

# Standard Guide for Evaluating Potential Hazard as a Result of Methane in the Vadose Zone<sup>1</sup>

This standard is issued under the fixed designation E2993; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

# 1. Scope

- 1.1 This guide provides a consistent basis for assessing site methane in the vadose zone, evaluating hazard and risk, determining the appropriate response, and identifying the urgency of the response.
- 1.2 *Purpose*—This guide covers techniques for evaluating potential hazards associated with methane present in the vadose zone beneath or near existing or proposed buildings or other structures (for example, potential fires or explosions within the buildings or structures), when such hazards are suspected to be present based on due diligence or other site evaluations (see 6.1.1).
- 1.3 Objectives—This guide: (1) provides a practical and reasonable industry standard for evaluating, prioritizing, and addressing potential methane hazards and (2) raises awareness of the key variables needed to properly evaluate such hazards.
- 1.4 This guide offers a set of instructions for performing one or more specific operations. This guide cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This guide is not intended to represent or replace the standard of care by which the adequacy of a given professional service should be judged, nor should this guide be applied without consideration of a project's many unique aspects. The word "Standard" in the title means only that the guide has been approved through the ASTM International consensus process.
  - 1.5 Not addressed by this guide are:
- 1.5.1 Requirements or guidance or both with respect to methane sampling or evaluation in federal, state, or local regulations. Users are cautioned that federal, state, and local guidance may impose specific requirements that differ from those of this guide;
- 1.5.2 Safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-

- priate safety and health practices and determine the applicability of regulatory limitations prior to use;
- 1.5.3 Emergency response situations such as sudden ruptures of gas lines or pipelines;
- 1.5.4 Methane entry into an enclosure from other than vadose zone soils (for example, methane evolved from well water brought into an enclosure; methane generated directly within the enclosure; methane from leaking natural gas lines or appliances within the enclosure, etc.);
- 1.5.5 Methane entry into an enclosure situated atop or immediately adjacent to a municipal solid waste (MSW) landfill;
- 1.5.6 Potential hazards from other gases and vapors that may also be present in the subsurface such as hydrogen sulfide, carbon dioxide, and/or volatile organic compounds (VOCs);
  - 1.5.7 Anoxic conditions in enclosed spaces;
  - 1.5.8 The forensic determination of methane source; or
- 1.5.9 Potential consequences of fires or explosions in enclosed spaces or other issues related to safety engineering design of structures or systems to address fires or explosions.
- 1.6 *Units*—The values stated in SI units are to be regarded as the standard.
- 1.6.1 *Exception*—Values in inch/pound units are provided for reference.
- 1.7 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

# 2. Referenced Documents

- 2.1 ASTM Standards:<sup>2</sup>
- D653 Terminology Relating to Soil, Rock, and Contained Fluids
- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D1946 Practice for Analysis of Reformed Gas by Gas Chromatography

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

- D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass
- D2487 Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System)
- D5088 Practice for Decontamination of Field Equipment Used at Waste Sites
- D6725 Practice for Direct Push Installation of Prepacked Screen Monitoring Wells in Unconsolidated Aquifers
- D7663 Practice for Active Soil Gas Sampling in the Vadose Zone for Vapor Intrusion Evaluations
- **E2600** Guide for Vapor Encroachment Screening on Property Involved in Real Estate Transactions
- F1815 Test Methods for Saturated Hydraulic Conductivity, Water Retention, Porosity, and Bulk Density of Athletic Field Rootzones
- 2.2 Other Standards:
- California DTSC, Evaluation of Biogenic Methane for Constructed Fills and Dairies Sites, March 28, 2012
- County of Los Angeles Building Code, Volume 1, Title 26, Section 110 Methane<sup>3</sup>
- ITRC Document VI-1 Vapor Intrusion Pathway: A Practical Guideline<sup>4</sup>
- ITRC Document PVI-1 Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management<sup>5</sup>
- EPA 530-R-10-003 Conceptual Model Scenarios for the Vapor Intrusion Pathway
- 29 CFR 1910.146 Permit-Required Confined Spaces<sup>6</sup>

#### 3. Terminology

- 3.1 Definitions:
- 3.1.1 This section provides definitions and descriptions of terms used in or related to this guide. An acronym list is also included. The terms are an integral part of this guide and are critical to an understanding of the guide and its use.
- 3.1.2 advection, n—transport of molecules along with the flow of a greater medium as occurs because of differential pressures.
- 3.1.3 *ambient air*, *n*—any unconfined portion of the atmosphere; open air.
- 3.1.4 *barometric lag*, *n*—time difference between changes in total atmospheric pressure (barometric pressure) and subsequent changes in total gas pressure measured at a specific point in the subsurface.
- 3.1.4.1 *Discussion*—Atmospheric pressure variations include routine diurnal highs and lows as well as changes associated with exceptional meteorological conditions (weather fronts). The time lag means that differential pressure between the surface and the subsurface point may be out of phase and may reverse (± relative to zero) with resulting reversals in soil gas flow direction over time between the shallow subsurface and the surface.
  - <sup>3</sup> Available from dpw.lacounty.gov.
- <sup>4</sup> Available from the Interstate Technology & Regulatory Council, http://www.itrcweb.org/Documents/VI-1.pdf.
- <sup>5</sup> Available from the Interstate Technology & Regulatory Council, http://www.itrcweb.org/PetroleumVI-Guidance/
- <sup>6</sup> Available from Occupational Safety and Health Administration (OSHA), 200 Constitution Ave., Washington, DC 20210, http://www.osha.gov.

- 3.1.5 *barometric pumping, n*—variation in the ambient atmospheric pressure that causes motion of vapors in, or into, porous and fractured earth materials.
- 3.1.6 *biogas*, *n*—mixture of methane and carbon dioxide produced by the microbial decomposition of organic wastes, also known as microbial gas.
- 3.1.7 *biogenic*, *adv*—resulting from the activity of living organisms.
- 3.1.8 *contaminant*, *n*—substance not normally found in an environment at the observed concentration.
- 3.1.9 *continuous monitoring, n*—measurements of selected parameters performed at a frequency sufficient to define critical trends, identify changes of interest, and allow for relationships with other attributes in a predictive capacity.
- 3.1.10 *dead volume*, *n*—total air-filled internal volume of the sampling system.
- 3.1.11 differential pressure, n—relative difference in pressure between two measurement points ( $\Delta P$ ).
- 3.1.11.1 *Discussion*— $\Delta P$  measurements are typically the differences between pressure at some depth in the vadose zone and pressure above ground at the same location (indoors or outdoors), but also could refer to the difference in pressure between two subsurface locations. A  $\Delta P$  measurement represents a pressure gradient between the two locations.
- 3.1.12 *diffusion*, *n*—gas transport mechanism in which molecules move along a concentration gradient from areas of higher concentration toward areas of lower concentration; relatively slow form of gas transport.
- 3.1.13 *effective porosity, n*—amount of interconnected void space (within intergranular pores, fractures, openings, and the like) available for fluid movement: generally less than total porosity.
- 3.1.14 *flammable range*, *n*—concentration range in air in which a flammable substance can produce a fire or explosion when an ignition source is present.
- 3.1.15 *fracture*, *n*—break in the mechanical continuity of a body of rock or soil caused by stress exceeding the strength of the rock or soil and includes joints and faults.
- 3.1.16 *groundwater*, *n*—part of the subsurface water that is in the saturated zone.
- 3.1.17 *hazard*, *n*—source of potential harm from current or future methane exposures.
- 3.1.18 *microbial*, *adv*—pertaining to or emanating from a microbe.
- 3.1.18.1 *Discussion*—The preferred term for nonthermogenic, nonpetrogenic methane such as from anaerobic activity in shallow soils or sanitary landfills is "microbial."
- 3.1.19 *moisture content*, *n*—amount of water lost from a soil upon drying to a constant weight expressed as the weight per unit weight of dry soil or as the volume of water per unit bulk volume of the soil.
- 3.1.20 *perched aquifer*, *n*—lens of saturated soil above the main water table that forms on top of an isolated geologic layer of low permeability.

- 3.1.21 *permeability, n*—ease with which a porous medium can transmit a fluid under a potential gradient.
- 3.1.22 *preferential pathway, n*—migration route for chemicals of concern that has less constraint on gas transport than the surrounding soil.
- 3.1.22.1 *Discussion*—Preferential pathways may be natural (for example, vertically fractured bedrock where the fractures are interconnected) or man-made (for example, utility conduits, sewers, and dry wells).
- 3.1.23 *pressure-driven flow, n*—gas transport mechanism that occurs along pressure gradients resulting from introduction of gas into the soil matrix.
- 3.1.23.1 *Discussion*—The flow of gas is from the region of high pressure to regions of lower pressure and continues until the gas pressure is equal or the flowpath is blocked. With advection, molecules are transported along with the flow of a greater medium. With pressure-driven flow, the introduced gas is the medium.
- 3.1.23.2 *Discussion*—In the vadose zone, elevated pressures in a given volume of soil can occur as a result of biogas generation at that location. Therefore, whether or not a given site has active biogas generation is an important consideration in evaluating methane hazard.
- 3.1.24 *porosity, n*—volume fraction of a rock or unconsolidated sediment not occupied by solid material but usually occupied by liquids, vapor, and/or air.
- 3.1.24.1 *Discussion*—Porosity is the void volume of soil divided by the total volume of soil.
- 3.1.25 *probe*, *n*—device designed to investigate and collect information from a remote location.
- 3.1.25.1 *Discussion*—As used in this guide, a point or methane test well used to collect information from within the vadose zone or subslab space of a building.
- 3.1.26 *purge volume*, *n*—amount of air removed from the sampling system before the start of sample collection.
- 3.1.26.1 *Discussion*—This is usually referred to in terms of number of dead volumes of probe (test well) casing or test well plus granular backfill total volume.
- 3.1.27 *repressurization*, *n*—unpressurized soil vapors can be pressurized by phenomena such as rapidly rising groundwater.
- 3.1.28 *risk*, *n*—probability that something will cause injury or harm.
- 3.1.29 *saturated zone, n*—zone in which all of the voids in the rock or soil are filled with water at a pressure that is greater than atmospheric.
- 3.1.29.1 *Discussion*—The water table is the top of the saturated zone in an unconfined aquifer.
- 3.1.30 *soil gas*, *n*—vadose zone atmosphere; soil gas is the air existing in void spaces in the soil between the groundwater table and the ground surface.
- 3.1.31 *soil moisture, n*—water contained in the pore spaces in the vadose zone.
- 3.1.32 *subslab vapor sampling, v*—collection of vapor from the zone just beneath the lowest floor slab of a building or below paving or soil cap.

- 3.1.33 *thermogenic*, *adj*—methane that is generated at depth under elevated pressure and temperatures during and following the formation of petroleum (for example, in oil fields).
- 3.1.34 *tracer*, *n*—material that can be easily identified and determined even at very low concentrations and may be added to other substances to enable their movements to be followed or their presence to be detected.
- 3.1.35 *tracer gas, n*—gas used with a detection device to determine the rate of air interchange within a space or zone or between spaces or zones.
- 3.1.36 *vadose zone*, *n*—hydrogeological region extending from the soil surface to the top of the principal water table.
- 3.1.36.1 *Discussion*—Perched groundwater may exist within this zone.
- 3.1.37 *vapor intrusion*, *n*—migration of a volatile chemical(s) from subsurface soil or water into an overlying or nearby building or other enclosed space.
- 3.1.38 *volatile organic compound, VOC, n*—an organic compound with a saturation vapor pressure greater than 10<sup>-2</sup> kPa at 25°C (Terminology D1356-14).
- 3.1.39 *water table*, *n*—top of the saturated zone in an unconfined aquifer.
  - 3.2 Acronyms and Abbreviations:
  - 3.2.1 ACH—air changes per hour
  - 3.2.2 CSM—conceptual site model
  - 3.2.3 FID—flame ionization detector
  - 3.2.4 HVAC—heating, ventilation, and air conditioning
- 3.2.5 In.  $H_2O$ —inches of water, a measure of pressure exerted by a column of water 1 in. (2.54 cm) in height; 1 in.  $H_2O$  equals approximately 250 Pa
- 3.2.6 *LEL*—lower explosive limit (same as lower flammable limit)
  - 3.2.7 Pa—Pascal, a measure of pressure
  - 3.2.8 ppmv—part per million on a volume basis
  - 3.2.9 psi—pounds per square inch
  - 3.2.10 QA/QC—quality assurance/quality control
- 3.2.11 *UEL*—upper explosive limit (same as upper flammable limit)
  - 3.2.12 *USEPA*—U.S. Environmental Protection Agency
  - 3.2.13 VOC—volatile organic compound
  - 3.2.14 v/v—by volume, as in percent by volume (% v/v)

# 4. Summary of Guide

- 4.1 This guide describes site screening, testing, data analysis, evaluation, and selection of mitigation alternatives.
- 4.2 Three-Tiered Approach—This guide provides an approach for assessing and interpreting site methane, evaluating hazard and risk, determining the appropriate response, and identifying the urgency of the response. A three-tiered approach is given that uses a decision matrix based on methane concentrations in the vadose zone and other factors such as indoor air concentrations, differential pressure measurements, and estimates of the volume of methane within soil gas near a

building to determine the potential hazard. The first tier consists of a site evaluation that can typically be done using existing, available information. This information is compiled, reviewed, and used to develop a conceptual site model (CSM). The CSM should describe and summarize the source of any methane that is present, vadose zone conditions (for example, depth to groundwater and soil type), size of impacted area, design and use of any existing buildings, exposure scenario, and other relevant lines of evidence for a given site. A decision matrix is applied to get an initial prediction of hazard. For sites in which potentially significant data gaps are identified during the Tier 1 review, the second tier consists of a refined site evaluation. Additional field work is performed to address the data gaps. The results are compared with the CSM and the CSM revised, as necessary. The decision matrix is again applied to the new, expanded data set to get an updated prediction of hazard. If it is determined that more data are needed, the third tier consists of a special case evaluation. For all three tiers, the path forward at any point should respect applicable regulatory guidance and consider risk management principles, technical feasibility, and community concerns.

- 4.2.1 The evaluation process is typically implemented in a tiered approach involving increasingly sophisticated levels of data collection, analysis, and evaluation. Users may choose to proceed directly to the most sophisticated tier, to pre-emptive mitigation, or to routine monitoring based on site-specific circumstances.
- 4.2.2 For some sites, a limited number of samples may not be sufficient to address potential hazard because there are (1) significant potential methane source(s) in the vicinity of the site (for example, a large mass of buried organic matter such as plants, wood, etc.) (2) high-permeability preferential pathways present that may result in higher than typical rates of vapor transport (for example, gravel trench for utility lines), (3) relatively high permeability soils (for example, sand or gravel) with insufficient moisture to support methanotrophic bacteria, or (4) changes in groundwater elevation over short time periods, which can create pressure gradients in the vadose zone. For such sites, presumptive mitigation or Tier 3 evaluation (for example, continuous or regular monitoring) should be considered.
- 4.3 Site Categorization—This guide is designed to promote rapid site characterization so that low-risk sites can be identified and efficiently removed from further evaluation. Conversely, high-risk sites can be identified and appropriate follow-up actions taken promptly. This guide focuses on Tier 1 and 2 evaluations. Special case evaluations (Tier 3) are generally outside the scope of this guide, but applicable tools and considerations are described for information purposes.

# 5. Significance and Use

5.1 Several different factors should be taken into consideration when evaluating methane hazard, rather than, for example, use of a single concentration-based screening level as a de-facto hazard assessment level. Key variables are identified and briefly discussed in this section. Legal background information is provided in Appendix X3. The Bibliography includes

references where more detailed information can be found on the effect of various parameters on gas concentrations.

- 5.2 Application—This guide is intended for use by those undertaking an assessment of hazards to people and property as a result of subsurface methane suspected to be present based on due diligence or other site evaluations (see 6.1.1).
- 5.2.1 This guide addresses shallow methane, including its presence in the vadose zone; at residential, commercial, and industrial sites with existing construction; or where development is proposed.
- 5.3 This guide provides a consistent, streamlined process for deciding on action and the urgency of action for the identified hazard. Advantages include:
- 5.3.1 Decisions are based on reducing the actual risk of adverse impacts to people and property.
- 5.3.2 Assessment is based on collecting only the information that is necessary to evaluate hazard.
- 5.3.3 Available resources are focused on those sites and conditions that pose the greatest risk to people and property at any time.
- 5.3.4 Response actions are chosen based on the existence of a hazard and are designed to mitigate the hazard and reduce risk to an acceptable level.
- 5.3.5 The urgency of initial response to an identified hazard is commensurate with its potential adverse impact to people and property.
- 5.4 Limitations—This guide does not address potential hazards from other gases and vapors that may also be present in the subsurface such as hydrogen sulfide, carbon dioxide, and/or volatile organic compounds (VOCs) that may co-occur with methane. If the presence of hydrogen sulfide or other potentially toxic gases is suspected, the analytical plan should be modified accordingly.
- 5.4.1 The data produced using this guide should be representative of the soil gas concentrations in the geological materials in the immediate vicinity of the sample probe or well at the time of sample collection (that is, they represent point-in-time and point-in-space measurements). The degree to which these data are representative of any larger areas or different times depends on numerous site-specific factors. The smaller the data set being used for hazard evaluation, the more important it is to bias measurements towards worst-case conditions.
- 5.5 Variables and Site-Specific Factors that May Influence Data Evaluation:
- 5.5.1 Gas Transport Mechanisms—Methane migration in soil gas results from pressure-driven flow, advection and diffusion. Advective transport and pressure-driven flow has been associated with methane incidents (for example, fires or explosions), whereas no examples are known of methane incidents resulting from diffusive transport alone. Therefore, diffusion is not considered a key transport mechanism when evaluating methane hazard.

