Proposed Regulatory Framework for Evaluating the Methane Hazard due to Vapor Intrusion

Bart Eklund
URS Corporation, PO Box 201088, Austin, TX 78720-1088

ABSTRACT

Guidance for addressing vapor intrusion of air toxics is relatively well established and the guidance may address petroleum hydrocarbons and chlorinated solvents as separate categories of pollutants requiring distinct conceptual site models. Guidance for methane (CH_4) at VI sites, however, is non-existent, overly vague, or conceptually flawed throughout most of the US. The evaluation of methane at VI sites is fundamentally different than the evaluation of VOCs and requires a different conceptual site model. Unlike VOCs, there is no fixed starting mass of methane at a site – methane can be generated *in situ* over time. Unlike VOCs, any methane hazard is acute rather than chronic. The relative importance of diffusive versus advective transport also is a key difference.

In this paper, existing regulations and guidance for methane are summarized, along with an overview of the fate & transport of methane in shallow soils. The general conditions that have led to historical methane explosions due to VI are described. The specific types of information that should be collected at a given site to evaluate methane hazard are listed and described. Finally, a decision-making framework for evaluating methane hazard is presented.

INTRODUCTION

Although methane is non-toxic and therefore not a long-term human health risk, it can pose a risk of explosion when present in the atmosphere or indoor air at concentrations between the lower explosive limit (LEL) of 5% and the upper explosive limit (UEL) of 15%. For an explosion to occur, both oxygen and an ignition source must be present in conjunction with methane in the explosive range in a confined space. Flammability limits and explosive limits are equivalent terms and the lower flammability limit is equal to the lower explosive limit.

Methane is often present in the unsaturated zone, especially in wet, organic soils and the probability of detecting methane tends to increase with increasing depth below ground surface. This is because biogenic methane may be produced in the subsurface via anaerobic biological processes. Even “clean” fill soil can generate methane if it has some organic fraction and is wet and devoid of oxygen. The biogas produced by microbes in the subsurface consists of roughly 50% methane and 50% carbon dioxide. Any bubble of biogas or soil gas readings taken near the location where biogas is produced may contain relatively high concentrations of methane. These soil gases will not explode *in-situ* in the subsurface soils, but can create hazards if a sufficient volume of gas migrates into enclosed or poorly ventilated spaces where ignition sources are present.

DISCUSSION

The following discussion addresses the differences in conceptual site models for VI evaluations involving methane versus those involving VOCs, the physical properties of methane, the fate and transport of methane in soil, and existing regulations for methane. The key decision points for regulating VI of methane are listed and a framework for evaluating methane hazard is given.

Conceptual Model for Methane versus VOCs

Potential vapor intrusion of methane is fundamentally different than potential vapor intrusion of VOCs for several reasons, as summarized below.

Table 1. Comparison of VOCs and Methane for Vapor Intrusion

VOCs	Methane
Given starting mass	No given starting mass
Mass flux is related to concentration in soil gas	Concentration in soil gas is not a good proxy for mass flux
Focus on long-term average concentrations	Focus on short-term maximum concentrations
Typical attenuation factors are ~10^{-3} or lower	Attenuation factor must be $\geq$0.05 to reach 5% indoors
Transport via diffusion with advection important near buildings	Transport via advection is the main concern
Soil gas levels for some VOCs inversely proportional to oxygen levels	Soil gas levels for methane inversely proportional to oxygen levels

For VOC releases, we start with a given mass of VOCs in the subsurface and this tends to slowly decrease over time due to degradation, volatilization, and other processes. For methane, however, gas production can start whenever conditions are conducive as discussed later in this section.

In VI studies, it is common practice to use concentration data and compare indoor concentrations to outdoor concentrations, indoor concentrations to soil gas concentrations, and so forth, and draw conclusions based on these comparisons. In such comparisons, it is important to recognize that concentration is used as a surrogate, or proxy, for what is truly important, which is mass flow. For gas transport, mass flow is concentration multiplied by gas flow rate. We usually focus on concentration because: 1) flow rate is difficult to measure and 2) we can make conservative assumptions about flow rate (e.g., vapor intrusion is 5 L/min into a residential sized building, building ventilation is about 0.5 air changes per hour [ACH], etc.).

