simulations of Abreu et al. (2009a) or the Generic BioVapor model indicates that the concentration of benzene in indoor is acceptable, there is little benefit from installing and sampling shallow monitoring points to further validate the forecast.

In contrast, some of the forecasts made with the site specific BioVapor model or with PVI-Screen had lower concentrations of benzene compared to the prediction made from concentrations in shallow soil gas using an attenuation factor (α) of 0.1. Three of the four forecasts were closer to the line of equivalent values, and one of the forecasts was much lower. An attenuation factor (α) of 0.1 ignores any contribution from biodegradation. It is intentionally conservative. The forecasts made by the Site specific BioVapor model or with PVI-Screen may have been a better description of the true conditions at the site.

7.5.4.4 Recommendations on Screening Approaches

Presumably, the building was determined to be within a vertical inclusion zone based on previous characterization of petroleum hydrocarbons in ground water or soil cores (U.S. EPA, 2013b; Wilson et al., 2012a).

7.5.4.4.1 Building with No Vapor Monitoring Points

The following recommendations apply to a building where no vapor monitoring points have been installed. Often a ground water monitoring well will be installed in the borehole used to acquire the core samples. If a ground water monitoring well is available, the well should be used to sample for soil gas and gas samples should be analyzed as described above. If more than one well is in reasonable proximity to the site, sample all the wells.

The data should be evaluated by comparison to the simulations of Abreu et al. (2009a, 2009b) as presented in Figures 3.14 or 3.15. If forecasts are available from more than one location, make the risk evaluation based on the forecast with the highest concentration of the compound of concern in indoor air. Do not average the forecasts.

If the forecast indicates that the risk of PVI is acceptable, one option is to continue to monitor the soil gas additional times to establish that conditions do not change.

If the forecast indicates that the risk of PVI is not acceptable, evaluate the data a second time using PVI-Screen or a site specific implementation of the BioVapor model. If the forecast of PVI-Screen or the site specific implementation of the BioVapor model indicates that the risk of PVI is not acceptable, one option is to install a shallow vapor monitoring point immediately adjacent to the building. Sample soil gas from the shallow vapor monitoring point and analyze the gas for concentrations of compounds of concern. Apply the appropriate generic attenuation factor to predict the concentration in indoor air.

If a shallow vapor monitoring point is installed, there is no need to install a deep vapor monitoring point to sample petroleum vapors at the source of the vapors.

7.5.4.4.2 Building with Vapor Monitoring Points

If vapor monitoring points have been installed at the site, sample all the monitoring points and perform the evaluation for each monitoring point. If monitoring points are available in the range of three to five feet below the bottom of the building, sample soil gas from these monitoring points and apply the appropriate generic attenuation factor as the first line of evidence to evaluate the risk of PVI. If deeper monitoring points are available, sample them and apply the approach in this Issue Paper as a second line of evidence.

The data from the deeper vapor monitoring points should first be evaluated by comparison to the simulations of Abreu et al. (2009a, 2009b) as presented in Figures 3.14 or 3.15. If forecasts are available from more than one vapor monitoring point, make the risk evaluation based on the forecast with the highest

concentration of the compound of concern in indoor air. Do not average the forecasts. If the forecasts indicate that the risk of PVI is acceptable, one option is to continue to monitor the soil gas additional times to establish that conditions do not change.

If the forecasts from any deeper wells indicate that the risk of PVI is not acceptable, evaluate the data a second time using PVIScreen or a site specific implementation of the BioVapor model. If the forecast of PVIScreen or the site specific implementation of the BioVapor model indicates that the risk of PVI is not acceptable, one option is to install one or more sub-slab sampling points inside the building. Sample soil gas from each sub-slab monitoring point and analyze the gas for concentrations of compounds of concern. Apply the appropriate generic attenuation factor to predict the concentration in indoor air.

If the distance from the bottom of the building to the vapor monitoring point is less than the presumed distance from the bottom of the building to the source of vapors, but the true distance to the source of vapors is not known, then use the distance to the monitoring point as the separation distance in the evaluation.

8.0 COMPARISON OF SOIL GAS SAMPLES COLLECTED FROM VAPOR PROBES AND WATER WELLS

Information on the concentrations of benzene and total petroleum hydrocarbons in soil gas at the source of the petroleum vapors is useful in screening sites for petroleum vapor intrusion. Traditionally, samples of soil gas are acquired from soil vapor probes that are built for that purpose. However, if existing ground water monitoring wells could be used to sample soil gas, this can reduce the cost of site characterization for petroleum vapor intrusion (PVI).

8.1 Background

Installation of dedicated soil vapor probes increases cost for site characterization and creates additional disruption for the site owner. Most leaking underground storage tank (LUST) sites have an existing ground water monitoring well network. Often, a portion of the screened interval of

conventional ground water monitoring wells is above the water table. Figure 8.1 shows the similarity between monitoring wells where the water table is within the screened interval and vapor probes. If soil gas samples can be obtained from existing ground water monitoring wells, this would avoid the cost of installing vapor probes and reduce cost of site characterization.

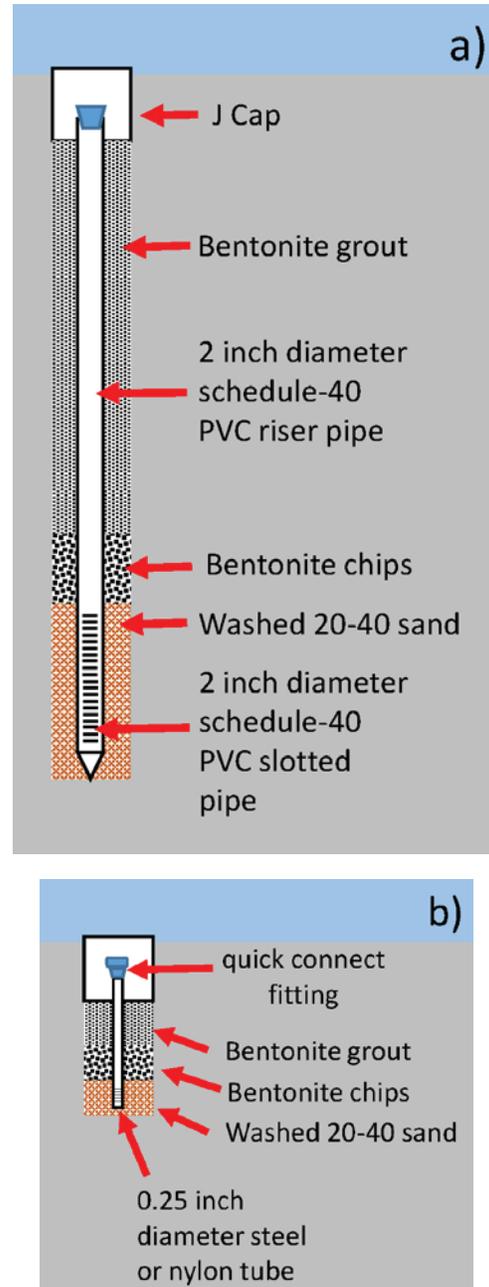


Figure 8.1. Similarities between a conventional ground water monitoring well (a) and a dedicated vapor probe (b).

A study was conducted to evaluate whether or not conventional ground water monitoring wells are functionally different from dedicated vapor probes and determine what those differences are. Recently, Jewell and Wilson (2011) proposed a practical method for sampling petroleum hydrocarbon soil vapors from conventional ground water monitoring wells that have some portion of the screen above the water table. They obtained samples from 12 gasoline sites in Oklahoma and results showed their method provided comparable soil gas concentrations compared to dedicated vapor probes. This method was used to compare soil gas samples from dedicated vapor probes with conventional groundwater monitoring wells at Hal's Chevron LUST site in Green River, Utah, and at the EZ Go Service Station in Antlers, Oklahoma.

Hal's Chevron site is located in Green River, Utah. In 1991, it was discovered that between 40,000 to 130,000 gallons of gasoline had leaked from the UST system and migrated downward through the vadose zone to the ground water table at about 18 feet (ft) below ground surface (bgs). From 1993 to 2004, 26,000 gallons of free product was removed. The gasoline plume migrated in an east/southeast direction for about 300 ft where it stabilized. The site is underlain by free phase gasoline which provided a strong source of petroleum hydrocarbon vapors. The free-phase gasoline plume underlies a motel, restaurant, and road at depths ranging from 15 to 18 ft bgs. The unsaturated zone is composed of interbedded silts and clays. The subsurface is well-characterized and the lateral extent of LNAPL is well-defined.

8.2 Comparison of Monitoring Wells and Vapor Probes at Hal's Chevron, Green River, UT

The data used in this case study are provided as an illustration. They do not necessarily reflect current conditions at the site, and have no bearing on past or current regulatory action taken by the Utah Department of Environmental Quality.

Conventional ground water monitoring wells and dedicated multi-depth vapor probes were installed by The Utah Department of Environmental Quality (UDEQ) at the site (Figure 8.2). Five vapor probes (VW-1, VW-2, VW-3, VW-7, and VW-8) and eight conventional monitoring wells (MW-2, MW-21, MW-39, MW-41, MW-42, MW-47, MW-48, and MW-51) were sampled in this study.

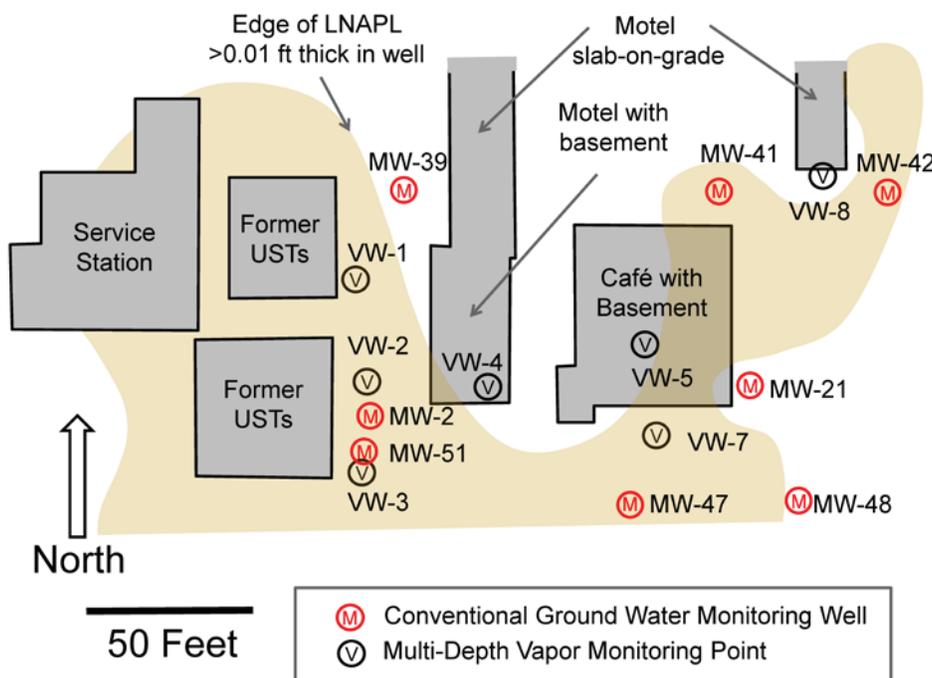


Figure 8.2. Map of Hal's Chevron site with location of conventional ground water monitoring wells (MW) and multi-depth vapor probes (VW). The brown area depicts the area with known distribution of NAPL.

The lithology of the site and the vertical distribution of petroleum are shown in Figure 8.3. Total petroleum hydrocarbon (TPH) concentration was determined as gasoline range organics (GRO). The highest TPH concentration is seen at 14 ft bgs. Depth intervals less than 12 ft below land surface have less than 250 mg/kg TPH.

The borehole log and details on the completion of the multi-depth vapor points at VW-7 are shown in Figure 8.4. As is consistent with Figure 8.3, screening of core samples with a PID meter showed clean soil down to 11 ft.

The vapor probes were comprised of 6-inch stainless-steel vapor sampling screens with polyethylene tubing to ground surface (Figure 8.5). The deepest vapor sample point in each vapor well was located either in the region with NAPL, or just above the NAPL.

Ground water monitoring wells were constructed using 2-inch or 4-inch diameter polyvinylchloride (PVC) pipe. The monitoring wells were fitted with an Ex-Cap® (Atlantic Screen and Manufacturing, Inc.) that provided a port to extract vapor samples. When 4-inch wells were sampled, a reducer was used to join the 2-inch Ex-Cap® to the 4-inch riser of the wells.

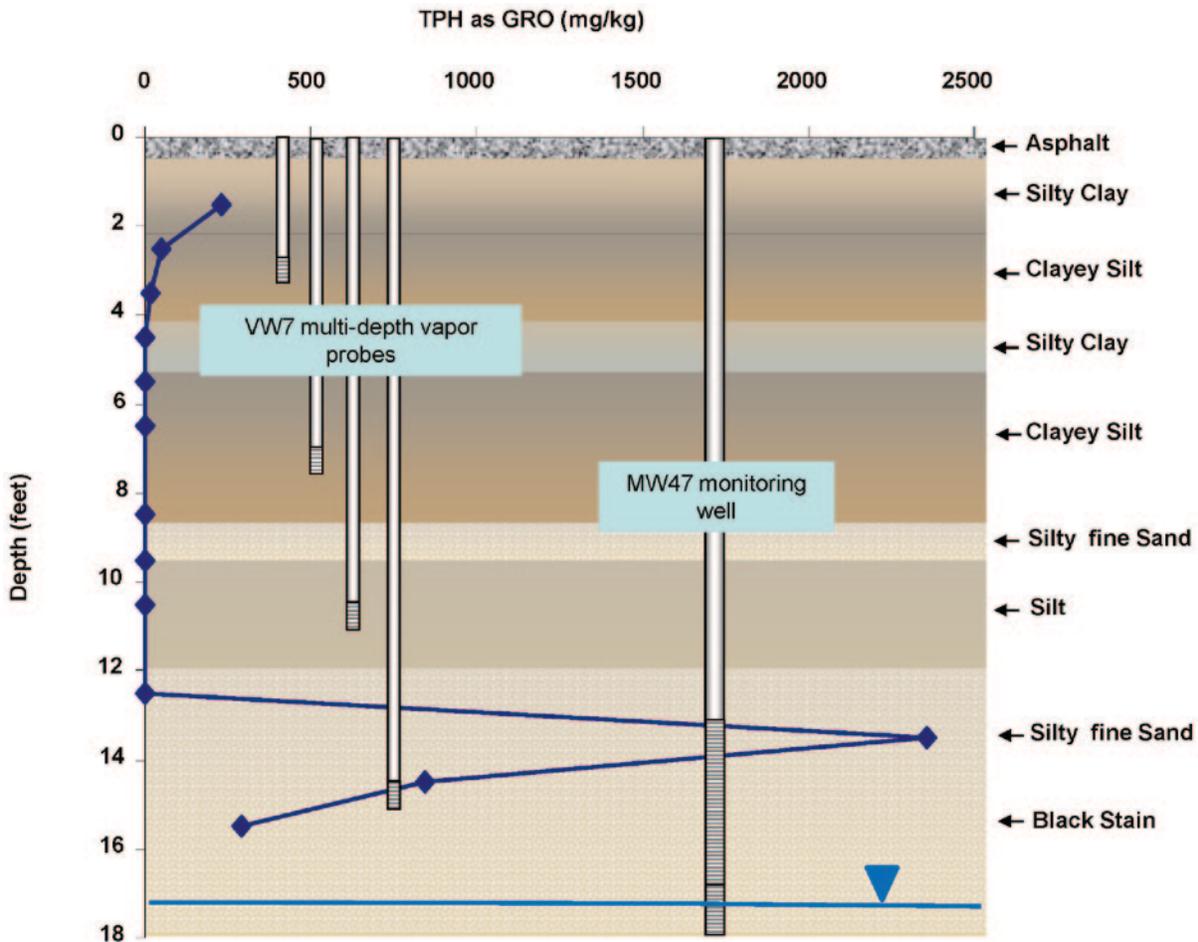


Figure 8.3. Distribution of TPH at Hal's Chevron site.

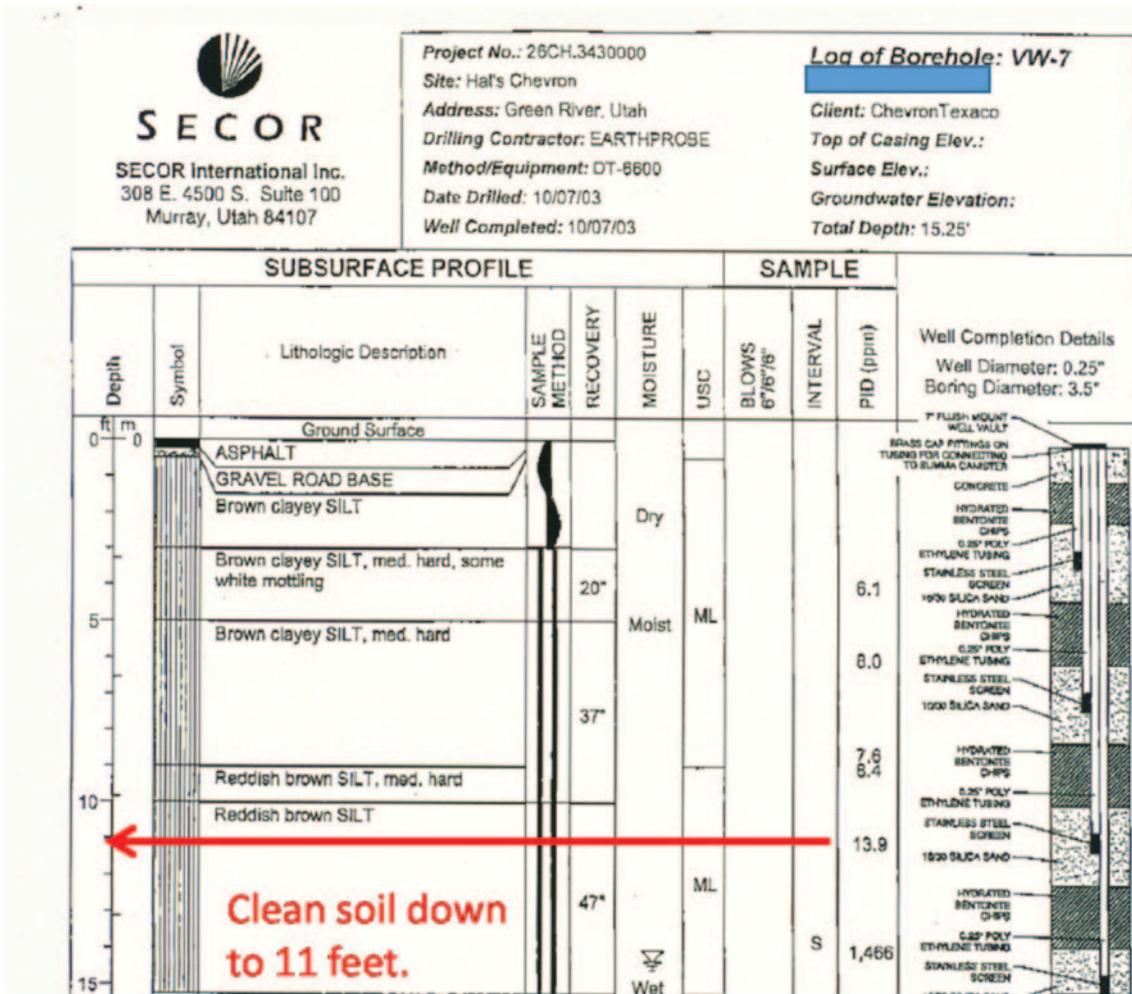


Figure 8.4. Borehole log of VW-7.

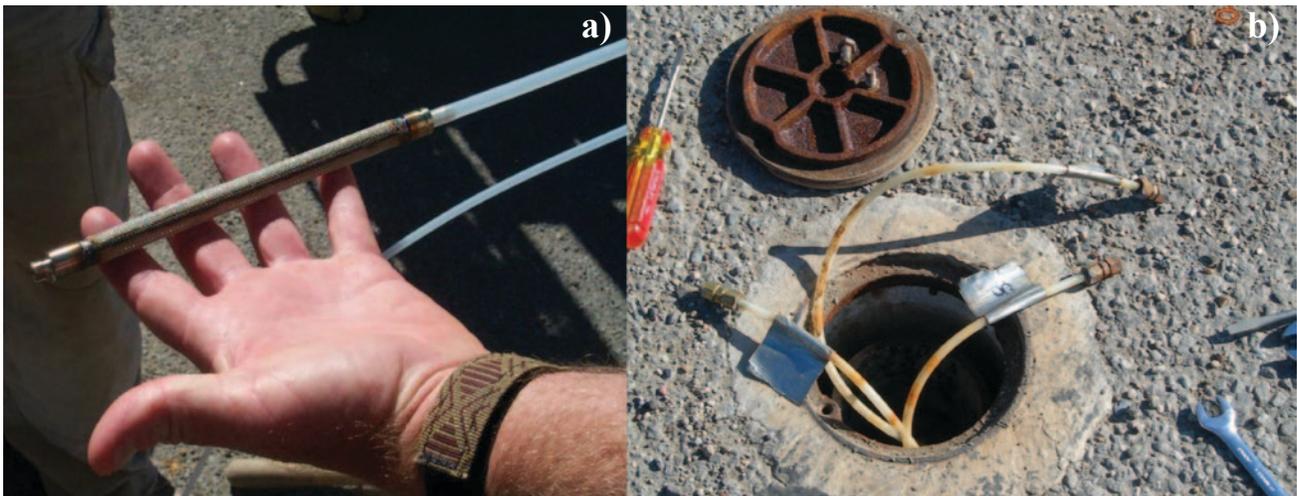


Figure 8.5. Vapor probes consist of a soil vapor sampling screen and polyethylene tubing to ground surface.

8.3 Field Sampling

Soil gas samples from ground water monitoring wells were collected using the method of Jewell and Wilson (2011). The soil gas sampling train used to sample ground water wells is shown in Figure 8.6. A vacuum pump was used to extract soil gas from the screened interval exposed above the water table. The soil gas passed through a 1-L glass flask that acts as a trap for water, then to the pump. The vacuum generated on the headspace of the well was monitored by a differential pressure gauge that was referenced to the atmosphere (range 0-50 inches of water). The flow rate was measured with a rotameter (flow rate meter) located on the effluent side of the pump and adjusted with a needle valve between the pump and rotameter. The gas on the effluent side of the needle valve was

at atmospheric pressure. The effluent of the rotameter went to a tee split to create a path that supplied gas to the field meters and a second path to provide an outlet for excess gas.

Samples from the vapor probes were collected using conventional soil gas sampling methods into Summa canisters (samples collected following U.S. EPA, 1994, 1996; canisters provided by H&P Mobile Geochemistry, Inc., Carlsbad, CA). Soil gas samples from vapor probes were analyzed by TO-15 (Air Toxics, Inc). Soil gas samples from conventional monitoring wells were analyzed as described in Jewell and Wilson (2011). They used a micro GC with a thermal conductivity detector. The detection limit for benzene was much higher using the micro GC compared to method TO-15.