- 5.5.1.1 The potential for significant rates of soil gas transport can often be recognized by relatively high differential pressures (for example, >500 Pa [2 in. H<sub>2</sub>O]), high concentrations of leaked or generated gas, and concurrent displacement of atmospheric gases (nitrogen, argon) from the porous soil matrix.
  - 5.5.2 Effect of Gas Transport Mechanisms:
- 5.5.2.1 Near-Surface Advection Effects—Within buildings, across building foundations, and in the immediate subsurface vicinity of building foundations, advective flow may be driven by temperature differences, the on-off cycling of building ventilation systems, the interaction of wind and buildings, and/or changes in barometric pressure. These mechanisms can pump air back and forth between the soil and the interior of structures. The effects may be significant in evaluation of VOC or radon migration between buildings and the subsurface, but are relatively minor factors in evaluation of methane migration and hazard.
- 5.5.2.2 Source Zone Flow Effects—Biogenic (microbial) gas generation (methanogenesis) results in a net increase in molar gas volume near the generation source. The resulting increased gas pressure causes gas flow away from the source zone. This gas flow typically originates near sources of buried organic matter. Pressure-driven flow can also result from pressurized subsurface gas sources including leaks from natural gas distribution systems, subsurface gas storage, or seeps from natural gas reservoirs. The evaluation of pressurized sources of gas themselves (for example, pipelines, reservoirs, or subsurface storage) is outside the scope of this guide (see 1.5.3 1.5.5).
- 5.5.2.3 Subsurface soil gas pressure change can also occur in other instances, such as with a rapidly rising or falling water table in a partially confined aquifer or barometric pumping of fractured bedrock or very coarse gravel. This effect may occur in conjunction with advection of either dilute or high-concentration soil gases and may be irregular or intermittent. The CSM should consider the potential for induced pressure-driven flow (which is sometimes referred to as repressurization).
- 5.5.3 Effect of Land Use—Combustible soil gas is a concern mostly for sites with confined habitable space because of the safety risk. Combustible soil gas can also be a concern at sites with other types of confined spaces, such as buried vaults where a source of ignition may be present.
- 5.5.4 *Pathways*—Pathways into buildings from the soil can include cracks in slabs, unsealed space around utility conduit penetrations, the annular space inside of dry utilities (electrical, communications), elevator pits (particularly those with piston wells), basement sumps, and other avenues.
- 5.5.5 Effect of Hardscape and Softscape—Any capping of the ground surface can impede the natural venting of soil gas. Hardscape and well irrigated softscape both present barrier conditions. Existing hardscape/softscape conditions should be noted during soil gas investigations. Proposed hardscape/softscape conditions should be considered when formulating alternatives for action at sites where methane hazard is to be mitigated.
- 5.5.6 Effect of Soil Physical Properties—The diffusion of gas through soil is controlled by the air-filled porosity of the

- soil, whereas the advection and pressure-driven flow of gas through soil is controlled by the permeability of the soil. Two soils can have similar porosities but different permeabilities and vice-versa. The effective porosity of a soil may be different than the total porosity depending on whether the soil pores are connected or not. For methane transport, advective and pressure-driven flow is of much more concern than diffusive flow, so permeability is a more important variable than porosity. Large spaces such as fractures in fine-grained soils can impart a high permeability to materials that would otherwise have a low permeability. Soil moisture can reduce the air-filled porosity of soil and the gas permeability thereby reducing both diffusive and advective flow of soil gas.
- 5.5.7 Effect of Environmental Variables—A number of environmental variables can affect the readings taken in the field and can be important in interpreting the readings once taken. The effect of environmental variables tends to be greatest for very shallow measurements in the vadose zone and typically is of limited importance at depths of 1.5 m and greater.
- 5.5.8 Atmospheric Pressures and Barometric Lag—A falling barometer may leave soil gas under pressure as compared with building interiors enabling increased soil gas flux out of the soil and into structures. The interpretation of barometric lag data should take into account the type of soil. Barometric lag is most pronounced in tight (clayey) soils in which the flow of gases is retarded; barometric lag is least pronounced in granular (sandy) soils that provide the greatest permeability for the flow of gas. The potential for pressure-driven gas transport through soil is significant only for permeable soil pathways.
- 5.5.9 *Precipitation*—Normal outdoor soil gas venting (that is, emissions at soil surface) is impeded when moisture fills the surface soil pore space. Infiltrating rainwater may displace soil gas and cause it to vent into structures. Increases in soil moisture following rain or other precipitation events can lead to enhanced rates of biogas generation, which may be evaluated through repeated measurements.
- 5.5.10 Effect of Sampling Procedures—Sampling probes (test wells) typically are designed to identify soil gas pressures and maximum soil gas concentrations at the point of monitoring. The sequence of steps (for example, purging, pressure and concentration readings, and so forth) can affect the results. For differential pressure measurements, gages capable of measuring 500 Pa (2 in. H<sub>2</sub>O) may be used. Ideally, the gage or gages should be capable of measurements over a range of pressures (for example, 0 to 1,250 Pa (0 to 5 in. H<sub>2</sub>O)) and have a resolution of at least 25 Pa (0.1 in. H<sub>2</sub>O). See the Bibliography for references on equipment for concentration and differential pressure measurements. Initial readings of pressure should be taken before any gas readings, as purging can reduce any existing pressure differential and steady-state conditions may not be reestablished for some time afterwards. Soil gas pressures and soil gas concentrations should also be measured after purging. The recovery, or change of pressure with time, may also be of interest. Gas pressure readings taken in groundwater monitoring wells may not be representative of vadose zone pressures.
- 5.6 Applicability of Results—Instantaneous data from monitoring probes represent conditions at a point in space and time.

Worst-case, short-term impacts are of interest in a methane evaluation because of the acute risk posed by methane. Single-sampling events in which data are collected from a number of points at different locations may be sufficient if there is a robust CSM (that is, accounting for worst-case conditions) and the site is well understood. If site results are inconsistent with the CSM, additional data may be needed to address uncertainties and increase the statistical reliability and confidence in the results.

# 6. Approach to Methane Hazard Evaluation

#### 6.1 Decision Framework:

6.1.1 Investigations may be triggered by site-specific findings (for example, observations of bubbling at ground surface or in water wells; measurement of methane in soil gas; odors; or, in extreme cases, fire or explosion or both) or may result from planned studies (for example, methane evaluations pursuant to property transfer, property refinance, or during the application process for a building permit). Investigation of methane in soil may also follow detection during other investigations, such as in confined space screening (29 CFR 1910.146) or environmental investigation of chemical-impacted soils and groundwater. The general process is shown in Fig. 1. The volume of gas that is important will depend on

the size of the building footprint. In general, the greater the spatial extent of soil gas with elevated methane, the greater the potential for vapor intrusion of methane to be an issue. A single, isolated hot spot of 5 to 30 % methane is unlikely to result in an indoor air issue.

6.1.2 Decision making uses a matrix of soil gas and indoor air values to address both current risk and potential future risk (see Table 1). The matrix is a risk management approach that uses conservative screening values for methane concentration and differential pressure to rank site hazard. The available volume of soil gas containing elevated levels of methane also is a consideration. It is important to recognize that the values are guidelines and not absolute thresholds. Concentrations and pressure need to be considered in terms of the CSM. The decision matrix shown in Table 1 is a suggested starting point and should be adjusted as appropriate for site-specific conditions. The 500 Pa (2 in. H<sub>2</sub>O) criterion for ΔP is based on measurements in the vadose zone at a depth or interval of 1.5 m (for example, difference between pressure measurements 1.5 m below ground surface and ambient air). For measurements at 1.5 m or greater, temporal variability is typically not significant. However, for shallower measurements or measurements at sites with highly permeable matrices, the potential for temporal variability warrants further consideration.

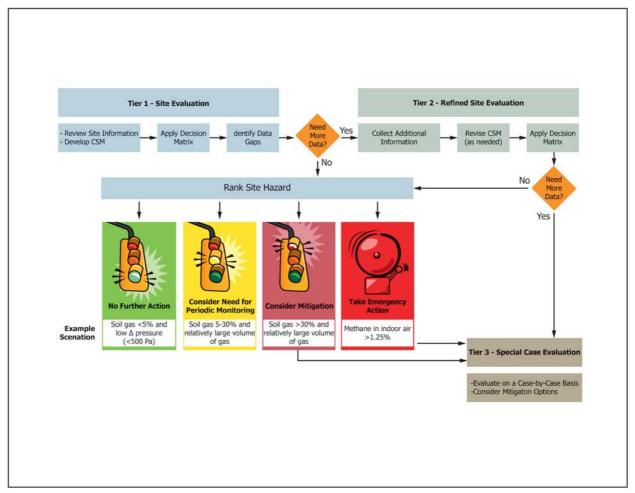


FIG. 1 Tiered Evaluation Process

#### TABLE 1 Suggested Default Decision Matrix for Methane in Soil Gas and Indoor Air

Note 1—Table based on Eklund, 2011 (1) and Sepich, 2008 (2)<sup>D</sup>. See also Appendix X2. Table is intended for sites with existing buildings. To address future development, no further action is recommended if the shallow soil gas concentration is <30% and ΔP <500 Pa.

Note 2—If the combined soil gas concentrations of methane and carbon dioxide are ≥90%, mitigation should be considered.

Note 3—Soil gas outside the building footprint but within a radius of 60 m (200 ft) of the building may be of interest. The total mass of methane present should be considered (that is, concentration  $\times$  volume).

Shallow Soil Gas Conc. <sup>A</sup>	Indoor Air Concentration						
Stidilow Soil Gas Colic.	No Measurements Available	<0.01% (that is <100 ppm)	0.01 to <1.25%	>1.25%			
<1.25% to 5%	No further action	No further action	No further action <sup>B</sup>	Immediately notify authorities, recommend owner/operator evacuate building			
>5% to 30% <sup>C</sup>	No further action unless $\Delta P$ >500 Pa <sup>B</sup>	No further action unless $\Delta P$ >500 Pa <sup>B</sup>	No further action unless $\Delta P$ >500 $Pa^B$	Immediately notify authorities, recommend owner/operator evacuate building			
>30% <sup>C</sup>	Collect indoor air data	Evaluate on case-by-case basis	Evaluate on case-by-case basis	Immediately notify authorities, recommend owner/operator evacuate building			

A Maximum methane soil gas value for area of building footprint. Shallow soil gas refers to soil gas in the vadose zone within the top 10 m (33 ft) of soil below ground

- 6.1.3 The screening values for methane concentration are, in most cases, derived from the lower flammable limit for methane in air, that is, 5 %, since methane hazard is related to flammability rather than toxicity. Concentration, pressure, and volume should be taken into account. Physical and toxicological characteristics of methane are summarized in Appendix X1. Additional discussion of the screening values is provided in Appendix X2. Note that for soil gas, methane concentration alone is insufficient to evaluate potential hazard. Information on pressures and volumes is also essential.
- 6.1.4 Screening values are location specific. That is, soil gas screening values should be used for comparison with site soil gas results and indoor air/confined space screening values should be compared only with indoor air/confined space results (for example, Table 1).
- 6.2 Develop Conceptual Site Model (CSM)—The user is required to identify the potential primary sources of methane in the subsurface, potential receptor points, and significant likely transport pathways from the primary sources to the receptors. Various vapor intrusion guidance documents describe the development of CSMs (ITRC Document VI-1 and PVI-1 and EPA/OSWER), though not for methane sites. The CSM provides a framework for the process of evaluating methane hazard. The CSM summarizes what is known about the site in terms of source, depth to groundwater, geology, data trends, receptors, building design and operation, and so forth. The CSM should consider reasonable worst-case conditions such as falling and low relative barometric pressure conditions or potential soil gas repressurization. The results of any further investigations are compared with the CSM to see whether or not the results are consistent with the expectations derived from the CSM. If the results are found to differ in material ways from these expectations, the CSM will require modification.
- 6.2.1 Source—Methane is produced by two primary mechanisms: thermogenic and microbial (see Appendix X1). Thermogenic or "fossil" methane typically originates from petroleum deposits at depths generally far below the vadose zone. Natural gas is largely thermogenic methane and may occur in coal mines, oil and gas fields, and other geological formations. Thermogenic methane, once produced, is carried in natural gas transmission and distribution lines. Microbial or "biogenic" methane typically is generated at relatively shallow depths by the recent microbial decomposition of organic matter in soil. The "biogas" produced is essentially all methane and carbon dioxide. If CH<sub>4</sub> + CO<sub>2</sub> approach 100 %, the gas is said to be "whole" or "undiluted." Microbial methane is a product of decomposition of organic matter in both natural (for example, wetlands and river and lake sediments) and man-made settings (for example, sewer lines, septic systems, and manure piles).
- 6.2.2 Transport—Methane will migrate along pressure gradients from areas where it is present at higher pressures to areas where it is present at lower pressures, or along concentration gradients, also from high to low. The primary mechanism for significant methane migration in subsurface unsaturated soils is pressure-driven flow. Diffusion also occurs but at rates too low to result in unacceptable indoor air concentrations under reasonably likely scenarios. Soils can be a significant sink for methane, with aerobic biodegradation also an important fate and transport consideration.
- 6.2.3 Receptors—Residential, commercial, and industrial buildings, and the individuals therein, are the primary receptors of interest. Buildings typically have roughly 0.5 to 1 air changes per hour (ACH) and a relatively high rate of vapor intrusion is necessary for the indoor atmosphere to approach the lower flammability limit for methane of 5 %. Therefore, portions of the buildings with lower rates of air exchange are of most interest, such as closed cabinets beneath sinks, closets,

surface.

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 should be considered.  $\Delta P$  refers to pressure gradients in the subsurface at a depth or interval of 1.5m. For gravel or other highly permeable matrices, use of a more conservative criterion less than 500 Pa (2 in. H<sub>2</sub>O) may be appropriate.

<sup>&</sup>lt;sup>C</sup> The potential for pressure gradients to occur in the future at a given site should be considered.

<sup>&</sup>lt;sup>D</sup>The boldface numbers in parentheses refer to a list of references at the end of this standard.

and stagnant areas of basements. Utility vaults and other small, poorly ventilated subsurface structures may be viewed as receptors or as worst-case indicators of potential conditions in nearby buildings.

- 6.3 Use a Tiered Approach—The evaluation process is typically implemented in a tiered approach involving increasingly sophisticated levels of data collection, analysis, and evaluation. Upon evaluation of each tier, the user reviews the results and recommendations and decides whether more detailed and site-specific analysis is necessary to refine the hazard analysis (see Fig. 1). Fires or explosions caused by intrusion of methane gas from the soil are relatively rare events, so it is assumed that most sites will be "screened out" by this process and result in no further action. (Such events, when they do occur, may be due to large leaks from natural gas transmission or distribution lines, which are outside the scope of this guide. This guide could be used, however, to evaluate residual hazard after the lines have been repaired.)
- 6.3.1 Site Evaluation (Tier 1)—Site information is assembled and evaluated.
- 6.3.1.1 At a minimum, this should include a desktop review of source (7.1.1 7.1.3), pathway (7.1.6 and 7.1.7) and receptor (7.1.8) characteristics, and collection and review of site soil gas measurements.
- 6.3.1.2 A conceptual site model is developed specific to methane (see 6.2).
- 6.3.1.3 An initial evaluation of hazard is made using Table
- 6.3.1.4 The user should select a response action option that best addresses the short-term concerns for the site, if any. Note that the initial response actions listed in Table 1 are not necessarily comprehensive or applicable for all sites.
- 6.3.1.5 If the initial data evaluation indicates data gaps, collect additional soil gas or other data, as needed, and reevaluate based upon the Fig. 1 and Table 1. For example, in many cases, methane concentration data are available at this stage, but information about carbon dioxide and oxygen concentrations, and differential pressures, may not exist. The amount of organic material in the subsurface that is potentially still subject to microbial degradation also may not be well characterized unless adequate soil-boring logs are available.
- 6.3.2 Refined Site Evaluation (Tier 2)—In many cases, additional site-specific data will be needed to support an evaluation of methane hazard. These additional data needs may include any or all of the following: (1) speciating the soil gas including measuring methane, carbon dioxide, higher order hydrocarbons, hydrogen sulfide, oxygen, nitrogen and argon in the soil gas to determine if the biogas is diluted or undiluted; (2) measuring differential pressures; (3) measuring methane at additional locations to determine the spatial distribution of methane in the subsurface and characterize better the potential volume/mass of methane present; (4) repeat measurements to help identify and quantify temporal variability of methane concentrations and pressures; and/or (5) collecting data to estimate methane emissions and flux (CA DTSC, 2012).
- 6.3.2.1 The amount of additional measurement data needed will depend on the initial evaluation of hazard and consistency

- of site measurements with the CSM. In general, the greater the uncertainty and potential risk, the more likely additional data will be needed.
- 6.3.2.2 If the data evaluation indicates data gaps, collect additional soil gas or other data and reevaluate based upon Fig. 1 and Table 1. Considerations for sampling and analysis are provided in Section 7 and the Bibliography.
- 6.3.3 Special Case Evaluation (Tier 3)—Some sites will require further investigation beyond the refined site evaluation because of remaining data gaps, certain atypical features of the CSM (for example, ongoing biogas generation, preferential pathways), or other risk management considerations. These sites should be evaluated on a case-by-case basis by an experienced professional. Such evaluations are outside the scope of this guide.
- 6.3.4 If there is still uncertainty, more advanced methods of site analysis may be used, such as (1) mathematical modeling, (2) continuous monitoring techniques, or (3) other acceptable methods. See the Bibliography.
- 6.4 Exiting the Investigative Phase—Exit points are summarized in Fig. 1 and Table 1. At any time, if there is still uncertainty in whether hazard exists, or if it is simply not desired to do further site evaluation, then mitigation or continued monitoring can be considered.
- 6.5 *Hazard*—Methane is not flammable directly within a typical soil matrix; the primary hazard is the flammability of methane in air (that is, in buildings). Methane in the soil gas is of concern if it migrates into enclosed spaces and mixes with air (including oxygen) to form a mixture within or above the flammable range: 5 to 15 %.
- 6.6 Classify Sites and Situations-A classification, or ranking, system is applied based on the potential hazard and the urgency of need for response action (see Fig. 1). The classification is based on information collected and reviewed during the site evaluation or refined site evaluation. Response actions are associated with classification and are to be implemented concurrently with an iterative process of continued assessment and evaluation. The classification system is applied at the initial stage of the process and also at any stage of the process in which site conditions change or new information is added. As the user gathers data, site conditions are evaluated and an initial response action implemented consistent with site conditions. The process is repeated when new data indicates a significant change in site conditions. Site urgency classifications are indicated in Table 1 along with example initial response actions. The user should select a response action option that best addresses the short-term concerns for the site. Note that the initial response actions listed in Table 1 are not necessarily comprehensive or applicable for all sites. Actual emergency response to an ongoing incident involves measurement of ambient gas levels at structures, points of emission from ground surface, etc. Normally, fire department and/or emergency response professionals will be involved in this effort and decision making. Emergency response monitoring is beyond the scope of this guide.

