Procedures for Evaluating Potential Methane Hazard at Vapor Intrusion Sites

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ABSTRACT

The evaluation of methane at vapor intrusion sites differs in fundamental ways from the evaluation of chlorinated hydrocarbons, petroleum hydrocarbons, or other volatile compounds. Evaluation of potential methane hazard requires consideration of concentration, pressure, and volume whereas concentration measurements alone are generally sufficient for other species. In this paper, various options for measuring methane concentration, differential pressure, and subsurface gas volume – or related, surrogate parameters – are presented and guidance given for interpreting the results. The measurement of methane and carbon dioxide concentration indoors and in soil gas using portable analyzers and GC methods is addressed as is the measurement of differential pressure at monitoring wells and sampling probes using analog and digital devices. Guidance is provided for the number of samples and the number of rounds of testing to characterize a typical site. Various methods for measuring gross or net generation rates of biogas (i.e., methane + carbon dioxide) are presented, including microcosms, test cells, wet gas meters, bag fill tests, and flux chambers. Various methods for measuring methane oxidation also are given, including column studies.

INTRODUCTION

The US EPA has recognized that petroleum hydrocarbon sites are fundamentally different from chlorinated hydrocarbon and other vapor intrusion (VI) sites and require separate guidance.[1] It has been proposed that methane sites also are fundamentally different and require a unique set of evaluation criteria.2 Evaluation of potential methane hazard requires consideration of concentration, pressure, and volume[3] whereas concentration measurements alone are generally sufficient for petroleum hydrocarbons and chlorinated hydrocarbons.

The conceptual site model for each category of chemicals differs from the others. In other words, different intellectual frameworks are needed for understanding the fate & transport of vapors of different types. It follows that the types of information needed to characterize these sites differs and that the interpretation of the information also may differ. This paper summarizes various options for measuring methane concentration, differential pressure, and subsurface gas volume – or related surrogate parameters – at methane sites and gives general guidelines for interpreting the results.

On-going releases from utility lines or pipelines and other emergency situations are outside the scope of this paper. The primary focus is sites with naturally occurring methane or methane arising from degradation of released chemicals. Information is given to help screen out sites with low or minimal risk and to identify sites where controls should be considered.

BACKGROUND

Methane (CH_4) is ubiquitous in the atmosphere and in indoor air. The global background concentration is about 2 ppmv (0.0002%). It also is often present at percent levels in soil gas in the unsaturated zone, especially in wet, organic soils. Even "clean" fill soil can generate methane if it has some organic fraction and is wet and devoid of oxygen.

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

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

Anaerobic biodegradation of organic matter produces biogases that are roughly 60% methane and 40% carbon dioxide (CO_2). These gases will not burn or explode *in-situ* in the subsurface soils, but can create hazards if the gas production volumes are large enough and the gas finds pathways to flow into enclosed or poorly ventilated spaces where ignition sources are present. Methane is flammable when present in the atmosphere or indoor air at concentrations between the lower explosive limit (LEL) of 5% and the upper explosive limit (UEL) of 15%, if sufficient oxygen also is present.[4]

For volatile organic compounds (VOCs), the concentration present in soil gas is directly related to the potential risk. In general, the higher the VOC concentration in soil gas, the greater the potential for indoor air impacts due to vapor intrusion.

For methane, this is not the case. Even small rates of methanogenesis will result in soil gas concentrations approaching 50% at the point of generation. There is essentially no correlation between methane gas production rate and methane concentration in soil gas *at the point of generation*.

SITE CHARACTERIZATION OPTIONS

Various options for measuring methane concentration, differential pressure, and subsurface gas volume are described below. Interpretation of the measurement data is addressed in a later section.

Gas Concentration Measurement

Gas measurement equipment options are summarized in Table 1. Commonly used soil gas and indoor air measurement techniques are discussed below.

Soil Gas

For soil gas, the so-called “fixed gases” methane (CH_4), carbon dioxide (CO_2), and oxygen (O_2) are typically of interest rather than just methane because concentration data for the trio of gases provides information about gas generation and removal processes in the subsurface – i.e. gas origin and history. The presence of carbon dioxide normally suggests that biodegradation is taking place (both aerobic and anaerobic biodegradation produce and emit carbon dioxide). Thermogenic gas usually contains very little carbon dioxide. Oxygen is of interest because methane is amenable to aerobic biodegradation. The methane concentration typically will be inversely correlated with the oxygen concentration. There is competition between subsurface biomass, petroleum hydrocarbons, and any methane produced from these organic materials, for the available subsurface oxygen. Practitioners should bear in mind the following:

Sensitivity / Detection Limits

Low detection limits are not generally an issue for soil gas measurements. Instead it is important to be able to measure concentrations of CH_4 up to 100%; of CO_2 up to about 50%; and of O_2 up to 21%.