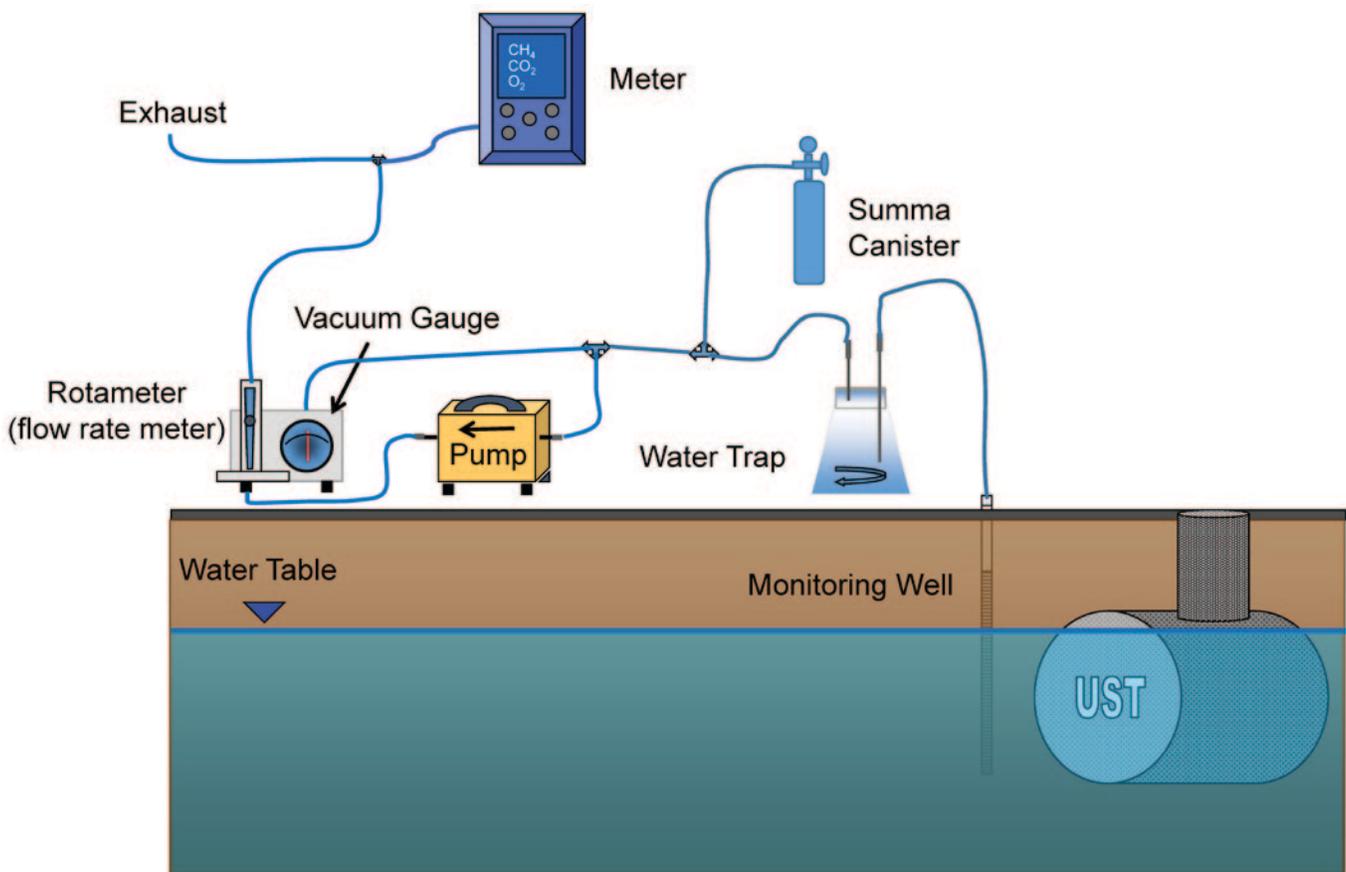


Figure 8.6. Sampling train for obtaining soil gas samples from a conventional monitoring well.

8.4 Comparison of Vapor Probes to Conventional Monitoring Wells at Green River, UT

For the conventional ground water monitoring wells, data on concentrations of oxygen and the equation in Section 4.3 were used to correct the measured concentrations of benzene, TPH-g and methane for dilution and leakage.

Table 8.1 compares concentrations of soil gas in locations between the service station and the office of the motel. Figure 8.7 shows the sampling locations. Well MW-39 is located outside the area with LNAPL.

Wells MW-2 and MW51 and vapor probes VW-1, VW-2 and VW-3 are located within the area with NAPL (Figure 8.7).

The concentrations of benzene, TPH-g and methane were much lower in well MW-39, which was not located in the area with NAPL. Comparing the monitoring wells and vapor probes that were located in the area with NAPL, the concentrations of benzene, TPH-g and methane were very uniform. They agreed within a factor of eight between any of the wells and any of the vapor probes. Although the vapor probes had higher concentrations of TPH-g, the wells had higher concentrations of benzene.

Table 8.1. Comparison of soil gas data from sampling locations between the service station and the adjacent office of the motel.

Well	Vapor Point	Screened Interval	Depth to Water	Depth Vapor Point	LNAPL	Benzene	TPH	Methane
		feet	feet	feet		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
MW-39		13 - 28	19.6		no	$< 6.5\text{E}+03$	$< 5.1\text{E}+04$	$< 9.8\text{E}+02$
	VW-1			16		$1.1\text{E}+06$	$2.2\text{E}+08$	$2.3\text{E}+06$
	VW-2			17		$2.3\text{E}+06$	$2.8\text{E}+08$	$1.9\text{E}+06$
MW-2		16 - 35	19.6		yes	$4.4\text{E}+06$	$1.3\text{E}+08$	$2.0\text{E}+06$
MW-51		13 - 28	19.6		yes	$8.5\text{E}+06$	$1.5\text{E}+08$	$1.4\text{E}+06$
	VW-3			18		$3.6\text{E}+06$	$2.8\text{E}+08$	$1.6\text{E}+06$

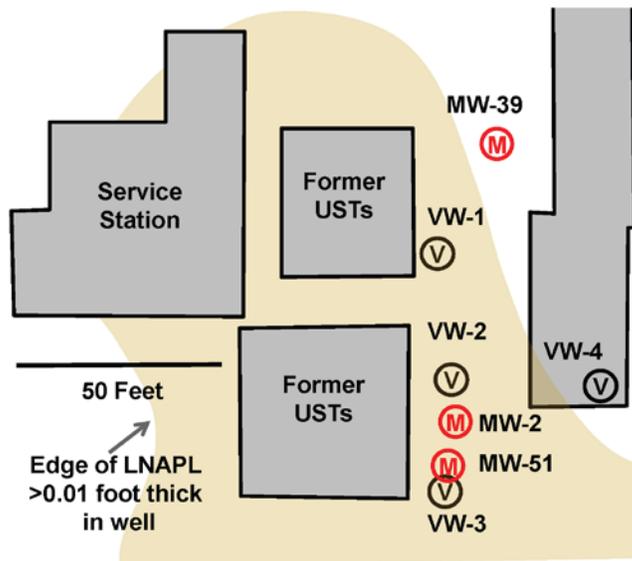


Figure 8.7. Location of sampling points in Table 8.1.

Table 8.2 compares concentrations of soil gas in locations near the café. Figure 8.8 shows the sampling locations. Monitoring wells MW-21 and MW-48 are located outside the area with NAPL while well MW-47 and vapor probe VW-7 are located within the area with NAPL (Figure 8.8).

Again, the concentrations of benzene, TPH-g and methane in soil gas were reasonably consistent between the monitoring wells and the vapor probe.

The concentration of methane was higher in the vapor probe, but the concentrations of TPH-g were higher in the monitoring wells.

As mentioned above, the analytical protocol used for the wells had a higher detection limit for benzene. As a result, benzene was not detected in soil gas from two of the three wells. In the one well where it was detected, the concentration of benzene was higher in the well than in the vapor probe.

Table 8.2. Comparison of soil gas data from sampling locations near the café.

Well	Vapor Point	Screened Interval	Depth to Water	Depth Vapor Point	LNAPL	Benzene	TPH	Methane
		feet	feet	feet		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
MW-47		13 - 28	17.6		yes	8.5E+04	1.0E+07	5.5E+03
	VW-7			15		4.6E+03	3.1E+06	9.3E+03
MW-48		13 - 28	15.0		no	< 4.1E+04	1.5E+07	3.5E+04
MW-21		12 - 27	17.1		no	< 5.9E+04	1.1E+07	<8.9E+03

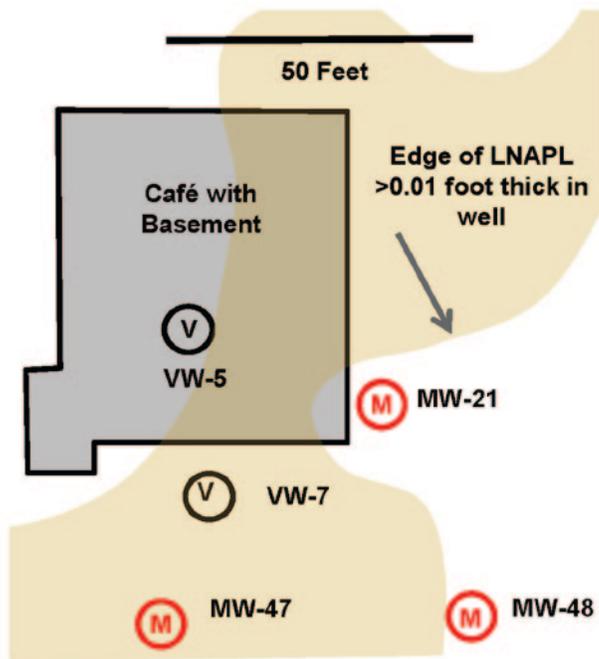


Figure 8.8. Location of sampling points in Table 8.2.

Table 8.3 compares concentrations of soil gas in locations near the sleeping rooms of the motel. Figure 8.9 shows the sampling locations. Monitoring wells MW-41 and MW-42 are within the fringe of the area with NAPL while vapor probe VW-8 is just outside of the area with NAPL (Figure 8.9).

The concentrations of methane and TPH-g were much higher in the soil gas from the monitoring wells. Benzene was not detected in soil gas from the wells. It is not possible to compare the recovery of benzene from the wells and the vapor probe at this location.

Results at the Hal's Site in Green River, UT show that the vapor concentrations of benzene, total

petroleum hydrocarbons and methane measured in the conventional monitoring wells were similar to the concentrations measured in the deep vapor points. When the conventional ground water wells and the soil vapor probes were located above LNAPL, the concentration of benzene and total petroleum hydrocarbons in soil gas produced from the conventional monitoring wells and the concentrations in soil gas produced by the deepest vapor probes were within an order of magnitude. At this site, the approach of sampling soil gas from conventional ground water monitoring wells can be as effective as sampling from vapor probes.

Table 8.3. Comparison of soil gas data from sampling locations near the sleeping rooms of the motel.

Well	Vapor Point	Screened Interval	Depth to Water	Depth Vapor Point	LNAPL	Benzene	TPH	Methane
		feet	feet	feet		$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$
MW-41		12 - 28	14.5		yes	$< 2.5\text{E}+04$	$7.0\text{E}+06$	$1.7\text{E}+05$
MW-42		13 - 28	16.9		yes	$< 7.0\text{E}+03$	$7.3\text{E}+06$	$6.7\text{E}+04$
	VW-8			15		$4.9\text{E}+00$	$9.0\text{E}+02$	$< 9.8\text{E}+02$

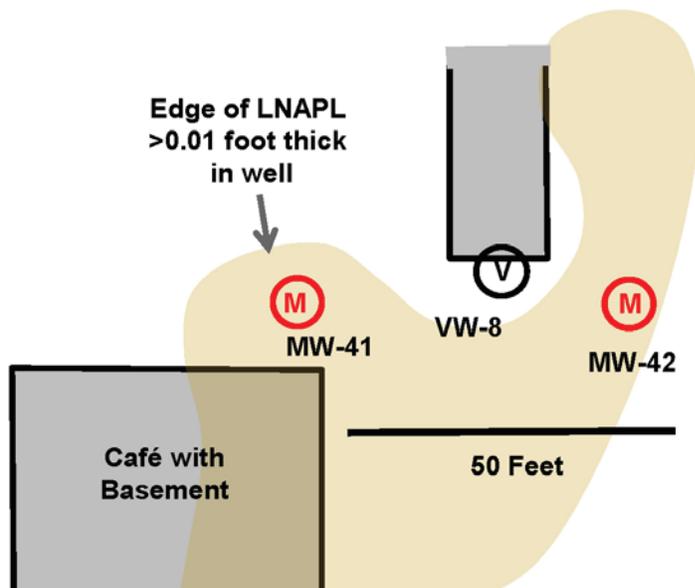


Figure 8.9. Location of sampling points in Table 8.3.

9.0 REFERENCES

- Abreu, L.D.V., and P.C. Johnson. 2005. Effect of vapor source–building separation and building construction on soil vapor intrusion as studied with a three-dimensional numerical model. *Environmental Science and Technology* 39(12): 4550–4561.
- Abreu, L.D.V., and P.C. Johnson. 2006. Simulating the effect of aerobic biodegradation on soil vapor intrusion into buildings: Influence of degradation rate, source concentration, and depth. *Environmental Science and Technology* 40 (7): 2304–2315.
- Abreu, L.D.V., R. Ettinger, and T. McAlary. 2009a. Simulated Soil Vapor Intrusion Attenuation Factors including Biodegradation for Petroleum Hydrocarbons. *Ground Water Monitoring & Remediation* 29(1): 105-117.
- Abreu, L.D.V., R. Ettinger, and T. McAlary. 2009b. Simulating the Effect of Aerobic Biodegradation on Soil Vapor: Evaluation of Low Strength Sources Associated with Dissolved Gasoline Plumes Intrusion into Buildings. The American Petroleum Institute. Publication Number 4775. Available at http://www.api.org/Environment-Health-and-Safety/Clean-Water/Ground-Water/Vapor-Intrusion/~/_link.aspx?_id=4689DFDA5BFC4DAA9ADDA CC310112471&_z=z
- Abreu, L., C.C. Lutes and E.M. Nichols. 2013. 3-D Modeling of Aerobic Biodegradation of Petroleum Vapors: Effect of Building Area Size on Oxygen Concentration below the Slab. EPA-510-R-13-002. Office of Underground Storage Tanks. Available at <http://www.epa.gov/oust/cat/pvi/building-size-modeling.pdf>
- API. 2005. *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*. The American Petroleum Institute. Publication Number 4741. Available at <http://www.api.org/ehs/groundwater/lnapl/upload/4741final111805.pdf>
- API. 2012. User's Manual BioVapor: A 1-D Vapor Intrusion Model with Oxygen-Limited Aerobic Biodegradation. Version 2.1. November 2012. The American Petroleum Institute. Available at: <http://www.api.org/environment-health-and-safety/clean-water/ground-water/vapor-intrusion/biovapor-form>
- ASTM. 2010. Standard Test Method for Analysis of Natural Gas by Gas Chromatography. American Society for Testing and Materials Designation D 1945-03(2010). Available at <http://www.astm.org/Standards/D1945.htm>
- CRC CARE. 2013. Petroleum Hydrocarbon Vapor Intrusion Assessment: Australian Guidance. Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Technical Report no. 23. July 2013. Available: <http://www.crccare.com/823C21A0-F98D-11E2-B4EA005056B60026>
- Davis, G.B., B.M. Patterson, and M.G. Trefry. 2009. Evidence for instantaneous oxygen-limited biodegradation of petroleum hydrocarbon vapors in the subsurface. *Ground Water Monitoring & Remediation* 29(1): 126–137.
- DeVaul, G.E. 2007. Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. *Environmental Science & Technology* 41, 3241–3248.
- DeVaul, G. E. 2011. Biodegradation Rates for Petroleum Hydrocarbons in Aerobic soils: A Summary of Measured Data. D-50, in H.V. Rectanus and R. Sirabian (Chairs), *Bioremediation and Sustainable Environmental Technologies-2011*. International Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, Nevada, June 27-30. ISBN 978-0-9819730-4-3. Battelle Memorial Institute, Columbus, OH.
- H&P Mobile Geochemistry, Inc., Carlsbad, CA. Instructions for Collecting Soil Vapor into Summa Canisters. Available at http://www.pstif.org/apps/soil_vapor_sampling_handouts.pdf
- ITRC. 2014. *Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management*. PVI-1. Interstate Technology & Regulatory Council, Washington, D.C. Petroleum Vapor Intrusion Team. Available at: www.itrcweb.org/PetroleumVI-Guidance.
- Jewell, K.P. and J.T. Wilson. 2011. A new screening method for methane in soil gas using existing groundwater monitoring wells. *Ground Water Monitoring & Remediation* 31(3): 82-94. Available at http://www.epa.gov/ada/pubs/methane_screening_soil_gas.pdf
- Johnson, P.C. and R.A. Ettinger. 1991. Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings. *Environmental Science & Technology* 25. 1445-1452.
- Johnson, P.C., M.W. Kemblowski, and R.L. Johnson. 1998. Assessing the significance of subsurface contaminant vapor migration to enclosed spaces: Site-specific alternatives to generic estimates. The American Petroleum Institute. Publication Number 4674. Available at <http://www.api.org/environment-health-and-safety/clean-water/ground-water/vapor-intrusion>

- Johnson, P.C., M.W. Kemblowski, and R.L. Johnson. 1999. Assessing the significance of subsurface contaminant vapor migration to enclosed spaces: Site-specific alternatives to generic estimates. *Journal of Soil Contamination* 8(3): 389–421.
- Jury, W.A., W.F. Spencer and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: I. Model description. *Journal of Environmental Quality* 12, 558-564.
- Kirchstetter, T.W., B.C. Singer, R.A. Harley, G.R. Kendall and J.M. Hesson. 1999. Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 2. Volatile organic compound speciation and reactivity. *Environmental Science & Technology* 33(2):329-336.
- Lahvis, M.A., I. Hers, R.V. Davis, J. Wright and G.E. DeVuall. 2013. Vapor Intrusion Screening at Petroleum UST Sites. *Groundwater Monitoring & Remediation* 33(2): 53–67.
- Ma, J., H. Luo, G.E. DeVuall, W.G. Rixey and P.J. J. Alvarez. 2014. Numerical Model Investigation for Potential Methane Explosion and Benzene Vapor Intrusion Associated with High-Ethanol Blend Releases. *Environmental Science & Technology* 48: 474-481.
- McAlary, T.A., P. Nicholson, H. Groenevelt, and D. Bertrand. 2009. A case study of soil-gas sampling in silt and clay-rich (low permeability) soils. *Ground Water Monitoring and Remediation* 29: 144–152.
- McHugh, T., R. Davis, G. Devuall, H. Hopkins, J. Menatti, and T. Peargin. 2010. Evaluation of Vapor Attenuation at Petroleum Hydrocarbon Sites: Considerations for Site Screening and Investigation. *Soil and Sediment Contamination* 19:725–745.
- NRC. 1983. Risk assessment in the federal government: Managing the process. Committee on the Institutional Means for Assessment of Risks to Public Health, Commission on Life Sciences, the National Research Council. Washington, DC: National Academy Press.
- Orchard, V.A., and F.J. Cook. 1983. Relationship between Soil Respiration and Soil Moisture. *Soil Biology and Biochemistry*. 15(4): 447-453.
- Ostendorf, D.W., and D.H. Kampbell. 1991. Biodegradation of hydrocarbon vapors in the unsaturated zone. *Water Resources Research* 27(4): 453–462.
- Ririe, G.T., R.E. Sweeney, and S.J. Daugherty. 2002. A comparison of hydrocarbon vapor attenuation in the field with predictions from vapor diffusion models. *Soil and Sediment Contamination* 11, 529–544.
- Roggemans, S., C.L. Bruce, P.C. Johnson, and R.L. Johnson. 2001. Vadose zone natural attenuation of hydrocarbon vapors: an empirical assessment of soil gas vertical profile data. API Soil and Groundwater Research Bulletin 15, American Petroleum Institute. Washington, D.C. Available at http://www.api.org/ehs/groundwater/upload/15_bull.pdf
- U.S. EPA. 1984. Method TO-3, Revision 1.0, Method for the Determination of Volatile Organic Compounds in Ambient Air using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection. April, 1984. Available at <http://www.epa.gov/ttnamti1/files/ambient/airtox/to-3.pdf>
- U.S. EPA. 1992. Guidelines for Exposure Assessment. EPA/600/Z-92/001. Federal Register 7(104):22888-22938. May 29, 1992. Available at http://www.epa.gov/raf/publications/pdfs/GUIDELINES_EXPOSURE_ASSESSMENT.PDF
- U.S. EPA. 1994. General Field Sampling Guidelines, SOP#:2001, REV#:0.0. Environmental Response Team, United States Environmental Protection Agency. Available at: http://www.epa.gov/region6/qa/qadevtools/mod5_sops/misc_field_procedures/ertsop2001fieldsampling-guide.pdf
- U.S. EPA. 1996. Soil Gas Sampling, SOP#:2042, REV#:0.0. Environmental Response Team, United States Environmental Protection Agency. Available at: <http://www.dem.ri.gov/pubs/sops/wmsr2042.pdf>
- U.S. EPA. 1999a. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition: Compendium Method TO-15, Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS). EPA/625/R-96/010b. Available at <http://www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf>
- U.S. EPA. 1999b. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition: Compendium Method TO-14A, Determination Of Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By GasChromatography. EPA/625/R-96/010b. Available at <http://www.airtoxics.com/literature/methods/Method%20TO-14A.pdf>
- U.S. EPA. 1999c. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition: Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes. EPA/625/R-96/010b. Available at <http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf>

- U.S. EPA. 2001. Soil Gas Sampling. Standard Operating Procedure 2042. Available at <http://www.clu-in.org/download/ert/2042-R00xx.pdf>
- U.S. EPA. 2002. OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Ground water and Soils (Subsurface Vapor Intrusion Guidance) EPA 530-D-02-004. Available at <http://www.epa.gov/epawaste/hazard/correctiveaction/eis/vapor/complete.pdf>
- U.S. EPA. 2011. Petroleum Hydrocarbons And Chlorinated Hydrocarbons Differ In Their Potential For Vapor Intrusion. Office of Underground Storage Tanks, Washington, D.C. 20460, September 2011, www.epa.gov/oust. Available at <http://www.epa.gov/oust/cat/pvi/pvicvi.pdf>
- U.S. EPA. 2012. Conceptual Model Scenarios for the Vapor Intrusion Pathway (EPA 530-R-10-003). Office of Solid Waste and Emergency Response U.S. Environmental Protection Agency Washington, DC Available at <http://www.epa.gov/oswer/vaporintrusion/documents/vi-cms-v11final-2-24-2012.pdf>
- U.S. EPA. 2013a. Evaluation of Empirical Data to Support Soil Vapor Intrusion Screening Criteria for Petroleum Hydrocarbon Compounds. EPA-510-R-13-001. Office of Underground Storage Tanks. Available at http://www.epa.gov/OUST/cat/pvi/PVI_Database_Report.pdf
- U.S. EPA. 2013b. [DRAFT] Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites. (EPA-510-R-13-xxx) Office of Underground Storage Tanks. Available at <http://www.epa.gov/oust/cat/pvi/petroleum-vapor-intrusion-review-draft-04092013.pdf>
- U.S. EPA. 2014a. What Is The History of The Federal Underground Storage Tank Program? Web page Available at <http://www.epa.gov/oust/faqs/genesis1.htm>
- U.S. EPA. 2014b. PVI Database Export. Available at <http://www.epa.gov/oust/cat/pvi/>
- U.S. EPA. 2014c. Integrated Risk Information System (IRIS). Available at <http://www.epa.gov/iris/>
- U.S. EPA. 2014d. Method 3C-Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen From Stationary Sources. Available at <http://www.caslab.com/EPA-Methods/PDF/m-03c.pdf>
- U.S. EPA. 2014e. Vapor Intrusion Screening Level (VISL) Calculator. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Office of Superfund Remediation and Technology Innovation. Available at <http://www.epa.gov/oswer/vaporintrusion/guidance.html>
- U.S. EPA. 2014f. Vapor Intrusion Screening Level (VISL) Calculator User's Guide. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Office of Superfund Remediation and Technology Innovation. Available at <http://www.epa.gov/oswer/vaporintrusion/documents/VISL-UsersGuide.pdf>
- U.S. EPA. 2014g. PVI Screen Model. In development, contact Weaver.Jim@epa.gov.
- Wilson, J.T., K. Jewell, C. Paul, R. Davis, and J. Menatti. 2009. Biodegradation of Petroleum Hydrocarbon Vapors in the Vadose Zone. Presented at the 2009 Annual National Tanks Conference & Exposition, Sacramento, CA, March 30, 2009. Available at: <http://www.neiwpc.org/tanks2009/presentations/Wilson%20Vapor%20Intrusion%20Mon.pdf>
- Wilson, J.T, J. W. Weaver, and H. White. 2012a. An Approach for Developing Site-Specific Lateral and Vertical Inclusion Zones within which Structures Should be Evaluated for Petroleum Vapor Intrusion due to Releases of Motor Fuel from Underground Storage Tanks. EPA/600/R-13/047. Available at <http://www.epa.gov/OUST/cat/pvi/epa600r13047.pdf>
- Wilson, J.T., M. Toso, D. Mackay, N. de Sieyes and G.E. DeVaul. 2012b. What's the Deal with Methane at LUST Spill Sites? Part 1. LUSTLine Bulletin 72, February 2013, pages 6-8 and 13.
- Wilson, J.T., M. Toso, D. Mackay, N. de Sieyes and G.E. DeVaul. 2013. What's the Deal with Methane at LUST Spill Sites? Part 2: Vapor Intrusion. LUSTLine Bulletin 72, February 2013, pages 5-11 and 21.