- 6.7 Implement Response Action, if Applicable—Response actions are selected to mitigate the identified hazard at the identified receptor. Consult Guide E2600 regarding mitigation of soil vapor hazard.
- 6.7.1 If the methane evaluation parameters are above levels of concern at the receptor points, along the transport pathway, or in primary source zones, the user develops measures designed to mitigate the hazard at the exposure point.
- 6.7.2 Hazard may also be mitigated by eliminating or controlling conditions at the exposure point, along the transport pathway, or in the primary source zone.
- 6.7.3 The mitigation measures may be a combination of engineering controls or institutional controls.
- 6.7.4 Remediation, or source removal, is seldom done for methane in soil gas. Sources may be too large or too deep or remote (off-site), making source removal impossible or at least economically unfeasible.
- 6.7.5 Institutional controls include covenants, restrictions, prohibitions, and advisories, and may include requirements for mitigation at some point.
- 6.7.6 Engineering Controls—Mitigation is the normal method of dealing with methane soil gas (see Fig. 2). At new buildings, mitigation techniques include: (1) subslab membrane and vent piping and (2) intrinsically safe design features. Intrinsically safe design allows no vapor pathway from the soil to confined space. Methods may include crawl spaces, first-floor "open-air" garages, or well-ventilated podium structures including basements. At existing buildings, mitigation techniques include: (1) barriers, passive crack repair, or other pathway plugging; (2) passive venting; (3) active venting; (4) positive pressure HVAC systems; (5) gas extraction systems;

- and (6) louvers in non-conditioned space that may also be used to increase air exchange rates inside structures. If pathways are blocked or plugged, an alternate route for venting of blocked gases is needed. Existing buildings may have VOC or radon mitigation systems already installed. If vent piping is part of the design, then mitigation systems for VOCs or radon should also serve to control methane as well. The potential for vented vapors to exceed an LEL should be evaluated to determine if an upgrade to an explosion-proof fan is warranted.
- 6.7.7 *Performance Monitoring*—Monitoring of soil gas, membrane performance, and/or interior air gas may be done.
- 6.7.7.1 Interior air monitoring such as with electronic gas detectors can be useful but is not itself a mitigation of gas intrusions since the detectors do not serve to prevent gas from entering a structure. Gas detection coupled with alarms may mitigate hazard by warning occupants to evacuate a structure when hazardous conditions ensue.
- 6.7.7.2 Monitoring of gas concentrations or pressures or both below the slab of a structure may be useful in determining changing soil gas conditions and risk.
- 6.7.8 *No Further Action*—This decision may be reached at various points, including before or after mitigation or control measures have been implemented, or after some period of monitoring. This step may be determined at any stage, including without mitigation or control, after mitigation or control, or after some period of monitoring.

#### 7. Procedures for Information Collection and Evaluation

7.1 Information Needs for Site Assessment—Gather and collect information necessary for site classification, initial

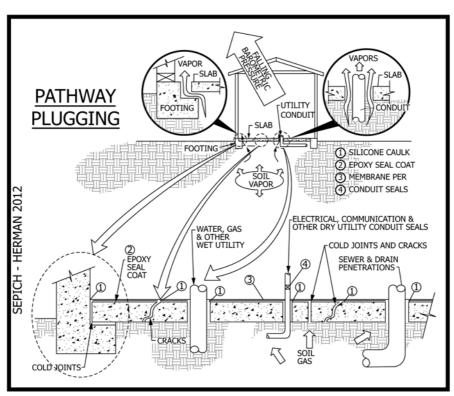


FIG. 2 Mitigation Method for Methane Soil Gas

response action, and comparison of data with screening criteria. Specific considerations follow.

- 7.1.1 General Gas Data—Review historical records, conduct site visits, conduct interviews, and consolidate a summary of any prior adverse events in the vicinity that might include: (1) complaints; (2) gas bubbles at ground surface after rainfall or irrigation; (3) odors as a result of trace non-methane vapors; (4) seeping gas, seeping tar, and oily groundwater; (5) ignition at cracks in slab; (6) explosions; and (7) eruption of gas from geotechnical or other soil borings upon encountering free gas or supersaturated groundwater during drilling.
- 7.1.2 Potential Gas Sources—Identify major potential sources and contributing sources to methane in the subsurface. Sources of methane in the subsurface can include: municipal solid waste landfills, volcanoes, petroleum gas reservoirs, very large subsurface releases of petroleum fluids, organic fill areas, bogs, swamps, wetlands, rice paddies, petroleum and gas seeps, natural gas pipeline and distribution systems, sewers, septic leachate fields, municipal sewers that include a high organic loading and leakage directly into the shallow subsurface, buried organic matter including vegetation, and other sources.
- 7.1.3 Soils and Groundwater Data—Identify relevant site and regional hydrogeological and geological characteristics, for example: (1) depth to groundwater, (2) soil type(s), (3) aquifer type and thickness, and (4) description of stratigraphy and confining units.
- 7.1.4 Groundwater Gas Data—Dissolved gas in groundwater has a bearing upon vadose zone gas concentrations. Ebullition (bubbling) from groundwater may occur if the dissolved gas is at a saturation limit. Quantifying the methane requires additional information on the occurrence of methane ebullition and, if so, the rate of methane gas flow, and is outside the scope of this guide. Groundwater methane concentration data alone cannot be directly correlated to unsaturated zone soil concentrations or the potential hazard from methane in buildings situated above the impacted groundwater. Saturated groundwater may pose a hazard if the groundwater is withdrawn for use. When the groundwater is no longer confined, the methane may volatilize and unacceptable indoor air concentrations may result in pump houses and other indoor spaces.
- 7.1.5 Vadose Zone Gas Data—Determine the methane evaluation parameters present in the subsurface and compare to levels of potential concern using the decision matrix (Table 1). Methane in the subsurface may be ubiquitous in soils under anoxic conditions. Methane concentration data alone is not sufficient to evaluate hazard from vadose zone gas. Soil gas pressures, soil types, pathways, receptors and other information are also necessary (see 6.1).
- 7.1.6 Soil Gas Pathways—Identify: (1) where methane gas may move directly into buildings, confined spaces, or tunnels or into subsurface structures (vaults, valve and meter boxes, ducts, conduits, vent pipes, sumps, sewers, and so forth); (2) situations in which a receptor (confined space) is exposed to a source of methane soil gas directly through air-connected soil porosity; and (3) preferential pathways such as coarse gravel backfill around utility lines leading to structures or large cracks or fractures in soil. Pathways may sometimes be discerned or

- assumed when elevated gas concentrations are found in vaults. Pathways may also be determined through evaluation of existing soils and geological reports for a site, the study of underground utility as-builts, or new investigations involving borings or trenching for observation of subsurface conditions.
- 7.1.7 Gas Receptors and Points of Exposure—Identify locations where hazard is of direct concern such as vaults, building interiors, tunnels, and any other confined spaces that are buried/below or above grade.
- 7.1.8 Interior Gas Data—Measure methane concentration at receptors and points of exposure (that is, in building or other enclosed spaces and structures) and compare to levels of concern, such as fraction of LEL. Other considerations apply. See Table 1. Measurements outside a building or structure (for example, soil gas measurements) may be used to extrapolate or predict conditions inside the building or structure. Conservative factors can be used for the extrapolation or may be modified based on site-specific conditions.
- 7.2 Guidelines for Test Probe Installation, Monitoring, Sampling, and Analysis:
- 7.2.1 Why to Sample Methane Soil Gas—Combustible soil gas sampling can be triggered by changes in ownership or refinancing, change in land use, simultaneous with other site investigations, or by some field event or observation.
  - 7.2.2 Where to Sample Soil Gas—Considerations include:
- 7.2.2.1 Radius-Based Sampling—In some jurisdictions, sampling for methane gas is typically done within prescribed distances from a methane source [for example, 305 m (1000 feet) of a sanitary landfill (County of Los Angeles Building Code Section 110); over or within 457 m (1,500 feet) of the administrative boundaries of an oilfield (City of Los Angeles methane buffer zone); or within some radius of an oil well, such as 8 to 61 m (25 to 200 feet; City of Los Angeles) or 107 m (350 feet; Orange County California)].
- 7.2.2.2 Source Recognition Gas Sampling—Often, there is no governance and the consultant should be aware of unregulated but known potential methane areas such as organic soils, swamps, marshes, and glacial till and any site where incidents or previous investigations and reports suggest the potential for combustible soil gas.
- 7.2.2.3 Site Surface Features—Consideration should be given to site specifics such as drainage patterns, location of hardscape and softscape, distance from structures, and any other site culture or conditions that may affect methane readings.
- 7.2.2.4 Site Subsurface Features—Consideration should be given to site specifics such as soils and geologic strata, groundwater and perched water depths, soil type, soil moisture, location of nearby underground utilities, and any other subsurface conditions that may affect methane readings.
- 7.2.2.5 Vadose Zone Gas Sampling—Methane samples are collected from various sources, including vadose zone push probes, vadose zone monitoring well head space and casing gas, landfill gas wells and pipelines, and oilfield hydrocarbon wells.
- 7.2.2.6 *Surface Sweeps*—Surface sweeps or screening may identify points of direct leakage and flow of soil gas from below grade to atmosphere or structure interiors. The finding of

methane in surface sweeps may provide direct evidence of methane flow. Such findings should normally be followed up by evaluation of soil gas concentrations and pressures, which are normally elevated at locations where surface seepage of methane is occurring.

7.2.3 When to Sample Soil Gas—Consideration should be given to diurnal variations, seasonal variations, recent rainfall, time since grading operations were conducted on a site, and other factors that could affect methane readings. Periods of falling barometric pressure may represent worst-case conditions. Other factors to consider would include soil moisture (and time since most recent precipitation, infiltration wetting front, hysteresis, soil type, and so forth), temperature and tidal fluctuations (for example, when near shorelines). For sites at which risk level is not obvious based upon the normal monitoring, it may be desired to perform more detailed analyses or continuous monitoring (see Bibliography).

# 7.2.4 Other Samples and Measurements:

7.2.4.1 *Indoor Air*—Air may be tested and samples may be collected from inside structures. Unlike the process for evaluating hazard from gas in the soil, it is not necessary to understand or measure pressures and volumes (flows) for direct evaluation of interior gas hazard. Gross interior air combustible gas concentrations alone (for example, greater than 1.25 % v/v, or 25 % of the LEL) are primary evidence of gas hazard inside a habitable structure. But even low (for example, less than 100 ppmv (0.01 % v/v, or 0.2 % of LEL) levels of methane, measured using sensitive gas detection equipment at cracks in slabs, conduits, or other entry pathways, are important in understanding the possible modes of methane intrusion into structures. An indoor air reading greater than 100 ppmv suggests a potential methane source and merits further evaluation.

7.2.4.2 *Confined Space Gas*—High concentrations of methane in smaller non-habitable confined spaces are also an important indicator of potential gas hazard at a site.

7.2.4.3 Groundwater Dissolved Gas—Methane samples are sometimes collected from water wells, either by sampling dissolved gases in groundwater or by measuring methane in water well head space. Groundwater samples may be taken under pressure and then depressurized in the laboratory with measurement of off gas and measurement of dissolved gas in the depressurized sample, giving an indication of the total dissolved methane in situ. Knowledge of groundwater pressure head at the point of sampling is also important in understanding the potential of the groundwater for methane off gassing.

#### 7.2.5 Field Measurements:

7.2.5.1 Soil Gas Speciation—Instruments are commonly available to measure field gas pressure and concentrations of methane and non-methane combustible gases, carbon dioxide, oxygen, and hydrogen sulfide. Non-methane (VOC) combustible vapors can be measured using devices such as photoionization detectors, or VOCs can be subtracted from the total combustibles using activated carbon absorption filters at the sample intake stream of FIDs or catalytic or solid state devices. It is normal to take the bulk of data through field measurements and use laboratory techniques only to confirm selected field data or to perform analyses that cannot be done in the field.

7.2.5.2 Vadose Gas Pressure—Pressure measurements should be taken in the field. To take pressure measurements properly, it is necessary to have the soil gas monitoring well or probe equipped with a sampling valve. Normally, this will be some type of small labcock with a hose barb or quick-connect fitting. Pressure measurement equipment should be connected to the valve while it is still shut. Then the valve is opened to observe downhole pressure. If the valve is opened before the pressure measurement equipment is attached, the downhole pressures or vacuums may be lost through equilibration with atmosphere. Pressures encountered in the soil because of barometric lag conditions are typically well below 250 Pa. These pressures (positive or negative) are not remarkable with respect to methane flammability hazard. Pressures in excess of 500 Pa may be significant. Conversely, in tight, clayey soils, relatively high differential pressures may be encountered for relatively weak, localized sources which do not typically represent significant risk. As discussed in 4.2, all data should be evaluated in context of the CSM.

7.2.5.3 Barometric Pressure—Barometric pressure profiles are typically available from the national weather service on line and are acceptable for determining trends before, during, and after field-monitoring events. Barometric pressures and variations in barometric pressure may also be measured in the field using a variety of equipment designed for that use.

# 7.2.6 Laboratory Analysis:

7.2.6.1 Laboratory analysis is typically done to confirm field measurements and, therefore, is needed for only a limited number of samples. Laboratory analysis can also be done if field instruments are not available to measure the parameter of interest (for example, isotopic analysis).

7.2.6.2 Basic laboratory characterization of field samples includes:

(1) Soil Gas Speciation—Routine speciation should include gas chromatographic measurement of the concentrations of  $CH_4$ ,  $O_2$ , and  $CO_2$ . Other gases of possible interest include:  $N_2$ , Ar,  $H_2$ , He,  $C_2H_6$ ,  $C_2H_4$ ,  $C_3H_8$ ,  $i\text{-}C_4H_{10}$ ,  $n\text{-}C_4H_{10}$ ,  $i\text{-}C_5H_{12}$ ,  $n\text{-}C_5H_{12}$ , and C6+. Consult laboratory for minimum sample concentrations and volumes necessary to conduct these tests.

- (2) Biogas Production Rates—Biogas production rates may be predicted based upon laboratory studies.
- (3) Soil Total Organics—Laboratory measurement of the total organic content of a soil sample from the source zone can give an indication of potential for methane generation.
- (4) Soil Moisture Content—Laboratory measurement of soil moisture content is useful when calculation of the soil flow characteristics will be done.
- (5) Soil Permeability—Laboratory measurement of the soil permeability is useful when calculation of the soil flow characteristics will be done. This can be done on an undisturbed sample or a remolded sample if the in-situ relative compaction of the soil is known. Note that flow characteristics can also be evaluated through field estimates of soil permeability (Falta, 1996) or purge and recovery tests.
- (6) Soil Bulk Density or Soil Percent Relative Compaction—Bulk density is the unit weight of the soil per unit volume including the soil particles and moisture. Percent relative compaction is a related measure, commonly used in

earthwork projects, defined as the ratio of the dry unit weight of soil in the field after compaction divided by the maximum dry unit weight measured in laboratory tests (for example, standard Proctor or modified Proctor). Either measurement can be useful when calculation of the soil flow characteristics will be done.

7.2.7 Methane Sampling Containers:

7.2.7.1 Primary concerns are: (1) container leakage and (2) problematic seals. Containers with silicone seals or a silicone septae should be avoided for methane use. Methane diffuses through silicone and is isotopically fractionated with fractionation becoming more problematic with longer holding times.

7.2.7.2 Glass and Metals—Glass and metals are preferred and are capable of long-term storage (for example, weeks or months)

7.2.7.3 Bags—Leakage is a far bigger concern with bags than with metal or glass containers. Holding times in Cali-5-Bond© bags<sup>7</sup> are generally considered to be on the order of several months. But even Tedlar© bags<sup>8</sup> can be used for storage of samples for several weeks with no significant change in their compositions. However, some types of sample bags are not suitable for collection of light hydrocarbons, even with short holding times. Some plastic containers (such as polyethylene) are semipermeable and should be avoided.

7.2.8 *Methane Sample Holding Times*—Restrictions on handling of gas samples and holding times are typically based on the type of sample containers used. Considerations for holding time include:

7.2.8.1 Leakage—Methane sample holding times are determined by the potential for container leakage or the potential for bacterial degradation of the sample. Short holding times, which are sometimes mandated by regulations, may not allow for transit of samples to a qualified laboratory. Holding times of weeks to years can be acceptable. Consult a qualified laboratory for specific container holding times.