Field Instruments

A very common option for field measurements is a landfill gas analyzer (e.g., Landtec GEM 500 or equivalent device). A multi-gas meter (e.g., 4 – or 5-gas meter) is also a very good option for field use when configured for the gases of interest. Two of the meter’s gas modules are used just for methane, one to measure combustible gas as methane from zero to the lower explosive limit, and a second to measure combustible gas as methane up to 100% by volume; the meter would need to be set up to also measure oxygen and carbon dioxide, and perhaps hydrogen sulfide if a fifth gas can be accommodated. Nitrogen (N_2) is never measured directly in the field, but calculated as $\% N_{2\,=}$ [100% - ($\% O_2 + \% CO_2 + \% CH_4 + \%$ other).

Table 1. Options for Measuring Methane Concentration

Measurement Option	Basis of Detection	Typical Operating Range	Relative Advantages	Relative Disadvantages
Portable Analyzers				
FID	Flame Ionization	1 – 10,000 ppmv (top end = 1% CH_4)	• Fast, linear response • Can be used to find specific points of leakage or gas entry	• Upper limit is only 1% methane (10% if a dilution probe is used) • Response to nearly all hydrocarbons and organic vapors, including CH_4, that is approximately linear with mass concentration • Will respond to certain non-hydrocarbons such as H_2S
Landfill Gas Analyzer	Infrared (IR) Absorption	0.1 – 100%	• Useful for a wide range of concentrations • Also provides data for O_2 and CO_2 • Continuous monitoring options are available	• Positive bias in CH_4 reading from hydrocarbons or other chemicals which absorb in the same IR band • Response depends on gas temperature and pressure (can be compensated).
LEL meter/ 4-gas meter	Catalytic Oxidation	1 – 100% of LEL (~500 ppmv – 5% CH_4)	• Inexpensive • Relatively simple to operate • Useful for personal and enclosed space monitoring	• Upper limit is only 5% methane • Cross-sensitivity from other hydrocarbons present • Tendency to overestimate gas concentration • Potential deactivation of noble metal catalyst from sulfur and other species
Solid State Sensor	Metal-Oxide Semiconductor (MOS)	1 – 20% of LEL (~500 ppmv – 1% CH_4)	• Inexpensive option for fixed indoor air monitoring	• Not well suited for vadose zone applications • Response drift if chip gets poisoned
PID	Photo Ionization	0.1 – 2,000 ppmv	None – Should not be used for CH_4 monitoring	PIDs are commonly used field instruments for VOC monitoring, but they will not respond to methane.
Off-Site or Mobile Lab Analysis of Discrete Samples				
ASTM D-1946	Gas Chromatography (GC-FID)	2 ppm – 100%	• Specificity for methane • Highly defensible data • Useful for a wide range of concentrations • Data also can be obtained for other fixed gases	• Data turnaround time of days or weeks for off-site analysis • Additional cost for each additional sample

Measurement Option	**Basis of Detection**	**Typical Operating Range**	**Relative Advantages**	**Relative Disadvantages**
Field GC	Gas Chromatography (GC-FID)	~20 ppm - % levels	• Specificity for methane • Quick response time • Useful for a wide range of concentrations if quantitative sample dilution can be performed	• Calibration and quality control protocols generally not as rigorous those used by an off-site analytical laboratory • Not cost-effective for sites with relatively few monitoring locations due to time & expense of system mobilization
	Gas Chromatography (GC-TCD)	1 ppm to %	• Specificity for multiple gases • Response in minutes • C1 to C6 hydrocarbons, O_2, N_2, CO2	• Identification by elution time; co-elution interferences • Same limitations as for GC-FID (see above)
Other Methane Detection Options				
Gas Imaging	Passive IR Camera / bandpass filter in methane absorption band	Methane leak at 0.8 g/hr	• Survey large areas quickly • Quick response time • Remote sensing	• Responds to other hydrocarbons • Not directly quantitative • Relatively expensive • Reduced or no sensitivity at night or during rain events
TDLAS	Tunable Diode Laser Absorption Spectroscopy	5 – 100,000 ppm · m	• Quick response time • Remote sensing	• Reduced sensitivity during rain events • Sensitivity limited by path length • Relatively expensive
Cavity Ring-Down Spectrophotometer	Switched laser excitation / decay	0.001 – 20 ppm	• Simultaneous gas analysis CH_4, CO_2 • Response in seconds • Can include isotope separation • Mobile, rugged	• Not well-suited for high CH4 concentrations • Relatively expensive