10.0 QUALITY ASSURANCE, METHODS AND PROCEDURES

Data presented in the manuscript was either obtained from peer reviewed documents published elsewhere or under a Ground Water and Ecosystems Restoration Division Quality Assurance Project Plan (GWERD QAPP). This section provides some of the details of experimental procedures and provides the documentation for quality assurance parameters for data generated under a GWERD QAPP. Data were developed under three different Quality Assurance Project Plans.

The data on chemicals in soil gas (Table 4.1) were generated under the Project Plan titled: *Production of methane and fatty acids as degradation products of ethanol and petroleum at UST sites in Oklahoma*, third amendment to task 10013/G-15667. All other data on chemicals in soil gas were generated under the Project Plan titled: *Production of methane and fatty acids as degradation products of ethanol and petroleum at UST*

sites in Oklahoma, fourth amendment task 10013/G-15667.

Data on concentrations of total petroleum hydrocarbons in the range of gasoline (TPH-g), also called gasoline range organics (GRO), in core samples were generated under the Project Plan titled: *Retrospective Evaluation of a Surfactant Flush to Remove Gasoline Contamination from an Aquifer at Golden, Oklahoma*, first Amendment, task 14393.

For convenience, the discussion of data quality is organized by individual data tables or figures.

10.1 Section 4 and Appendix A

10.1.1 Soil gas components in Table 4.1

Soil gas was pumped from conventional ground water monitoring wells using the protocol in Jewell and Wilson (2011). A schematic of the sampling train used to collect the samples is presented in Figure 10.1.

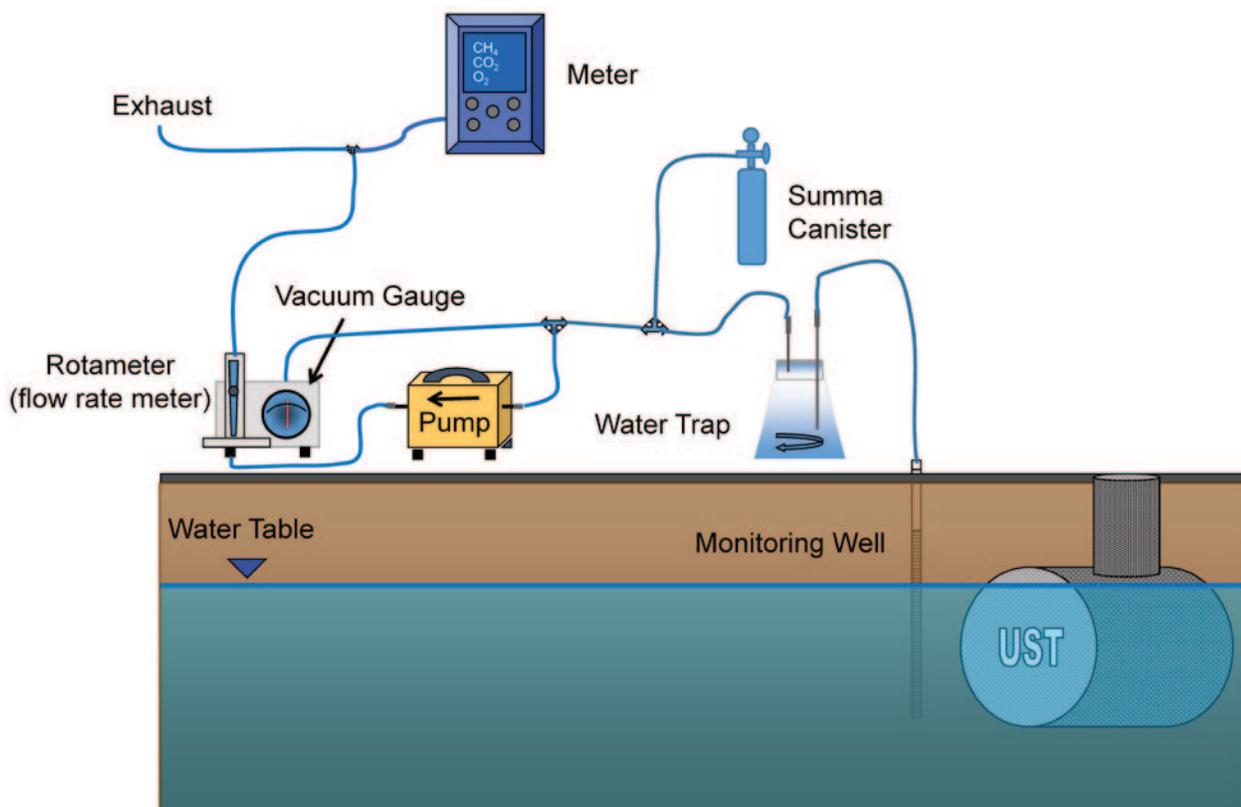


Figure 10.1. Sampling train to provide soil gas to a field meter and a gas sampling port.

Table 10.1 describes the performance of the quality assurance parameters during the analysis of the samples.

The continuing calibration checks and the second source standards were within +/- 15% of the nominal value. Carbon dioxide was detected in the field blanks, but at low concentrations, equal to 0.06% and 0.09% by volume. The lowest concentration of carbon dioxide in Table 4.1 was 11.7%. The carbon dioxide in the field blanks do not affect the interpretation of the data, and the data were used as intended. The concentration in the other blanks were less than the detection limit. The quality of the data were acceptable for the intended purpose, and all the data were used.

The purpose of Table 4.1 was to compare two samples where a leak was suspected in the sampling train (MW-2B and GMW-1B) to a sample where the leak was not evident (MW-9). The relative percent difference for oxygen in the field duplicates of sample MW-9 was above the acceptance criteria of +/- 15%, but was much less than the relative percent difference in samples MW-2B and GMW-1B. The data quality were acceptable for the intended purpose, to illustrate the effect of a leak on the ratio of oxygen to nitrogen.

Hydrogen was included in the sample to allow a calculation of the balance of total gas. The actual values of the hydrogen data were not interpreted.

Table 10.1. Quality assurance parameters from laboratory-based analyses of soil gas (applies to data in Table 4.1).

Analyte	QA Parameter	Number of Analyses	Range of Values
Methane	CCC ¹	3	101% to 105% Recovery
Methane	SS ²	1	105% Recovery
Methane	GB ³	4	All < 2.0 ppm (v/v)*
Methane	FB ⁴	2	All < 2 ppm (v/v)*
Ethylene	CCC	2	100% to 103% Recovery
Ethylene	SS	1	102% Recovery
Ethylene	GB	4	All < 3.3 ppm (v/v)*
Ethylene	FB	2	All < 3.3 ppm (v/v)*
Ethane	CCC	2	95.9% to 98.7% Recovery
Ethane	SS	1	102% Recovery
Ethane	GB	4	All < 1.8 ppm (v/v)*
Ethane	FB	2	All < 1.8 ppm (v/v)*
Acetylene	CCC	2	95.7% to 96% Recovery
Acetylene	SS	1	98.1% Recovery
Acetylene	GB	4	All < 2.4 ppm (v/v)*
Acetylene	FB	2	All < 2.4 ppm (v/v)*
Propane	CCC	2	98% to 100% Recovery
Propane	SS	1	101% Recovery
Propane	GB	4	All < 1.7 ppm (v/v)*
Propane	FB	2	All < 1.7 ppm (v/v)*
<i>iso</i> -Butane	CCC	2	96.5% to 98.3% Recovery
<i>iso</i> -Butane	SS	1	98.7% Recovery
<i>iso</i> -Butane	GB	4	All < 10 ppm (v/v) **

Table 10.1. Quality assurance parameters from laboratory-based analyses of soil gas (applies to data in Table 4.1) (continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
Butane	CCC	2	98.6% to 100% Recovery
Butane	SS	1	100% Recovery
Butane	GB	4	All < 1.44 ppm (v/v)*
Butane	FB	2	All < 1.44 ppm (v/v)*
<i>iso</i> -Pentane	CCC	2	96.1% to 98.1% Recovery
<i>iso</i> -Pentane	SS	1	98.3% Recovery
<i>iso</i> -Pentane	GB	4	All < 2 ppm (v/v) **
Pentane	CCC	2	95.4% to 101% Recovery
Pentane	SS	1	95.1% Recovery
Pentane	GB	4	All < 2 ppm (v/v) **
C6+	CCC	2	106% to 107% Recovery
C6+	SS	1	110% Recovery
C6+	GB	4	All < 2 ppm (v/v) **
Benzene	CCC	2	111% to 111% Recovery
Benzene	SS	1	112% Recovery
Benzene	GB	4	All < 2 ppm (v/v) **
Oxygen	CCC	2	101% to 102% Recovery
Oxygen	SS	1	104% Recovery
Oxygen	GB	4	All < 1251 ppm (v/v)*
Nitrogen	CCC	2	98.6% to 99.4% Recovery
Nitrogen	SS	1	101% Recovery
Nitrogen	GB	4	All < 5 ppm (v/v) **
Carbon Dioxide	CCC	3	94.4% to 109% Recovery
Carbon Dioxide	SS	1	97.5% Recovery
Carbon Dioxide	GB	4	All < 2.52 ppm (v/v)*
Carbon Dioxide	FB	2	6.18 and 9.16 ppm (v/v)
Hydrogen	CCC	2	101% to 103% Recovery
Hydrogen	SS	1	106% Recovery
Hydrogen	GB	4	All < 3.03 ppm (v/v)*

* < MDL

**< An estimated value for the MDL provided by the analyst. Method detection limit not determined.

¹CCC is Continuing Calibration Check.

²SS is a Second Source Standard and is a measure of accuracy.

³GB is a laboratory blank.

⁴FB is a field blank, equivalent to an equipment blank. The other data were collected February 13, 2012. Due to an error, field blanks were not collected at that time. The same equipment was used to sample the same wells on May 30, 2012. These are values for the field blanks collected May 30, 2012.

Table 10.2. Relative percent difference between duplicate samples of laboratory-based analysis of soil gas.
(Applies to data in Table 4.1).

Monitoring Well	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
Antlers MW-2	2/13/2012	Oxygen	Field Duplicate	127
Antlers MW-2	2/13/2012	Methane	Field Duplicate	29
Antlers MW-2	2/13/2012	Hydrogen	Field Duplicate	NC
Antlers MW-2	2/13/2012	Total Petroleum Hydrocarbons*	Field Duplicate	44
Antlers MW-2	2/13/2012	Nitrogen	Field Duplicate	199**
Antlers MW-2	2/13/2012	Carbon Dioxide	Field Duplicate	17.2
Antlers MW-9	2/13/2012	Oxygen	Field Duplicate	27.1
Antlers MW-9	2/13/2012	Methane	Field Duplicate	2.1
Antlers MW-9	2/13/2012	Hydrogen	Field Duplicate	NC
Antlers MW-9	2/13/2012	Total Petroleum Hydrocarbons*	Field Duplicate	1.3
Antlers MW-9	2/13/2012	Nitrogen	Field Duplicate	6.3
Antlers MW-9	2/13/2012	Carbon Dioxide	Field Duplicate	7.3
Antlers GMW-1	2/13/2012	Oxygen	Field Duplicate	4.5
Antlers GMW-1	2/13/2012	Methane	Field Duplicate	2.4
Antlers GMW-1	2/13/2012	Hydrogen	Field Duplicate	NC
Antlers GMW-1	2/13/2012	Total Petroleum Hydrocarbons*	Field Duplicate	0.75
Antlers GMW-1	2/13/2012	Nitrogen	Field Duplicate	199***
Antlers GMW-1	2/13/2012	Carbon Dioxide	Field Duplicate	3.4

NC = Not calculated, one or both of the pair is < MDL

*Sum of concentrations of individual hydrocarbons in ppm (v/v).

**Concentration in MW-2A sample was 31.4 ppm, concentration in MW-2B sample was 66200 ppm, indicating a leak in the MW-2B sample. Data in Table 4.1 from sample MW-2B.

***Concentration in GMW-1A sample was 38.9 ppm, concentration in GMW-1B sample was 241000 ppm, indicating a leak in the MW-1B sample. Data in Table 4.1 from sample GMW-1B.

10.1.2 Quality Assurance of Carbon Dioxide, Oxygen and Methane using Field Meter in Figure 4.4, Figure 4.5 and Appendix A

Oxygen, Carbon Dioxide and Methane in the soil gas sample were determined using a Landtec GEM2000 gas analyzer (Landtec Inc., 850 S. Via Lata, Suite 112, Colton, CA 92324).

The Landtec GEM2000 gas analyzer was calibrated daily prior to use. The gas analyzer was calibrated again whenever the ambient air temperature changed more than 20 degrees Fahrenheit. Additionally, the gas analyzer was checked against the calibration standard any time the gas analyzer was turned off.

The GEM2000 gas analyzer was calibrated using standard gas samples that were acquired from LandTec (850 S. Via Lata, Suite 112, Colton, CA 92324). The carbon dioxide and methane sensors were calibrated with LandTec's commercial standard containing 50% methane, 35% carbon dioxide, and balance nitrogen gas. Ambient air was used to calibrate the oxygen sensor. The zero response for the carbon dioxide sensor and the methane sensor was calibrated against a gas standard that had 4% oxygen and the balance nitrogen. The zero response for the oxygen sensor was calibrated against the standard containing 50% methane, 35% carbon dioxide, and balance nitrogen gas.

The following calibration procedure was located in the "calibration" window. After all channels were zeroed, the calibration gas standard mixture containing 50% methane, 35% carbon dioxide and balance nitrogen is supplied to the instrument. When readings stabilize, the "SPAN CH4" channel was selected allowing the reading to adjust to the input parameter. Then the "SPAN CO2" channel was selected allowing the reading to adjust to the input parameter. Next, ambient oxygen was supplied to the instrument. When readings stabilize, the "SPAN O2" channel was selected allowing the reading to adjust to the input parameter. This procedure completed the GEM2000 calibration.

As mentioned above, calibration was carried out using a commercial gas standard with 50% methane, 35% carbon dioxide and the balance nitrogen mixture, and with ambient air that contains 20.9% oxygen. At some sites, the calibration was compared against a second source standard mixture containing 2.5% methane,

20.1% carbon dioxide, and 10.1% oxygen. Calibration checks, also known as "Bump Cal", were used periodically throughout the sampling process to ensure meter calibration was within acceptable parameters. The acceptable range was +/- 1% of display reading.

Table 10.3 presents the results from the field calibration of the gas analyzer.

Four of the calibration checks were outside the acceptable range, but were within +/- 2% of the nominal value of the standard. In the figures, the meter readings were plotted to reveal changes over time as the concentrations of the compounds in the sampled gas approached equilibration. A range of +/- 2% of the nominal value of the standard is useful for this purpose. The quality of the data were acceptable for the intended purpose, and all the data were used in the figures.

Table 10.3. Results of field calibration and calibration checks of the Landtec GEM2000 gas analyzer.

Figure	Well	Site	Location	Date	Calibration	Nominal Value	Reading
4.4	MW-2	EZ Go	Antlers, OK	5/30/12	Standard	50% CH ₄	51.9%*
					Standard	35% CO ₂	35.1%
					Standard	20.9% O ₂	20.9%
					Check	50% CH ₄	49.8%
					Check	35% CO ₂	35.1%
					Check	20.9% O ₂	20.9%
4.5	MW-4	Kev's Auto	Helena, MT	10/26/12	Standard	50% CH ₄	50.9%
					Standard	35% CO ₂	35.1%
					Standard	20.9% O ₂	20.0%
					Check	2.51% CH ₄	2.4%
					Check	20.1% CO ₂	20.2%
					Check	10.1% O ₂	10.7%
A.1	MW-9	Visocan Site	Helena, MT	10/25/12	Standard	50% CH ₄	50.1%
					Standard	35% CO ₂	35.4%
					Standard	20.9% O ₂	20.9%
					Check	2.51% CH ₄	2.3%
					Check	20.1% CO ₂	19.6%
					Check	10.1% O ₂	10.6%
A.2	MW-4	Visocan Site	Helena, MT	10/26/12	Standard	50% CH ₄	50.9%
					Standard	35% CO ₂	35.1%
					Standard	20.9% O ₂	20.0%
					Check	2.51% CH ₄	2.4%
					Check	20.1% CO ₂	20.2%
					Check	10.1% O ₂	10.7%
A.3	SVE-NE	Noon's Store	Helena, MT	10/25/12	Standard	50% CH ₄	50.1%
					Standard	35% CO ₂	35.4%
					Standard	20.9% O ₂	20.9%
					Check	2.51% CH ₄	2.3%
					Check	20.1% CO ₂	19.6%
					Check	10.1% O ₂	10.6%

Table 10.3. Results of field calibration and calibration checks of the Landtec GEM2000 gas analyzer. (Continued).

Figure	Well	Site	Location	Date	Calibration	Nominal Value	Reading
A.4	SVE-SE	Noon's Store	Helena, MT	10/24/12	Standard	50% CH ₄	50.1%
					Standard	35% CO ₂	36.9%*
					Standard	20.9% O ₂	21.1%
					Check	2.51% CH ₄	2.4%
					Check	20.1% CO ₂	19.6%
					Check	10.1% O ₂	10.7%
A.5	HMM-6	Noon's Store	Helena, MT	10/25/12	Standard	50% CH ₄	50.1%
					Standard	35% CO ₂	35.4%
					Standard	20.9% O ₂	20.9%
					Check	2.51% CH ₄	2.3%
					Check	20.1% CO ₂	19.6%
					Check	10.1% O ₂	10.6%
A.6	GMW-1	EZ Go	Antlers, OK	5/30/12	Standard	50% CH ₄	51.9%*
					Standard	35% CO ₂	35.1%
					Standard	20.9% O ₂	20.9%
					Check	50% CH ₄	49.8%
					Check	35% CO ₂	35.1%
					Check	20.9% O ₂	20.9%
A.7	MW-9	EZ Go	Antlers, OK	5/30/12	Standard	50% CH ₄	51.9%*
					Standard	35% CO ₂	35.1%
					Standard	20.9% O ₂	20.9%
					Check	50% CH ₄	49.8%
					Check	35% CO ₂	35.1%
					Check	20.9% O ₂	20.9%
A.8	MW-1	Miller Mart	Wapanucka, OK	4/29/13	Standard	50% CH ₄	WAR**
					Standard	35% CO ₂	WAR**
					Standard	4.0% O ₂	WAR**

* Values outside the acceptable range of +/- 1% of the nominal value of the standard.

** WAR means Within Acceptable Range. Field notebook indicates that values were within the acceptable range, but a value was not recorded.

10.1.3 Benzene and TPH-g in Figure 4.4, Figure 4.5 and Appendix A

Soil gas samples were acquired by water displacement into 165 ml serum vials. The vials did not drain completely and always retained a few drops of water. Bacteria in the water in contact with the gas samples might have degraded the hydrocarbons in the gas samples. The water contained 1% trisodium phosphate as a preservative.

The vials were returned to the Kerr Center for analysis by micro gas chromatography with thermal conductivity detection as is described in Jewell and Wilson (2011).

Data in Figure 4.4, Figure A.6 and A.7 are from wells that were installed at the direction of the Petroleum Storage Tank Division of the Oklahoma Corporation Commission at an EZ Go service station in Antlers, OK. The quality assurance parameters for data in Figure 4.4, Figure A.6 and Figure A.7 are presented in Table 10.4.

The continuing calibration checks and the second source standards were within +/- 15% of the nominal value. The concentration in all the blanks were less than the detection limit. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.4. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure 4.4, Figure A.6 and Figure A.7.

Analyte	QA Parameter	Number of Analyses	Range of Values
Methane	CCC ¹	7	90.6% to 107% Recovery
Methane	SS ²	1	93.9% Recovery
Methane	LB ³	12	All < 1.98 ppm (v/v)*
Methane	FB ⁴	2	All < 1.98 ppm (v/v)*
Ethylene	CCC	6	94.6% to 99.9% Recovery
Ethylene	SS	1	95.5% Recovery
Ethylene	LB	12	All < 3.29 ppm (v/v)*
Ethylene	FB	2	All < 3.29 ppm (v/v)*
Ethane	CCC	6	93.7% to 101% Recovery
Ethane	SS	1	92.7% Recovery
Ethane	LB	12	All < 1.75 ppm (v/v)*
Ethane	FB	2	All < 1.75 ppm (v/v)*
Acetylene	CCC	6	90.8% to 98.5% Recovery
Acetylene	SS	1	95.4% Recovery
Acetylene	LB	12	All < 2.39 ppm (v/v)*
Acetylene	FB	2	All < 2.39 ppm (v/v)*
Propane	CCC	6	91.9% to 107% Recovery
Propane	SS	1	85.7% Recovery
Propane	LB	12	All < 1.74 ppm (v/v)*
Propane	FB	2	All < 1.74 ppm (v/v)*
Butane	CCC	6	105% to 110% Recovery
Butane	SS	1	98.2% Recovery
Butane	LB	12	All < 1.44 ppm (v/v)*
Butane	FB	2	All < 1.44 ppm (v/v)*

* < MDL

¹CCC is Continuing Calibration Check.

²SS is a Second Source Standard and is a measure of accuracy.

³LB is a laboratory method blank.

⁴FB is a field blank equivalent to an equipment blank.

Table 10.5 presents the relative percent difference between duplicate laboratory samples for the data in Figure 4.4, Figure A.6 and Figure A.7.