7.2.8.2 Bacterial Degradation—For aerobic degradation of methane in a sample, three things are required: oxygen, water, and bacteria. If the samples contain a liquid (aqueous) phase and oxygen, bacterial oxidation can occur if bacteria are present. Samples taken from a warm saturated (that is, landfill gas) source may arrive at the laboratory containing free liquid condensate that forms in the sample container upon cooling of the sample. Bacterial degradation is uncommon if the moisture in a sample came only from condensation. Bacterial degradation can be a problem if containers that were previously contaminated with bacteria were reused.

7.2.8.3 *Bacterial Oxidation*—Bacterial oxidation can be a problem with dissolved gas samples and headspace samples in which there is a liquid (aqueous) phase present. Benzalkonium chloride bactericide is typically added to the samples before

shipping to the laboratory. Consult the laboratory to determine appropriate amounts of bactericide and other sample preservation methods.

7.2.8.4 *Dry Samples*—For dry samples with no water, the holding time for methane or natural gas is entirely a function of the sample container and how the sample was collected. Gas samples have been stored in aluminum cylinders for nearly 20 years with no measurable change in their chemical or isotopic composition. Testing has shown that other sample container types have holding times ranging from weeks to years.

7.3 A bibliography is provided at the end of this standard. Other ASTM International standards relevant to evaluation of methane hazard in the vadose zone include Terminologies D653 and D1356 (terminology); Practices D2487, D5088, D6725, and D7663 (field methods); Practice D1946 and Test Methods D2216 and F1815 (laboratory methods).

#### 8. Calculations

8.1 Calculate Dead Volume—Calculate the internal dead volume of sampling lines and other sampling components. The internal volume of items with circular cross sections can be calculated using the internal diameter (d) of the component and the length (L) of the component as follows:

$$V = \pi (d / 2)^2 \times L \tag{1}$$

8.2 *Measure Dead Volume*—Alternatively, the internal space of a sampling component or sampling assembly can be determined empirically by filling the void space with water and then carefully decanting the water into a graduated cylinder.

8.3 Calculate Purge Time—The time  $(\tau)$  to change out one residence (purge) volume in an enclosure is calculated using the volume (V) and flow rate (Q) as follows:

$$\tau = V / Q \tag{2}$$

8.4 Unit Conversions:

8.4.1 Conversions between ppbv and  $\mu g/m^3$ —For any ideal gas with molecular weight (MW), the conversions at 25°C are as follows:

$$C(\text{ppbv}) = C(\mu g / m^3) \times (24.45 / MW)$$
 (3)

$$C(\mu g / m^3) = C(ppbv) \times (MW / 24.45)$$
 (4)

8.4.1.1 The same equations can be used for conversions between mg/m<sup>3</sup> to ppmv with the appropriate substitutions. For temperatures other than 25°C, the value of 24.45 should be adjusted. (See Note 1.)

Note 1—The conversion is based on the ideal gas law (see below) and standard temperature ( $0^{\circ}C = 273K$ ) and standard pressure (1 atmosphere = 760 mm Hg). The ideal gas law is:

$$PV = nRT$$

where:

P = pressure in atmospheres,

V = volume of gas (L),

n = moles of the gas (number of moles = mass/MW),

R = gas constant (0.082056 liter-atm/mole-K), and

T = temperature (K).

For one mole of gas (n=1): (1 atm)(V) = (1)(0.0820)(273) and V=22.4 L. In other words, one mole of any ideal gas occupies 22.4 L at standard temperature and pressure. At room temperature  $(25^{\circ}\text{C}=298\text{K})$ , the ideal gas law yields: (1 atm)(V) = (1)(0.0820)(298) and V=24.45 L.

<sup>&</sup>lt;sup>7</sup> The Cali-5-Bond© bag is covered by a patent. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patented item to the ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

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For benzene, for example, one mole of gas (78.11 g) occupies 24.45 L, which is equal to  $0.024~45~m^3$ . For pure gas, the concentration is 1~000~000 ppm. So: 1~000~000 ppm =  $78.11~g/0.024~45~m^3$  and 1~000~000 ppm =  $3190~g/m^3$ .

Divide each side by 1 000 000 (which converts g to  $\mu$ g): 1 ppm = 3190  $\mu$ g/m<sup>3</sup>. Divide each side by 1000 to convert to part per billion: 1 ppb = 3.19  $\mu$ g/m<sup>3</sup>.

- 8.4.2 Conversion between various units of pressure. One atmosphere (atm) of pressure equals the following:
  - 101325 Pa,
  - 1013 mbar,
  - 29.9 in. Hg.
  - 1033 cm H<sub>2</sub>O,
  - 407 (in. H<sub>2</sub>O) (in. w.c.),
  - 14.7 psi, and
  - 760 mm Hg (Torr).
- 8.4.3 Conversion between Percent (on a volume basis) and ppmv—For any gas, 1 % = 10 000 ppmv. So, the conversions are as follows:

$$C(\%) = C(\text{ppmv}) \times 0.0001 \tag{5}$$

$$C(ppmv) = C(\%) \times 10\ 000$$
 (6)

# 9. Methane Reports and Documentation

- 9.1 Data Records/Reporting Requirements—The records or field logs that contain information, measurements, or readings (data) collected in the field before, during, and after data collection should be kept in order and made available to anyone who needs to review them in conjunction with final generation or report review or both. The data reports should contain, but are not limited to, the sample identifications (IDs); where the samples were collected; the depth at which they were collected; how they were collected; and any applicable field readings, such as purge volumes, sampling flow rates, differential pressure, and/or temperature.
- 9.2 Purpose of Records—Of primary concern is that records include the information necessary to describe the methods and results of the evaluation performed for a particular application. At a minimum, the information listed in 9.3 should be included.
- 9.3 *Minimum Information*—The test report should contain the following information:
- 9.3.1 A statement to indicate the confidentiality of the information supplied, if appropriate;
  - 9.3.2 Executive summary;
  - 9.3.3 Site description;
  - 9.3.4 Site ownership and use;
  - 9.3.5 Description of source areas;
  - 9.3.6 Monitoring/testing program;
  - 9.3.7 Vadose zone and/or confined space gas at site;
  - 9.3.8 Evaluation of gas hazard at site;

- 9.3.9 Conclusions and recommendations;
- 9.3.10 Figures—Maps and photos;
- 9.3.11 Tables—Data and data comparisons.
- 9.4 *Field Notes*—Field notes may be included as an appendix to the site report:
  - 9.4.1 Site name and address/location:
  - 9.4.2 Name of technician(s) doing the sampling;
- 9.4.3 Name and affiliation of other persons participating in the fieldwork;
  - 9.4.4 Date and time(s) of sampling;
- 9.4.5 *Weather*—Sunny or cloudy, humidity, precipitation, temperature, and wind; barometric pressure trend leading up to the field event and where in the trend the field measurements occurred:
  - 9.4.6 Locations of sampling (accompanied by sketch);
- 9.4.7 Sample location identification names, numbers, and depths;
- 9.4.8 Manufacturer/model number of field equipment for gas concentrations/pressures;
- 9.4.9 Pre-monitoring calibration check and post-monitoring check, as appropriate;
- 9.4.10 Initial pressure/vacuum measurements, units (incheswater and so forth);
  - 9.4.11 Lower/upper detection limit;
- 9.4.12 Concentrations of each target analyte, units (ppm, % LEL, %, and so forth);
  - 9.4.13 Initial concentration:
  - 9.4.14 Peak concentration, purge time;
  - 9.4.15 Steady concentration, purge time;
  - 9.4.16 Lower/upper detection limits of equipment; and
- 9.4.17 Comments/remarks (unusual or notable observations).
- 9.5 *Laboratory Report*—The laboratory report may be included as an appendix to the site report:
  - 9.5.1 Chain of custody;
  - 9.5.2 Site name;
  - 9.5.3 Laboratory name;
  - 9.5.4 Date of analysis;
  - 9.5.5 Name of analyst:
  - 9.5.6 Instrument identification;
- 9.5.7 Sample location identification names, numbers, and depths;
  - 9.5.8 Analyte list and QA/QC data;
  - 9.5.9 Concentrations or other results of each analysis;
  - 9.5.10 Laboratory QC limits; and
  - 9.5.11 Notes or explanation of any outliers.

# 10. Keywords

10.1 hazard; measurement; methane; soil gas; vadose zone

#### APPENDIXES

(Nonmandatory Information)

# X1. METHANE CHARACTERISTICS: PHYSICAL AND CHEMICAL PROPERTIES, TOXICOLOGICAL ASSESSMENT SUMMARY, AND HAZARD

#### **X1.1 Introduction**

X1.1.1 Methane gas concentrations are typically expressed as percent volume (that is, methane in air), percentage of the lower explosive limit (LEL), or parts per million by volume. A value of 100 % LEL is the same as 5 % v/v and 50 000 ppmv (see Table X1.1).

X1.1.2 A basic understanding of physical and toxicological properties is a key component in the evaluation of chemical risk and hazard.

X1.1.3 This appendix provides a basic introduction to the physical, chemical, and toxicological characteristics of methane and is focused on the information that is most relevant to assessing potential impacts caused by the release of methane to shallow subsurface soils and in transport of methane from the shallow subsurface to surface and subsurface enclosed spaces. Much of the information is summarized from listed references.

#### X1.2 Referenced Documents

X1.2.1 ANSI Standards:<sup>9</sup>

ANSI/API RP 505 Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities

ANSI/GPTC Z380 Guide for Gas Transmission and Distribution Piping Systems

X1.2.2 NFPA Standards: 10

NFPA 30 Flammable and Combustible Liquids Code

NFPA 70 National Electric Code

NFPA 497 Recommended Practice for the Classification of Flammable Liquids, Gases or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas

**TABLE X1.1 Methane Gas Concentrations** 

%CH₄	PPMV	% LEL	Remarks
0.00001	0.1	_	Laboratory
0.0005	5	0.01	Flame ionization detector (FID)
0.05	500	1	Catalytic detector accuracy
1.25	12 500	25	Example indoor air action level
5	50 000	100	Lower explosive limit
14	140 000	_	Upper explosive limit (UEL)
100	1 000 000	_	Pure methane

X1.2.3 Federal Standards: 11

29 CFR Section 1915.12(b)(3) Confined and Enclosed Spaces and Other Dangerous Atmospheres

29 CFR Section 1019.146(b)(1) Permit-required Confined Spaces

30 CFR 57.22001 Safety Standards for Methane in Metal and Nonmetal Mines

30 CFR § 57.22003 MSHA Illustration 27

40 CFR 258.23 Explosive Gases Control

#### X1.3 Overview of Methane Characteristics

X1.3.1 The specific characteristics for methane are referred to in the following sections of this appendix:

X1.3.1.1 Physical and Chemical Properties—See X1.4.

X1.3.1.2 Toxicity Summary—See X1.5.

X1.3.1.3 Flammability Summary—See X1.6.

X1.3.1.4 Sources and Generation of Methane—See X1.7.

X1.3.1.5 *Transport and Degradation of Methane in Soils*—See X1.8.

# **X1.4 Physical Properties of Methane**

X1.4.1 Descriptive information and basic physical properties of methane are listed in Table X1.2.

X1.4.1.1 Henry's Law Coefficient—The equilibrium partition of a soluble chemical between an aqueous solution and the vapor phase is determined by the Henry's Law constant, H. In consistent units, the ratio of the chemical concentration in the vapor phase,  $c_{v}$ , (moles/L-air) to that in the aqueous phase,  $c_{w}$ , (moles/L-water) ratio is given by  $H = c_v/c_w$ , or, in terms of the vapor partial pressure  $P_{\nu}$  (atm), aqueous concentration (mol/  $\text{m}^3$ ), and H' (atm- $\text{m}^3$ /mol),  $H' = P_{\nu}/c_{\nu}$ , where  $H'/(R \cdot T) = H$ , T(K) is the equilibrium temperature and  $R = 8.20562 \times 10^{-5}$ (m<sup>3</sup>·atm / mol·K) is the gas constant. Henry's law is limited to low concentrations, that is, concentrations for which the mole fraction in water is small and ideal gas assumptions apply for the vapor phase. Henry's law coefficient at 25°C is included in Table X1.2. Values for Henry's law coefficient from a number of empirical data sets (8)<sup>12</sup> as a function of temperature are summarized in Table X1.3.

X1.4.1.2 Aqueous Solubility—The aqueous solubility of a chemical in water is defined as the maximum amount of the chemical that will dissolve in pure water at a specified temperature. Solubility is a thermodynamic property. Methane is a gas at nominal environmental temperature and pressure, therefore, aqueous solubility depends on both temperature and the partial pressure of methane. The aqueous solubility of

<sup>&</sup>lt;sup>9</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

<sup>&</sup>lt;sup>10</sup> Available from National Fire Protection Association (NFPA), 1 Batterymarch Park, Quincy, MA 02269, http://www.nfpa.org.

<sup>&</sup>lt;sup>11</sup> Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

<sup>12</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

#### **TABLE X1.2 Physical Properties of Methane**

Physical Property	Value	Reference
Chemical name	Methane	
Synonyms	Fire damp, marsh gas, Refrigerant 50, methyl	
	hydride	
Chemical Abstracts Service Registration Number	74-82-8	
(CAS RN)		
Molecular formula	CH <sub>4</sub>	
Molecular weight, MW	16.04 g/mol	
Molecular diffusion coefficient in air, Dair	D <sub>air</sub> : 0.217 cm <sup>2</sup> /s (experimental, at 25°C, 1 atm)	Cowie and Watts (3) <sup>A</sup>
Molecular diffusion coefficient in water, $D_{water}$	1.88E-5 cm <sup>2</sup> /s (experimental, at 25°C)	Witherspoon and Saraf (4)
Organic carbon to water partition coefficient, $K_{oc}$	90 L-wat/kg-oc	HSDB (5)
Octanol to water partition coefficient, $K_{ow}$	12.3 L-water/kg-octanol (experimental)	US EPA (6)
Henry's law coefficient, H	0.658 atm-m <sup>3</sup> /mol (experimental, at 25°C)	US EPA (6)
Vapor pressure, $P_{\nu}$	466 000 mmHg, 613.2 atm (experimental, at 25°C)	US EPA (6)
Aqueous solubility limit, S	22 mg/L (experimental, at 25°C)	US EPA (6)
Melting point, $T_{mp}$	-182.4 °C	Daubert and Danner (7)
Boiling point, $T_{nbp}$	-161.5 °C ( at 1 atm)	Daubert and Danner (7)
Critical temperature	-82.6 °C	Daubert and Danner (7)
Critical pressure	34495 mmHg, 45.4 atm	Daubert and Danner (7)
Lower flammability limit, $X_{LFL}^{B}$	4.4%v in air	Daubert and Danner (7)
Upper flammability limit, $X_{UFL}^{B}$	16.5 %/v in air	Daubert and Danner (7)

A The boldface numbers in parentheses refer to the list of references at the end of this standard.

TABLE X1.3 Henry's Law Coefficient for Methane

T(°C)	Lide and Frederikse (9)	Dean (10)	Kavanaugh and Trussell (11)	Wilhelm, Battino, et al (12)
		H(atm	n-m³/mol)	
5	0.479	0.480	0.492	0.468
10	0.531	0.542	0.552	0.521
15	0.585	0.609	0.616	0.579
20	0.643	0.681	0.685	0.640
25	0.705	0.759	0.759	0.705
30	0.770	0.844	0.839	0.775
35	0.839	0.934	0.924	0.848
40	0.912	1.030	1.014	0.927
45	0.988	1.134	1.110	1.009

X1.4.2 Methane (or other gas concentration) values quoted on a volume basis (% v/v or ppbv) require conversion based on the average molecular weight and composition of the vapor to a mass concentration basis ( $\mu g/m^3$ ).

$$(ppbv) = C_{CH4} \left(\frac{\mu g}{m^3}\right) \times \frac{R \times T}{MW \left(16.04 \frac{g}{mol}\right) \times P} = C_{CH4} \left(\frac{\mu g}{m^3}\right) \times \frac{24.45}{16.04 \frac{g}{mol}}$$

$$c_{CH4} \left( \frac{\mu g}{m^3} \right) = X_{CH4} (ppbv) \times \frac{MW \left( 16.04 \frac{g}{mol} \right) \times P}{R \times T} = X_{CH4} (ppbv) \times \frac{16.04 \frac{g}{mol}}{24.45}$$
(X1.2)

where:

 $X_{CH4}$  = concentration of methane as a volume fraction (ppbv),

C = mass concentration,

methane is shown in Table X1.4 using values of Henry's law coefficient from Table X1.3 with the partial pressure of methane equal to 1 atm.

TABLE X1.4 Aqueous Solubility for Methane at Pressure of 1 atm

				Depth below V	Vater Table (Unco	onfined Aquifer)			
Depth, ft	0	3.3	6.6	9.8	16.4	32.8	65.6	98.4	164.0
Depth, m	0	1	2	3	5	10	20	30	50
Temperature, °C			V	Vater-Saturated N	Methane Concenti	ration (mg/L-wate	r)		
5	33.3	36.6	39.8	43.0	49.5	65.6	97.9	130.1	194.7
10	29.8	32.7	35.6	38.5	44.3	58.7	87.6	116.5	174.2
15	26.8	29.4	32.0	34.6	39.8	52.7	78.7	104.6	156.5
20	24.2	26.5	28.8	31.2	35.8	47.5	70.9	94.3	141.0
25	21.8	24.0	26.1	28.2	32.4	43.0	64.1	85.3	127.6
30	19.8	21.7	23.7	25.6	29.4	39.0	58.2	77.4	115.8
35	18.1	19.8	21.5	23.3	26.8	35.5	53.0	70.5	105.4
40	16.5	18.1	19.7	21.3	24.5	32.4	48.4	64.3	96.2
45	15.1	16.6	18.0	19.5	22.4	29.7	44.3	58.9	88.1

<sup>&</sup>lt;sup>B</sup> The flammability range for methane is typically taken as 5–15%.