Interference / Cross Sensitivity

Non-methane petroleum hydrocarbons will tend to give a positive bias to the measured methane value on many types of field equipment, because the equipment is not methane-specific but merely measures total combustible vapors present in the soil.

Lab or Bench-Top Instruments

Bench-top analyses capable of speciating the various combustible vapors will provide the most defensible data. Off-site analysis (such as ASTM D-1946) utilizes gas chromatography (GC), flame ionization detection (FID) and thermal conductivity detection (TCD) techniques. Field GC's are sometimes employed when multiple combustible gas species are present in the soil.

Sample Containers

Soil gas may be collected in evacuated stainless-steel canisters if long holding times are anticipated. Properly bagged samples are very reliable for shorter holding times and are less expensive. Syringes are often used for very short holding times which are acceptable in rapidly performed field GC analyses.

Indoor Air

For indoor air, methane data alone is often sufficient and data for the other fixed gases is superfluous. The methane concentration range of interest runs from the background level of 2 ppmv to 1.25% (12,500 ppmv or 25% of the LEL). Immediate evacuation of the building usually generally is required for readings of 1.25% or higher based on the National Fire Code. Practitioners should bear in mind the following:

Imminent Hazard

Indoor air surveys for identification of hazardous conditions requiring evacuation of the building may utilize simple and inexpensive LEL or Multi-Gas meters.

Pathways

Interior surveys for determination of gas intrusion pathways are better served by a portable FID analyzer with low detection limits and quick response time. FID surveys are useful for finding indoor emission sources, such as unlit pilot lights, leaky gas utility pipe joints, and dried-out water traps in drains or sewer lines. But the use of such sensitive equipment also can be used to pinpoint soil gas intrusion pathways into buildings, such as cracks in slabs, unsealed space around utility conduit penetrations, the annular space inside of dry utilities (electrical, communications), stud wall gas measured at existing electrical outlets, gas in elevator pits (particularly those with pistons), basement sumps, and other avenues.

Time Averaged Samples

Time-integrated indoor air samples are standard for VOC work, but are not routinely utilized for methane since instantaneous combustible gas concentrations are of critical importance. Methane is not toxic, and exposure to less than flammable amounts of methane presents no hazard regardless of duration. If desired, time weighted sampling may employ the same approach as discussed above for soil gas collection in canisters and off-site ASTM D-1946 analysis.

Differential Pressure

Differential pressure is a measurement of the difference between the soil gas pressure at some depth, and indoor or ambient air pressure.

Importance

Gas transport rates due to diffusion are very low compared with building ventilation rates and diffusion of soil gas is not expected to result in an unsafe indoor environment. Pressure-driven flow is necessary to quickly move the volumes of gas required to result in indoor air approaching the LEL for methane. Therefore, if methane concentrations in soil gas exceed some threshold value (e.g., 5% by volume), differential pressure (ΔP) between the soil and the ambient air or receptor structure is an important variable to measure. A screening value of 2” H_2O[a] (5 cm H_2O) for ΔP has been proposed.[3,5]

Measurement

Analog devices such as Magnehelic gauges are inexpensive and relatively fool-proof. Having gauges in various ranges (e.g., 0 to 0.25, 0 to 2, and 0 to 50 “H_2O) provides flexibility and precision. A digital manometer is another good option. Figure 1 shows examples of analog and digital ΔP measurements.