The relative percent difference of the lab duplicates were all less than 15%. Each well was sampled four times at each time period. There were four field duplicates. The individual data are plotted on the figures. In Figure A.6, the data at the initial sampling interval were variable, ranging over as much as a

factor of four. In subsequent sampling periods the range of values were less than 150% to 50% of their mean. The figures plot a line connecting the mean of the four samples at each time period. The figures were intended to illustrate the tendency to reach equilibration. The data in the later time periods were closely clustered about their mean. The data were of acceptable quality for the intended purpose and all of the data were used.

Table 10.5. Relative percent difference of laboratory duplicates on samples of soil gas analyzed in the laboratory for data in Figure 4.4, Figure A.6 and Figure A.7.

Monitoring Well	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
Antlers MW-1-10 min-F in Figure A.6	5/30/12	Benzene	Lab Duplicate	0.18
Antlers MW-1-10 min-F in Figure A.6	5/30/12	Total Hydrocarbons*	Lab Duplicate	0.49
Antlers MW-2-0 min-A in Figure 4.4	5/30/12	Benzene	Lab Duplicate	0.43
Antlers MW-2-0 min-A in Figure 4.4	5/30/12	Total Hydrocarbons*	Lab Duplicate	0.23
Antlers MW-2-30 min-B in Figure 4.4	5/30/12	Benzene	Lab Duplicate	0.67
Antlers MW-2-30 min-B in Figure 4.4	5/30/12	Total Hydrocarbons*	Lab Duplicate	0.54
Antlers MW-9-10 min-E in Figure A.7	5/30/12	Benzene	Lab Duplicate	0.12
Antlers MW-9-10 min-E in Figure A.7	5/30/12	Total Hydrocarbons*	Lab Duplicate	0.48
Antlers MW-9-40 min-F in Figure A.7	5/30/12	Benzene	Lab Duplicate	0.78
Antlers MW-9-40 min-F in Figure A.7	5/30/12	Total Hydrocarbons*	Lab Duplicate	2.5

*Sum of concentrations of individual petroleum hydrocarbons plus methane in $\mu\text{g}/\text{m}^3$.

Data in Figure A.8 are from a well that was installed at the direction of the Petroleum Storage Tank Division of the Oklahoma Corporation Commission at the Miller Mart service station in Wapanucka, OK. The quality assurance parameters for data in Figure A.8 are presented in Table 10.6.

The continuing calibration checks and the second source standards were within +/- 15% of the nominal value. The concentration in all the blanks were less than the detection limit. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.6. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure A.8.

Analyte	QA Parameter	Number	Range of Values
Methane	CCC ¹	3	106% to 111% Recovery
Methane	SS ²	1	107% Recovery
Methane	LB ³	6	All < 1.76 ppm (v/v)*
Methane	FB ⁴	1	< 1.76 ppm (v/v)*
Ethylene	CCC	3	103% to 105% Recovery
Ethylene	SS	1	104% Recovery
Ethylene	LB	6	All < 1.22 ppm (v/v)*
Ethylene	FB	1	< 1.22 ppm (v/v)*
Ethane	CCC	3	98.2% to 100% Recovery
Ethane	SS	1	100% Recovery
Ethane	LB	6	All < 3.1 ppm (v/v)*
Ethane	FB	1	< 3.1 ppm (v/v)*
Acetylene	CCC	3	99% to 101% Recovery
Acetylene	SS	1	98.6% Recovery
Acetylene	LB	6	All < 2.51 ppm (v/v)*
Acetylene	FB	1	< 2.51 ppm (v/v)*
Propane	CCC	3	107% to 109% Recovery
Propane	SS	1	110% Recovery
Propane	LB	6	All < 1.16 ppm (v/v)*
Propane	FB	1	< 1.16 ppm (v/v)*
Propylene	CCC	3	108% to 111% Recovery
Propylene	SS	1	110% Recovery
Propylene	LB	6	All < 2 ppm (v/v) **
Propylene	FB	1	< 2 ppm (v/v) **
<i>iso</i> -Butane	CCC	3	99.7% to 102% Recovery
<i>iso</i> -Butane	SS	1	102% Recovery
<i>iso</i> -Butane	LB	6	All < 10 ppm (v/v)**
<i>iso</i> -Butane	FB	1	< 10 ppm (v/v)**
Butane	CCC	3	104% to 107% Recovery
Butane	SS	1	107% Recovery
Butane	LB	6	All < 0.72 ppm (v/v)
Butane	FB	1	< 0.72 ppm (v/v)

Table 10.6. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure A.8. (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
<i>trans</i> -2-Butene	CCC	3	104% to 106% Recovery
<i>trans</i> -2-Butene	SS	1	106% Recovery
<i>trans</i> -2-Butene	LB	6	All < 2 ppm (v/v) **
<i>trans</i> -2-Butene	FB	1	< 2 ppm (v/v) **
1-Butene	CCC	3	110% to 113% Recovery
1-Butene	SS	1	114% Recovery
1-Butene	LB	6	All < 2 ppm (v/v) **
1-Butene	FB	1	< 2 ppm (v/v) **
<i>iso</i> -Butylene	CCC	3	112% to 114% Recovery
<i>iso</i> -Butylene	SS	1	115% Recovery
<i>iso</i> -Butylene	LB	6	All < 2 ppm (v/v) **
<i>iso</i> -Butylene	FB	1	< 2 ppm (v/v) **
<i>cis</i> -2-Butene	CCC	3	108% to 111% Recovery
<i>cis</i> -2-Butene	SS	1	110% Recovery
<i>cis</i> -2-Butene	LB	6	All < 2 ppm (v/v) **
<i>cis</i> -2-Butene	FB	1	< 2 ppm (v/v) **
<i>iso</i> -Pentane	CCC	3	101% to 103% Recovery
<i>iso</i> -Pentane	SS	1	103% Recovery
<i>iso</i> -Pentane	LB	6	All < 2 ppm (v/v) **
<i>iso</i> -Pentane	FB	1	< 2 ppm (v/v) **
Pentane	CCC	3	89.3% to 108% Recovery
Pentane	SS	1	108% Recovery
Pentane	LB	6	All < 2 ppm (v/v) **
Pentane	FB	1	< 2 ppm (v/v) **
2-Methyl-2-Butene	CCC	3	98.5% to 101% Recovery
2-Methyl-2-Butene	SS	1	110% Recovery
2-Methyl-2-Butene	LB	6	All < 2 ppm (v/v) **
2-Methyl-2-Butene	FB	1	< 2 ppm (v/v) **
<i>trans</i> -2-Pentene	CCC	3	107% to 110% Recovery
<i>trans</i> -2-Pentene	SS	1	101% Recovery
<i>trans</i> -2-Pentene	LB	6	All < 2 ppm (v/v) **
<i>trans</i> -2-Pentene	FB	1	< 2 ppm (v/v) **
1-Pentene	CCC	3	108% to 110% Recovery
1-Pentene	SS	1	111% Recovery
1-Pentene	LB	6	All < 2 ppm (v/v) **
1-Pentene	FB	1	< 2 ppm (v/v) **

Table 10.6. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure A.8. (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
<i>cis</i> -2-Pentene	CCC	3	108% to 110% Recovery
<i>cis</i> -2-Pentene	SS	1	111% Recovery
<i>cis</i> -2-Pentene	LB	6	All < 2 ppm (v/v) **
<i>cis</i> -2-Pentene	FB	1	< 2 ppm (v/v) **
C6+ Hydrocarbons	CCC	3	92% to 97.8% Recovery
C6+ Hydrocarbons	SS	1	91.4% Recovery
C6+ Hydrocarbons	LB	6	All < 2 ppm (v/v) **
C6+ Hydrocarbons	FB	1	< 2 ppm (v/v) **
Benzene	CCC	3	97.4% to 97.7% Recovery
Benzene	SS	1	100% Recovery
Benzene	LB	6	All < 2 ppm (v/v) **
Benzene	FB	1	2.02 ppm (v/v)

* < MDL

**< An estimated value for the MDL provided by the analyst. Method detection limit not determined.

¹CCC is Continuing Calibration Check.

²SS is a Second Source Standard and is a measure of accuracy.

³LB is a laboratory method blank.

⁴FB is a field blank, equivalent to an equipment blank.

⁵An estimated value provided by the analyst. Method detection limit not determined.

Table 10.7 presents the relative percent difference between duplicate laboratory samples for the data in Figure A.8.

The relative percent difference of the lab duplicates were all less than 5%. Each well was sampled four times at each time period. There were four field duplicates. The individual data are plotted on the figures. In all sampling periods the range of values

were less than 150% to 50% of their mean. The figure plots a line connecting the mean of the four samples at each time period. The figure was intended to illustrate the tendency to reach equilibration. The data in the later time periods were closely clustered about their mean. The data were of acceptable quality for the intended purpose and all of the data were used.

Table 10.7. Relative percent difference of laboratory duplicates on samples of soil gas analyzed in the laboratory for data in Figure A.8.

Monitoring Well	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
Wapanucka MW-1-20 min-F in Figure A.8	4/29/2013	Benzene	Lab Duplicate	0.0
Wapanucka MW-1-20 min-F in Figure A.8	4/29/2013	Total Hydrocarbons*	Lab Duplicate	0.64
Wapanucka MW-1-60 min-F in Figure A.8	4/29/2013	Benzene	Lab Duplicate	0.40
Wapanucka MW-1-60 min-F in Figure A.8	4/29/2013	Total Hydrocarbons*	Lab Duplicate	0.35

*Sum of concentrations of individual petroleum hydrocarbons plus methane in $\mu\text{g}/\text{m}^3$.

Data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5 are from conventional ground water wells that were installed at the direction of the Petroleum Release Section of the Montana Department of Environmental Quality at three sites in Helena, MT. Soil gas samples were acquired by water displacement into 165 ml serum vials. The vials were returned to the Kerr Center for analysis by micro gas chromatography with thermal conductivity detection as was described in Jewell and Wilson (2011).

The quality assurance parameters for data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5 are presented in Table 10.8.

The continuing calibration checks and the second source standards were within +/- 15% of the nominal value. The concentration in all the blanks were less than the detection limit. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.8. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5.

Analyte	QA Parameter	Number	Range of Values
Methane	CCC ¹	15	101% to 107% Recovery
Methane	SS ²	4	102% to 107% Recovery
Methane	LB ³	30	All < 1.98 ppm (v/v)*
Methane	FB ⁴	2	All < 1.98 ppm (v/v)*
Ethylene	CCC	15	96.6% to 101% Recovery
Ethylene	SS	4	96.1% to 101% Recovery
Ethylene	LB	30	All < 3.29 ppm (v/v)*
Ethylene	FB	2	All < 3.29 ppm (v/v)*
Ethane	CCC	15	92.7% to 96.7% Recovery
Ethane	SS	4	92.6% to 97.1% Recovery
Ethane	LB	30	All < 1.75 ppm (v/v)*
Ethane	FB	2	All < 1.75 ppm (v/v)*
Acetylene	CCC	15	93.6% to 97.7% Recovery
Acetylene	SS	4	92.8% to 95.6% Recovery
Acetylene	LB	30	All < 2.39 ppm (v/v)*
Acetylene	FB	2	All < 2.39 ppm (v/v)*
Propane	CCC	15	98.2% to 101% Recovery
Propane	SS	4	100% to 101% Recovery
Propane	LB	30	All < 1.74 ppm (v/v)*
Propane	FB	2	All < 1.74 ppm (v/v)*
Propylene	CCC	15	97.7% to 101% Recovery
Propylene	SS	4	98% to 98.7% Recovery
Propylene	LB	30	All < 2 ppm (v/v) **
Propylene	FB	2	All < 2 ppm (v/v) **
<i>iso</i> -Butane	CCC	15	99.7% to 103% Recovery
<i>iso</i> -Butane	SS	4	101% to 102% Recovery
<i>iso</i> -Butane	LB	30	All < 10 ppm (v/v) **
<i>iso</i> -Butane	FB	2	All < 10 ppm (v/v)**

Table 10.8. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5. (Continued).

Analyte	QA Parameter	Number	Range of Values
Butane	CCC	15	94.2% to 96.4% Recovery
Butane	SS	4	94.6% to 95.4% Recovery
Butane	LB	30	All < 1.44 ppm (v/v)
Butane	FB	2	All < 1.44 ppm (v/v)
<i>trans</i> -2-Butene	CCC	15	96.2% to 98.5% Recovery
<i>trans</i> -2-Butene	SS	4	96.9% to 97.9% Recovery
<i>trans</i> -2-Butene	LB	30	All < 2 ppm (v/v) **
<i>trans</i> -2-Butene	FB	2	All < 2 ppm (v/v) **
1-Butene	CCC	15	100% to 104% Recovery
1-Butene	SS	4	101% to 103% Recovery
1-Butene	LB	30	All < 2 ppm (v/v) **
1-Butene	FB	2	All < 2 ppm (v/v) **
<i>iso</i> -Butylene	CCC	15	98.8% to 102% Recovery
<i>iso</i> -Butylene	SS	4	99.4% to 100% Recovery
<i>iso</i> -Butylene	LB	30	All < 2 ppm (v/v) **
<i>iso</i> -Butylene	FB	2	All < 2 ppm (v/v) **
<i>cis</i> -2-Butene	CCC	15	97.1% to 100% Recovery
<i>cis</i> -2-Butene	SS	4	97.5% to 99% Recovery
<i>cis</i> -2-Butene	LB	30	All < 2 ppm (v/v) **
<i>cis</i> -2-Butene	FB	2	All < 2 ppm (v/v) **
<i>iso</i> -Pentane	CCC	15	97.3% to 99.9% Recovery
<i>iso</i> -Pentane	SS	4	98.1% to 98.6% Recovery
<i>iso</i> -Pentane	LB	30	All < 2 ppm (v/v) **
<i>iso</i> -Pentane	FB	2	All < 2 ppm (v/v) **
Pentane	CCC	15	85.9% to 107% Recovery
Pentane	SS	4	85.3% to 101% Recovery
Pentane	LB	30	All < 2 ppm (v/v) **
Pentane	FB	2	All < 2 ppm (v/v) **
2-Methyl-2-Butene	CCC	15	97.5% to 101% Recovery
2-Methyl-2-Butene	SS	4	107% to 109% Recovery
2-Methyl-2-Butene	LB	30	All < 2 ppm (v/v) **
2-Methyl-2-Butene	FB	2	All < 2 ppm (v/v) **
<i>trans</i> -2-Pentene	CCC	15	96.3% to 99.8% Recovery
<i>trans</i> -2-Pentene	SS	4	89.6% to 90.3% Recovery
<i>trans</i> -2-Pentene	LB	30	All < 2 ppm (v/v) **
<i>trans</i> -2-Pentene	FB	2	All < 2 ppm (v/v) **

Table 10.8. Quality assurance parameters from laboratory-based analyses of soil gas for data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5. (Continued).

Analyte	QA Parameter	Number	Range of Values
1-Pentene	CCC	15	98.8% to 103% Recovery
1-Pentene	SS	4	99.8% to 101% Recovery
1-Pentene	LB	30	All < 2 ppm (v/v) **
1-Pentene	FB	2	All < 2 ppm (v/v) **
<i>cis</i> -2-Pentene	CCC	15	98.7% to 102% Recovery
<i>cis</i> -2-Pentene	SS	4	99.4% to 101% Recovery
<i>cis</i> -2-Pentene	LB	30	All < 2 ppm (v/v) **
<i>cis</i> -2-Pentene	FB	2	All < 2 ppm (v/v) **
C6+ Hydrocarbons	CCC	15	97.6% to 107% Recovery
C6+ Hydrocarbons	SS	4	91.2% to 102% Recovery
C6+ Hydrocarbons	LB	30	All < 2 ppm (v/v) **
C6+ Hydrocarbons	FB	2	All < 2 ppm (v/v) **
Benzene	CCC	15	96% to 97.8% Recovery
Benzene	SS	4	96% to 96.9% Recovery
Benzene	LB	30	All <2 ppm (v/v) **
Benzene	FB	2	All <2 ppm (v/v) **

* < MDL

**< An estimated value for the MDL provided by the analyst. Method detection limit not determined.

¹CCC is Continuing Calibration Check.

²SS is a Second Source Standard and is a measure of accuracy.

³LB is a laboratory method blank.

⁴FB is a field blank, equivalent to an equipment blank.

Table 10.9 presents the relative percent difference between duplicate laboratory samples for the data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5.

The relative percent difference of the lab duplicates were all less than 15%. Each well was sampled four times at each time period. The individual data are plotted on the figures. In Figure A.5, the data at the initial sampling interval were variable, ranging over

as much as a factor of ten. In subsequent sampling periods the range of values were less than 150% to 50% of their means. The figures plot a line connecting the mean of the four samples at each time period. The figures were intended to illustrate the tendency to reach equilibration. The data in the later time periods were closely clustered about their mean. The data were of acceptable quality for the intended purpose and all of the data were used.

Table 10.9. Relative percent difference of laboratory duplicates on samples of soil gas analyzed in the laboratory for data in Figure 4.5, Figure A.1, Figure A.2, Figure A.3, Figure A.4 and Figure A.5.

Monitoring Well	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
Kev's Auto MW-4-20 min-F in Figure 4.5	10/26/2012	Benzene	Lab Duplicate	0.27
Kev's Auto MW-4-20 min-F in Figure 4.5	10/26/2012	Total Hydrocarbons*	Lab Duplicate	0.18
Visocan Site MW-9-0 min-F in Figure A.1	10/25/2012	Benzene	Lab Duplicate	0.05
Visocan Site MW-9-0 min-F in Figure A.1	10/25/2012	Total Hydrocarbons*	Lab Duplicate	0.43
Visocan Site MW-9-40 min-A in Figure A.1	10/25/2012	Total Hydrocarbons*	Lab Duplicate	1.6
Visocan Site MW-4-10 min-B in Figure A.2	10/26/2012	Total Hydrocarbons*	Lab Duplicate	1.0
Visocan Site MW-4-40 min-E in Figure A.2	10/26/2012	Total Hydrocarbons*	Lab Duplicate	0.16
Noon's Store HMM-6-10 min-A in Figure A.5	10/25/2012	Benzene	Lab Duplicate	0.20
Noon's Store HMM-6-10 min-A in Figure A.5	10/25/2012	Total Hydrocarbons*	Lab Duplicate	0.34
Noon's Store HMM-6-40 min-B in Figure A.5	10/25/2012	Benzene	Lab Duplicate	0.0
Noon's Store HMM-6-40 min-B in Figure A.5	10/25/2012	Total Hydrocarbons*	Lab Duplicate	1.2

*Sum of concentrations of individual petroleum hydrocarbons plus methane in $\mu\text{g}/\text{m}^3$.

10.1.4 Soil gas components in Tables 6.1, 6.2 and 6.3

The quality assurance parameters for data in Tables 6.1, 6.2 and 6.3 are presented in Table 10.10.

The continuing calibration checks and the second source standards were within +/- 15% of the nominal value. However, the maximum concentration of methane in any blank was 384 ppm. The measured concentrations of methane in wells MW-9 and MW-2 was 400,000 and 630,000 ppm. The methane in the blank was not a significant fraction of the methane in the samples.

The maximum measured concentrations of *iso*-butane, *iso*-pentane, pentane and C6+ compounds in any blank were 37, 2.1, 3.3 and 470 ppm respectively. These would correspond to a concentration of TPH of 2.1E+06 µg/L. The measured concentrations of TPH in well MW-9 was 3.0E+07 µg/L and in well MW-2 was 4.6E+08 µg/L (Table 6.1). The measured concentration of TPH in well MW-9 (3.0E+07 µg/L)

was then added to the concentration of methane in well MW-9 (3.0E+08 µg/L) to calculate a concentration of total hydrocarbons (3.3E+08 µg/L), see table 6.2. The concentration of total hydrocarbons was fit to Figure 6.4 with a precision of one significant digit to estimate the attenuation factor of benzene. The concentrations of hydrocarbons in the blanks would not affect the estimate of the attenuation factor.

The concentrations of oxygen in the blanks was a high as 3.9% by volume. Using the equation in Section 4.3, this would require a correction of the hydrocarbon data by multiplying by a factor of 1.2. The concentration of total hydrocarbons was fit to Figure 6.4 with a precision of one significant digit to estimate the attenuation factor of benzene. The concentrations of oxygen in the blanks would not affect the estimate of the attenuation factor. The concentration in all the other blanks were less than the detection limit.

The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.10. Quality assurance parameters from laboratory-based analyses of soil gas for data in Table 6.1, 6.2 and 6.3.