R = gas constant, T = temperature, P = pressure, and MW = molecular weight.

# X1.5 Toxicity Summary of Methane

X1.5.1 Methane acts as a simple asphyxiant when inhaled (13, 14). Asphyxiants displace oxygen in the air and can cause symptoms of oxygen deprivation (asphyxiation). Simple asphyxiants include, among others, carbon dioxide ( $CO_2$ ), helium (He), and gaseous hydrocarbons (that is, methane,  $CH_4$ ; ethane,  $C_2H_6$ ; propane,  $C_3H_8$ ; and butane,  $C_4H_{10}$ ).

X1.5.1.1 Toxicity of a simple asphyxiant is related to the severity of displacement of ambient oxygen and the duration of exposure. The available oxygen should be a minimum of 18 % or harmful effects will result.

X1.5.1.2 Methane as an initially pure chemical displaces oxygen to 18 % in air when present at 14 % (140 000 ppm). Methane is not expected to cause unconsciousness (narcosis) as a result of central nervous system depression until it reaches much higher concentrations (30 % or 300 000 ppm), well above the lower explosive limit and asphyxiating concentrations.

X1.5.1.3 Therefore, acute toxicity of narcosis/oxygen deprivation occurs in the range of 140 000- to 300 000-ppm methane.

X1.5.1.4 ACGIH (15) has recommended a threshold limit value of exposure for methane at 5000 ppm (based on no effect in animals at 10 000 ppm, divided by an uncertainty factor of two). Because this no observable effect level (NOEL) is based on an absence of response, not on observed toxicity, we discount it in this summary.

X1.5.2 The lower flammability limit,  $X_{\rm LFL}$ , of methane (5 %v, 50 000 ppm) in air is much lower than any toxicity-based concentration level. Potential flammability of methane in air and the potential for fire or explosion is, therefore, the primary hazard of methane to people, as well as the primary hazard to property.

# X1.6 Flammability of Methane

X1.6.1 Measures of flammability are based on measured flame propagation in a test cell of specific design and geometry.

X1.6.2 Comprehensive measures of methane flammability are included in Zabetakis (1965), as indicated in Fig. X1.1(a), as a function of methane, oxygen, and nitrogen (inert gas) concentrations, at 1 atm. The methane flammability range in air is illustrated as a function of spark energy in Fig. X1.1(b).

X1.6.2.1 Flammability depends on methane concentration, oxygen concentration, gas temperature, and ignition energy.

X1.6.2.2 Initiation of a fire or explosion for a flammable gas in air varies from the specific measured flammability limit ranges.

X1.6.3 In ambient air with oxygen at 21 %v, flammability is defined by a lower flammability limit ( $X_{\rm LFL}$ ) and upper flammability limit ( $X_{\rm LFL}$ ).

X1.6.4 The  $X_{\rm LFL}$  value is the lower limit concentration in open air that will support a flame. Zabetakis (16) compiles values of chemical-specific  $X_{\rm LFL}$ . The  $X_{\rm LFL}$  on a mass concentration basis for methane is 38 g/m<sup>3</sup>.

X1.6.4.1 Values of  $X_{LFL}$  for >C3 hydrocarbons nominally range from 45 to 52 g/m<sup>3</sup>-air.

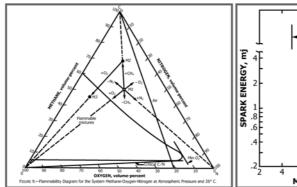
X1.6.4.2 The  $X_{\rm LFL}$  value applies in ambient air with oxygen within the normal range (21 % v/v). No adjustment of  $X_{\rm LFL}$  for other atmospheres (reduced or increased oxygen or temperature) is included in the defined  $X_{\rm LFL}$ .

X1.6.5 Flammability for chemical mixtures, including methane and petroleum vapors, follows Le Châtelier (17) with  $X_{\rm LFL-i}$  (v/v) of constituent flammable chemicals (volume/ volume) and  $x_i$  (mol/mol) as mole fractions (volume fractions) of hydrocarbon fuel constituents (including methane).

$$X_{LFL-n}(v/v) = \frac{1}{\frac{x_1}{X_{LFL-1}} + \frac{x_2}{X_{LFL-2}} + \dots + \frac{x_n}{X_{LFL-n}}}$$
 (X1.3)

X1.6.5.1 Only flammable chemicals are included in the summation. No unusual compounds and no inhibitors are presumed.

X1.6.5.2 Source methane gas present with nonflammable gases (such as nitrogen and carbon dioxide) will mix with air within flammable limits to a narrower range of dilutions than pure methane. The effect on flammability levels of varied levels of methane and oxygen is shown in 30 CFR § 57.22003, MSHA Illustration 27, [http://www.msha.gov/30cfr/57.22003.htm], see Fig. X1.2.



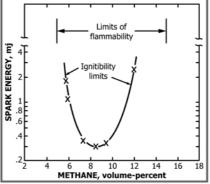
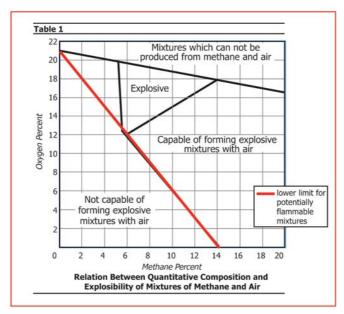


FIG. X1.1 Diagrams for Methane Flammability from Zabetakis (16) where (a) Flammable Range of Methane, Oxygen, and Nitrogen and (b) Flammable Range in Air (21 %v O<sub>2</sub>) Versus Ignition Spark Energy



Note 1—The straight red line illustrates varied mixture ratios of source methane gas (for example, soil gas;14.1 %v methane) with ambient air (21 %v oxygen) and defines the lowest concentration (14.1 %v) of methane that can be diluted with air to form a flammable ("explosive") mixture in air.

FIG. X1.2 Flammability Levels of Methane and Oxygen (from 30 CFR § 57.22003, MSHA Illustration 27)

X1.6.6 Source methane gas (for example, methane in soil gas) must exceed 14.1 %v methane to dilute (with ambient air) into the flammable range.

X1.6.6.1 Soil gas with methane at concentration levels at above a few percent (>1 to 2 %) is generally completely anoxic (no oxygen) as a result of microbial activity in soil.

X1.6.6.2 Mixing anoxic soil gas (no oxygen) with air (21 %v oxygen) lowers the oxygen level in the resultant mixture.

X1.6.6.3 To interpret Fig. X1.2, for example, mixtures of ambient air (21 %v oxygen, 79 %v inert) with soil gas (14.1 %v methane, 85.9 %v inert) within the range of all possible dilution ratios will fall on the straight red line in the figure. This shows that methane concentrations in soil gas are required to be greater than 14.1 %v for the soil gas to dilute (with ambient air) into the flammable ("explosive") range.

X1.6.6.4 Fig. X1.2 is consistent with the flammable range from Fig. X1.1.

X1.6.6.5 The 14.1 %v methane in soil gas criteria neglects biodegradation of methane as it migrates through aerobic soil. In Table X1.5, the results are shown of several relevant published examples showing methane decreasing from, at, and near this soil gas concentration (5 to 14 %v) to levels below potential concern in soil, within 1 to 2 ft (0.3 to 0.6 m) of soil, below building foundations. This substantial attenuation is attributed to aerobic methane degradation.

X1.6.7 Methane within the void of a soil gas matrix is not flammable.

X1.6.7.1 The quenching distance is the minimum tube diameter through which a laminar flame will propagate. At tube diameters less than the quenching distance, the rate of heat removal by the ambient temperature tube walls is greater than the rate of heat generation, and the flame will not propagate. The quenching distance for flammable mixtures of methane in air is approximately 1.8 mm.

**TABLE X1.5 Methane Degradation** 

Site Specifics	Methane		
	Depletion	Location	Reference
O-cm depth change below a slab on grade home overlying residual petroleum non- aqueous phase liquid (NAPL)	From 14 %v (source depth was 1.8 m) to near 0 %v (non-detect).	Santa Maria, CA	Lundegard et al (18)
20 cm, below a slab-on-grade building at a gasoline service station building	From 35 g/m³-air (5.2 %v, source depth was 0.6 m) to non-detect (0.15 %)	Alameda Naval Air Station, Alameda, CA	Fischer et al (19)

X1.6.7.2 The maximum safe experimental gap (MSEG) is a standardized test for measuring flame propagation through cracks or gaps. It is somewhat more stringent than the quenching distance. Methane is regarded as having an MSEG of 1.14 mm (20).

X1.6.7.3 Soils with pore diameters less than either the quenching distance or the MSEG will not propagate a flame.

X1.6.8 Criteria levels for screening the presence of potential flammability in open air are conservatively defined at a fraction of the  $X_{\rm LFL}$ .

X1.6.8.1 A value of 10%  $X_{\rm LFL}$  is an applicable screening criteria for occupied enclosed spaces (for example, US 29 CFR Section 1915.12(b)(3), US 29 CFR 1910.146(b)(1)).

X1.6.8.2 Twenty-five percent  $X_{LFL}$  is applied in electrical classification (ANSI/API RP 505-1998; NFPA 30).

X1.6.8.3 Criteria for methane in subsurface mines (US 30 CFR 57.22001), range from 0.25 to 2.5 % methane (or approximately, 5 to 50 %  $X_{\rm LFL}$  for methane), with varied responses depending on the monitored level.

X1.6.9 Criteria levels for screening soil gas based in the potential for flammable conditions in open air follow:

X1.6.9.1 U.S. Federal regulations indicate the 100 %  $X_{\rm LFL}$  criteria for methane are not to be exceeded at the boundary of municipal solid waste landfills (21) (40 CFR 258.23).

X1.6.9.2 ANSI/GPTC Z380 includes extensive guidance on leak investigation, classification, and action criteria (Grades 1, 2, and 3). Natural gas (methane—lighter than air) and petroleum gas (heavier than air) are included. For selected comparative purposes, criteria for a leak that represents an existing or probable hazard (Grade 1) are set at >60 % of the  $X_{\rm LFL}$  within a confined space. For a nonhazardous but probable future hazard (Grade 2), a criteria is set at >40 %  $X_{\rm LFL}$  in soil gas under a sidewalk or wall-to-wall paved area. Many states have adopted the ANSI/GPTC Z380 Guide.

X1.6.9.3 Operating retail service stations, other petroleum installations, and natural gas installations include controlled areas defined as "hazardous locations." These are defined as areas within which ignitable concentrations of flammable vapors may exist in air all or some of the time under normal operating conditions [NFPA 30, (22), NFPA 497, NFPA 70, NFPA 497]. Engineered systems within these "hazardous locations" are designed for the presence of flammable vapors during normal operations; this should be considered in a response to the presence of flammable vapors.

#### X1.7 Sources of Methane in the Environment

X1.7.1 Methane is the principal constituent of natural gas. X1.7.1.1 It occurs in natural petroleum and gas reservoirs,; methane hydrates in arctic regions and marine sediments and volcano emissions.

X1.7.1.2 It is a product of petroleum refining and natural gas processing; transported in underground pipelines and distribution systems; and a constituent of heating, illuminating, and cooking gas.

X1.7.2 Biogenic methane is a product of microbial degradation.

X1.7.2.1 Methane is released to the environment as natural emissions from biodegrading animal and plant wastes. Sources

include bogs, swamps, and sediments; from animals (ruminants); and during the growing of rice. Biogenic methane is produced from coal, oil, and kerogen over geological time frames in reservoirs and mineral deposits and in biodegradation of anthropogenic releases of oil and other organic matter to the environment.

X1.7.2.2 Anaerobic fermentation of cellulose, hemicelluloses, polysaccharides, other organic molecules, to form  $CO_2$ ,  $H_2$ , and organic acids, including acetate (or acetic acid).

X1.7.2.3 Microbes (methanogens) carry out one or both of the following reactions to produce methane under strictly anaerobic conditions (23).

$$CH_3COOH \rightarrow CH_4 + CO_2$$
 (X1.4)

$$CO_2 + H_2 \rightarrow CH_4 + 2H_2O$$
 (X1.5)

X1.7.2.4 Biogenic methane generation results in a net molar volume increase from reactants to products. This can result in a net advective soil gas flow.

X1.7.3 Thermal methane may be produced from heated organic matter. Methane is a product of partial combustion.

X1.7.3.1 Thermal methane may occur in petroleum reservoirs, originating from hydrocarbons and kerogens at elevated temperatures over geological time periods.

X1.7.3.2 Thermal methane also occurs in petroleum processing, organic synthesis, and coking.

# X1.8 Transport and Degradation of Methane in the Subsurface

X1.8.1 Aerobic Biodegradation:

X1.8.1.1 Methane is oxidized by methanotrophs in soils (23).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
 (X1.6)

X1.8.1.2 Environmental biodegradation rate of methane in aerobic soils, based on measured data, shows a geometric mean first-order water phase degradation rate of 53/h, with a measured range between 0.31 to 190/h.

# X2. TECHNICAL BACKGROUND—SCREENING LEVELS

# **X2.1** Introduction

X2.1.1 The decision matrix presented in Table 1 of this standard is based on Eklund (24), an evaluation of historic methane incidents which supported the decision points in the matrix, and a comparison with regulatory guidance regarding the use of differential pressure (for example, California DTSC). Screening levels for shallow soil gas are provided in the decision matrix that include several points of departure, including methane concentrations within soil gas at 0.05 (5 % v/v) and 0.30 (30 % v/v) and differential pressures from the subsurface to atmosphere of 500 Pa (2 in. H<sub>2</sub>O) or less. This appendix provides additional support for the screening levels through the use of modeling. Modeling parameters provided in Table X2.1 are based on Eklund (24).

X2.1.2 Flammability Criteria—The hazard criteria is not exceeded if methane concentration does not exceed a specified fraction of the lower flammability limit concentration of methane within the interior volume of the enclosed space. The criterion is applied directly at points within the enclosed space. The flammability criteria for methane is specified as  $(X_{CH_+}$  LFL· $\epsilon$ ) with  $X_{CH_+LFL}=0.054$  (5.4 %v/v) in ambient air (25). In some of the examples of this section,  $\epsilon=0.10$  is selected as an fractional multiplying factor, applicable for an occupied enclosed space [for example, US 29 CFR Section 1915.12(b)(3) Confined and Enclosed Spaces and Other Dangerous Atmospheres, US 29 CFR Section 1910.146(b)(1) Permitrequired Confined Spaces]. A value of  $\epsilon=1.0$  is applied in other examples. Other fractional multiplying factors may apply in different enclosure classifications. See Appendix X1.

TABLE X2.1 Estimated Limiting Methane Fluxes and Flows into an Enclosure to Yield Methane Lower Flammability Limits or Fractions Thereof

	Methane		Enclosure Flammability	Enclosure Air	Foundation Area in				Methane Volume		Methane	_
Case	Flammability	Safety	Criteria	Exchange	Contact	Mixing	Enclosure	Building Air	Flow	Methane	Volume	Methane
	Limit X <sub>CH4. LFL</sub>	Factor	·X <sub>CH4,</sub> LFL	Rate ER	with Soil A	Height L <sub>mix</sub>	Volume V	Flow Q <sub>bldg</sub>	Q <sub>bldg</sub> X <sub>CH4. LFL</sub>	Volume Flux	Flux (L/100 m <sup>2</sup> -	Molar Flux (g-mol
	(m <sup>3</sup> /m <sup>3</sup> )	(-)	(m <sup>3</sup> /m <sup>3</sup> )	(1/h)	(m <sup>2</sup> )	(m)	(m <sup>3</sup> )	(m <sup>3</sup> /h)	(m <sup>3</sup> /h)	(m <sup>3</sup> /m <sup>2</sup> -h)	min)	/m <sup>2</sup> -s)
	Lower Range Limits											
1	0.054	0.1	0.0054	0.25	100	2.4	240	60	0.324	0.00324	5.4	3.8E-5
2	0.054	1	0.054	0.25	100	2.4	240	60	3.24	0.0324	54	3.8E-4
	Upper Range Limits											
3	0.054	0.1	0.0054	1	100	2.4	240	240	1.296	0.01296	21.6	1.5E-4
4	0.054	1	0.054	1	100	2.4	240	240	12.96	0.1296	216	1.5E-3

# X2.1.3 Relation to Surface Emission Flux:

X2.1.3.1 Concentration within an enclosure is estimated with a balance of gas flow into and out of the enclosure. Methane into the enclosure is presumed to originate through the enclosure surface in contact with soils or through cracks or penetrations in the enclosure in contact with soils and to exit the enclosure through air exchange to the outdoors through openings such as walls, ceilings, windows, and doors. Methane concentration is presumed zero in outdoor air. The enclosure concentration is:

$$X_{CH_{4,e}} = X_{CH_{4,f}} \cdot \frac{1}{\frac{L_{mix} \cdot ER}{\left(\frac{N_{CH_{4}}^{T}}{X_{CH_{4},f}}\right) \cdot \left(\frac{R \cdot T}{P}\right)}} + 1$$
 (X2.1)

where:

 $X_{CH_{+}e}$  = enclosure methane concentration as a volume fraction (m3/m3) or mole fraction (mol/mol) of methane in indoor air,

 $X_{CH_4,f}$  = methane concentration entering the building envelope from below the soil cap or enclosure foundation,

 $N_{CH_4}^T(g - m \text{ o } 1/m^2 - s) = \text{molar flux of methane into the enclosure from soils,}$ 

 $L_{mix}$ (m) = mixing height or volume to surface area ratio for the enclosure  $(L_{mix} = V/A)$ , and

ER (1/s) = volumetric air exchange rate for the enclosure.