For VOCs the concentration present in soil gas is directly related to the potential risk. In general, the higher the VOC concentration in soil gas, the greater the potential for indoor air impacts due to vapor intrusion. For methane, this is not the case. Even small rates of methanogenesis will result in soil gas concentrations approaching 50% at the point of generation. There is essentially no correlation between methane gas production rates and methane concentrations in soil gas at the point of generation.

With VOCs, the focus is almost always on chronic exposure and therefore VI evaluations address long-term average concentrations. For methane, we're concerned about the worst-case short-term conditions. Typical attenuation factors relating indoor air concentrations to shallow soil gas concentrations suggest that, *on average*, methane will never be a problem. This is true, of course, but not meaningful. The average indoor air concentration will not exceed the LEL, but any one, short-term event can be a problem.

Investigations of past methane explosions invariably show that pressure-driven (advective) flow occurred. If a utility line or pipeline has a break, large volumes of gas under high pressure can be released and move through the soil. Similarly, the large gas generation that occurs at municipal solid-waste (MSW) landfills can result in pressure-driven flow into overlying or nearby buildings. In some cases, methane in soil gas can be induced to move by pressure gradients resulting from barometric pressure changes or infiltrating water.

No cases have been identified where diffusion alone directly led to an explosion within a building. In general, the rate of diffusion is too slow and the amount of ventilation air moving through buildings is too large for this to occur. For vapor intrusion of methane to lead to an explosion, large volumes of soil gas need to enter a building and this must occur over a relatively short period of time for the indoor concentration to reach or exceed 5%. Soil gas cannot exceed 100% methane, so an attenuation factor of 0.05 or greater is required for the indoor air concentration within a given building zone to reach the LEL. If preferential pathways are present, there may be increased potential for localized areas indoors to have elevated concentrations.

The same general concept holds true for oxygen depletion within a building due to soil gas intrusion. For soil gas to dilute indoor air from 20.8% oxygen down to unsafe levels (<19.5%), an attenuation factor of 0.06 or greater is required. Low oxygen levels in soil gas are common, but oxygen depletion of indoor air due to vapor intrusion of this soil gas is very rare. Similarly, high methane levels in soil gas are common, but elevated concentrations in indoor air due to diffusion of this soil gas are very rare. If diffusion alone were enough to lead to a VI problem for these compounds, these scenarios would not be very rare and some type of controls would be needed at many buildings.

Physical Properties of Methane

The physical properties of methane are of interest to the extent they affect its fate and transport. Methane is a single carbon compound (C_1) with a formula of CH_4 and a CAS number of 74-82-8. It has a molecular weight of 16 and therefore is lighter than air. At room temperature and 1 atm of pressure, the conversion factor between concentration and mass per volume is 1 ppm = 650 $\mu g/m^3$.

The explosive range for methane at 1 atm of pressure is 5% to 15%. The lower explosive limit (LEL) of 5% is higher than – for example – gasoline or the BTEX compounds. Soil acts as a natural flame arrestor, so methane in a typical soil matrix cannot explode. So, there is not LEL for soil gas (methane in a large void in the soil is a different scenario).

Methane has a water solubility of about 35 mg/L and the solubility increases with decreasing water temperature. Groundwater at depth can have confining pressure due to the overlying water. For each 10m of hydrostatic head, the effective pressure increases by 1 atm and the water solubility is roughly linear with pressure. Water that is saturated or supersaturated with methane can pose a hazard if it is drawn from depth to the surface in a water well or it flows into a mine or other void space and undergoes rapid volatilization.