Analyte	QA Parameter	Number of Analyses	Range of Values
Methane	CCC ¹	3	92.3% to 98.2% Recovery
Methane	SS ²	1	96.2% Recovery
Methane	LB ³	4	All < 0.57 ppm (v/v)*
Methane	FB ⁴	4	< 0.57 to 194 ppm (v/v)
Methane	TB ⁵	3	159 to 384 ppm (v/v)
Ethylene	CCC	3	97.1% to 102% Recovery
Ethylene	SS	1	99.1% Recovery
Ethylene	LB	4	All < 1.44 ppm (v/v)*
Ethylene	FB	4	All < 1.44 ppm (v/v)*
Ethylene	TB	3	All < 1.44 ppm (v/v)*
Ethane	CCC	3	96.5% to 101% Recovery
Ethane	SS	1	98.2% Recovery
Ethane	LB	4	All < 0.70 ppm (v/v)*
Ethane	FB	4	All < 0.70 ppm (v/v)*
Ethane	TB	3	All < 0.70 ppm (v/v)*

Table 10.10. Quality assurance parameters from laboratory-based analyses of soil gas for data in Table 6.1, 6.2 and 6.3. (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
Acetylene	CCC	3	98.1% to 104% Recovery
Acetylene	SS	1	101% Recovery
Acetylene	LB	4	All < 1.2 ppm (v/v)*
Acetylene	FB	4	All < 1.2 ppm (v/v)*
Acetylene	TB	3	All < 1.2 ppm (v/v)*
Propane	CCC	3	97.3% to 101% Recovery
Propane	SS	1	96.8% Recovery
Propane	LB	4	All < 0.60 ppm (v/v)*
Propane	FB	4	All < 0.60 ppm (v/v)*
Propane	TB	3	All < 0.60 ppm (v/v)*
Propylene	CCC	3	96.5% to 101% Recovery
Propylene	SS	1	96.5% Recovery
Propylene	LB	4	All < 2 ppm (v/v)**
Propylene	FB	4	All < 2 ppm (v/v)**
Propylene	TB	3	All < 2 ppm (v/v)**
<i>iso</i> -Butane	CCC	3	89.1% to 92.9% Recovery
<i>iso</i> -Butane	SS	1	89.7% Recovery
<i>iso</i> -Butane	LB	4	All < 10 ppm (v/v)**
<i>iso</i> -Butane	FB	4	< 10 to 6.5 ppm (v/v)**
<i>iso</i> -Butane	TB	3	All < 10 ppm (v/v)**
Butane	CCC	3	94.7% to 100% Recovery
Butane	SS	1	95.7% Recovery
Butane	LB	4	All < 0.44 ppm (v/v)*
Butane	FB	4	< 0.44 to 37 ppm (v/v)*
Butane	TB	3	All < 0.44 ppm (v/v)*
<i>trans</i> -2-Butene	CCC	3	94.1% to 98.7% Recovery
<i>trans</i> -2-Butene	SS	1	94.8% Recovery
<i>trans</i> -2-Butene	LB	4	All < 2 ppm (v/v)**
<i>trans</i> -2-Butene	FB	4	All < 2 ppm (v/v)**
<i>trans</i> -2-Butene	TB	3	All < 2 ppm (v/v)**
1-Butene	CCC	3	95.6% to 101% Recovery
1-Butene	SS	1	97.1% Recovery
1-Butene	LB	4	All < 2 ppm (v/v)**
1-Butene	FB	4	All < 2 ppm (v/v)**
1-Butene	TB	3	All < 2 ppm (v/v)**

Table 10.10. Quality assurance parameters from laboratory-based analyses of soil gas for data in Table 6.1, 6.2 and 6.3. (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
<i>iso</i> -Butylene	CCC	3	96.4% to 103% Recovery
<i>iso</i> -Butylene	SS	1	99.4% Recovery
<i>iso</i> -Butylene	LB	4	All < 2 ppm (v/v)**
<i>iso</i> -Butylene	FB	4	All < 2 ppm (v/v)**
<i>iso</i> -Butylene	TB	3	All < 2 ppm (v/v)**
<i>cis</i> -2-Butene	CCC	3	93.8% to 100% Recovery
<i>cis</i> -2-Butene	SS	1	96.3% Recovery
<i>cis</i> -2-Butene	LB	4	All < 2 ppm (v/v)**
<i>cis</i> -2-Butene	FB	4	All < 2 ppm (v/v)**
<i>cis</i> -2-Butene	TB	3	All < 2 ppm (v/v)**
<i>iso</i> -Pentane	CCC	3	94% to 97.6% Recovery
<i>iso</i> -Pentane	SS	1	95.3% Recovery
<i>iso</i> -Pentane	LB	4	All < 2 ppm (v/v)**
<i>iso</i> -Pentane	FB	4	< 2 to 2.1 ppm (v/v)**
<i>iso</i> -Pentane	TB	3	All < 2 ppm (v/v)**
Pentane	CCC	3	95.3% to 102% Recovery
Pentane	SS	1	97.3% Recovery
Pentane	LB	4	All < 2 ppm (v/v)**
Pentane	FB	4	< 2 to 3.3 ppm (v/v)**
Pentane	TB	3	All < 2 ppm (v/v)**
2-Methyl-2-Butene	CCC	3	94.0% to 96.0% Recovery
2-Methyl-2-Butene	SS	1	94.0% Recovery
2-Methyl-2-Butene	LB	4	All < 2 ppm (v/v)**
2-Methyl-2-Butene	FB	4	All < 2 ppm (v/v)**
2-Methyl-2-Butene	TB	3	All < 2 ppm (v/v)**
<i>trans</i> -2-Pentene	CCC	3	97.1% to 101% Recovery
<i>trans</i> -2-Pentene	SS	1	94.8% Recovery
<i>trans</i> -2-Pentene	LB	4	All < 2 ppm (v/v)**
<i>trans</i> -2-Pentene	FB	4	All < 2 ppm (v/v)**
<i>trans</i> -2-Pentene	TB	3	All < 2 ppm (v/v)**
1-Pentene	CCC	3	96.5% to 97.8% Recovery
1-Pentene	SS	1	94.5% Recovery
1-Pentene	LB	4	All < 2 ppm (v/v)**
1-Pentene	FB	4	All < 2 ppm (v/v)**
1-Pentene	TB	3	All < 2 ppm (v/v)**

Table 10.10. Quality assurance parameters from laboratory-based analyses of soil gas for data in Table 6.1, 6.2 and 6.3. (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
<i>cis</i> -2-Pentene	CCC	3	96.1% to 98.1% Recovery
<i>cis</i> -2-Pentene	SS	1	94.2% Recovery
<i>cis</i> -2-Pentene	LB	4	All < 2 ppm (v/v)**
<i>cis</i> -2-Pentene	FB	4	All < 2 ppm (v/v)**
<i>cis</i> -2-Pentene	TB	3	All < 2 ppm (v/v)**
C6+ Hydrocarbons	CCC	3	91.7% to 104% Recovery
C6+ Hydrocarbons	SS	1	98.6% Recovery
C6+ Hydrocarbons	LB	4	All < 2 ppm (v/v)**
C6+ Hydrocarbons	FB	4	< 2 to 470 ppm (v/v)**
C6+ Hydrocarbons	TB	3	< 2 to 68.9 ppm (v/v)**
Benzene	CCC	3	88.6% to 92.4% Recovery
Benzene	SS	1	92.7% Recovery
Benzene	LB	4	All < 2 ppm (v/v)**
Benzene	FB	4	< 2 to 4.9 ppm (v/v)**
Benzene	TB	3	All < 2 ppm (v/v)**
Oxygen	FB	4	4,130 to 34,800 ppm (v/v)
Oxygen	TB	3	28,000 to 39,300 ppm (v/v)

* < MDL

**< An estimated value for the MDL provided by the analyst. Method detection limit not determined.

¹CCC is Continuing Calibration Check.

²SS is a Second Source Standard and is a measure of accuracy.

³LB is a laboratory method blank.

⁴FB is a field blank, equivalent to an equipment blank.

⁵TB is a trip blank.

The quality assurance parameters for data in Tables 6.1, 6.2 and 6.3 are presented in Table 10.11.

The relative percent difference of the field and lab duplicates were all less than 15%. The data were of acceptable quality for the intended purpose and all of the data were used.

Table 10.11. Relative percent difference of field and laboratory duplicates on samples of soil gas analyzed in the laboratory for data in Table 6.1.

Monitoring Well	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
Antlers MW-2	1/4/2011	Oxygen	Field Duplicate	7.7
Antlers MW-2	1/4/2011	Methane	Field Duplicate	4.7
Antlers MW-2	1/4/2011	i-Butane	Field Duplicate	2.4
Antlers MW-2	1/4/2011	i-Pentane	Field Duplicate	2.0
Antlers MW-2	1/4/2011	C6+	Field Duplicate	9.8
Antlers MW-2	1/4/2011	Benzene	Field Duplicate	5.8
Antlers MW-2	1/4/2011	Methane	Lab Duplicate	4.6
Antlers MW-2	1/4/2011	i-Butane	Lab Duplicate	0.33
Antlers MW-2	1/4/2011	i-Pentane	Lab Duplicate	0.90
Antlers MW-2	1/4/2011	C6+	Lab Duplicate	0.67
Antlers MW-2	1/4/2011	Benzene	Lab Duplicate	1.8
Antlers MW-9	1/4/2011	Oxygen	Field Duplicate	7.0
Antlers MW-9	1/4/2011	Methane	Field Duplicate	1.2
Antlers MW-9	1/4/2011	i-Butane	Field Duplicate	3.2
Antlers MW-9	1/4/2011	i-Pentane	Field Duplicate	2.3
Antlers MW-9	1/4/2011	C6+	Field Duplicate	0.7
Antlers MW-9	1/4/2011	Benzene	Field Duplicate	2.4

10.1.5 TPH-g in Core Samples Figure 4.7

Core samples were acquired from a spill of motor gasoline at the former A-1 Movers site in Madison, Wisconsin. Samples were acquired in May, 2006. The samples were acquired using the GeoProbe Macrocore® system. The cores were cut open with a cleaned or decontaminated hacksaw, plug samples were taken from the face of the exposed core and then extracted in the field into a 50% methanol in water solution. To determine the wet weight of the sample that was extracted, the vials were weighed and then weighed again after they received the sample. The weight of the plug sample was the final weight minus the initial weight. The wet weight of the plug samples varied from 38 to 44 grams.

The methanol extracts were spiked into water and analyzed at Kerr Center for Total Petroleum Hydrocarbons in the gasoline range (TPH-g) using purge and trap/gas chromatography. The concentrations of TPH-g in the extracts were reported in µg/L of extract. The method detection limit was 309 µg/L. The density of methanol is 791 g/L. The density of the 50% solution of methanol in water used to extract the core samples was assumed to be 896 g/L. The mass of the extracting solution was calculated by weighing each vial empty and again after it received the extracting solution. The mass of the extracting

solution in grams was divided by 896 g/L to determine the liters of extracting solution. The volume of the extracting solution in liters was multiplied by the concentration in µg/L to calculate the mass of TPH-g in the extract in µg.

Separate plug samples taken from the same depth interval as the samples that were extracted in methanol were taken back to the laboratory and air dried. The loss on drying was used to calculate the water content of the plug samples. The moisture of the samples ranged from 12.5% to 18.4% of the dry weight. The average water content and the wet weight of the plug samples were used to calculate the dry weight of the plug samples that were extracted into the 50% methanol and water solution.

For each plug sample, the mass of TPH-g (µg) was divided by the dry weight of the sample (g) to calculate the concentration of TPH-g in the sample (mg/kg).

The quality assurance parameters for TPH-g data in Figure 4.7 are presented in Table 10.12.

The continuing calibration checks and the second source standards were within +/- 15% of the nominal value. The concentration in all the blanks were less than the detection limit. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.12. Quality assurance parameters from analyses of core extracts for data in Figure 4.7.

Analyte	QA Parameter	Number of Analyses	Range of Values
TPH-g	CCC ¹	15	96.6% to 113% Recovery
TPH-g	SS ²	1	96.0% Recovery
TPH-g	LB ³	19	All <309 µg/L in methanol extract or 0.2 mg/kg soil extracted*
TPH-g	LCS ⁴	3	101% to 105% Recovery
TPH-g	TB ⁵	1	<309 µg/L in methanol extract or 0.2 mg/kg soil extracted*
TPH-g	Lab Duplicate	1	RPD=3.52%

* < the limit of quantitation.

²SS is a Second Source Standard and is a measure of accuracy.

⁴LCS is laboratory control spike.

¹CCC is Continuing Calibration Check.

³LB is a laboratory method blank.

⁵TB is a trip blank.

10.2 Section 5

10.2.1 TPH on Core Samples, Figure 5.3

Core samples were acquired using the GeoProbe Macrocore® system. The cores were cut open with a hacksaw, plug samples were taken from the core, and extracted in the field into 50% methanol in water. To determine the wet weight of the sample that was extracted, the vials were weighed and then weighed again after they received the sample. The weight of the plug sample was the final weight minus the initial weight. The wet weight of the plug samples varied from 38 to 44 grams.

The methanol extracts were spiked into water and analyzed at Kerr Center for Total Petroleum Hydrocarbons in the gasoline range (TPH-g) using purge and trap/gas chromatography and the *Modified Wisconsin Method for Determining Gasoline Range Organics by Purge and Trap Gas Chromatography-OI*. Modifications to the method included utilizing a composite Gasoline Standard (Restek #30205) and a baseline to baseline area sum from the end of methanol (retention time (RT) ~11.5 min.) to a final RT of 25.5 min. The final time corresponds to the last peak eluted from the composite Gasoline standard.

The concentrations of TPH-g in the extracts were reported in µg/L of extract. The quantitation limit was 50 µg/L. The density of methanol is 791 g/L. The density of the 50% solution of methanol in water used to extract the core samples was assumed to be

896 g/L. The mass of the extracting solution was calculated by weighing each vial empty and again after it received the extracting solution. The mass of extracting solution in grams was divided by 896 g/L to determine the liters of extracting solution. The volume of extracting solution in liters was multiplied by the concentration in µg/L to calculate the mass of TPH-g in the extract in µg.

Separate plug samples taken from the depth interval of the samples that were extracted in methanol were taken back to the laboratory and air dried. The loss on drying was used to calculate the water content of the plug samples. The moisture of the samples ranged from 12.5% to 18.4% of the dry weight. The average water content and the wet weight of the plug samples were used to calculate the dry weight of the plug samples that were extracted into the 50% methanol and water solution.

For each plug sample, the mass of TPH-g (µg) was divided by the dry weight of the sample (g) to calculate the concentration of TPH-g in the sample (mg/kg).

The quality assurance parameters for TPH data in Figure 5.3 are presented in Table 10.13.

The surrogate spikes, the continuing calibration checks, the second source standards, and the laboratory control spikes were within +/- 15% of the nominal value. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.13. Quality assurance parameters from analyses of TPH-g in soil extract (applies to Figures 5.3 and 8.3).

Analyte	QA Parameter	Number	Range of Values
FB*-reference	Surrogate Spike	22	85.6% to 106% Recovery
BFB**-reference	Surrogate Spike	22	92.1% to 119% Recovery
TPH-gasoline range	Continuing Calibration Check	13	90.0% to 113% Recovery
TPH-gasoline range	Second Source Standard	1	102% Recovery
TPH-gasoline range	Laboratory Control Spike	5	94.6% to 108% Recovery

*Fluorobenzene

**4-Bromofluorobenzene

Table 10.14 presents TPH-g sample data compared to concentrations of TPH-g in the Trip Blank and the methanol blank used to extract the solvents.

There were detectable concentrations of TPH-g in the blanks. Borehole EPA-1 was immediately adjacent to the multi-depth vapor probes at location VW-7. The purpose of the sampling was to determine the depth intervals near the water table that were contaminated with NAPL, and the greatest depth interval that was not contaminated. The water table was near 15 feet below land surface. The concentrations in the blanks were less than 1% of the concentrations from the deep core samples near the water table and therefore had negligible impact on that sample data.

The highest concentration in any blank was 1.2E+04 µg/L. If the highest concentration in any blank had come from a core sample, the concentration in that core sample would have been approximately 9 mg/kg. This is less than the criterion of 250 mg/kg. In the deepest samples where the concentration of TPH was less than the criterion of TPH < 250 mg/kg, the concentration in the samples was < 0.04 mg/kg. The concentrations in the blanks could not have impacted the identification of the deepest depth interval that met the criterion of TPH < 250 mg/kg.

Table 10.14. Concentrations of TPH-g in samples depicted in Figure 5.3 compared to the concentrations of TPH-g in the trip blanks and methanol blanks.

Sample Name	Sample Depth	TPH-g in Methanol Extract	TPH-g in Core Samples
VW-7 location	(feet below land surface)	(µg/L)	mg/kg
EPA-1 1-2A	1.5	3.4E+05	263
EPA-1 2-3A	2.5	6.9E+04	53
EPA-1 3-4A	3.5	2.4E+04	19
EPA-1 4-5A	4.5	< 50	< 0.04
EPA-1 5-6A	5.5	< 50	< 0.04
EPA-1 6-7A	6.5	8.0E+02	1
EPA-1 8-9A	8.5	< 50	< 0.04
EPA-1 9-10A	9.5	< 50	< 0.04
EPA-1 10-11A	10.5	< 50	< 0.04
EPA-1 10-11B	10.5	< 50	< 0.04
EPA-1 12-13A	12.5	< 50	< 0.04
EPA-1 12-13B	12.5	< 50	< 0.04
EPA-1 13-14A	13.5	3.1E+06	2400
EPA-1 13-14B	13.5	1.4E+06	1084
EPA-1 14-15A	14.5	1.4E+06	1084
EPA-1 14-15B	14.5	8.8E+05	681
EPA-1 15-16A	15.5	2.8E+05	217
EPA-1 15-16B	15.5	8.4E+04	65
MeOH Blank-1		2.1E+03	NC
MeOH Blank-2		< 50	NC
Trip Blank-1		1.2E+04	NC
Trip Blank-2		3.2E+03	NC

NC = Not calculated, core sample not extracted

Table 10.15 presents the relative percent difference between duplicate field samples for the data in Figure 5.3.

No laboratory duplicates were analyzed. The relative percent difference of the field duplicates were not within 15%. The values of the relative percent differences were large compared to the values of the Continuing Calibration Checks and Laboratory Control Spikes in Table 10.13. The large relative percent differences in Table 10.15 reflect variation in TPH-g

in the samples due to the expected heterogeneity of the contaminated zone on the scale of the plug samples that were collected and submitted for analysis. The purpose of the analyses was to distinguish the deepest depth interval with TPH less than 250 mg/kg. That interval was 12 to 13 feet. There was no further interpretation put on the depth intervals with concentrations greater than 250 mg/kg. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.15. Relative percent difference of field duplicates for analysis of TPH-g on samples of soil extracts (applies to Figures 5.3 and 8.3).

Vapor Monitoring Point	Date Collected	Soil Component	Duplicate	Relative Percent Difference
VW-7, 10 to 11 feet	6/15/2007	TPH-g	Field	NC*
VW-7, 11 to 12 feet	6/15/2007	TPH-g	Field	NC*
VW-7, 12 to 13 feet	6/15/2007	TPH-g	Field	NC*
VW-7, 13 to 14 feet	6/15/2007	TPH-g	Field	39
VW-7, 14 to 15 feet	6/15/2007	TPH-g	Field	22
VW-7, 15 to 16 feet	6/15/2007	TPH-g	Field	54

*NC means not calculated because both replicates were less than the detection limit of 0.04 mg/kg.

10.2.2 Soil Gas Samples, Tables 5.1 through 5.6 and 8.1 through 8.3

10.2.2.1 Total Hydrocarbons and Benzene in Soil Gas from Vapor Probes

Soil gas samples from vapor monitoring points installed by the Utah Department of Environmental Quality were acquired by purging three tubing volumes with a syringe, and then collecting approximately 1 liter of soil gas into a Summa Canister. The vacuum in the canister drew in the sample. The samples were analyzed by Air Toxics LTD. (180 Blue Ravine Road, Suite B, Folsom, CA 95630). Benzene was analyzed by EPA Method TO-15. Total petroleum hydrocarbons were analyzed by modified EPA Method TO-15. Methane was analyzed by modified ASTM D-1946.

The quality assurance parameters for data in Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3 are presented in Table 10.16.

All of the quality assurance parameters were within the acceptable range except for the recovery of the surrogate spike of 1,2-dichloroethane-d4. The recovery of 1,2-dichloroethane-d4 exceeded the nominal value. Presumably, the recovery of compounds of interest would also exceed the true value. However, the other two surrogate recoveries were acceptable and are more representative of the compounds of interest. Therefore, the impact on sample data for this one high surrogate recovery is considered minimal. Because the data are used to screen the site, there is limited or no harm if the recoveries exceed the true value by a small factor, in this case less than a factor of three. The data were accepted and used in the screening process.

Table 10.16. Quality assurance parameters from analyses of soil gas from vapor probes (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3).

Analyte	QA Parameter	Number of Analyses	Range of Values
1,2-Dichloroethane-d4	Surrogate Spike	26	78% to 262% Recovery
4-Bromofluorobenzene	Surrogate Spike	26	92% to 109% Recovery
Toluene-d8	Surrogate Spike	26	76% to 104% Recovery
Benzene	CCV ¹	4	95% to 97% Recovery
Benzene	LCS ²	4	98% to 106% Recovery
Benzene	LCSD ³	4	96% to 101% Recovery
Benzene	Lab Blank	4	All < 1.6 µg/m3 *
TPH ref. to Gasoline	CCV	4	100% to 100% Recovery
TPH ref. to Gasoline	LCS		Not Performed
TPH ref. to Gasoline	LCSD		Not Performed
TPH ref. to Gasoline	Lab Blank	4	All < 100 µg/m3 *
Methane	LCS	1	99% Recovery
Methane	LCSD	1	102% Recovery
Methane	Lab Blank	1	< 0.00028%(v/v)*

*<MDL

¹CCV is Continuing Calibration Verification.

²LCS is a Laboratory Control Spike, equivalent to a Second Source Standard, and is a measure of accuracy.

³LCSD is a duplicate of the Laboratory Control Spike, and is a measure of precision.

Table 10.17 presents the relative percent difference between duplicate field samples and duplicate laboratory samples for the data in Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3.

The relative percent differences of benzene and TPH in the field duplicates from VW-3 at 18 feet were not within 15%. The large relative percent differences in the field duplicates from VW-3 at 18 feet may reflect changes in the concentrations of petroleum hydrocarbons from one sampling day to the next. As presented in Table 8.2, the concentrations of TPH and benzene in soil gas from VW-3 at 18 feet were from two to three fold lower than the concentrations of benzene and TPH in the groundwater monitoring wells. The highest concentration of benzene in the field duplicates from VW-3 at 18 feet was 1.8 fold higher than the lowest concentration. The highest concentrations of TPH in the field duplicates from

VW-3 at 18 feet was 2.2 fold higher than the lowest concentration. The variation within the samples from VW-3 at 18 feet was not larger than the variation between VW-3 at 18 feet and the samples from the groundwater monitoring wells. The conclusion drawn from the comparison was as follows: *Again, the concentrations of benzene, TPH-g ... in soil gas were reasonably consistent between the monitoring wells and the vapor probe.* The variability between replicate samples from VW-3 at 18 feet did not affect the comparison of data from VW-3 to the groundwater wells.

The relative percent differences of benzene and TPH in all the other field duplicates or laboratory duplicates were within 15%. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.17. Relative percent difference of field and laboratory duplicates on samples of soil gas from vapor probes (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3).

Vapor Monitoring Point	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
VW-3 at 18 feet	09/08/2011	Benzene	Laboratory	0
VW-3 at 18 feet	09/07-08/2011*	Benzene	Field	28.5
VW-7 at 15 feet	09/08/2011	Benzene	Laboratory	2.2
VW-7 at 15 feet	09/07/2011	Benzene	Laboratory	1.1
VW-7 at 15 feet	09/07-08/2011	Benzene	Field	0
VW-3 at 18 feet	09/08/2011	TPH ref. to Gasoline	Laboratory	0
VW-3 at 18 feet	09/07-08/2011	TPH ref. to Gasoline	Field	36.6
VW-7 at 15 feet	09/08/2011	TPH ref. to Gasoline	Laboratory	2.2
VW-7 at 15 feet	09/07/2011	TPH ref. to Gasoline	Laboratory	3.3
VW-7 at 15 feet	09/07-08/2011	TPH ref. to Gasoline	Field	14.8
VW-1 at 8 feet	09/07/2011	Methane	Laboratory	0
VW-3 at 18 feet	09/08/2011	Methane	Field	3.1
VW-7 at 15 feet	09/07-08/2011	Methane	Field	7.7

*Most of the field duplicates were collected on subsequent days.

10.2.2.2 Individual Hydrocarbons and Oxygen in Soil Gas from Monitoring Wells

Soil gas samples were acquired using the protocol of Jewell and Wilson (2011) from conventional ground water wells that were installed at the direction of the Utah Department of Environmental Quality. Soil gas samples were acquired by water displacement into 165 ml serum vials. The vials were returned to the Kerr Center for analysis by micro gas chromatography with thermal conductivity detection. The quality assurance parameters for data in Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3 are presented in Table 10.18.

There was no CCC, SS, or GB for oxygen. For the other compounds, the continuing calibration checks

and the second source standards were within +/- 15% of the nominal value. The concentration of oxygen in the field blanks and trip blank were as much as 3.29% by volume. Using the equation in Section 4.3, this would require a correction of the hydrocarbon data by multiplying by a factor of 1.2. The concentration of total hydrocarbons was fit to Figure 6.4 with a precision of one significant digit to estimate the attenuation factor of benzene. The concentrations of oxygen in the blanks would not affect the estimate of the attenuation factor. The concentration in all the other blanks were less than the detection limit. The quality of the data were acceptable for the intended purpose, and all the data were used.

Table 10.18. Quality assurance parameters from analyses of soil gas from ground water wells (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3).