X2.1.3.2 The total molar flux, including methane and other gases and vapors, through the foundation and into the enclosure is:

$$N_{total}^{T} = \left(N_{CH_A}^{T} / X_{CH_A,f}\right) \tag{X2.2}$$

where:

 $(R \cdot T / P)$  = molar volume (m<sup>3</sup>/g-mol) based on the ideal gas law with temperature, T; total pressure, P; and ideal gas constant, R and

 $(N_{CH_4}^T / X_{CH_4,f}) \cdot (R \cdot T / P)$  = total volumetric flow into the foundation including methane and other gases and vapors.

X2.1.3.3 With methane-only soil gas flow,  $X_{CH_4,f}=1$  and  $N_{total}^T=N_{CH_4}^T$  for:

$$X_{CH_{4},e} = \frac{1}{\frac{L_{mix} \cdot ER}{N_{CH_{4}}^{T} \cdot \left(\frac{R \cdot T}{P}\right)} + 1}$$
(X2.3)

X2.1.3.4 If flow out of the soil is a small fraction of the total enclosure flow:

$$X_{CH_4,e} = N_{CH_4}^T \cdot \left(\frac{R \cdot T}{P}\right) \cdot \left(\frac{1}{L_{\text{min}} \cdot ER}\right) \tag{X2.4}$$

X2.1.3.5 Flux values may be specified as volumetric flux (m³/m²-s),  $u_{v,CH_4} = (R \cdot T / P) \cdot N_{CH_4}^T$  or mass flux (g/m²-s),  $J_{CH_4} = MW_{CH_4} \cdot N_{CH_4}^T$ . Total methane flow is the flux multiplied by the area of the foundation in contact with soil, A. Volume fraction (and mole fraction) may be presented as a mole concentration (g-mol/m³), ( $X_{CH_4} \cdot (P / R T)$ ), or a mass concentration (g/m³),  $c_{CH_4} = X_{CH_4} \cdot MW_{CH_4} \cdot (P / R T)$ ).

X2.1.4 Relationship between Enclosure Concentration and Surface Emission Flux—Hers et al (26) specify high and low ranges of parameters for residential houses. These parameters are typical for many occupied enclosures, including basements and crawlspaces. The limiting ranges of methane emission flux into an enclosure are shown in Table X2.1 for this range of enclosure parameters. The more stringent flux criteria, Cases 1 and 2, are for the lower building air flow.

# X2.2 Estimate of Methane Hazard Screening Criteria in Soil Gas

X2.2.1 Flammability Criteria:

X2.2.1.1 Potential flammability of soil gas methane is evaluated by applying a flammability criterion within an enclosure or at the interface between open air (outdoors or within an enclosure) and the top of the soil, soil cap, or foundation interface. Soil gas concentration and differential pressure screening values within the soil matrix are estimated based on soil properties and the imposed surface methane concentration criteria using soil gas transport models. We consider several similar scenarios, with a subsurface source of methane:

(1) An open soil surface,

(2) An intact low-permeability cap or building foundation (concrete, asphalt, clay, and so forth) in contact with the soil, and

(3) A cracked low-permeability cap or building foundation in contact with the soil.

X2.2.1.2 The scenarios and geometries are illustrated in Fig. X2.1. In these cases, Scenario 1 for a homogeneous soil layer is a simplification of Scenario 2, for which the upper surface is

a low-permeability and low-diffusion coefficient cap. Scenario 3 in these examples and the included estimates is considered in a one-dimensional geometry with average parameters for the cracked cap. More complex estimates may include two- or three-dimensional representations; these may be more useful in

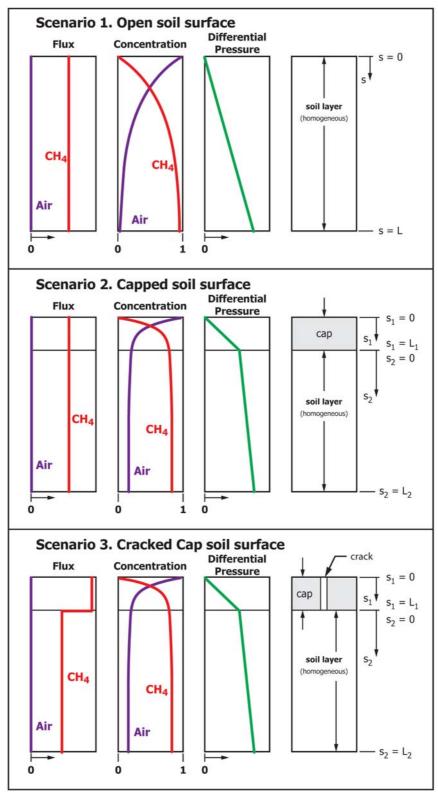


FIG. X2.1 Scenarios for Methane Flammability Hazard Screening

some site-specific evaluations, rather than the one-dimensional screening estimates that are presented herein.

X2.2.2 Soil Gas Concentration and Pressure Criteria:

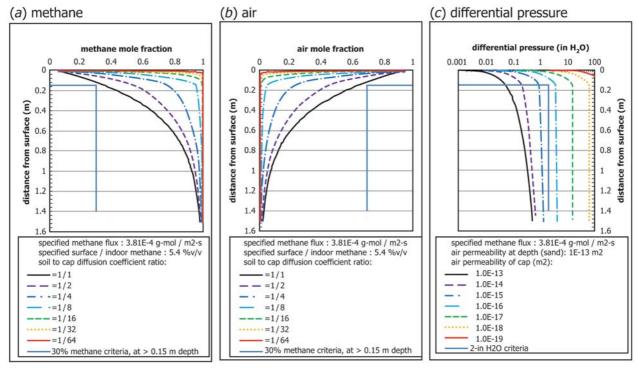
X2.2.2.1 Comparison to Algebraic Model Estimates—Estimates have been calculated using a presumption of binary soil gas flow (air and methane) using a simplified 'dusty gas' model (27), as developed and discussed in a later section of this appendix. Biogenic reaction of methane with oxygen is neglected in this model. Neglecting aerobic biodegradation of methane in soil is a conservative assumption.

X2.2.2.2 Two cases are calculated. Case 1 (from Table X2.1) applies a 100 % lower flammability limit (LFL) methane concentration inside the enclosure and at the soil surface, along with a constant methane flux through soil of 3.8E-5 g-mol /m²-s. Case 2 (from Table X2.1) applies a 10 % LFL methane concentration inside the enclosure and at the soil surface, along with a constant methane flux through soil of 3.8E-4 g-mol /m²-s. The modeled soil gas concentration profiles have been calculated for a homogeneous sand layer, as well as a range of capping materials with the diffusion coefficient for the cap specified as a fraction of the diffusion coefficient for porous sand. The calculated differential pressure profile is also shown in Fig. X2.2 and Fig. X2.3 for specified values of the cap

permeability. The resulting soil gas profiles for methane and air, and differential pressure, are shown for these scenarios in Fig. X2.2 and Fig. X2.3. Relevant model parameters are included in Table X2.2.

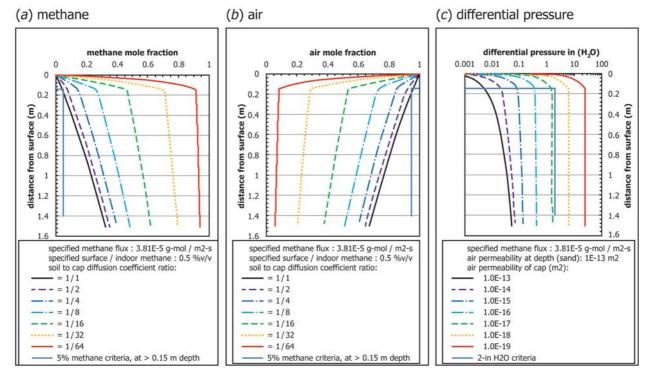
X2.2.2.3 Eklund (24) proposed screening levels for shallow soil gas that include several points of departure, including methane concentrations within soil gas at 0.05 (5 % v/v) and 0.30 (30 % v/v) within the soil gas matrix and differential pressures from the subsurface to atmosphere of 2 in.  $H_2O$  or less. The model estimates are compared to these screening values to better bound their range of applicability.

X2.2.2.4 The upper range soil gas screening level of 0.30 (30 % v/v) methane is a conservative indicator for the 100 % LFL criteria within a low-airflow enclosure (Fig. X2.2). The lower range soil gas screening level of 0.05 (5 % v/v) methane is a conservative indicator for the 10 % LFL criteria within a low-airflow enclosure (Fig. X2.3). In both figures, the air fraction is complementary to the methane concentration; methane flux partially displaces ambient air and its components (nitrogen, oxygen, argon, and so forth). Differential pressure from the enclosure to below a capping layer is < 2 in.  $\rm H_2O$  for lower-permeability capping layers of approximately  $\rm 10^{-16}$  to  $\rm 10^{-17}$  m² for the specified 0.15-m capping layer thickness.



Note 1—Sandy soil is presumed at depths greater than 0.15 m. Varied transport properties are presumed for the shallow cap layer from the surface to 0.15 m. Concentration profiles are shown for methane (a) and air (b) with the diffusion coefficient through the shallow layer equal to that for sand (1/1) and reduced by factors from 2 through 64. The concentration profiles are compared with a 30 % v/v methane criteria specified at 0.15 m and greater (below the cap) and shown to be conservative (overestimating enclosure methane concentration) with respect to the 30 % v/v methane soil gas criteria for all presumed diffusion coefficients. Differential pressure versus depth is shown in (c) for selected values of cap permeability ranging from that equal to sand (1E-13 m<sup>2</sup>) to 1.0E-19 m<sup>2</sup>. The pressure profiles are compared with a 2-in. H<sub>2</sub>O differential pressure criteria at depths below 0.15 m and are shown to be conservative (overestimating enclosure methane concentration) for cap permeability less than approximately 1.0E-16 m<sup>2</sup>. Values are calculated with the algebraic model of Thorstenson and Pollock (27) and biodegradation of methane is very conservatively neglected. Assumptions: soil (sand) permeability = 1.0E-13 m<sup>2</sup> and soil (sand) effective diffusion coefficient for methane in air = 3.49E-06 m<sup>2</sup>/s.

FIG. X2.2 Soil Gas Versus Depth for (a) Methane, (b) Air, and Differential Pressure (c) for an Applied Surface Methane Concentration of 5.4 %v/v (100 % LFL) and an Upward Methane Flux of 3.8E-4 g-mol /m²-s (Corresponding to a 5.4 %v/v Methane Concentration in a Low-Flow Rate Surface Enclosure)



Note 1—Sandy soil is presumed at depths greater than 0.15 m. Varied transport properties are presumed for the shallow cap layer from the surface to 0.15 m. Concentration profiles are shown for methane (a) and air (b) with the diffusion coefficient through the shallow layer equal to that for sand (1/1) and reduced by factors from 2 through 64. The concentration profiles are compared with a 5% v/v methane criteria specified at 0.15 m and greater (below the cap), and shown to be conservative (overestimating enclosure methane concentration) with respect to the 5% v/v methane soil gas criteria for all presumed diffusion coefficients. Differential pressure versus depth is shown in (c) for selected values of cap permeability ranging from that equal to sand (1E-13 m<sup>2</sup>) to 1.0E-19 m<sup>2</sup>. The pressure profiles are compared with a 2-in H<sub>2</sub>O differential pressure criteria at depths below 0.15 m and are shown to be conservative (overestimating enclosure methane concentration) for cap permeability less than approximately 1.0E-18 m<sup>2</sup>. Values are calculated with the algebraic model of Thorstenson and Pollock (27) and biodegradation of methane is very conservatively neglected. Assumptions: Soil (sand) permeability = 1.0E-13 m<sup>2</sup>. Soil (sand) effective diffusion coefficient for methane in air = 3.49E-06 m<sup>2</sup>/s.

FIG. X2.3 Soil Gas Versus Depth for (a) Methane, (b) Air, and Differential Pressure (c) for an Applied Surface Methane Concentration of 0.54 %v/v (10 % LFL) and an Upward Methane Flux of 3.8E-5 g-mol /m<sup>2</sup>-s (Corresponding to a 0.54 %v/v Methane Concentration in a Low-Flow Rate Surface Enclosure)

#### **TABLE X2.2 Applied Parameters**

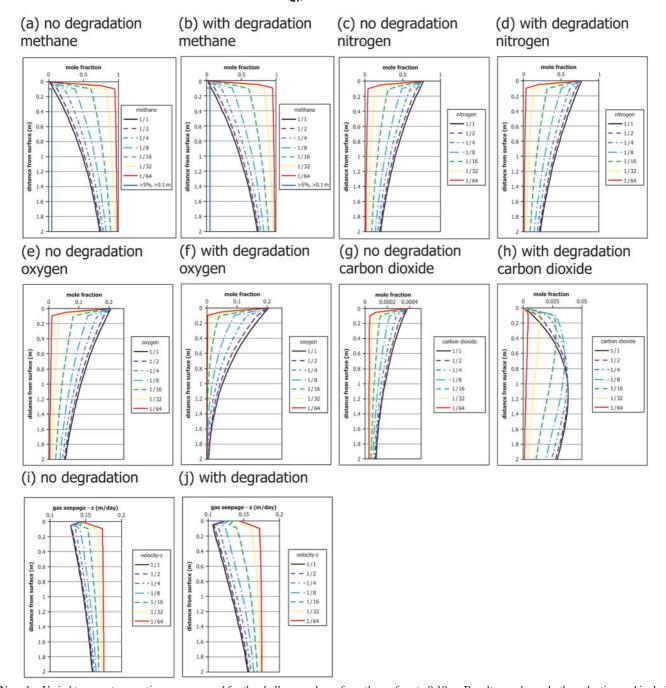
R	831.473 ((kg/m-s <sup>2</sup> )·m <sup>3</sup> /g-mol·K)	Ideal gas constant
P	10132500 (kg/m-s <sup>2</sup> )	Atmospheric pressure
T	293.15 (K)	Ambient temperature
D <sub>CH4</sub> -air	2.17E-5 (m <sup>2</sup> /s)	Molecular diffusion coefficient of methane in air
$X_{CH_4,LFL}$	0.054 (mol/mol)	Flammability criteria for methane in air
	0.10	Fractional multiplying factor for flammability criteria
$MW_{CH_4}$	16.04 (g/g-mol)	Molecular weight of methane
MW <sub>air</sub>	28.9644 (g/g-mol)	Average molecular weight of air
$\mu_{CH4}$	1.02E-05 (kg/m-s)	Gas viscosity of methane
$\mu_{air}$	1.80E-05 (kg/m-s)	Gas viscosity of air
sand	_	Applied parameters for sand,
		after Tillman and Weaver
		(2007) <b>(28)</b>
$\theta_{\mathcal{T}}$	0.375 (cm <sup>3</sup> -void/cm <sup>3</sup> -soil)	Soil porosity
$\theta_{w}$	0.054(cm <sup>3</sup> -water/cm <sup>3</sup> -soil)	Soil water fraction
$K_w$	26.78 (cm/hr)	Saturated soil hydraulic
		conductivity
$B_k$	1E-13 m <sup>2</sup>	Gas permeability

#### X2.2.3 Effect of Aerobic Methane Oxidation:

X2.2.3.1 The dusty gas model is too complex for algebraic solution with more than two gases or with reactions between gas components. A numerical model, MIN3P-DUSTY (29, 30)

has been applied in solution of Case 2 (from Table X2.1), consistent with the scenarios in Fig. X2.1. Comparable simulations have been calculated both including and neglecting aerobic methane oxidation. Results are plotted in Fig. X2.4. An upward methane flux of 3.8E-4 g-mol /m<sup>2</sup>-s was specified at a depth of 2.8 m, consistent with Case 2 (Table X2.1), based on the 10 % LFL methane criteria within an enclosure.

X2.2.3.2 As in the prior algebraic modeling, the numerical modeling shows agreement with the soil gas screening level for methane of 0.05 (5 % v/v) proposed by Eklund (24) in all instances. The effect of biodegradation on methane concentration and flux is relatively negligible in this case because of the high imposed methane flux. The effects of biodegradation are also limited for higher values of methane flux, including Case 1 (Table X2.1). The effect of aerobic biodegradation is more significant at lower specified values of methane flux (discussed later). Some degree of biodegradation is evident from the plotted profiles for oxygen and carbon dioxide. Net total upward gas seepage is less for higher-diffusion coefficient capping layers when biodegradation is included. This reflects greater downward oxygen transport through the higher diffusion coefficient capping layer.



Note 1—Varied transport properties are presumed for the shallow cap layer from the surface to 0.10 m. Results are shown both neglecting and including biogenic methane oxidation. The difference in concentration is negligible for methane and nitrogen. Oxygen shows shallower penetration from the surface with degradation included. Significant differences are evident in the carbon dioxide concentration profile. Net upward gas seepage is less when both biodegradation and a higher-diffusion coefficient cap are included; this reflects greater downward oxygen flux as a component of the total gas flux.

FIG. X2.4 Soil Gas Versus Depth for an Applied Upward Methane Flux at a 2.8-m Depth of 3.8E-5 g-mol /m2-s

# **X2.3** Modeling Considerations and Development

X2.3.1 Homogeneous Soil Layer:

X2.3.1.1 Significant presence of methane in soil, when observed, can occur with both displacement of relatively nonreactive atmospheric gases from soil gas (nitrogen, argon) and subsurface soil gas pressures greater than atmospheric pressure. General calculations for methane soil gas migration

and attenuation under these conditions are not always adequately addressed by simple models, such as, for example, Fick's law. More complex estimates, including, for example, the "dusty gas" model (31, 32) are applicable for these general scenarios and address the coupled effects of diffusion and viscous gas flow for multiple gas species in porous soil. For the purpose of developing a simple but useful screening method

using only algebraic equations, a simplification of the "dusty gas" model is applied.