Methane has a boiling point of -162 °C (-259 °F) and because it is not a liquid over the normal range of temperatures encountered in the environment, it doesn't have a vapor pressure (i.e., it is a gas at normal temperatures and pressures). The Henry's Law constant for methane is about 37,600 atm or 28 in dimensionless units. Therefore, the head space concentration above saturated water will be about 100%.

The diffusivity in air (D_a) of methane is 0.23 cm^2/s; this value is about twice as high as that of BTEX compounds. The rate of diffusion for a compound is proportional to its diffusivity in air, so the diffusion rate of methane is about twice as fast as diffusion of most VOCs.

The advection of methane is inversely proportional to its viscosity. The viscosity of methane is about 1.1E-04 g/cm-s, which is less than the viscosity of air (but within a factor of 2x). So, the pressure-driven flow of methane is somewhat faster than that of air.

Fate and Transport of Methane in Soil

Methane can be generated in soils (via microbes called methanogens) and methane also can be consumed in soils (via microbes called methanotrophs). All soils tend to be either net sources or sinks of methane. Within a given soil column, methane may be produced at depth where the soils are anaerobic and any vapors migrating upwards may be consumed within shallower soil layers where the soils are aerobic.

Methane production may begin in an area if the conditions are conducive. Subsurface conditions may change over time and methanogenesis may begin without a recent leak or spill. The generally accepted mechanisms for degradation of petroleum hydrocarbons in groundwater start with aerobic degradation. Once the available oxygen is gone, other process such as denitrification, iron reduction and sulfate reduction may occur. Only after these pathways have been exhausted will methanogenesis (i.e., biogas production) begin. Methanogenesis is not a favored pathway.

As indicated in Figure 1, the dominant pathway may change over time. A site may have relatively widespread dissolved NAPL, for example, but only isolated pockets of methane. This may be due, in part, to the specific micro-environments present across the site.

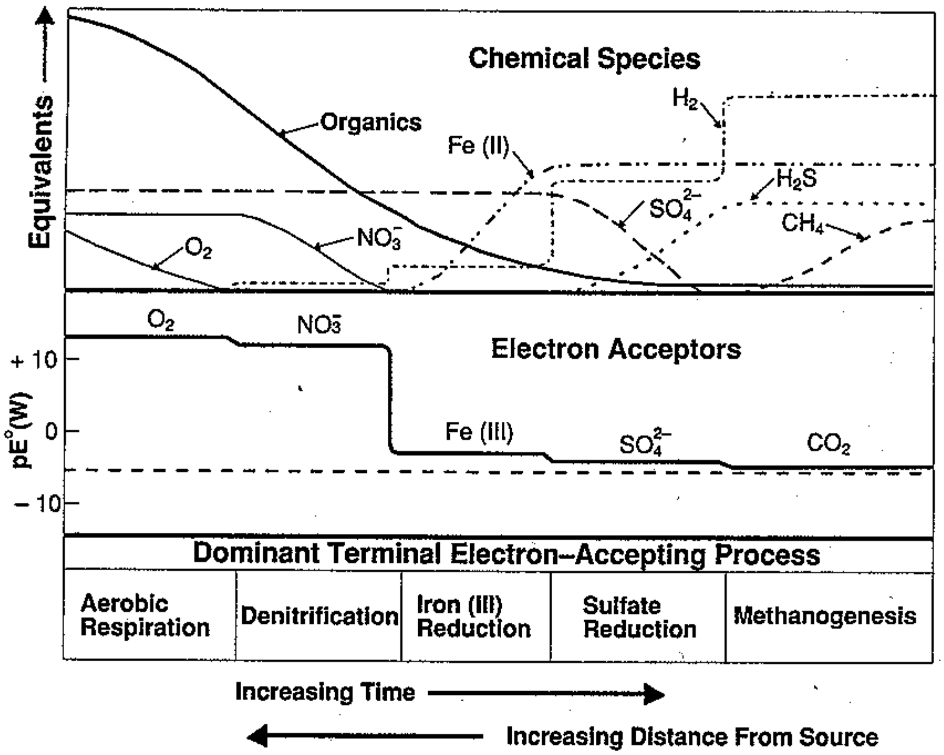

Figure 1. Conceptual Model of Degradation of Petroleum Hydrocarbons in Groundwater (Source: Weidemeier, et al., 1999).