Analyte	QA Parameter	Number of Analyses	Range of Values
Methane	CCC ¹	5	98.4% to 106% Recovery
Methane	SS ²	2	101% to 105% Recovery
Methane	GB ³	7	All < 1.47 ppm (v/v)*
Methane	FB ⁴	4	All < 1.47 ppm (v/v)*
Methane	TB ⁵	1	< 1.47 ppm (v/v)*
Ethylene	CCC	5	103% to 105% Recovery
Ethylene	SS	2	104% to 105% Recovery
Ethylene	GB	7	All < 1.77 ppm (v/v)*
Ethylene	FB	4	All < 1.77 ppm (v/v)*
Ethylene	TB	1	< 1.77 ppm (v/v)*
Ethane	CCC	5	98.4% to 101% Recovery
Ethane	SS	2	100% to 101% Recovery
Ethane	GB	7	All < 2.65 ppm (v/v)*
Ethane	FB	4	All < 2.65 ppm (v/v)*
Ethane	TB	1	< 2.65 ppm (v/v)*
Acetylene	CCC	5	100% to 102% Recovery
Acetylene	SS	2	102% to 102% Recovery
Acetylene	GB	7	All < 2.5 ppm (v/v)*
Acetylene	FB	4	All < 2.5 ppm (v/v)*
Acetylene	TB	1	< 2.5 ppm (v/v)*

Table 10.18. Quality assurance parameters from analyses of soil gas from ground water wells (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3). (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
Propane	CCC	5	98.4% to 107% Recovery
Propane	SS	2	102% to 107% Recovery
Propane	GB	7	All < 2.05 ppm (v/v)*
Propane	FB	4	All < 2.05 ppm (v/v)*
Propane	TB	1	< 2.05 ppm (v/v)*
Propylene	CCC	5	97.3% to 105% Recovery
Propylene	SS	2	99% to 104% Recovery
Propylene	GB	7	All < 2 ppm (v/v)**
Propylene	FB	4	All < 2 ppm (v/v)**
Propylene	TB	1	< 2 ppm (v/v)**
<i>iso</i> -Butane	CCC	5	92.1% to 99.9% Recovery
<i>iso</i> -Butane	SS	2	99.9% to 105% Recovery
<i>iso</i> -Butane	GB	7	All < 10 ppm (v/v)**
<i>iso</i> -Butane	FB	4	All < 10 ppm (v/v)**
<i>iso</i> -Butane	TB	1	< 10 ppm (v/v)**
Butane	CCC	5	98.1% to 106% Recovery
Butane	SS	2	101% to 106% Recovery
Butane	GB	7	All < 1.99 ppm (v/v)*
Butane	FB	4	All < 1.99 ppm (v/v)*
Butane	TB	1	< 1.99 ppm (v/v)*
<i>trans</i> -2-Butene	CCC	5	98.4% to 101% Recovery
<i>trans</i> -2-Butene	SS	2	100% to 101% Recovery
<i>trans</i> -2-Butene	GB	7	All < 2 ppm (v/v)**
<i>trans</i> -2-Butene	FB	4	All < 2 ppm (v/v)**
<i>trans</i> -2-Butene	TB	1	< 2 ppm (v/v)**
1-Butene	CCC	5	97.1% to 108% Recovery
1-Butene	SS	2	100% to 107% Recovery
1-Butene	GB	7	All < 2 ppm (v/v)**
1-Butene	FB	4	All < 2 ppm (v/v)**
1-Butene	TB	1	< 2 ppm (v/v)**
<i>iso</i> -Butylene	CCC	5	96.9% to 106% Recovery
<i>iso</i> -Butylene	SS	2	100% to 105% Recovery
<i>iso</i> -Butylene	GB	7	All < 2 ppm (v/v)**
<i>iso</i> -Butylene	FB	4	All < 2 ppm (v/v)**
<i>iso</i> -Butylene	TB	1	< 2 ppm (v/v)**

Table 10.18. Quality assurance parameters from analyses of soil gas from ground water wells (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3). (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
<i>cis</i> -2-Butene	CCC	5	96.1% to 105% Recovery
<i>cis</i> -2-Butene	SS	2	98.5% to 104% Recovery
<i>cis</i> -2-Butene	GB	7	All < 2 ppm (v/v)**
<i>cis</i> -2-Butene	FB	4	All < 2 ppm (v/v)**
<i>cis</i> -2-Butene	TB	1	< 2 ppm (v/v)**
<i>iso</i> -Pentane	CCC	5	96.1% to 105% Recovery
<i>iso</i> -Pentane	SS	2	99.1% to 104% Recovery
<i>iso</i> -Pentane	GB	7	All < 2 ppm (v/v)**
<i>iso</i> -Pentane	FB	4	All < 2 ppm (v/v)**
<i>iso</i> -Pentane	TB	1	< 2 ppm (v/v)**
Pentane	CCC	5	91.1% to 99.6% Recovery
Pentane	SS	2	90.5% to 104% Recovery
Pentane	GB	7	All < 2 ppm (v/v)**
Pentane	FB	4	All < 2 ppm (v/v)**
Pentane	TB	1	< 2 ppm (v/v)**
2-Methyl-2-butene	CCC	5	91.1% to 105% Recovery
2-Methyl-2-butene	SS	2	109% to 114% Recovery
2-Methyl-2-butene	GB	7	All < 2 ppm (v/v)**
2-Methyl-2-butene	FB	4	All < 2 ppm (v/v)**
2-Methyl-2-butene	TB	1	< 2 ppm (v/v)**
<i>trans</i> -2-Pentene	CCC	5	96.8% to 101% Recovery
<i>trans</i> -2-Pentene	SS	2	94.1% to 91.9% Recovery
<i>trans</i> -2-Pentene	GB	7	All < 2 ppm (v/v)**
<i>trans</i> -2-Pentene	FB	4	All < 2 ppm (v/v)**
<i>trans</i> -2-Pentene	TB	1	< 2 ppm (v/v)**
1-Pentene	CCC	5	96.8% to 107% Recovery
1-Pentene	SS	2	100% to 106% Recovery
1-Pentene	GB	7	All < 2 ppm (v/v)**
1-Pentene	FB	4	All < 2 ppm (v/v)**
1-Pentene	TB	1	< 2 ppm (v/v)**
<i>cis</i> -2-Pentene	CCC	5	96.8% to 105% Recovery
<i>cis</i> -2-Pentene	SS	2	101% to 105% Recovery
<i>cis</i> -2-Pentene	GB	7	All < 2 ppm (v/v)**
<i>cis</i> -2-Pentene	FB	4	All < 2 ppm (v/v)**
<i>cis</i> -2-Pentene	TB	1	< 2 ppm (v/v)**

Table 10.18. Quality assurance parameters from analyses of soil gas from ground water wells (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3). (Continued).

Analyte	QA Parameter	Number of Analyses	Range of Values
C6+	CCC	5	91.6% to 102% Recovery
C6+	SS	2	91.3% to 97.8% Recovery
C6+	GB	7	All < 2 ppm (v/v)**
C6+	FB	4	All < 2 ppm (v/v)**
C6+	TB	1	< 2 ppm (v/v)**
Benzene	CCC	5	100% to 109% Recovery
Benzene	SS	2	102% to 103% Recovery
Benzene	GB	7	All < 2 ppm (v/v)**
Benzene	FB	4	All < 2 ppm (v/v)**
Benzene	TB	1	< 2 ppm (v/v)**
Oxygen	FB	2	29,900 and 29,200 (v/v)**
Oxygen	TB	1	32,900 ppm (v/v)

*<MDL

**<An estimated value for the MDL provided by the analyst. Method detection limit not determined.

¹CCC is Continuing Calibration Check.

²SS is a Second Source Standard and is a measure of accuracy.

³GB is a laboratory blank.

⁴FB is a field blank.

⁵TB is a trip blank.

Table 10.19. Relative percent difference of field and laboratory duplicates on soil gas samples from ground water monitoring wells (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3).

Vapor Monitoring Point	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
MW-2	09/08/2011	Oxygen	Field	9.7
MW-2	09/08/2011	Methane	Field	2.4
MW-2	09/08/2011	Ethane	Field	0.4
MW-2	09/08/2011	Propane	Field	0.3
MW-2	09/08/2011	<i>iso</i> -Butane	Field	0.9
MW-2	09/08/2011	Butane	Field	0.8
MW-2	09/08/2011	<i>trans</i> -2-Butene	Field	0.6
MW-2	09/08/2011	1-Butene	Field	4.6
MW-2	09/08/2011	<i>iso</i> -Butylene	Field	1.1
MW-2	09/08/2011	<i>cis</i> -3-Butene	Field	0.6
MW-2	09/08/2011	<i>iso</i> -Pentane	Field	0.7
MW-2	09/08/2011	Pentane	Field	0.7
MW-2	09/08/2011	2-Methyl-2-Butene	Field	33.7
MW-2	09/08/2011	<i>trans</i> -2-Pentene	Field	18.1
MW-2	09/08/2011	1-Pentene	Field	32
MW-2	09/08/2011	<i>cis</i> -2-Pentene	Field	60
MW-2	09/08/2011	C6+	Field	0.2
MW-2	09/08/2011	Benzene	Field	0.4
MW-2	09/08/2011	Total Petroleum Hydrocarbons*	Field	7.1
MW-21	09/07/2011	Oxygen	Field	0.5
MW-21	09/07/2011	C6+	Field	2.4
MW-21	09/07/2011	Sum Petroleum Hydrocarbons	Field	4.9
MW-41	09/09/2011	Oxygen	Field	0.7
MW-41	09/09/2011	C6+	Field	6.5
MW-41	09/09/2011	Total Petroleum Hydrocarbons*	Field	85.0
MW-42	09/09/2011	Oxygen	Field	55
MW-42	09/09/2011	Methane	Field	6.3
MW-42	09/09/2011	Butane	Field	8.8
MW-42	09/09/2011	<i>trans</i> -2-Butene	Field	10.8
MW-42	09/09/2011	Pentane	Field	24
MW-42	09/09/2011	C6+	Field	6.3
MW-42	09/09/2011	Total Petroleum Hydrocarbons*	Field	44.5

Table 10.19. Relative percent difference of field and laboratory duplicates on soil gas samples from ground water monitoring wells (applies to Tables 5.1, 5.2, 5.4, 5.5, 8.1, 8.2 and 8.3). (Continued).

Vapor Monitoring Point	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
MW-47	09/09/2011	Oxygen	Field	0.0
MW-47	09/09/2011	Pentane	Field	29
MW-47	09/09/2011	C6+	Field	0.6
MW-47	09/09/2011	Total Petroleum Hydrocarbons*	Field	0.53
MW-47	09/09/2011	Oxygen	Laboratory	1.2
MW-47	09/09/2011	Pentane	Laboratory	4.8
MW-47	09/09/2011	C6+	Laboratory	2.9
MW-48	09/07/2011	Oxygen	Field	1.9
MW-48	09/07/2011	Methane	Field	3.4
MW-48	09/07/2011	Pentane	Field	0.8
MW-48	09/07/2011	C6+	Field	0.2
MW-48	09/07/2011	Total Petroleum Hydrocarbons*	Field	0.53
MW-51	09/08/2011	Oxygen	Field	0.0
MW-51	09/08/2011	Methane	Field	2.3
MW-51	09/08/2011	Ethane	Field	69
MW-51	09/08/2011	Propane	Field	61
MW-51	09/08/2011	<i>iso</i> -Butane	Field	16.8
MW-51	09/08/2011	Butane	Field	2.8
MW-51	09/08/2011	1-Butene	Field	45
MW-51	09/08/2011	<i>iso</i> -Butylene	Field	25
MW-51	09/08/2011	<i>cis</i> -3-Butene	Field	64
MW-51	09/08/2011	<i>iso</i> -Pentane	Field	0.2
MW-51	09/08/2011	Pentane	Field	1.3
MW-51	09/08/2011	2-Methyl-2-Butene	Field	14.7
MW-51	09/08/2011	<i>trans</i> -2-Pentene	Field	0.1
MW-51	09/08/2011	1-Pentene	Field	3.4
MW-51	09/08/2011	C6+	Field	0.2
MW-51	09/08/2011	Benzene	Field	0.4
MW-51	09/08/2011	Total Petroleum Hydrocarbons*	Field	3.9

*Values of each individual analyte in ppm converted to $\mu\text{g}/\text{m}^3$, and then summed to get Total Petroleum Hydrocarbons.

The relative percent difference for many of the individual petroleum hydrocarbons was greater than 15%. The concentrations of the individual petroleum hydrocarbons are summed to calculate TPH in units of µg/L. Table 10.19 also compare the relative percent difference of the calculated TPH for duplicate field samples. The relative percent difference for TPH in samples from MW-41 and MW-42 were 85.0 and 44.5% respectively. The relative percent difference for samples from the other sampling locations were less than 15%.

Table 8.3 compares the calculated concentration of TPH in soil gas from well MW-41 and MW-42 to measured concentrations of TPH in soil gas from vapor sampling point VW-8. The data were interpreted to make the following claim. *The concentrations of methane and TPH-g were much higher in the soil gas from the monitoring wells.* To be conservative in the comparison of TPH between the vapor sampling point and the monitoring wells, the samples from MW-41 and MW-42 with the lower calculated concentration of TPH were used in Figure 8.9. The lower of the two calculated values for TPH in duplicate field samples from well MW-42 was 77% of the mean of the samples, and the lower of the two calculated values for TPH in duplicate field samples from well MW-41

was 58% of the mean of the samples. These lower values were almost ten thousand fold higher than the concentration in gas from vapor sampling point VW-8. The relative percent difference in the duplicate samples is small compared to the difference in concentrations between the gas samples from the monitoring wells and the gas sample from the vapor sampling point.

The quality of the data were acceptable for the intended purpose, and all the data were used.

10.3 Section 6

Soil gas samples were acquired using the protocol of Jewell and Wilson (2011) from conventional ground water wells that were installed at the direction of the Oklahoma Corporation Commission. Soil gas samples were acquired by water displacement into 165 ml serum vials. The vials were returned to the Kerr Center for analysis by micro gas chromatography with thermal conductivity detection.

The quality assurance parameters for data in Table 6.1 are presented in Table 10.10 (Section 10.1.4). Table 10.20 presents the relative percent difference between duplicate field samples and duplicate laboratory samples for the data in Table 6.1.

Table 10.20. Relative percent difference of field and laboratory duplicates on samples of soil gas analyzed in the laboratory for data in Table 6.1.

Monitoring Well	Date Collected	Soil Gas Component	Duplicate	Relative Percent Difference
Antlers MW-2	1/4/2011	Oxygen	Field Duplicate	3.8
Antlers MW-2	1/4/2011	Methane	Field Duplicate	2.4
Antlers MW-2	1/4/2011	Benzene	Field Duplicate	2.9
Antlers MW-2	1/4/2011	Total Petroleum Hydrocarbons*	Field Duplicate	2.4
Antlers MW-2	1/4/2011	Oxygen	Lab Duplicate	9.6
Antlers MW-2	1/4/2011	Methane	Lab Duplicate	2.3
Antlers MW-2	1/4/2011	Benzene	Lab Duplicate	0.9
Antlers MW-2	1/4/2011	Total Petroleum Hydrocarbons*	Lab Duplicate	0.2
Antlers MW-9	1/4/2011	Oxygen	Field Duplicate	3.5
Antlers MW-9	1/4/2011	Methane	Field Duplicate	0.6
Antlers MW-9	1/4/2011	Benzene	Field Duplicate	1.2
Antlers MW-9	1/4/2011	Total Petroleum Hydrocarbons*	Field Duplicate	0.6

*Values of each individual analyte in ppm converted to µg/m³, and then summed to get Total Petroleum Hydrocarbons.

The relative percent difference of the field and lab duplicates were all less than 15%. The data were of acceptable quality for the intended purpose and all of the data were used.

10.4 Section 8

Data in Figure 8.3, Table 8.1, Table 8.2 and Table 8.3 are repeat data discussed in Section 4. The quality assurance parameters for data in Figure 8.3 are presented in Table 10.13. Table 10.15 presents the relative percent difference between duplicate field samples for the data in Figure 8.3.

The quality assurance parameters for data in Tables 8.1, 8.2 and 8.3 are presented in Table 10.16. Table 10.17 presents the relative percent difference between duplicate field samples and duplicate laboratory samples for the data in Tables 8.1, 8.2 and 8.3.

ACKNOWLEDGEMENTS

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NOTICE

The U.S. Environmental Protection Agency through its Office of Research and Development conducted the research described here as an in-house effort. This Issue Paper has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document.

APPENDIX A. KINETICS OF STABILIZATION DURING FIELD SAMPLING

The data used in these case studies are provided as an illustration. They do not necessarily reflect current conditions at the site and have no bearing on past or current regulatory action taken by the Oklahoma Corporation Commission or the Montana Department of Environmental Quality.

Data are presented from an additional eight sites related to the kinetics of stabilization of oxygen and carbon dioxide and the kinetics of stabilization of benzene and petroleum hydrocarbons in soil gas samples. All locations, including data presented in Figures 4.4 and 4.5 in Section 4, used existing ground water monitoring wells for soil gas collection. Wells were screened across the water table.

Prior to purging each well, the water level was measured and well construction logs were reviewed to determine exposed screen length above the water table that was available for entry of soil gas. A modified EX-Cap[®] was connected to the top of the well casing to provide a pneumatic port to connect the sample train. Wells were purged at rates up to 10 L/min as measured using a rotameter. The vacuum that developed in the well was determined with a vacuum gauge that read in inches of water. Vacuum measurements in inches of water directly indicate the rise of water in the well during purging. Knowing the exposed screen length, the pump rate was adjusted so that the vacuum in the well did not exceed the length in inches of the exposed screen, thereby preventing water from inundating the entire screened interval.

The outlet from the pump and rotameter was split to two outlet lines. One supplied the sampled soil gas to the field meters for CO₂ and O₂ measurements to monitor for stable concentrations. The other was for collection of samples for laboratory analysis of benzene and Total Hydrocarbons in the sampled soil gas. Following the procedures of Jewell and Wilson (2011), samples were collected by water displacement into glass serum bottles. The bottles were sealed with butyl rubber Teflon[®]-faced septum and aluminum crimp caps. The septa were faced with Teflon[®] and had a layer of lead foil presented to the sample. The

water used for displacement contained a 1% solution of sodium phosphate dodecahydrate to act as a bactericide and preventing biological degradation of the samples before sample analysis.

Four samples were collected for Total Hydrocarbons and Benzene analysis at each time interval. The greatest variability in concentrations between the four samples occurred at the initial time, one minute. Later samples had better agreement in concentration.

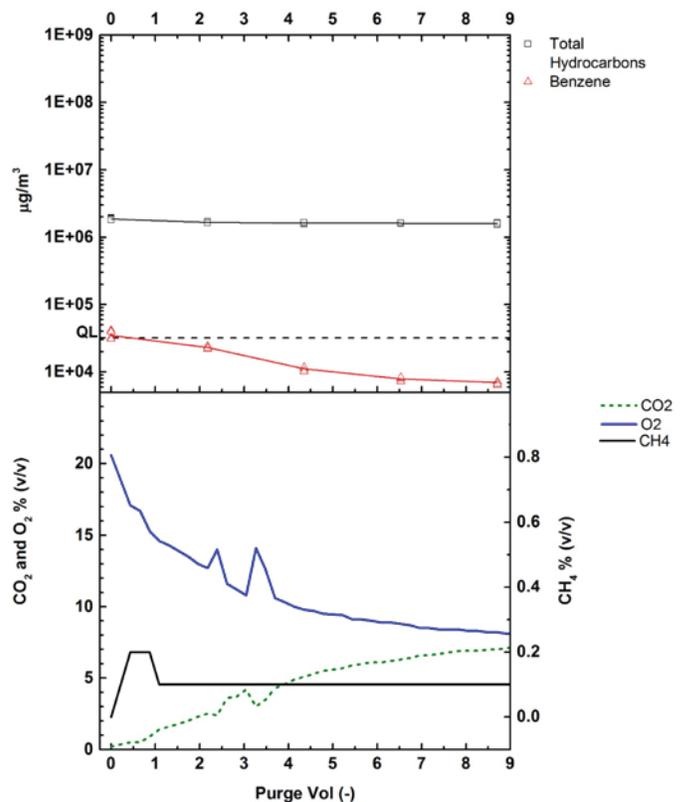


Figure A.1. Location MW-9 at the Visocan Site at Helena, MT.

See Figure A.1. Equilibration for CO₂ and O₂ occurred after 8.5 purge volumes. Benzene was initially detected above quantitation limits and decreased below quantitation limits and eventually method detection limits. Concentrations of Total Hydrocarbons were stable after 2 purge volumes. Both Total Hydrocarbons and Benzene decreased from the first measurement. The lithology around the screen/sand pack was stratified tan to purple silty clay with less than 10% sand and clasts up to ½ inch diameter.

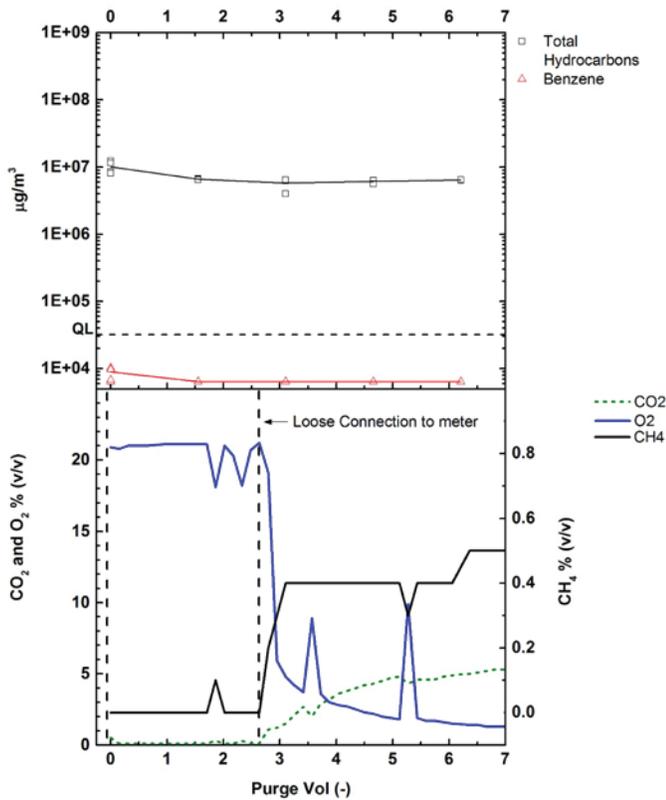


Figure A.2. Location MW-4 at the Visocan Site at Helena, MT.

See Figure A.2. Equilibration for CO₂ and O₂ occurred after approximately 6 purge volumes. Notice a loose connection to the field meter prevented accurate readings before 2.5 purge volumes. Benzene was below quantitation limits and eventually non-detect.

Concentrations of Total Hydrocarbons were stable after 3 purge volumes. Both Total Hydrocarbons and Benzene decreased from initial measurements. The lithology around the screen/sand was stratified green to purple silty clay with less than 5% sand and clasts up to ½ inch diameter.

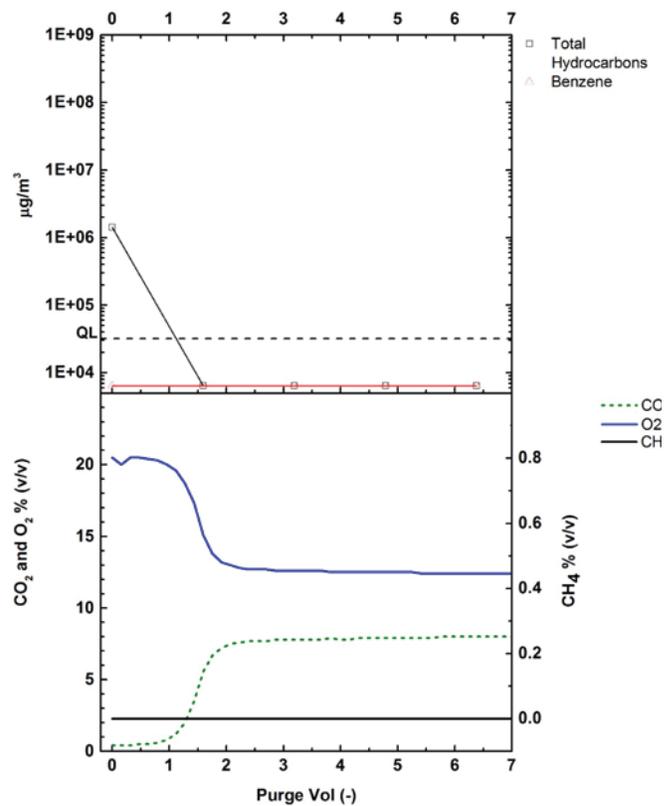


Figure A.3. Location SVE-NE at the Former Noon's Store, Helena, MT.