X2.3.1.2 Chemical reaction of gases in the soil matrix is neglected. For cases in which methane concentration in the soil matrix is significant, that is, greater than several percent by volume, and methane advection is significant, this is a reasonable assumption, as the methane will displace atmospheric gases, including oxygen. Where oxygen is present in the subsurface, microbial reaction of methane with oxygen can attenuate methane in the subsurface (33, 34). In these conditions, this conservative assumption of neglecting biodegradation may overestimate potential methane hazard.

X2.3.1.3 Migration of methane only is considered, with other major atmospheric gases (nitrogen, oxygen, argon, and carbon dioxide) included as a single stagnant (air) component in soil gas. The method follows that of Thorstenson and Pollock (27), hereafter, TP. The effect of total pressure gradients and temperature gradients on diffusion rates is neglected. Gas transport is presumed to be dominated by gas-gas, not gas-solid interactions; this is a reasonable assumption at and near atmospheric pressure. Development and discussion of the method follows.

X2.3.1.4 In these estimates, a steady, constant flux,  $N_{CH_4}^T$ , of methane (CH<sub>4</sub>) is specified along the migration pathway from a source at depth to the open surface interface. For the one-component nonreactive flow, mole and mass averaged velocity (or flux) is the same. Mass flux and volume (or Darcy) flux are, respectively:

$$J_{CH_4} = MW_{CH_4} \cdot N_{CH_4}^T$$
 (X2.5)

$$u_{v} = (R \cdot T / P) \cdot N_{CH}^{T}$$
 (X2.6)

X2.3.1.5 For a biogenic source, the flux could include both methane and carbon dioxide. For a chemical source (hydrocarbons, for example), the flux could also include volatilizing component chemicals.

X2.3.1.6 Air is presumed as a stagnant gas with no net flux into or out of the soil,  $N_{air}^T = 0$ . The concentration of air in soil is given by the solution to the Stefan-Maxwell Equations [noting TP (Eq. 85) has a typographical error; integration of TP (Eq. A2) is shown]. The mole fraction of CH4 is given by difference [TP(Eq. 86)]:

$$X_{air}(s) = X_{air}(s = 0) \cdot \exp\left(-\left(\frac{R \cdot T}{P}\right) \cdot \left(\frac{N_{CH_4}^T}{D_{CH_4 - air(eff)}}\right) \cdot s\right)$$
(X2.7)

$$X_{CH_s}(s) = 1 - X_{air}(s)$$
 (X2.8)

X2.3.1.7 The value, s, is the increasing depth or distance along the migration pathway originating at the point of entry to an enclosed space (s=0) as in Fig. X2.1. At the s=0 boundary,  $X_{CH_4}(s=0) \le X_{CH_4,LFL}$ :  $\varepsilon$  is a limiting criterion. In upper bound calculations (representing worst case conditions), we apply:

$$X_{CH_4}(s = 0) = X_{CH_4, LFL} \cdot \varepsilon \tag{X2.9}$$

$$X_{air}(s = 0) = 1 - X_{CH_s}(s = 0)$$
 (X2.10)

X2.3.1.8 Other parameters include the temperature, T(K), presumed constant; the total atmospheric pressure, P, here presumed nearly constant over the soil layer depth; and the

ideal gas constant, R. The solution for  $X_{air}(s)$  also applies for the conserved (or nearly conserved) gases in air, including nitrogen and argon. The value  $D_{CH_{d}-air(eff)}(35)$  is the effective diffusion coefficient of methane in the soil matrix.

$$D_{CH_4-air(eff)} = D_{CH_4-air} \cdot \left(\frac{\theta_a^{103}}{\theta_T^2}\right) \tag{X2.11}$$

where:

 $D_{CH_q\text{-}air}$  = molecular diffusion coefficient of methane in air,  $\theta_T$  = total soil porosity, and  $\theta_a$  = air-filled soil porosity.

X2.3.1.9 In this example,  $D_{CH_{a}-air}$  is presumed constant independent of the component mixture composition.

X2.3.1.10 Viscous flux is calculated as [TP(70)]:

$$N^{V} = \frac{N_{CH_4}^{T} \cdot (MW_{CH_4})^{1/2} + N_{air}^{T} \cdot (MW_{air})^{1/2}}{\frac{\mu \cdot b_m}{P} + X_{CH_4} \cdot (MW_{CH_4})^{1/2} + X_{air} \cdot (MW_{air})^{1/2}}$$
(X2.12)

X2.3.1.11 Molecular weight for methane and air are respectively,  $MW_{CH_4}$  and  $MW_{air}$ . Gas viscosity,  $\mu$ , is defined as mean molar viscosity of the mixture [TP Eq. (81)]:

$$\mu = X_{CH_4} \cdot \mu_{CH_4} + X_{air} \cdot \mu_{air} \qquad (X2.13)$$

X2.3.1.12 The Klickenberg parameter for air,  $b_{air}$ , is based on empirical correlation [TP (Eqs. 68 and 69)] of measured gas permeability in porous media.

$$b_{qir}[atm] = 0.77 \cdot B_k[millidarcies]$$
 (X2.14)

where  $b_{air}$  is in atmospheres and the soil matrix permeability,  $B_k$ , is in millidarcies.

X2.3.1.13 This is a dimensional correlation; with unit change we have:

$$b_{air} [kg/m - s^{2}] = 10132500 \frac{kg/m - s^{2}}{atm} \cdot 0.77 \cdot \left( \frac{millidarcy}{9.869233E - 16m^{2}/millidarcy} \right)^{-0.39} \cdot B_{k} [m^{2}]^{-0.39}$$

$$b_{air} [kg/m - s^{2}] = 0.11 \cdot B_{k} [m^{2}]^{-0.39}$$
(X2.15)

X2.3.1.14 The Klickenberg parameter is generalized to a hypothetical gas of unit molecular weight and unit viscosity as [TP (Eq. 63)]:

$$b_m = b_{air} \cdot (MW_{air})^{1/2} / \mu_{air}$$
 (X2.16)

X2.3.1.15 Differential pressure along the pathway s is calculated using Darcy's law [TP (Eq. C2)].

$$\frac{\partial P(s)}{\partial s} = -N^{V} \cdot \left(\frac{R \cdot T}{P}\right) \cdot \frac{\mu}{B_{L}} \tag{X2.17}$$

X2.3.1.16 The differential pressure over a finite soil layer thickness, *s*, is numerically calculated as:

$$\Delta P(s) = \int_{s=0}^{s} \left( \frac{\partial P}{\partial s} \right) \cdot ds \tag{X2.18}$$

X2.3.2 Upper-Bound Flux and Layered Soils:

X2.3.2.1 For homogeneous soils, as in Fig. X2.1 (a), the the profile relationship Eq X2.7 is applied.

$$N_{CH_4}^T = -\ln\left(\frac{X_{air}(s=L)}{X_{air}(s=0)}\right) \cdot \left(\frac{P}{R \cdot T}\right) \cdot \left(\frac{D_{CH_4-air(eff)}}{L}\right) (X2.19)$$

X2.3.2.2 This relationship imposes an upper bound methane flux:

$$N_{CH_4}^T(s = L) \le -\ln\left(\frac{X_{air}(s = L)}{X_{air}(s = 0)}\right) \cdot \left(\frac{P}{R \cdot T}\right) \cdot \left(\frac{D_{CH_4-air(eff)}}{L}\right)$$
(X2.20)

X2.3.2.3 For a given soil type with specified  $D_{CH_4\text{-}air(eff)}$  and  $X_{CH_4}(s=0) \le X_{CH_4\text{-}LFL} \cdot \varepsilon$ , this maximum acceptable flux is a function of depth (s=L) and source concentration  $X_{air}(s=L)$ .

X2.3.2.4 For layered soils, including capping layers, as in Fig. 1(b) and (c), each layer is defined by bulk parameters, as  $D_{CH_4\text{-}air(eff)}$ , effective vapor diffusion coefficient;  $B_k$ , gas permeability; and L, thickness. Eq X2.9 and Eq X2.10 apply for each of the layers. With constant flux,  $N_{CH_4}^T$ , through all of the layers, and matched concentrations of methane and air at the layer interfaces, flux through a two-layer system is:

$$N_{CH_4}^{T} = -\ln\left(\frac{X_{air}(s_2 = L_2)}{X_{air}(s_1 = 0)}\right) \cdot \left(\frac{P}{R \cdot T}\right) \frac{1}{\left(\frac{L_1}{D_{CH_4 - air(eff)_1}} + \frac{L_2}{D_{CH_4 - air(eff)_2}}\right)}$$
(X2.21)

X2.3.2.5 This defines an acceptable upper bound flux:

$$N_{CH_4}^T \Big( s_2 = L_2 \Big) \leq -\ln \left( \frac{X_{air} \Big( s_2 = L_2 \Big)}{X_{air} \Big( s_1 = 0 \Big)} \right) \cdot \left( \frac{P}{R \cdot T} \right) \frac{1}{\left( \frac{L_1}{D_{CH_4 - air(eff)_1}} + \frac{L_2}{D_{CH_4 - air(eff)_2}} \right)}$$

$$(X2.22)$$

as a function of depth  $(s_2 = L_2)$  and source concentration  $X_{air}(s_2 = L_2)$ .

X2.3.3 Transport Estimates for a Cracked Capped Soil Layer:

X2.3.3.1 Capping layers of soil, asphalt paving, or concrete may be intact or cracked. In the instance that the soil layer bounded by a cracked cap, the cracked  $(A_{crk})$  and total  $(A_{total})$  areas are specified. The crack fraction is defined as:

$$\eta = \left(\frac{A_{crk}}{A_{total}}\right) \tag{X2.23}$$

X2.3.3.2 For both diffusion coefficient and permeability estimates we consider an area-weighted parallel resistance flow model. The effective average parameter values are:

$$D_{eff,avg} = \eta \cdot D_{eff,crk} + (1 - \eta) \cdot D_{eff,intact}$$
 (X2.24)

$$B_{k,avg} = \eta \cdot B_{k,crk} + (1 - \eta) \cdot B_{k,intact}$$
 (X2.25)

X2.3.3.3 With the intact area of the cap presumed impermeable, flow occurs only through the cracked area and:

$$D_{eff,avg} = \eta \cdot D_{eff,crk} \tag{X2.26}$$

$$B_{k,avg} = \eta \cdot B_{k,crk} \tag{X2.27}$$

X2.3.3.4 Other than the redefined transport parameters, calculations are similar to those for the intact cap. For an intact concrete capping layer with no cracks ( $\eta=0$ ), the lower bound flux is not zero but is instead limited by diffusion through the intact concrete.

X2.3.4 Model Sensitivity—Comparison of Stefan-Maxwell Equation to Fick's Law:

X2.3.4.1 From Eq X2.7 and Eq X2.8, with no degradation, for a binary mixture (methane/air) in homogeneous soil, we have the mole fraction of methane in soil gas:

$$X_{CH_{4}}(s) = 1 - \left(1 - X_{CH_{4}}\left(s = 0\right)\right) \cdot \exp\left(-\left(\frac{R \cdot T}{P}\right) \cdot \left(\frac{N_{CH_{4}}^{T}}{D_{CH_{4}-air(eff)}}\right) \cdot s\right)$$
(X2.28)

X2.3.4.2 The Darcy flux of methane is:

$$u_{\nu} = \left(\frac{R \cdot T}{P}\right) \cdot N_{CH_4}^T \tag{X2.29}$$

X2.3.4.3 A Taylor series expansion of  $exp(\eta)$  at  $\eta = 0$  is:

$$\exp(\eta) = \sum_{n=0}^{\infty} \frac{\eta^n}{n!} \cong 1 + \eta + \frac{\eta^2}{2} + \dots$$
 (X2.30)

X2.3.4.4 Apply the first two terms of the Taylor series expansion to Eq X2.7 and Eq X2.8.

$$X_{CH_4}(s) \approx 1 - \left(1 - X_{CH_4} \left(s = 0\right)\right) \cdot \left\{1 + \left(-\left(\frac{R \cdot T}{P}\right) \cdot \left(\frac{N_{CH_4}^*}{D_{CH_4-air(eff)}}\right) \cdot s\right)\right\}$$
(X2.31)

X2.3.4.5 With algebra, this yields:

$$N_{CH_{4}}^{T} \approx \left(\frac{P}{R \cdot T}\right) \cdot \frac{D_{CH_{4}-air(eff)}}{s} \cdot \frac{\left[X_{CH_{4}}\left(s\right) - X_{CH_{4}}\left(s = 0\right)\right]}{\left[1 - X_{CH_{4}}\left(s = 0\right)\right]}$$
(X2.32)

X2.3.4.6 The further simplification in Fick's law presumes low concentrations as a fraction of the total:

$$[1 - X_{CH_4}(s = 0)] = X_{air}(s = 0) = X_{total} = 1 \text{ (X2.33)}$$

or

$$N_{CH_{4}}^{T} \approx \left(\frac{P}{R \cdot T}\right) \cdot \frac{D_{CH_{4}-air(eff)}}{s} \cdot \left[X_{CH_{4}}\left(\mathbf{s}\right) - X_{CH_{4}}\left(\mathbf{s}=0\right)\right] \tag{X2.34}$$

X2.3.4.7 The Darcy flux for Fick's law and Stefan-Maxwell equations are:

$$u_{\nu[D-G]} = \left(\frac{R \cdot T}{P}\right) \cdot N_{CH_4}^T = -\frac{D_{CH_4-air(eff)}}{s} \cdot \ln\left(\frac{1-X_{CH_4}(s)}{1-X_{CH_4}(s=0)}\right) \tag{X2.35}$$

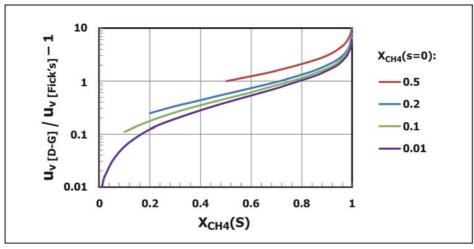
$$u_{v[Ficks]} = \left(\frac{R \cdot T}{P}\right) \cdot N_{CH_4}^T \approx \frac{D_{CH_4 - air(eff)}}{s} \cdot \ln(X_{CH_4}(s) - X_{CH_4}(s = 0))$$
(X2.36)

X2.3.4.8 The ratio is:

$$\frac{u_{v[D-G]}}{u_{v[Ficks]}} = \frac{-\ln\left(\frac{1-X_{CH_4}(s)}{1-X_{CH_4}(s=0)}\right)}{\left(X_{CH_4}(s)-X_{CH_4}(s=0)\right)}$$
(X2.37)

X2.3.4.9 A comparison of bias is shown in Fig. X2.5 for ratios of  $[X_{CH_4}(s=0)/X_{CH_4}(s=L)]=0.01,\ 0.1,\ 0.2,\ and\ 0.5$  and  $X_{CH_4}(s=L)>X_{CH_4}(s=0)$ , that is, upward diffusive concentration flux.

X2.3.4.10 It is evident from Fig. X2.5 that, for lower concentrations of the mobile methane gas, the bias between the two estimates is smaller. For methane mole fraction concentrations less than 0.20 bias, error is less than approximately 25 %. More general problems, including reactive flow and heterogeneous conditions, would have different bias than this simple example. The solution does point to the likely need to use more complex models than Fick's law when the mobile gas is a substantial fraction of the total soil gas composition.



Note 1—For values of  $\{u_{v[D-G]} / u_{v[F i c k s]} - 1\} < 0.5$ , bias error is less than 50 %.

FIG. X2.5 Relative Bias between Fick's Law and Stefan-Maxwell Flux Estimates Versus Source Concentration,  $X_{\text{CH4}}(s)$  and Concentration at the Top of the Domain  $X_{\text{CH4}}(s=0)$ 

#### **X2.4** Effect of Methane Biodegradation

X2.4.1 The prior section presented estimates for vapor transport of methane in air (a binary mixture) in subsurface soils using a simplified algebraic solution of the "dusty-gas" model. Scenarios with more than two chemical components or with biological reactions between components are more complex and require numerical solution. The contribution of biological methane oxidation has been estimated using the MIN3P-DUSTY numerical model to simulate transport and reaction of methane and oxygen in air through soils. MIN3P-DUSTY is a three-dimensional finite-volume model for multicomponent reactive transport in variably saturated porous media (29, 30). Gas and vapor transport in this use of the MIN3P-DUSTY model are simulated using the dusty gas model. Gas flow and induced pressures in these simulations result from molecular diffusion and non-equimolar reactions of the gas species.

X2.4.2 The capped and uncapped one-dimensional scenarios illustrated in Fig. X2.1 are used in the simulations. Stoichiometric methane oxidation (when included) occurs in the water phase.

$$CH_4 + 2 \cdot O_2 \rightarrow CO_2 + 2 \cdot H_2O$$
 (X2.38)

X2.4.3 No biomass growth is presumed. Dual Monod-type kinetics are applied.

$$R_{m} = V_{\text{max}} \cdot \left( \frac{c_{CH_{4}}}{c_{CH_{4}} + K_{m,CH_{4}}} \right) \cdot \left( \frac{c_{O_{2}}}{c_{O_{2}} + K_{m,O_{2}}} \right)$$
(X2.39)

X2.4.4 Kinetic rates are based on observation and literature values (35). Values include the maximum methane oxidation rate,  $V_{max}$  (8 × 10<sup>-8</sup> mol-CH<sub>4</sub>/L<sub>water</sub>-s) and the half-saturation constants for methane and oxygen, respectively,  $K_{m\_O_2}$  and  $K_{m,O_2}$  (both 1 × 10<sup>-5</sup> mol/L<sub>water</sub>).