Temporal Variability

Various authors have noted that differential pressure may vary over time as a function of HVAC usage, wind speed, etc. This variability is small, however, relative to the 2” H_2O screening value. “Re-pressurization” such as from rapidly rising shallow groundwater is an uncommon but

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[a] One atmosphere (atm.) of pressure:

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

Figure 1. Analog and Digital Measurements of Differential Pressure

not unknown phenomenon. Continuous ΔP measurements can document such variability. Continuous ΔP has been routinely measured for sub-slab depressurization systems (SSDS), using such devices as Engineering Solutions Omniguard 4 Differential Pressure recorders.[6]

Soil Gas Areal Extents and Depths

Methane is a concern when 1) there is a large volume of subsurface methane present under or near a building, or 2) subsurface methane is being produced or introduced into the soil at a relatively high rate under or near a building. Isolated high concentration methane "hot spots" in soil generally will not lead to a problem because the hot spot will contain insufficient mass of methane to result in elevated indoor air concentrations.

The extent to which methane is present at a given building can be assessed by collecting fixed gas data at multiple locations across the building site. Hand-installed shallow boreholes and deeper test points – i.e. small diameter wells drilled or pushed into the subsurface-- are commonly deployed for site data collection in methane hazard potential assessments. Once probes are installed, one or more sets of measurements are made. Ideally, numerous repetitive measurements are made with field equipment over a period of days or weeks during various barometric and weather conditions. The larger the number of data points (locations, depths and times), the greater the certainty in the evaluation of site risk. Suggested minimum sampling densities are discussed below.

Based upon field monitoring results, a relatively small number of samples can then collected for laboratory verification of field data, and for suites of laboratory tests that cannot be performed in the field. Samples for off-site analyses are usually collected from probes showing relatively high soil gas concentrations in the field data. The approach depends, in part, on the type of development, as described below:

New Development

For proposed building sites with no existing improvements, subsurface monitoring probes may be installed in a grid pattern across the site, with nested shallow, medium, and deeper completions below grade surface. The monitoring program for proposed development sites is determined by site specifics. A City of Los Angeles methane standard[5] calls for a shallow probe for each 10,000 square feet (900 m^2) of lot area – this would be equivalent to a 100-foot (30 m) grid; plus a deeper multi-depth probe cluster for each 20,000 square feet (1,900 m^2) of lot area. Shallow probe monitoring results may be used to determine placement of deeper probes.

Existing Buildings

If methane is a potential concern for an existing building, it is common to conduct FID testing of indoor air as described in the "Indoor Air" section above, and serpentine FID testing of the yard or grounds as described below. If subsurface gas monitoring is also utilized, a minimum of four subsurface probe locations are recommended for a typical residential size building. For larger industrial or commercial buildings, six to 12 locations (e.g., one location per every 1,000 – 5,000 ft^2 [90 – 460 m^2]) are recommended as a reasonable minimum sampling density. If methane soil gas exceeds some threshold value (e.g., 30%) at any location, additional step-out locations should be sampled to better define the areal extent of the methane.

Soil Gas Production/Generation/Transport Rates

Microbial gas production can generate significant volumes of methane at a site. Thermogenic gas also can be introduced into the soil at a site in significant volumes, through pathways from some deeper or remote source. Potentially important considerations are discussed below.

Whole Gas

When combined microbial gas concentrations of $CH_4 + CO_2$ approach 100%, the soil gas is said to be "whole" or "undiluted." For thermogenic gas, this is the case if the concentrations of methane plus higher order hydrocarbons, hydrogen sulfide, and carbon dioxide approach 100%. The presence of whole gas suggests that the rate of soil gas production or introduction is high enough to displace nitrogen and other gases from the soil pore spaces by pressurized flow rather than by diffusion or cyclical, push-pull advective phenomena.

Volumetric-Potential Studies

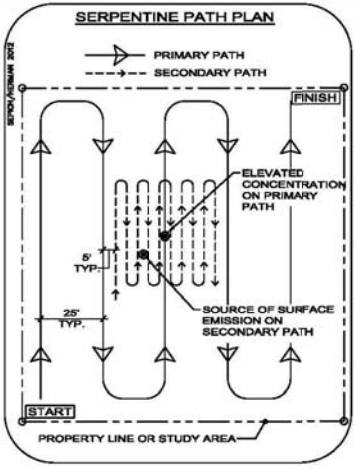
If whole soil gas is encountered or suspected, measurement of how long it takes for soil gas emitted from a sample probe under positive pressure to fill a small impermeable gas bag (e.g., 1 L) can serve as a related parameter to available gas volume. Measuring gas volume using a wet gas meter is another option. Tests involving water displacement generally should be avoided because of the relatively high ΔP required for gas to start flowing in such tests.