See Figure A.3. Equilibration for CO₂ and O₂ occurred after 2.5 purge volumes. Benzene was non-detect and Total Hydrocarbons were non-detect after the initial sample. This is a classic profile of a clean well. The lithology around the screen/sand pack was reddish tan sandy clay, brown sand with gravel, and brown clayey sand.

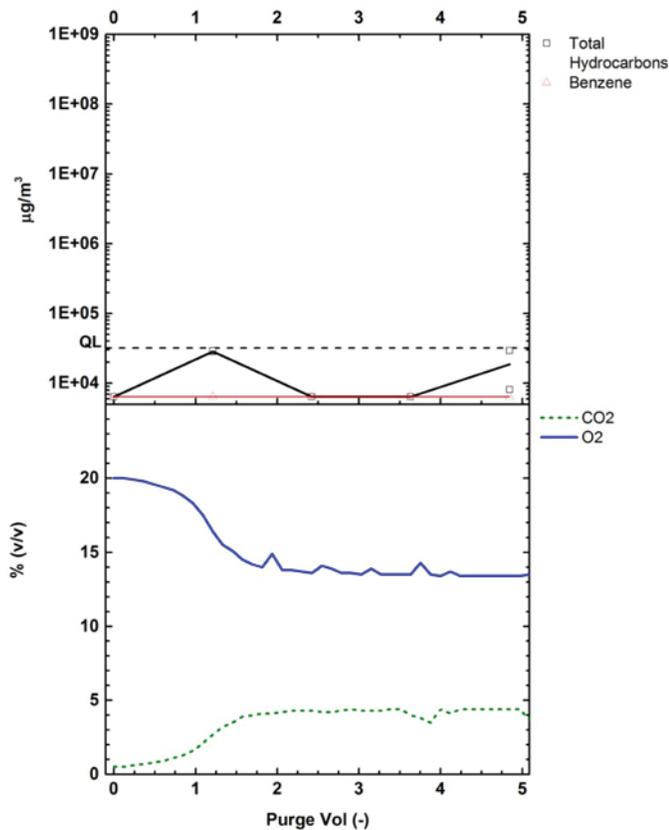


Figure A.4 Location SVE-SE at the Former Noon's Store, Helena, MT.

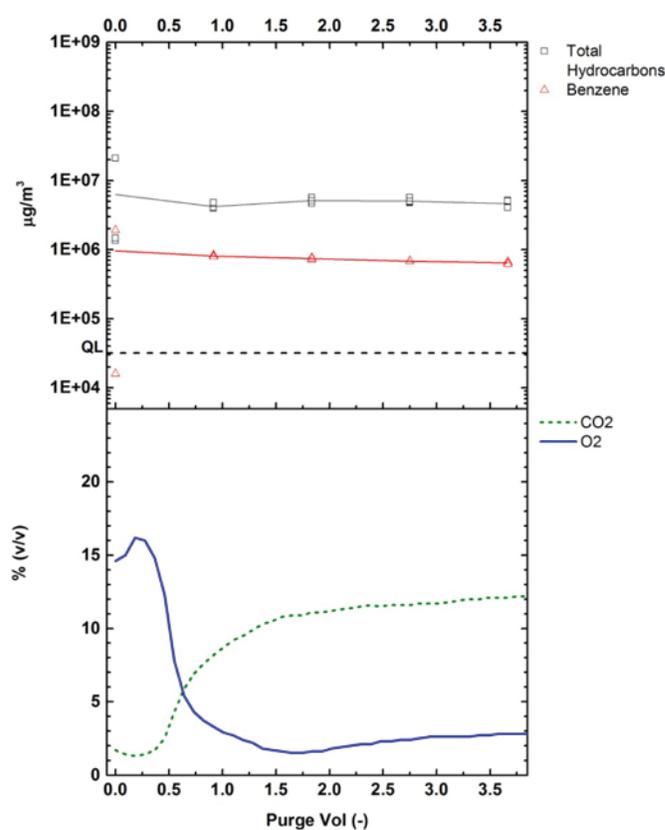


Figure A.5. Location HMM-6 at the Former Noon's Store, Helena, MT.

See Figure A.4. Equilibration for CO₂ and O₂ occurred after 2.5 purge volumes. Benzene was non-detect and concentrations of Total Hydrocarbons had varying non-detects and detection below quantifying limits. The lithology around the screen/sand pack was reddish tan sandy clay, brown sand with gravel, and brown clayey sand.

See Figure A.5. Equilibration for CO₂ and O₂ occurred after 2 purge volumes. Concentrations of Benzene and Total Hydrocarbons decreased from initial measurements and stabilized after 2 purge volumes. The lithology around the sand/screen pack was a light tan mudstone and limestone.

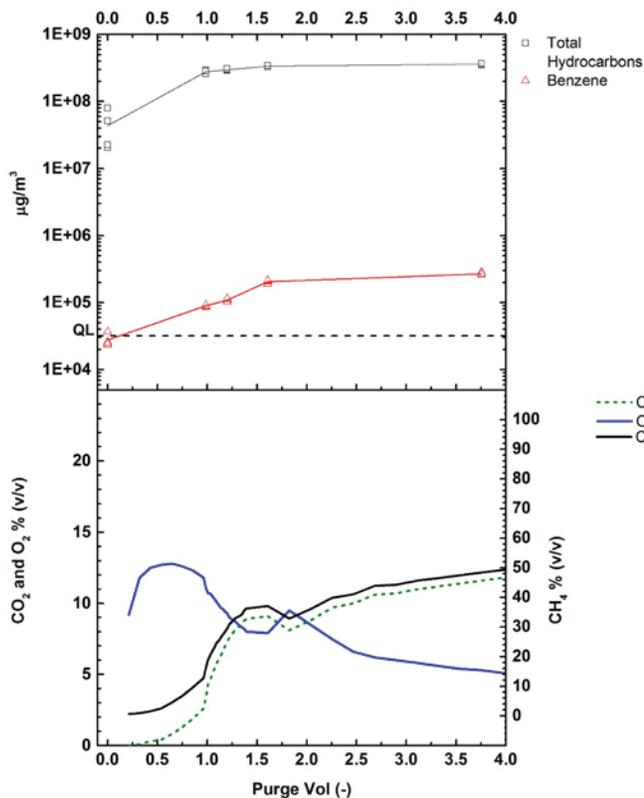


Figure A.6. Location GMW-1 at the EZ-Go Service Station at Antlers, OK.

See Figure A.6. Equilibration for CO₂ and O₂ occurred after 4 purge volumes. Concentrations of both Benzene and Total Hydrocarbons increased throughout the purge and approached stability near 4 purge volumes. The lithology around the screen/sand pack was gravel fill and sandy clay.

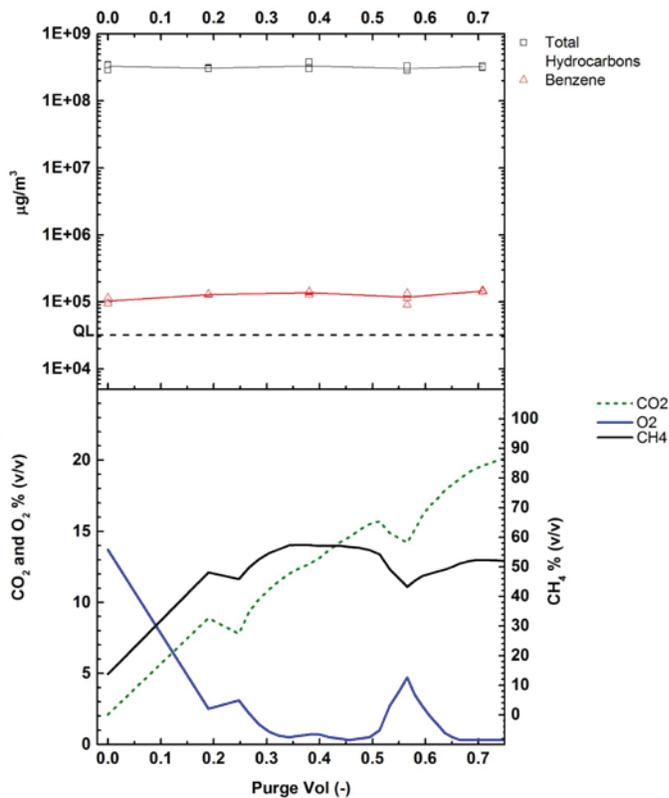


Figure A.7. Location MW-9 at the EZ-Go Service Station at Antlers, OK.

See Figure A.7. Equilibration for O₂ occurred after 0.7 purge volume. CO₂ continued to increase throughout the entire purge. Concentrations of Benzene increased from initial measurements and stabilized after 0.4 purge volumes. Concentrations of Total Hydrocarbons were stable throughout the purge. The lithology around the screen/sand pack was brown clay, red brown clay, and red brown sand clay.

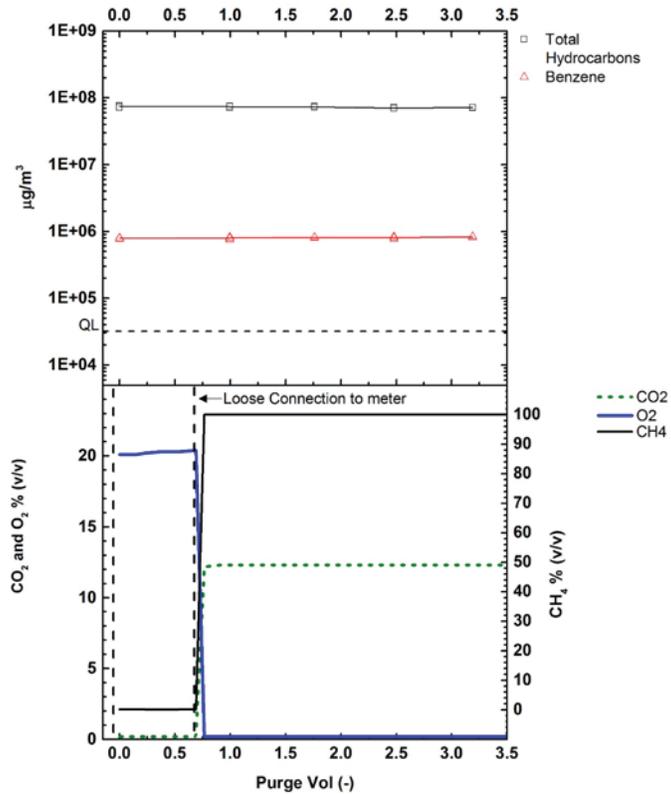


Figure A.8. Location MW-1 at the Miller Mart Service Station at Wapanucka, OK.

See Figure A.8. Equilibration for CO₂ and O₂ occurred after 1 purge volume. Concentrations of Benzene and Total Hydrocarbons were stable throughout the purge. Notice the loose connection to the field meter that prevented accurate measurements during the initial stages of the purge. The lithology around the screen/sand pack was red brown and light gray clay, silt, sand gravel mix, and some mottling.

APPENDIX B. RECOMMENDED PRACTICE FOR COLLECTING SOIL GAS SAMPLES

There are extensive recommendations available for good practice for collecting soil gas samples from vapor probes. There are few recommendations for collecting soil gas from conventional ground water monitoring wells. This section will provide references to useful guidance documents for vapor probes and will provide detailed recommendations for sampling of soil gas from ground water monitoring wells.

B1. Collecting Soil Gas Samples from Vapor Probes

U.S. EPA has published a standard operating procedure for sampling soil gas (U.S. EPA, 2001). The American Petroleum Institute has produced a publication with recommendations for collecting soil gas samples from the vadose zone (API, 2005). Both of these documents have many useful recommendations, but they describe the state of practice ten years ago.

Recently, the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment in Australia published Australian guidance for petroleum hydrocarbon vapor intrusion (CRC CARE, 2013). The guidance is detailed and easy to read. The technical approach is consistent with good practice in the USA. The appendices of this document provide detailed protocols for installation and sampling of soil gas probes. The document also provides links to much of the technical and regulatory guidance that is currently available from state agencies in the USA.

The Interstate Technology & Regulatory Council (ITRC) has produced a guidance document on petroleum vapor intrusion. This document provides detailed protocols for installation and sampling of soil gas probes (ITRC, 2014).

B2. Collecting Soil Gas Samples from Groundwater Monitoring Wells

Jewell and Wilson (2011) describe a procedure to extract and analyze soil gas from conventional ground water monitoring wells. This section describes that procedure in detail and provides recommendations for good practice.

B.2.1 Equipment Requirements

The sampling train should have the following components. The flow of air through the sampling train should be in the order that the various components of the sampling train are discussed in the text below.

B.2.1.1 A Sampling Cap

Jewell and Wilson (2011) used an EX-Cap® to connect the sampling train to the monitoring well (Figure B.1). An EX-Cap® is an adaptation of a conventional J-Plug® well cap that is commonly used to seal two-inch PVC wells.



Figure B.1. The cap used by Jewell and Wilson (2011) to sample soil gas from ground water wells.

The EX-Cap® was not designed to be air-tight. As a result, the EX-Cap® as supplied by the manufacturer may leak air. If the EX-Cap® is to be used as the sampling cap, it must be taken apart and fitted with O-rings or other seals to make it air tight. Another issue is the internal resistance of the compression fitting to the flow of air. At normal pumping rates, there is a measureable pressure drop across the EX-Cap®.

It is possible to fabricate a sampling cap made from materials that can be acquired at any hardware store. A nipple with a tube fitting made from metal or PVC is screwed or glued to a PVC plug. The plug is connected to the riser of the well with a flexible rubber collar. Most monitoring wells are either 2 inches or 4 inches in diameter. The diameter of the rubber collar

should match the diameter of the riser. To minimize contact of the air sample with the flexible collar, the plug should fit down against the top of the riser.

B.2.1.2 A Trap to Collect Water or NAPL

Accidents happen. On occasion, pumping on the well may inadvertently yield water or hydrocarbons instead of soil gas. This can destroy the pump, the rotameter and any instruments that are connected downstream of the pump. It is also necessary to keep water out of the Summa Canister used to collect the sample. The pump and equipment downstream should be protected by a water trap or fluid trap. One approach is to insert a 1.0 liter glass vacuum flask between the sampling cap on the well and the pump (Figure B.2).



Figure B.2. An arrangement of a sampling cap connected to the riser of a well, a water trap and a sampling port connected to a Summa Canister.

Be sure to use a vacuum flask. It will have heavy walls and a side arm. A tube should run from the sampling cap through a rubber stopper to the bottom of the flask. A second line should run from just below the bottom of the stopper to the pump. The second line can also be connected to the side arm. If the second line is plumbed through the stopper, the side arm must be sealed off.

It is possible to produce a vapor from a ground water monitoring well that will burn (Jewell and Wilson, 2011). If the vapors in the trap are ignited, the flexible rubber stopper in the cap should separate from the

flask and allow the gasses to escape. Do not clamp the stopper down. Do not push it into the flask tightly. The stopper should be just tight enough to make an air-tight seal.

The soil gas that is produced from the unsaturated zone contains water vapor. It can be very close to being saturated with water vapor. If the sampling train is cold with respect to the unsaturated zone, water may condense or freeze out in the sampling train. Condensation in the rotameter is particularly problematic. This can be remedied by putting a desiccant in the trap (Figure B.3).

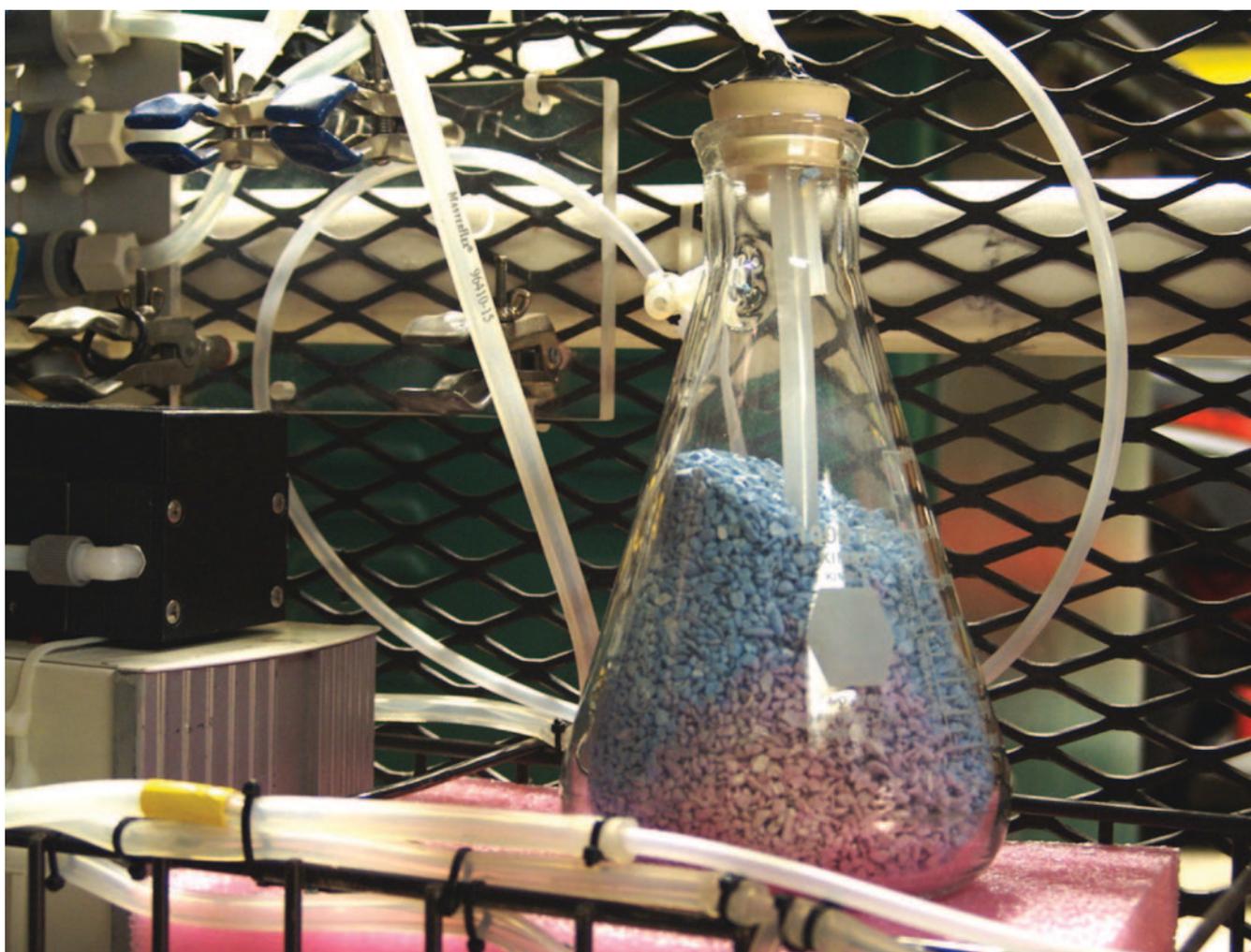


Figure B.3. A trap containing desiccant to remove water vapor from the soil gas sample.

B.2.1.3 A Valve to Collect Gas Samples

Tubing connects the sampling cap to a trap that protects the pump and downstream equipment. A three-port valve should be installed to allow the collection of a sample of the gas from the well into a Summa Canister for laboratory analysis (Figure B.2). The Summa Canister should be filled rapidly, over at most a few minutes. When the Summa Canister is being filled, position the three-port valve so that the Summa Canister is open to the monitoring point, but both the Summa Canister and the monitoring point are isolated from the vacuum pump. Turn off the vacuum pump while the Summa Canister is filling.

The three-port valve can be installed just downstream of the trap. This will protect the Summa Canisters. It is possible a desiccant could sorb or desorb compounds of interest. If desiccant is put in the trap, the three-port valve should be inserted between the sampling cap and the trap. If the three-port valve is located between the sampling cap and the trap, the Summa Canister is not protected from water. Inspect the line from the monitoring point to the valve as the Summa Canister fills to see if droplets of water wet the side of the line. If droplets of water enter a Summa Canister, that canister is compromised. Sample again with a new canister. To minimize the risk of pulling water into the canister, adjust the valve to the canister to lower the flow rate of soil gas to the canister.

B.2.1.4 A Vacuum Gauge

As will be discussed below, it is important to monitor the vacuum on the soil gas in the well. A line should run from a vacuum gauge to the sampling cap or to the line between the sampling cap and the trap. The vacuum gauge should be referenced to the atmosphere. It should display the vacuum in inches of water. This will alleviate a need to make unit conversions in the field. The gauge should display a vacuum up to 100 inches of water.

B.2.1.5 A Pump to Move Soil Gas

Each 1.0 vertical feet of a 2.0 inch well contains 0.6 L of soil gas. Depending on the depth to water, the dead air space in the screen and riser of a ground water monitoring well varies from several liters to tens of liters. This is too much soil gas to efficiently purge

with the small pumps that are built into conventional field meters. It is necessary to have a second pump to produce soil gas from the monitoring well for purging and for sampling.

The pump should be able to function effectively against a pressure difference of 100 inches of water. It is not necessary to have a pump that works against a higher vacuum. The pump should move approximately ten liters of soil gas a minute against a pressure difference of 100 inches of water. The pump should be constructed with components that will not sorb petroleum vapors, such as fluoropolymer elastomer. There are several air pumps on the market that will meet these specifications. Many of these pumps are diaphragm pumps.

B.2.1.6 A Rotameter to Measure the Pumping Rate

To monitor the progress of purging, it is necessary to know how rapidly soil gas is moving through the sampling train. A rotameter should be installed downstream of the pump. If the rotameter is downstream, it operates at atmospheric pressure instead of in a partial vacuum. If it operates at atmospheric pressure, there is no need to apply corrections to the readings from the rotameter. The rotameter should measure up to 10 standard liters of air per minute.

B.2.1.7 A Valve to Control the Flow of Soil Gas

There should be a valve in the sampling train that allows the operator to have fine control on the flow rate of soil gas through the pump. This should be a needle valve, not a ball valve. The needle valve can be built into the pump, it can be built into the rotameter or it can be a separate unit that is installed between the pump and the rotameter. It is more convenient if the needle valve is built into the rotameter. The needle valve should be installed between the pump and the rotameter.

The needle valve should allow precise control of the flow rate of soil gas down to a flow of 1.0 liters per minute.

B.2.1.8 Lines to Supply Soil Gas to a Field Meter

Field meters for methane, oxygen, carbon dioxide or total hydrocarbons have an internal pump. It is necessary to supply soil gas to the meter at atmospheric pressure. This can be done by inserting a tee between the rotameter and the field meter. One line from the tee goes to the meter, the other line goes to exhaust. The meter pumps the soil gas it needs and the excess is discharged through the exhaust line. Figure B.4 illustrates this arrangement.