The figure also suggests potential control strategies. Control evaluations often focus on source removal and engineering controls (venting) at buildings. Methane generation is a microbiological process and microbiological solutions merit consideration. For example, isolated pockets of methane could be vented to remove existing methane and nitrate added to prevent future methanogenesis. The efficacy and lifetime of such controls would need to be demonstrated, but may be far more cost-effective than engineering controls at buildings.

A huge amount of literature is available where the emission flux of methane has been measured from various types of soils or other sources. One use of this information is in developing global emission inventories for evaluating climate change. Based on previous literature searches, the emission fluxes of methane from various sources can be approximated as shown in Table 2. The highest reported methane flux was 14,000,000 $\mu g/m^2$-s from a crack at a landfill surface that allowed for preferential migration of landfill gas (Eklund, et al., 1995).

Table 2. Typical Emission Fluxes for Methane from Various Source Types

Emission Source	Typical Emission Flux ($\mu g\ CH_4 / m^2 - sec$)
Wetlands	0.1
Lakes	0.5
Tundra, moors	<3
Rice fields	6
Manure	>15
MSW landfills	<4,000

Given that biogas is generated in various moist soils and wastes and each bubble of biogas produced by microbes is roughly 50% methane, relatively high soil gas concentrations of methane may be encountered at some sites.

Removal mechanisms for methane in soil gas also can be an important process. Surface soils tend to be capable of destroying large amounts of methane via aerobic degradation. Oxidation rates up to about 1 L per minute per square meter are possible (40 g/m^2-hr). This is far higher than rates of diffusion through soil columns, so methane generally will be 100% removed if there is an aerobic soil layer beneath a building. So, for example, in houses with crawl spaces over dirt floors, no soil gas methane would be expected to reach the crawl space.

Methane Regulations

In general, methane in soil gas is not regulated in the US, but there are Federal regulations for certain specific types of sites. For municipal solid-waste (MSW) landfills, there is a requirement that methane must not exceed 25% of the LEL (i.e., 1.25% CH_4 in indoor air) within buildings or other facility structures and not exceed the LEL in soil gas at the property boundary (EPA, 2010). For tunnels and other underground construction, OSHA defines a potentially gassy operation as one where there is 10% or more of the LEL (i.e., 0.5% CH_4) measured 12 inches from the roof, face, floor, or walls for more than a 24-hr period (OSHA, 2010). The operation is considered to be gassy if $\geq$10% of the LEL is measured for three consecutive days. Local fire codes or building safety plans often include something similar to the EPA MSW action level (e.g., 20% or 25% of the LEL) as an action level for indoor air to trigger evacuation.

There are some existing regulations or guidance documents put forth in recent years for methane in soil gas in California. Portions of southern California have underlying thermogenic (fossil) CH_4. This methane originates deep in the earth and can move under pressure to the surface. For example, gas transport in 1985 resulted in an explosion at a retail store in Los Angeles. Pressures in the field at the explosion site were found to be 27 psi (750 in. w.c.) and perhaps 40 psi of pressure was present beneath the building immediately prior to the event (Sepich, 2008).

Gas continues to routinely reach the surface in the area, as can be observed in lagoons at the La Brea Tart Pits.

Action levels from various California regulations or guidance are summarized in Table 2. The existing methane guidance, as with vapor intrusion (VI) guidance in general, is evolving and existing guidance is often contradictory and not always based on valid technical assumptions. To give one example, the City of Los Angeles regulations can be interpreted to call for remedial action at sites "*given methane concentrations below 100 ppmv, even if the methane is not under pressure*." The 100 ppm value is <1% of the lower explosive limit (LEL) for methane in indoor air. Such regulatory soil gas action levels have been described as "*a reversal of science and truly indefensible in light of present knowledge*" (Sepich, 2008). In general, the California documents are considered to be overly conservative and are not good templates for developing a regulatory framework for methane.