Yard Gas Serpentine Monitoring

At sites with a large volume of relatively undiluted soil gas, it is not uncommon to find the gas evolving from grade in the yard at various locations. Specific locations include the interiors of irrigation, electrical or other vaults; cracks in pavement, sidewalks and other hardscape; dirt fissures around the edge of buildings where grade or hardscape abuts foundations; and locations where piping, conduit or posts come out of grade. Methane may also seep out of the ground at random locations in soil or landscaped areas.

These locations are identifiable during serpentine sweeps with an FID. The intake wand of the FID is attached to a land surveyor's measuring wheel at 3" above the ground surface and walked in a serpentine path across the property. The surveyor's wheel odometer readings, in feet, are used to notate locations of elevated combustible concentrations on a prepared form (map) of the site and sweep-path. Initial (wider) spacing of serpentine path legs may be 25 feet.

Any combustible gas "hit" areas are then re-walked at a reduced (narrower) leg spacing of say 5 feet. Ultimately by working down to a smaller and smaller area, a point source of soil gas seepage may be identified. Precipitation and barometric conditions before and during the monitoring may be important and should be taken into consideration.



Source: Reference 7

Other Site Characterization Tools

Several additional site characterization tools described below may be useful at some sites.

Isotopic Ratios

The ratio of both stable isotopes (i.e., $^{13}C/^{12}C$ and $^{2}H/^{1}H$) can be used to distinguish between methane of microbial (also referred to as biogenic) origin, as opposed to methane originating from "fossil" or "thermogenic" sources. Thermogenic methane is formed from organic material at high subsurface pressures and temperatures deep in the earth, and is associated with oil, coal or natural gas fields. Microbial methane is generally a product of anaerobic microbial reduction of CO_2 using hydrogen (hydrogenotrophic pathway, approximately 30% of worldwide biogenic methane production), or from dismutation of acetate (aceticlastic pathway, approximately 70% of worldwide biogenic methane production[8]).[a] Soil gases may also be of mixed origins. If stable isotope analysis does not yield definitive results, analysis of radioactive isotopes of methane, and the carbon isotopes of carbon dioxide found with the methane, may provide further definition.

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[a] Some readers may be more familiar with pathways being labeled as either fermentation or respiration. The aceticlastic pathway refers to the fermentation of acetate in which it is split into CH4 and CO2. The hydrogenotrophic pathway refers to reduction of CO2 using electrons from hydrogen, which can be thought of as a form of respiration.

Isotopes

Methane (CH_4) may be comprised of various isotopes.[9] Carbon has three naturally occurring isotopes: ^{12}C, ^{13}C, and ^{14}C. The first two are stable and constitute about 98.9% and 1.1% of carbon, respectively. ^{14}C is comparatively rare (10^{-10}%), is radioactive, and decays with a half-life of 5,730 years. Hydrogen also has three naturally occurring isotopes: ^{1}H, ^{2}H (deuterium) and ^{3}H (tritium). The first two are stable and constitute about 99.99% and 0.01% of hydrogen, respectively. Tritium is comparatively rare (10^{-15}%), is radioactive, and decays with a half-life of 12 years.

Sample Containers

Sample collection typically utilizes either evacuated stainless-steel canisters or impermeable gas bags.[10] Stable isotopes can be analyzed by gas chromatography/mass spectrometry (GC/MS). Radioactive isotopes can be analyzed using liquid scintillation counters or gas proportional counters. Isotopic analysis is a specialized field and is offered by relatively few analytical laboratories. It also is important to note that analysis of radioactive isotopes may require several grams of methane in the sample. So unless soil gas samples have a relatively high methane concentration, larger volume samples may be required for determination of either ^{14}C or ^{3}H isotopic ratios.

Surface Emissions Flux Measurements

In the early days of landfill gas study, the “bucket test” was widely used. A five-gallon plastic “homer” bucket with a stoppered monitoring port drilled into the bottom of the pail would be inverted on grade, perhaps with a clay seal. A watch, a portable combustible gas sniffer and a clipboard were used to measure and record the rise in bucket-gas concentrations versus time.

More sophisticated flux chamber methods were developed by the US EPA in the mid-1980’s to measure emission fluxes (i.e., emission rates per unit area) for use in human health risk assessments. A user guide was published.[11] Flux measurements may be useful for quantifying mass transfer rates for unpaved soils, such as emissions from bare dirt into a crawl space. The flux chamber measurements are not affected by above-ground background sources and they reflect any aerobic biodegradation that is occurring. Multiple measurements are needed to adequately characterize a given area.