It is necessary to know the pumping rate in the meter and adjust the sample pump to supply that flow of soil gas with a comfortable margin. If more soil gas than is needed by the pump is not delivered to the tee, the pump in the meter will pull air from the atmosphere through the exhaust line. The soil gas delivered to the meters will be diluted with air, which will produce erroneous readings.

To confirm that things are working as intended, insert the exhaust line into a beaker of water and check for bubbles. The presence of bubbles ensures that an adequate supply of soil gas is being provided to the meters.

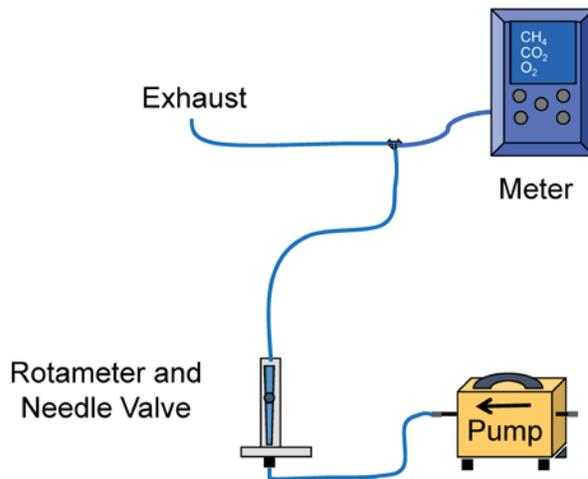


Figure B.4. Recommended arrangement of the lines that supply sampled soil gas to field meters.

B.2.2 Minimizing the Contamination of Soil Gas Samples by the Contents of the Monitoring Well

The intention is to sample oxygen, petroleum hydrocarbons and methane in soil gas at the source of the vapors. The sample can be compromised by interaction of the sampled gas with materials in the well. If there is floating hydrocarbon in the well, volatile hydrocarbons released from the floating hydrocarbon can contribute to the hydrocarbons in the gas sample. If there are dissolved hydrocarbons in the water, volatile hydrocarbons that escape the water can also contribute to the hydrocarbons in the gas sample.

If the level of ground water or floating NAPL hydrocarbons is above the top of the screen, the sampling train will produce water or NAPL hydrocarbons, not soil gas. The well will only produce soil gas when the initial level of ground water or floating NAPL hydrocarbons is below the top of the screen. The vacuum imposed in the well during purging or sampling will cause the water or NAPL hydrocarbons to rise inside the well. If the vacuum is high enough, the rise will inundate the top of the

screen. When the level of well water or floating NAPL hydrocarbons is above the top of the screen, the soil gas sample must be pulled through the floating NAPL hydrocarbons or the well water inside the well. This greatly increases the chances for transfer of hydrocarbons from floating NAPL or water to the soil gas sample, and should be avoided.

The effect of vacuum is illustrated in a laboratory experiment depicted in Figure B.5. A conventional two inch PVC well screen and riser was cut in half, and the sections were attached to a piece of Plexiglas. Then the Plexiglas was mounted as one side of a steel box. The box was filled with sand and colored water was added to create a water table that was below the top of the screen in both model wells. A ruler was added to measure the change in water elevations when soil gas was pumped from Well #1. A red arrow identifies the level of water in Well #1, and a second red arrow identifies the location of the black ball in the rotameter which measures the rate of purging of soil gas from Well #1. Figure B.5 represents static water level conditions, when soil gas has not yet been pumped from the well.

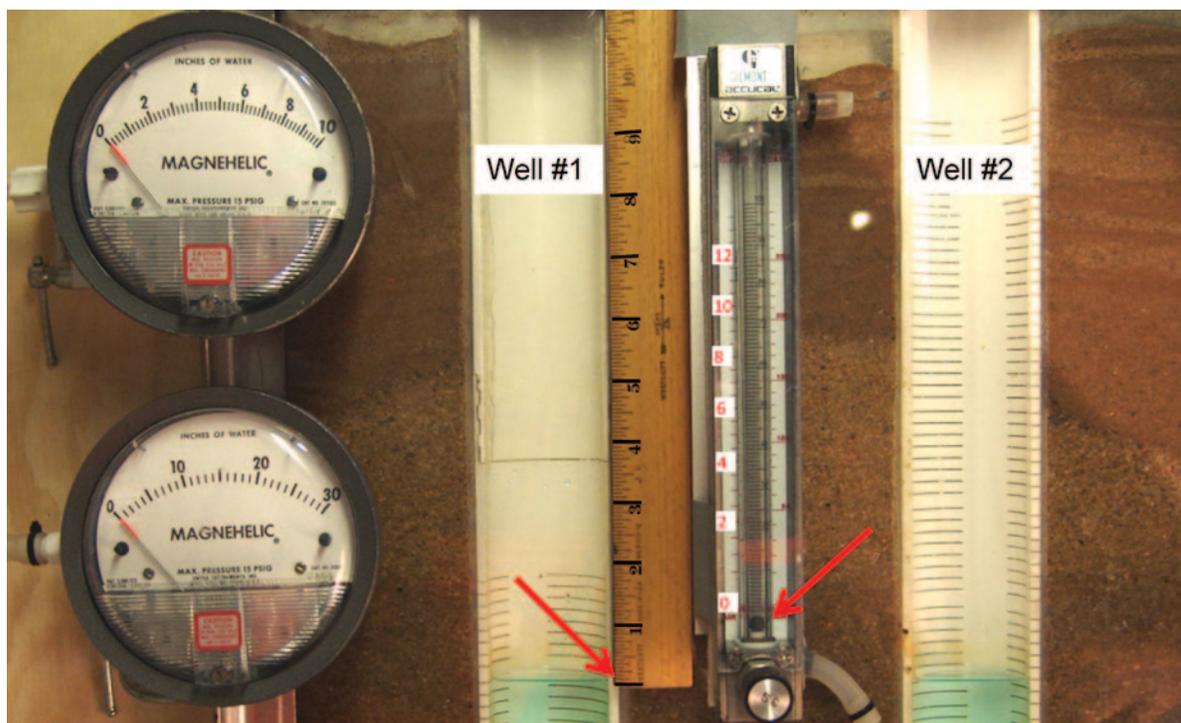


Figure B.5. Level of water in model monitoring wells with no purging of gas and no vacuum.

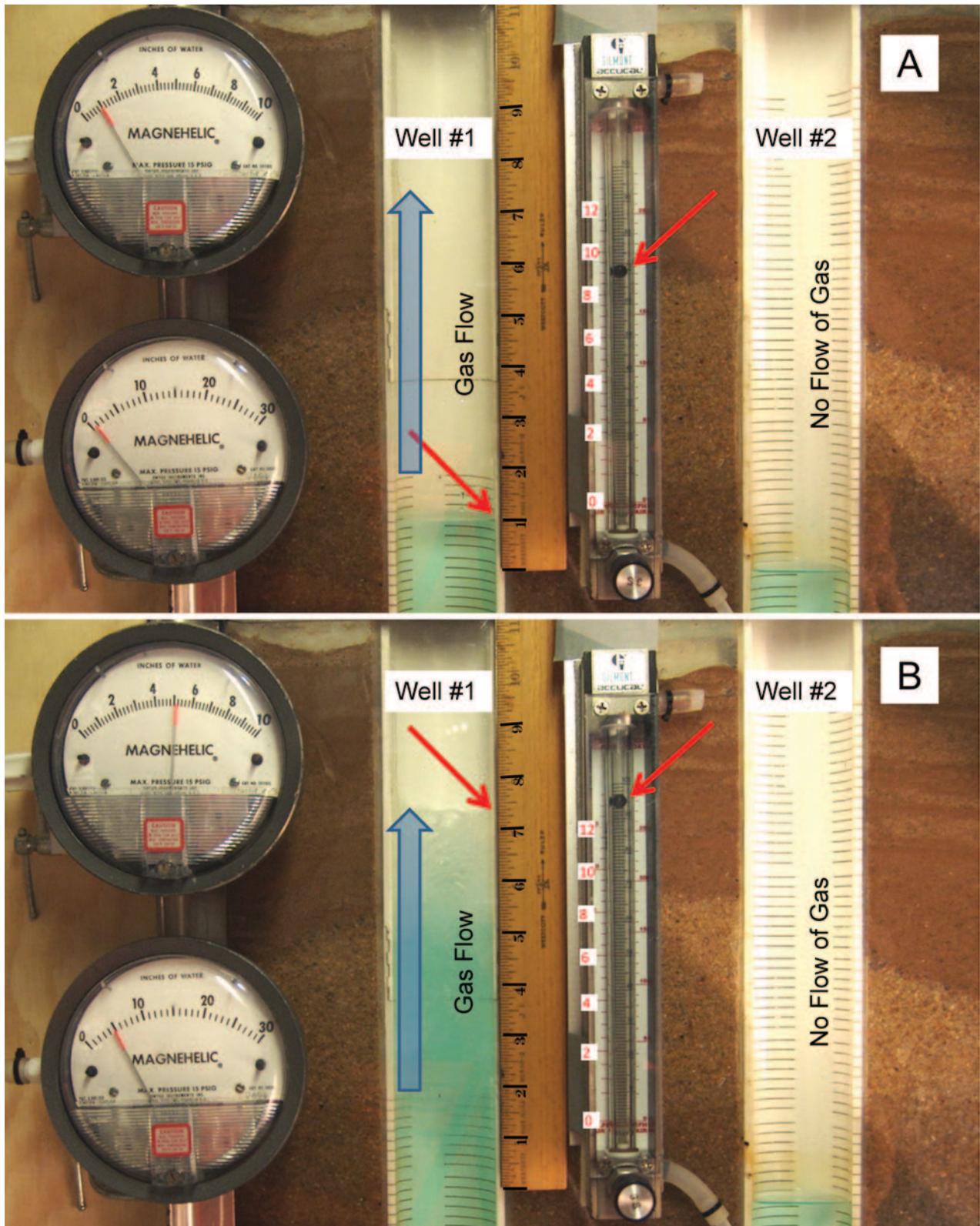


Figure B.6. Effect of purge rate of soil gas on the vacuum in the well and the elevation of water in the well. Panels A and B illustrate gas flow rates of 9 and 13 L/min, respectively.

Figure B.6 compares the effect of two different purge rates of soil gas from Well #1 on the vacuum produced and the level of water in the well. Well #2 on the right side of the figure acts as piezometer. It documents the free water surface under atmospheric conditions.

In Panel A of Figure B.6, the flow rate of soil gas was 9 liters per minute from Well #1. The free water surface in Well #1 is just below the top of the screen. The vacuum that developed was near 1.0 inch of water.

In Panel B of Figure B.6, the flow rate of soil gas was increased to 13 liters per minute. The free water surface was above the top of the screen. The vacuum that developed increased to 5 inches of water. The water was pulled through approximately 5 inches of well water as it moved from the sand pack around the well to the inside of the riser. The examples in Figure B.5 and Figure B.6 are from a more extensive

experiment. All the data are presented in Figure B.7. It should be noted that only one-half of a well was used in these experiments. The flow rate in a complete well would be twice as large.

Without any pumping, almost 2 inches of screen was exposed to the soil gas. As the rate of pumping increased, the vacuum increased. The rise of water in the well was equivalent to the vacuum. Only 1 inch of screen could supply enough soil gas to sustain pumping at 9 liters per minute. However, at 10 liters per minute the water rose in the well and inundated the screen.

At faster flow rates, the rise of water in the well was greater than the vacuum. This is because the water above the screen contained bubbles of gas, and thus had a lower density.

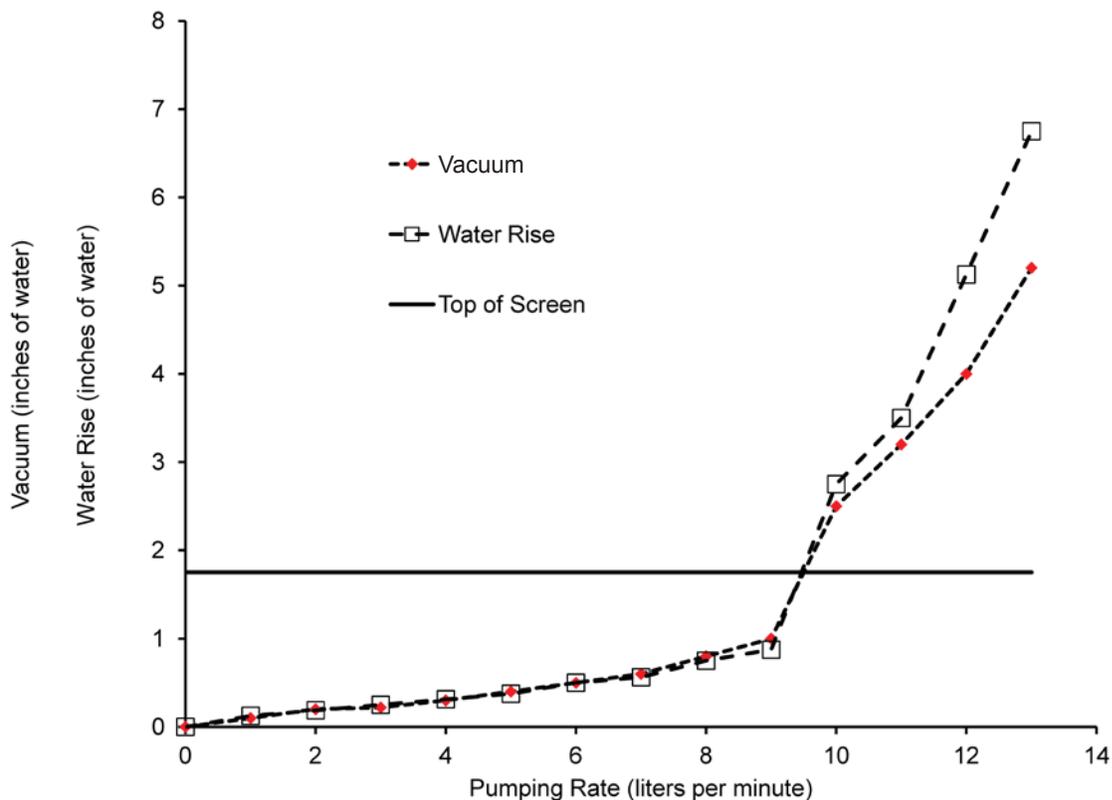


Figure B.7. Relationship between pumping rate of soil gas from Well #1 in the model, the vacuum that developed in Well #1, and rise of water inside Well #1.

B.2.3 Sampling Procedures to Prevent Transfer of Contamination to Soil Gas

Useful information regarding the well can be found in the well construction log. Take a well log to the field. From the log, determine the depth to the top of the screened interval. Determine the depth to water in the well. Subtract the depth to the top of the screen from the depth to water. That difference is the depth interval of screen that is exposed to soil gas. Monitor the vacuum that develops in the well and adjust the flow rate as necessary to ensure that the vacuum (in inches) does not exceed the exposed interval of screen (in inches).

To save labor costs, it is obviously better to purge and sample soil gas from a well as rapidly as possible. The practical rate of pumping is controlled by the depth interval of the screen that is exposed to soil gas, which controls the maximum vacuum that should be put on a well and the permeability of the unsaturated material.

Figure B.8 compares the relationship between the rate of soil gas extraction and the vacuum that developed on a number of ground water monitoring wells. These data were developed using the approach of Jewell and Wilson (2011). Many wells must be pumped at rates that are less than 10 liters a minute to avoid developing vacuums in excess of 50 or 100 inches of water.

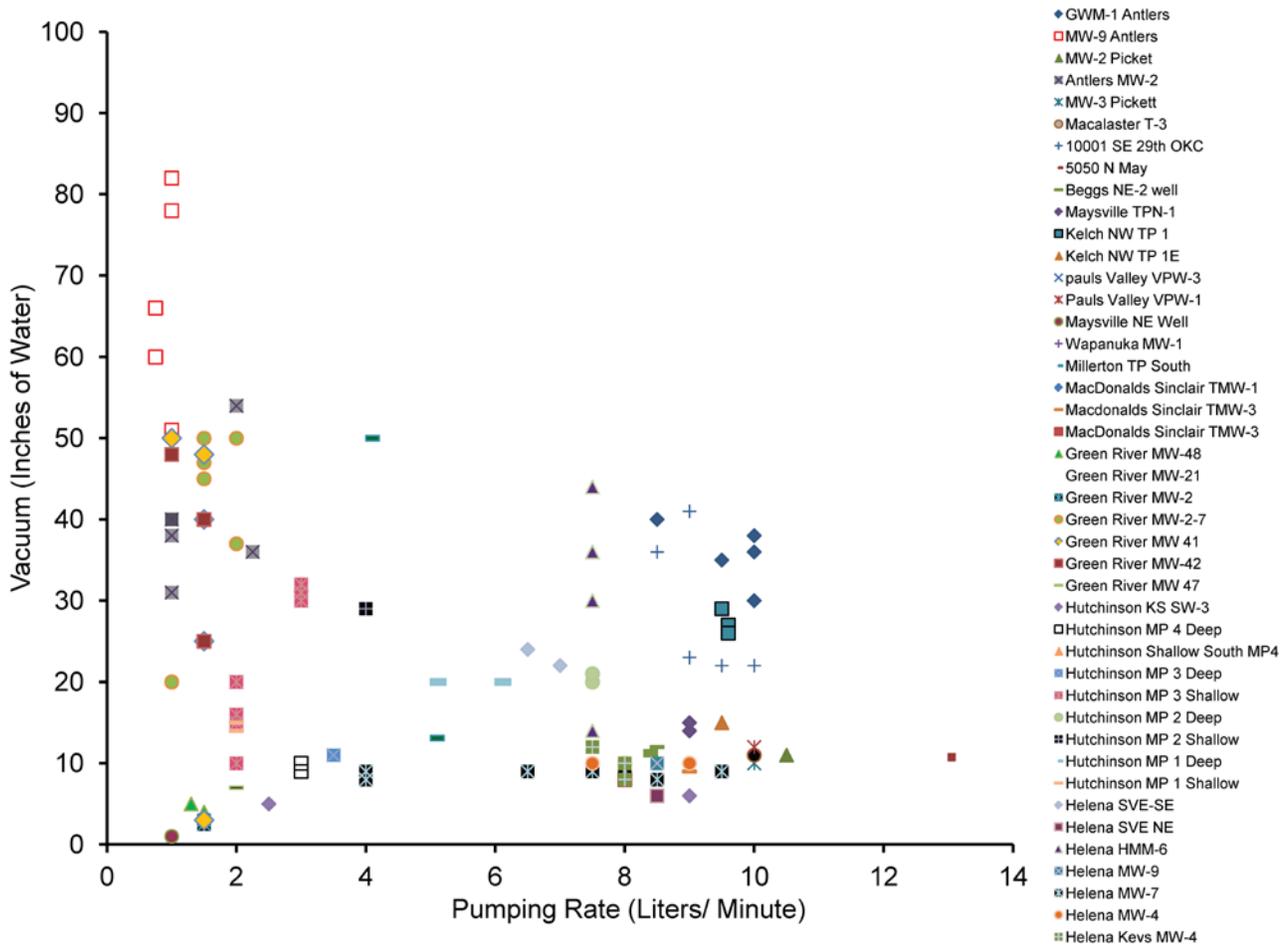


Figure B.8. Relationships between the pumping rate of soil gas and the vacuum that developed on gas in selected ground water monitoring wells.

B.2.4 Perform a Leak Test on the Sampling Train

Conduct a leak test on the equipment setup used to acquire the soil gas samples. Glue a cap on the end of a section of one inch riser, two inch riser or four inch riser (as is appropriate for the vapor monitoring point) to create an air-tight seal. This makes a test section. Turn off any field meters. Connect the sampling cap to the test section and run the pump to develop a vacuum of 50 inches of water, 100 inches of water or whatever is the maximum vacuum you intend to impose. Then turn off the pump and position the three port valve between the rotameter and the exhaust line so as to isolate the sampling system from the exhaust and from the field pumps. Watch for one minute to see if the vacuum readings drop on the gauge. If the vacuum readings drop, find the leak and correct it.

B3. Summary of ORD Recommendations for Sampling Soil Gas from Ground Water Monitoring Wells

At the beginning of each day of sampling, take equipment blanks of air that has passed through the sampling train for analysis of benzene and TPH-g.

Take trip and field blanks as required by the quality assurance project plan.

Zero the vacuum gauge at the beginning of the day. Check and adjust the zero every time the sampling train is moved.

Conduct a leak test every time you set up on a new vapor sampling point.

The field meters should be calibrated as specified by the manufacturer. Check the calibration by analyzing the concentration of a standard gas. At a minimum, the calibration should be checked at the beginning of a day of field sampling, during the middle of the day and at the end of the day. The best practice is to check the calibration when the sampling train is moved to a new location. The nominal and reported values of the calibration gas should be recorded in the field notebook. If the performance of an instrument is out of the acceptable range, it should be adjusted or recalibrated to bring its performance into the acceptable range.

If there is floating NAPL in a well, remove as much NAPL as possible before sampling gas from the well.

Know the depth interval of well screen exposed to soil gas and do not apply enough vacuum during sampling to inundate the screen.

As soil gas is pumped from a monitoring well, the concentrations of petroleum vapors in the gas can go up or they can go down (see Appendix A). It is impossible to know beforehand which pattern a well will follow. Collect one set of samples for laboratory analysis approximately one minute after pumping starts. Monitor soil-gas concentrations during purging until stable concentrations of oxygen and carbon dioxide are attained. Then collect a second set of samples for laboratory analysis. The purge volume required to reach stable concentrations may be greater or less than the typically recommended purge volume (~3 void volumes of air in the well).

Store the samples, trip blanks, field blanks and equipment blanks away from direct sunlight and at room temperature.

Determine if the sampling train is contaminated before moving the sampling train to a new location. After sampling is concluded at a location, disconnect the sampling train from the well and pump clean air through the sampling train for ten minutes. Monitor the air that passes out of the sampling train with an OVA meter. If the air is still contaminated after ten minutes, replace tubing and decontaminate the equipment in the sampling train. Do not sample a new location until the OVA meter indicates that the sampling train is no longer contaminated.

Infrared sensors in an OVA meter are sensitive to radio frequency interference. Any device that transmits radio waves can cause the infrared meter readings to fluctuate. Cell phones are the most common cause of the problem. Never use cell phones while taking readings with an infrared sensor. Cell phones should be turned off or kept at least 20 feet away from an instrument in active use.

If there is any concern of transfer of contamination from one location to the next, take equipment blanks for analysis of benzene and TPH-g before sampling the new location.

Do not use Tygon® tubing. Use nylon or silicone tubing. Tubing can become contaminated by being in the vicinity of electrical generators or containers for gasoline. Store tubing in a protective container or bag. Store the tubing away from electrical generators or containers for gasoline.

Where possible, set up the sampling train at a location that is up-wind from potential sources of airborne contamination. These sources include electrical generators, dispenser islands at gasoline service stations and the exhaust of automobiles.

Isolate electrical generators and fuel cans from all sampling equipment during storage, transport and field sampling. Wear disposable gloves when refueling generators and automobiles. Immediately discard the gloves after re-fueling equipment.

Change gloves when moving from one sampling location to the next. This is particularly important if floating NAPL is present in a well.

When the water table rises, the ground water may cover up the NAPL. When the water table goes down, it may expose NAPL to soil gas. Sample the soil gas more than one time. If possible, one sampling event should be when the water table is at or near a seasonal low.



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