Table 3. Example Soil Gas Action Levels in California Regulations / Guidance

Document	Intended Application	Soil Gas Action Level	Recommended Action
CA DTSC (2005)	School property	1,000 ppm methane or ΔP = 0.1 psi (2.8" H_2O)	Further investigation
		5,000 ppm methane or ΔP = 0.5 psi (14" H_2O)	Periodic monitoring or other further response
		ΔP = 1 psi (28" H_2O) on a sustained basis	High risk site. Controls should be considered.
City of LA (2004)	New buildings and paved areas in certain zones	>12,500 ppm methane	Mitigation system
		5,001 to 12,500 ppm	Active sub-slab system if ΔP is >2" H_2O
		≤5,000 ppm methane	Passive sub-slab system
County of Riverside (2004)	New development	>15,000 ppm methane	Include any remediation required by the Engineer of record
Orange County (2008)	New development near oil/gas well, gas seepage zone, or MSW landfill	5,000 ppm	Mandatory mitigation for all buildings within 300 ft.
		>12,500 ppm	Mitigation plan for all buildings within 300 ft.
County of San Diego (2002) [Repealed in 2005]	New development that uses fill dirt	12,5000 ppm methane	Mitigation

Note that pressure is a parameter of interest in addition to concentration in some cases. One atmosphere (atm) of pressure:

- = 101,300 Pascals (Pa)
- = 1013 millibars (mbar)
- = 29.9 inches of mercury ("Hg)
- = 1033 centimeters of water (cm H_2O)
- = 407 inches of water (in. H_2O)(in. w.c.)
- = 14.7 psi
- = 760 mm Hg (Torr)

DECISION MATRIX

There are three key parameters for evaluating hazards related to soil gas and these parameters should be considered in conjunction with one another rather than independently:

1. Methane concentration in soil gas;
2. Differential pressure; and
3. Whether or not the soil gas is saturated with methane or biogas.

If the soil gas concentration of methane is low enough, no hazard exists. A *de minimis* level for screening purposes is 1.25% (12,500 ppm). Any methane concentrations below this level are trivial in terms of hazard. There is no concentration of methane in soil gas that is intrinsically unsafe, but methane concentrations above 40% in soil gas suggest that biogas production is locally significant and merits further investigation. The biogas produced by microbes is roughly one-half methane, so methane at high concentrations can be found in soils, even clean fill, if conditions are conducive for methanogenesis. For decision making purposes, it is important to determine if there is significant methane generation over a reasonably large area.

Diffusion of soil gas is not expected to result in an unsafe indoor environment; pressure-driven flow is necessary to move the volumes of gas required to result in indoor air approaching the LEL for methane. Therefore, differential pressure (ΔP) is an important variable to measure. If significant biogas production is underway, elevated pressures will be observed. A screening value of 2" H_2O has been proposed (Sepich, 2008). Pressures below this screening value are considered to be negligible and pressures above this screening value require further consideration. If the pressure exceeds 2" H_2O, methane soil gas control measures should be implemented. This might involve engineering controls at buildings of concern (e.g., venting systems) and/or source reduction (e.g., provide alternative electron receptors).

Differential pressure for a given site will be a function of the permeability of the soil. A given rate of biogas production will result in a lower differential pressure in more permeable soils. For example, differential pressures within MSW landfills tend to be <10" H_2O even though the rate of biogas production is high, because the waste material is highly permeable. The 2" H_2O rule-of-thumb results in a rate of advective transport that is about 30x higher than diffusive transport in soils with a permeability of 10^{-8} cm^2 (e.g., sandy soils). This screening value may need to be made more conservative for sites with soils that are more permeable than 10^{-8} cm^2.