X2.4.5 Results are shown in Fig. X2.4 for a high-methane flux scenario. In Fig. X2.4, aerobic biodegradation of methane has a relatively insignificant effect on methane flux at the surface.

#### X3. LEGAL BACKGROUND ON FEDERAL AND STATE LIABILITY FOR METHANE GAS

# INTRODUCTION

This appendix provides background on the basis of potential liability for owners and operators of real property for methane gas Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S.C. 9601 et seq. (CERCLA), Resource Conservation and Recovery Act, 42 U.S.C. 6901 et seq. ("RCRA"), and potential state common law causes of action for personal injury and property damage claims as a result of the presence of methane gas. These potential state common law causes of action include negligence, strict liability in tort, nuisance, trespass, and premises liability.

Note X3.1—This appendix is intended for informational purposes only

and is not intended to be nor may it be interpreted as legal advice.

#### X3.1 CERCLA

X3.1.1 CERCLA authorizes the federal government to respond to releases of hazardous substances, <sup>13</sup> seek reimbursement from potentially responsible parties (PRPs), <sup>14</sup> or order PRPs to abate releases or threatened releases of hazardous substances that may be an imminent and substantial endangerment to the public health or welfare or the environment. <sup>15</sup> In addition, CERCLA requires anyone who is in charge of a facility or vessel to report immediately releases of hazardous substances that they become aware of which exceed the reportable quantity threshold established by the U.S. Environmental Protection Agency (EPA). <sup>16</sup> In addition, private persons and PRPs who incur cleanup costs may seek reimbursement from other PRPs provided they comply with certain requirements. <sup>17</sup>

X3.1.2 There are four categories of potentially responsible parties that may be liable under CERCLA identified in §9607(a).<sup>18</sup> A plaintiff shall establish the following elements before a defendant may be found liable under CERCLA:

X3.1.2.1 There has been a "release" or threatened release; <sup>19</sup>

X3.1.2.2 of a hazardous substance;<sup>20</sup>

X3.1.2.3 from a facility or vessel;<sup>21</sup> and

X3.1.2.4 that has caused the incurrence of response costs<sup>22</sup> that are consistent with the National Oil and Hazardous Substances Pollution National Contingency Plan (NCP).<sup>23</sup>

X3.1.3 Methane does not fall within the definition of a CERCLA hazardous substance because it does not fall within Categories (A)-(F) of the definition of a hazardous substance.<sup>24</sup> For example, the EPA has not designated methane has a hazardous substance under 42 U.S.C. 9602.<sup>25</sup> Methane is also not regulated as a hazardous waste under 42 U.S.C. 6921.<sup>26</sup> Methane has not been identified as a toxic pollutant<sup>27</sup> or a

hazardous air pollutant.<sup>28</sup> Finally, methane has not been identified as an "imminently hazardous chemical substance or mixture pursuant to 15 U.S.C. 2606.<sup>29</sup> Indeed, the recent regulatory focus involving methane has been its status as an intensive greenhouse gas.

X3.1.3.1 The definition of hazardous substance in Section 101(14) and pollutant or contaminant in Section 104(a)(2) excludes certain types of natural gas and petroleum. Naturally occurring methane gas found in or associated with petroleum deposits is a type of natural gas and is, therefore, exempted from CERCLA coverage. However, methane gas emanating from a landfill is not considered to be "natural gas" and such releases may, therefore, be eligible for response under Section 104(a)(1) if methane gas otherwise meets the definition of pollutant or contaminant under Section 104(a)(2).

X3.1.3.2 The EPA is authorized under Section 104(a)(1) to take response actions for actual or potential releases of "pollutants or contaminants" that may present an "imminent and substantial danger to the public health or welfare." In its guidance document entitled, "CERCLA Removal Actions at Methane Release Sites," OSWER Directive #9360.0-8 (Jan. 23, 1986), the EPA indicated that potentially explosive gas levels that are detected during daily monitoring at the perimeter of the landfill and nearby homes and businesses appeared to meet the criterion of imminent and substantial danger. However, the EPA emphasized that, while it had the authority to take action under Section 104, the agency would not be able to recover its costs under Section 107 since methane is not a hazardous substance.

X3.1.4 If landfill gas contains methane and other hazardous substances such as volatile organic compounds (VOCs), the landfill gas itself could be considered to be a hazardous substance.<sup>30</sup>

# X3.2 Resource Conservation and Recovery Act (RCRA)<sup>31</sup>

X3.2.1 Under Subtitle D of RCRA, the EPA established minimum national performance standards for landfills receiving wastes such as municipal wastes that are not regulated as hazardous wastes.<sup>32</sup> Subtitle D imposes certain requirements regarding methane gas. For example, for operating landfills, the concentration of methane gas may not exceed 25 % of the lower explosive limit (LEL) for methane in facility structures. Additionally, the concentration of methane gas may not exceed

<sup>&</sup>lt;sup>13</sup> Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S.C. § 9604(a)(1) (2006).

<sup>&</sup>lt;sup>14</sup> 42 U.S.C. § 9607(a)(4)(A).

<sup>15 42</sup> U.S.C. § 9606.

<sup>&</sup>lt;sup>16</sup> 42 U.S.C. § 9603.

<sup>&</sup>lt;sup>17</sup> 42 U.S.C. § 9607(a)(4)(B).

<sup>&</sup>lt;sup>18</sup> 42 U.S.C. § 9607(a)(1)-(4).

<sup>&</sup>lt;sup>19</sup> 42 U.S.C. § 9601(22). Excluded from the definition of "release" is any release that results in exposure solely within the workplace for claims that may be asserted against an employer; 42 U.S.C. § 9601(22)(A).

<sup>&</sup>lt;sup>20</sup> 42 U.S.C. §§ 9601(14)(A)-(F). A CERCLA hazardous substance includes any substance identified as a CERCLA hazardous substance by EPA pursuant to 42 U.S.C. § 9602 (See List of Hazardous Substances and Reportable Quantities, 40 C.F.R. pt. 302, Table 302), classified as a hazardous waste under 42. U.S.C. § 6921, designated as toxic pollutants under 33 U.S.C. §§ 1317 or 1321, a hazardous air pollutant under 42 U.S.C. § 7412, or an imminently hazardous chemical substance or mixture pursuant to 15 U.S.C. § 2606(f).

<sup>&</sup>lt;sup>21</sup> 42 U.S.C. § 9601(9).

<sup>&</sup>lt;sup>22</sup> 42 U.S.C. § 9601(25).

<sup>&</sup>lt;sup>23</sup> 40 C.F.R. pt. 300.

<sup>&</sup>lt;sup>24</sup> 42 U.S.C. 9601(14)(A)-(F).

<sup>&</sup>lt;sup>25</sup> 42 U.S.C. 9601(14(B). See also OSWER Directive 9360.0-8, "CERCLA Removal Actions at Methane Release Sites," Henry L. Longest II to Basil Constantelos (Jan. 23, 1986).

<sup>&</sup>lt;sup>26</sup> 42 U.S.C. 9601(14)(C). Indeed, the EPA has decided to regulate methane gas from landfills under the nonhazardous waste section of the Resource Conservation and Recovery Act (RCRA). See 40 CFR 258.23.

<sup>&</sup>lt;sup>27</sup> 42 U.S.C. 9601(14)(D).

<sup>&</sup>lt;sup>28</sup> 42 U.S.C. 9601(14)(E). Methane is not one of the 187 substances identified as hazardous air pollutants as required by this clause to be considered a CERCLA hazardous substance. Indeed, the EPA decided to address methane gas emissions under its New Source Performance Standards of Section 111 of the Clean Air Act. See 40 CFR 60.30. Methane is considered a "regulated substance" under the Chemical Accident Prevention Provisions of 42 U.S.C. 7412(r) that requires facilities producing, handling, processing, distributing, or storing certain chemicals above their listed threshold quantities to develop a risk management program and prepare a risk management plan (RMP). See Table 3 of 40 CFR 68.130. A "regulated substance" is not a hazardous air pollutant for purposes of 42 U.S.C. 9601(14)(E).

 <sup>&</sup>lt;sup>29</sup> 42 U.S.C. 9601(14)(F).
 <sup>30</sup> Marcas, LLC v Board of County Commissioners of St. Mary's County, 2011
 U.S. Dist. LEXIS 110378 (D. Md. 9/28/11)(migration of methane gas, vinyl chloride and other volatile organic compounds to residential development project).

<sup>31 42</sup> U.S.C. 6901 et seq.

 $<sup>^{32}</sup>$  42 U.S.C. 6941-6949a. The subtitle D regulations are codified at 40 C.F.R. Part 258.

the LEL for methane at the property boundary.<sup>33</sup> The presence of methane gas at a boundary of a landfill above the LEL has been held to be a violation of the Subtitle D regulations 40 C.F.R. § 258.23(a)(2).<sup>34</sup>

# X3.2.2 RCRA Citizen Suits for Injunctive Relief:

X3.2.2.1 RCRA Section 7002 provides that injunctive relief may be available against any person who: (1) is alleged to be in violation of any permit, standard, regulation, condition, requirement, prohibition, or order under RCRA<sup>35</sup> or (2) has contributed or is contributing to the past or present handling, storage, treatment, transportation, or disposal of any solid or hazardous waste that may present an imminent and substantial endangerment to health or the environment.<sup>36</sup>

X3.2.2.2 Unlike CERCLA, which only requires a showing that a release of hazardous substances has occurred, Section 7002 requires the plaintiff to show also that the presence of solid or hazardous wastes may be posing an imminent and substantial endangerment.<sup>37</sup> In general, to establish that the harm is "imminent," a plaintiff does not have to show actual harm, just that there is a threatened risk that may occur later.<sup>38</sup> Likewise, to establish that the harm posed a "substantial endangerment," a plaintiff simply needs to show that there is "reasonable cause for concern that someone or something may be exposed to a risk of harm if remedial action is not taken."<sup>39</sup> The finding of an imminent and substantial endangerment is a fact-intensive inquiry that will depend on specific site conditions. The migration of methane gas from a landfill at concentrations that exceed the LEL has been found to present an imminent and substantial endangerment to health or the environment.40

# X3.3 State and Local Regulation of Methane

X3.3.1 Most states have corollary statutes to CERCLA<sup>41</sup> or RCRA.<sup>42</sup> Other, more detailed, statutes or regulations address methane specifically by source. For example, methane from landfills is highly regulated at the state level.<sup>43</sup> Methane arising from oil production facilities is also specifically regulated.<sup>44</sup>

X3.3.1.1 Some special situations concerning the specific future uses of property may give rise to regulation of methane. For example, California's Education Code defines methane as a naturally occurring hazardous material requiring investigation and remediation at school sites.<sup>45</sup>

#### X3.3.2 Local Regulation:

X3.3.2.1 A myriad of local city and county regulations also address methane, especially with respect to residential development. The City of Los Angeles, which not, coincidentally, holds many producing oil wells, has a comprehensive set of "Methane Seepage Regulations," for example. <sup>46</sup> Variations of these regulations may be found throughout the state (country). <sup>47</sup>

X3.3.2.2 Local agencies do not uniformly regulate methane gas in soil vapor, however, since local conditions may vary. For example, the County of San Diego, California first adopted an ordinance regulating methane gas testing and mitigation following discovery of methane in a real estate development. It later repealed the ordinance after several years of testing at numerous real estate developments established that subsurface methane gas, which is not under pressure and is associated with small amounts of organic materials in engineered fills, have much lower risks than methane associated with landfills and oil wells. 49

<sup>&</sup>lt;sup>33</sup> 40 C.F.R. § 258.23(a)(1) and (2).

<sup>&</sup>lt;sup>34</sup> Marcas, L.L.C. v. Bd. of County Comm'rs, 2013 U.S. Dist. LEXIS 104380 (D.Md. 7/25/13).

<sup>&</sup>lt;sup>35</sup> 42 U.S.C. § 6972(a)(1)(A). See *Cox v. City of Dallas*, 1999 U.S. Dist. LEXIS 22747 (N.D. Tx. 8/12/99) (Defendant ordered to monitor for methane gas and take appropriate action to protect the health and safety of the residents of the adjoining area if hazardous conditions are detected.)

<sup>&</sup>lt;sup>36</sup> 42 U.S.C. § 6972(a)(1)(B).

<sup>&</sup>lt;sup>37</sup> Foster v. U.S., 922 F.Supp. 642 (D.D.C. 1996).

<sup>&</sup>lt;sup>38</sup> Dague v. City of Burlington, 935 F.2d 1343, 1355-1356 (2d Cir.1991), reversed on other grounds, 505 U.S. 557, 112 S.Ct. 2638, 120 L.Ed.2d 449 (1992); Price v. United States Navy, 39 F.3d 1011, 1019 (9th Cir.1994).

<sup>&</sup>lt;sup>39</sup> Foster v. U.S. 922 F.Supp. 642 (D.D.C. 1996); United States v. Conservation Chemical Co., 619 F.Supp. 162, 193 (W.D.Mo.1985).

<sup>&</sup>lt;sup>40</sup> Marcas, L.L.C. v. Bd. of County Comm'rs, 2013 U.S. Dist. LEXIS 104380 (D.Md. 7/25/13). See also Newark Group, Inc. v. Dopaco, Inc., 2011 U.S. Dist. LEXIS 110110 (E.D. Cal., 2011) (high concentrations of methane from degradation of toluene present "a threatened or potential harm" to Marcor employees on the property and that there is "some reasonable cause for concern that [Marcor employees] may be exposed to a risk of harm by a . . . threatened release of [methane] if remedial action is not taken)", Frontier Recovery, LLC v. Lane County, 2010 U.S. Dist. LEXIS 61857 (D. Or., Apr. 14, 2010) (denying defendant motion for summary judgment). But, see Adams v. NVR Homes, Inc., 135 F. Supp. 2d 675 (D.Md. 2001) (methane concentrations at residential development did not constitute imminent and substantial endangerment).

<sup>&</sup>lt;sup>41</sup> See for example, California "Hazardous Substance Account Act," Cal. Health & Safety Code Section 25300 et seq.; New Jersey "Spill Compensation and Control Act" N.J. Rev. Stat., Sections 58:10-23.11 et seq.

 $<sup>^{42}\,\</sup>mathrm{See}$  for example, California "Hazardous Waste Control Law," Cal. Health & Safety Code Sections 25200 et seq.

<sup>&</sup>lt;sup>43</sup> See for example, California Code of Regulations, Title 27, Division 2, Subdivision 1, Chapt. 3.0, Subchapter 4, Article 6, "Gas Monitoring and Control at Active and Closed Disposal Sites," (California Integrated Waste Management Board).

<sup>&</sup>lt;sup>44</sup> See California Code of Regulations Title 14, Chap. 4, Department of Conservation, Division of Oil, Gas, and Geothermal Resources (DOGGR).

<sup>&</sup>lt;sup>45</sup> California Education Code, Section 17210.1.

<sup>&</sup>lt;sup>46</sup> Los Angeles Municipal Code, Division 71, of Article 1, Chap. IX, Sections 91.7101 et seq.

<sup>&</sup>lt;sup>47</sup> "Development and Land Use Guideline for Combustible Soil Gas Hazard Mitigation," Guideline L-03, Orange County Fire Authority, Jan. 31, 2000 (www.ocfa.org/business/pandd/guideline.htm); City of Huntington Beach, California Building Code Section 17.04.085, July 1999.

<sup>&</sup>lt;sup>48</sup> San Diego County Code, Div. 6, Title 8, Chap. 3, Sections 86.301 et seq., added by Ordinance No. 9364 (July 2001) amended by Ordinance No. 9446 (Mar. 2002).

<sup>&</sup>lt;sup>49</sup> San Diego County Ordinance No. 9713 (20 April 2005).

# X3.4 State Common Law Liability

X3.4.1 Although environmental law is often considered primarily based on statutes and regulations, the common law (namely, court-made law) has been used for centuries to fashion remedies long before any applicable statutes were enacted.<sup>50</sup> These theories include nuisance, trespass, negligence, and strict liability.

X3.4.1.1 Nuisance:

- (1) The cause of action of nuisance has been used as a theory of recovery for damages caused by environmental pollution for more than a century.<sup>51</sup>
- (2) In some jurisdictions, a claim for private nuisance requires that the source of the contaminant (for example,

methane) be from a neighboring property.<sup>52</sup> In others, it is a valid theory even if the source is on the very property damaged.<sup>53</sup>

(3) Methane migration gives rise to a claim of private nuisance if permanent damages include reduction in value of the property and emotional distress.<sup>54</sup> Where explosive levels of methane from a former town dump forced homeowners to abandon their home, they were awarded the full value of their home under a theory of inverse condemnation, in addition to nuisance.<sup>55</sup>

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<sup>&</sup>lt;sup>51</sup> See for example, *Donahue v. Stockton Gas Co.*, 6 Cal.App. 276 (1907) (gasoline leaking onto adjacent land and polluting well constitutes nuisance).

<sup>&</sup>lt;sup>52</sup> See for example, *Philadelphia Electric Co. v. Hercules, Inc.*, 762 F.2d 303 (3rd Cir. 1985).

<sup>&</sup>lt;sup>53</sup> See *Mangini v. Aerojet-General Corp.*, 230 Cal. App. 3d 1125, 281 Cal.Rptr 827 (1991), Cf. *Mangini v. Aerojet-General Corp.*, 12 Cal. 4th 1087 (1996) (nuisance not abatable, but "permanent," therefore, barred by statute of limitations).

<sup>&</sup>lt;sup>54</sup> City of Warner Robbins v. Holt, 220 Ga.App. 794 (1996).

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- (6) D5088 Practice for Decontamination of Field Equipment Used at Waste Sites
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