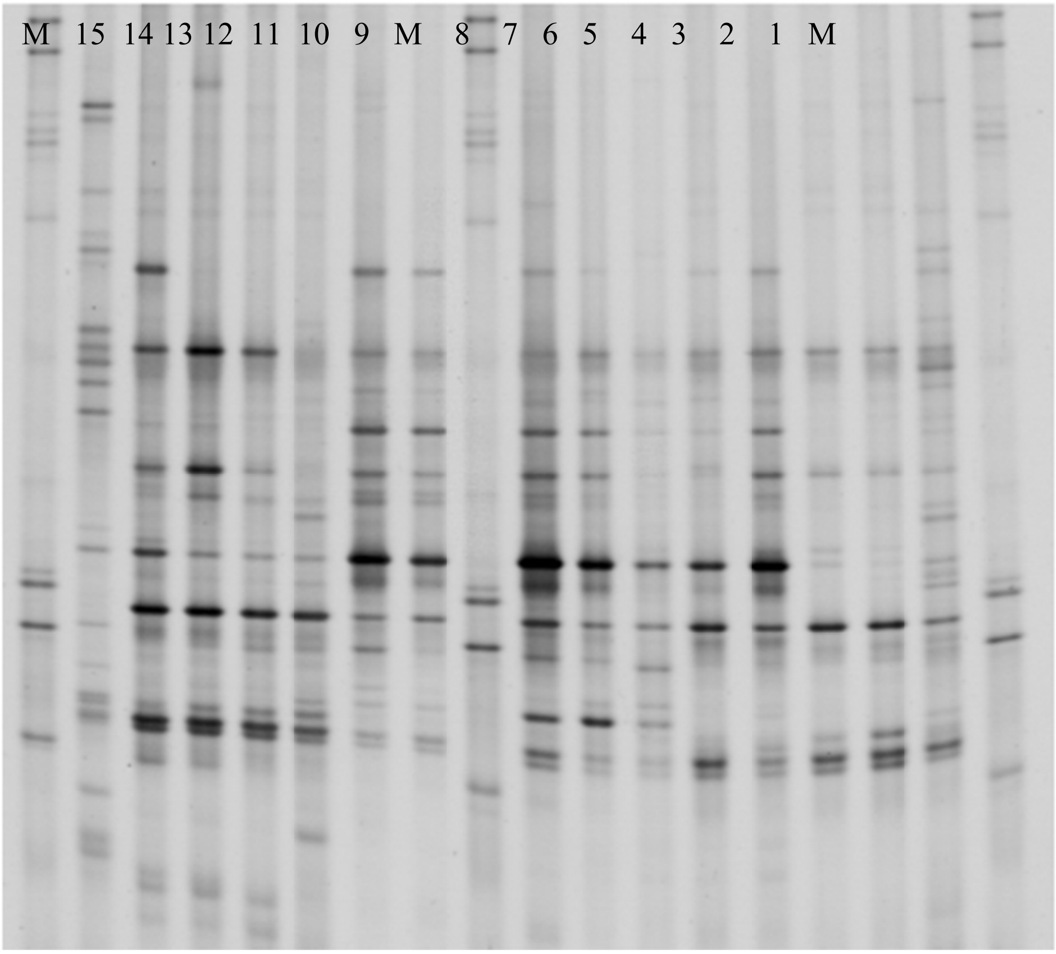
DNA Testing

As previously stated, soils may contain methanogenic bacteria that produce methane. The same soils, however, may also contain methanotrophic (methane-oxidizing bacteria). In a given soil column, the bacteria in deeper soil layers may generate methane and the bacteria in shallower, aerobic soil layers may consume methane. The soil may be a net source or a net sink for atmospheric methane. The type of bacteria present can be determined by off-site DNA testing of soil samples from given depths.