Isolated “hot spots” of high methane concentration in soil gas generally are not a concern, but widespread elevated concentrations suggest that biogas production is or has been significant. At methane concentrations of 40% and above, biogas likely is being generated at a sufficiently high rate to completely displace other gases from the soil. Below this level, the gas production rate is likely to be too small to displace other gases from the soil pore spaces.[1] For added conservativeness, 30% can be used as a rule-of-thumb (rather than 40%). If a large reservoir of methane exists in the soil gas near a building, it may pose a potential hazard even if there is no on-going gas production or elevated differential pressure. Under certain circumstances, the methane can be induced to move (e.g., extremely low barometric pressure, methane flashing out of formerly confined groundwater, etc.). Therefore, if the soil gas surrounding a building is largely “whole” or undiluted biogas (e.g., if $CH_4 + CO_2$ are >90%), it would be prudent to mitigate even if the differential pressure was below the rule-of-thumb discussed above.

A generic framework for decision making that outlines the logic and thought process most often used in VI evaluations was developed and is presented in Table 3. The framework builds upon prior work by John Sepich and others. The decision matrix is based on a combination of indoor air data and shallow soil gas data. These are two very important lines of evidence, but are not the only lines of evidence that may need to be considered for a given building. So, the decision matrix cannot completely replace the typical case-by-case evaluation that considers all available information (e.g., soil gas oxygen levels) and is intended for informative purposes to illustrate the general thought process proposed for use in VI evaluations.

The general form of the matrix is based on that used by the New York State Department of Health in 2006. Recommended actions are given based on the measured values in indoor air and shallow soil gas. In this way, the matrix addresses both current conditions and future conditions (e.g., if the shallow soil gas concentrations are sufficiently high, action may be recommended even if the current indoor air quality is acceptable). Methane should be evaluated in terms of short-term, maximum effects rather than long-term, average conditions as is done for volatile organic compounds. Therefore, averaging of methane soil gas concentrations is not recommended and Table 1 is based on maximum measured values within or very near the building footprint. Nonetheless, it should be recognized that vapor intrusion of isolated pockets of methane will be mass-limited.

There are several assumptions inherent in Table 3. One, there is no soil gas methane concentration that is inherently dangerous. It is important to consider concentration, differential pressure, and the volume of methane present in the soil. Two, if methane levels indoors reach 1.25%, this requires immediate action, regardless of whether or not VI is contributing to the indoor air levels. This action level is 25% of the lower explosive limit for methane in indoor air and if this concentration is detected, it suggests that explosive conditions may exist somewhere

---

[1] Biogas consists largely of methane and carbon dioxide, with each present at roughly 40 to 60%. If biogas is produced in the soil at appreciable rates, the produced gas will displace any atmospheric or other gases that are present and be “undiluted.” If soil gas is not largely methane and carbon dioxide, the biogas production rate is assumed to be low. Low biogas production rates tend to be associated with low hazard potential. A methane concentration of 30% in soil gas is a conservative rule-of-thumb for assessing whether the soil gas is undiluted biogas or not.

in the building. Three, indoor methane values that equal or exceed 100 parts per million are sufficiently above typical background levels that it suggests a methane source is present. In such cases, it is prudent to further investigate to determine whether methane readings anywhere in the building approach the LEL of 5%. In many cases, elevated indoor concentrations are found to be due to unlit pilot lights or other indoor sources.

The decision matrix for methane is intended for commercial/industrial buildings, which are assumed to be slab-on-grade construction and have some form of ventilation. The decision matrix is not applicable small, unventilated spaces in the subsurface, such as utility vaults, which are more prone to vapor intrusion issues.

SUMMARY

Vapor intrusion of methane requires a different conceptual model than VI for petroleum hydrocarbons and chlorinated solvents. At this time, there is very little guidance for methane (CH_4) at VI sites and what guidance does exist is of limited usefulness. Relevant information about the basic underlying concepts of methane fate and transport is briefly summarized in this paper. A decision matrix is presented that can be used to "screen out" sites with minimal potential hazard.

ACKNOWLEDGEMENTS

The author wishes to thank John Sepich for his review of the paper and thoughtful comments. The author has benefited from the many insights provided over the last decade by Mr. Sepich and by Robert Legrand during numerous discussions regarding methane.

REFERENCES

CA DTSC. Department of Toxic Substances Control (DTSC). Advisory on Methane Assessment and Common Remedies at School Sites. June 16, 2005.

City of LA. Los Angeles Municipal Code, Ordinance No. 175790, Appendix D, City of Los Angeles – Methane Seepage Regulations. Effective date March 29, 2004.

County of Riverside, Building and Safety Department. Methane Design Guidelines. Memorandum from Nick Anderson to Building and Safety Staff. November 1, 2004.

County of San Diego. Ordinance No. 9466, An Ordinance Amending the Code of Regulatory Ordinances Related to Testing Requirements for Methane Gas on Projects with Mass Grading. March 13, 2002.

Eklund, B., E. Anderson, B. Walker, and D. Burrows. Determination of Landfill Gas Composition and Pollutant Emission Rates at Fresh Kills Landfill. US EPA Region II, EPA 902-R-95-001. December 1995.

New York State Department of Health (DOH). Guidance for Evaluating Soil Vapor Intrusion in the State of New York. October 2006.

Orange County Fire Authority. Combustible Soil Gas Hazard Mitigation, Guideline C-03. January 1, 2008.

OSHA. 29 Code of Federal Regulations Part 1926.800, Safety and Health Regulations for Construction, Underground Construction. Available at: http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=10790&p_table=STANDARDS Accessed May 5, 2010.

Sepich, J., Hazard Assessment by Methane CVP (Concentration, Volume, Pressure). Presented at the Sixth Annual Battelle Conference, Monterrey, California. May 19 to 22, 2008.

USEPA. 40 Code of Federal Regulations Part 258.23 [Resource Conservation and Recovery Act Subtitle D], Criteria for Municipal Solid Waste Landfills, Explosive Gases Control. Available at: http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=72cda062b68ac7e9da9f0a73cc05dd67&rgn=div5&view=text&node=40:24.0.1.4.38&idno=40#40:24.0.1.4.38.1 Accessed May 5, 2010.

Weidemeier, T., H. Rifai, C. Newell, and J. Wilson, 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface, Chapter 5 – Biodegradation Processes for Petroleum Hydrocarbons*. John Wiley & Sons.

KEYWORDS

Methane, vapor intrusion, soil gas, emission flux

Table 3. Decision Matrix for Methane in Soil Gas and Indoor Air

Shallow Soil Gas Conc. [a]	Indoor Air Concentration			
	None Available	**<0.01% (i.e. <100 ppm)**	**0.01 to <1.25%**	**$\geq$ 1.25%**
<1.25% to 5%	No further action	No further action	No further action [b]	Immediately notify authorities, recommend owner/operator evacuate building
>5% to 30% [c]	No further action unless ΔP >2 inches H_2O [b]	No further action unless ΔP >2 inches H_2O [b]	No further action unless ΔP >2 inches H_2O [b]	Immediately notify authorities, recommend owner/operator evacuate building
>30% [c]	Collect indoor air data	Evaluate on case-by-case basis	Evaluate on case-by-case basis	Immediately notify authorities, recommend owner/operator evacuate building

Footnotes:

[a] Maximum methane soil gas value for area of building footprint.

[b] Landowner or building owner/manager should identify indoor sources and reduce/control emissions. If no sources are found, additional subsurface characterization and continued indoor air monitoring are recommended.

[c] The potential for pressure gradients to occur in the future at a given site should be considered.

General Notes:

1. Table is intended for sites with existing buildings. To address future development, no further action is required if the shallow soil gas concentration is <30% and ΔP <2 inches H_2O.
2. If the combined soil gas concentrations of methane and carbon dioxide are $\geq$90%, mitigation should be considered.