Methanotrophs can be divided into two distinct physiological groups. Type I methanotrophs are methylotrophs belonging to the gamma-proteobacteria. They assimilate the formaldehyde produced from the oxidation of methane by using the ribulose monophosphate pathway. They contain predominantly 16-carbon fatty acids and possess bundles of intracytoplasmic membranes. Type II methanotrophs belong to the alpha-proteobacteria and utilize the serine pathway for formaldehyde assimilation. They have intracytoplasmic membranes arranged around the periphery of the cell and contain predominantly 18-carbon fatty acids.[12]

For DNA testing, a small mass of soil (e.g., 2g) is used to extract the total microbial DNA for each sampling point. Polymerase Chain Reaction (PCR) methodology is used for amplification. DNA fragments generally are analyzed by Denaturing Gradient Gel Electrophoresis (DGGE), which is based on the electrophoretic mobility of partially denaturated DNA-molecules. DNA-fragments with a different base pair composition migrate at different rates through the gel. This gives finally a banding pattern, which is characteristic for the microbial community, as shown in Figure 2.

Figure 2. Results of DNA Testing for Type 1 Methanotrophic Bacteria



Biogas Laboratory Test Cells

Biological methane potential (BMP) or microcosm tests are laboratory-scale tests that can be used to determine the amount of organic material that can be degraded anaerobically for a particular soil or waste and also can be used to measure the anaerobic process efficiency. The BMP test involves placing a known mass of sample in a sealed container and measuring the methane production over time. The testing typically involves replicate tests and controls using a standard cellulose. The tests are typically run for 30-days or longer. An example of a microcosm test is shown in Figure 3.

Figure 3. Microcosm Study of Gas Production Rate

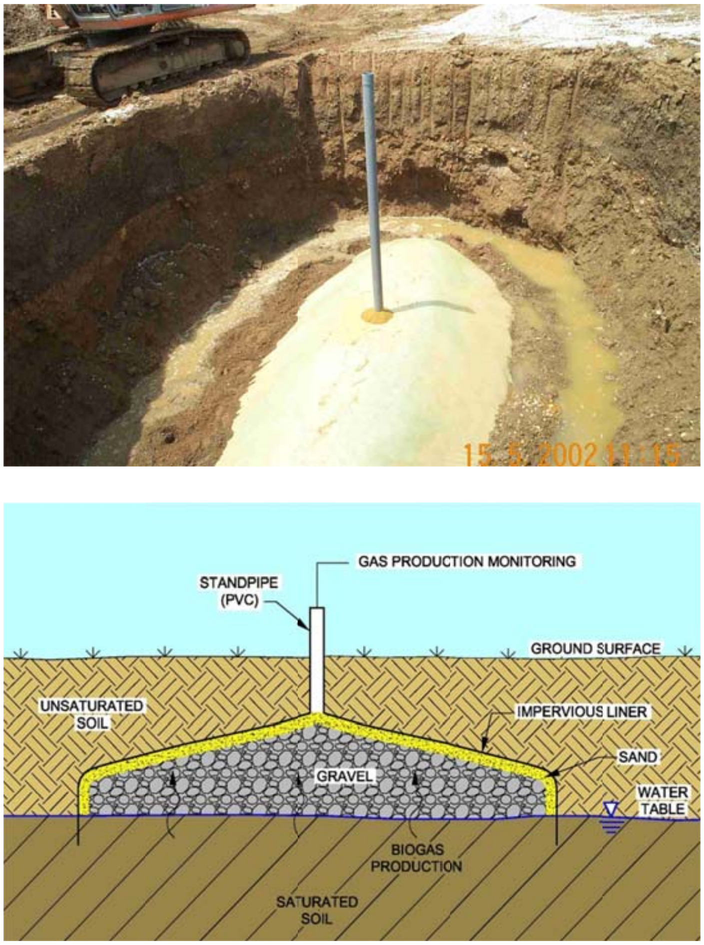
Biogas Field Test Cells

Specially constructed test cells have been used to measure gas production rates in situ. Figure 4 shows a schematic of a 10m x 5m test cell and a photograph from the field construction. The test cell prevents oxygen transport into the soil, so it is a measure of the maximum potential gas emission rate. The actual emission rate will be lower due to aerobic biodegradation near the ground surface.

Methanotroph Column Studies

Methanotrophs in shallower soils can remove a significant fraction of the methane produced in underlying strata, as the gas moves upward towards the surface. The capacity for such removal can be measured in the laboratory using soil column studies. Soil from specified depths is collected at the site and packed into columns. Methane at a known rate is introduced at one end of the column and the rate at the other end of the column is measured to determine the attenuation at steady-state conditions.

Figure 4. Large Scale In-Situ Test Cell



DATA INTERPRETATION

General guidance for interpreting concentration, pressure, and volume data are given below. Concentration, volume and pressure aspects of methane soil gas are difficult to discuss independently. Methane concentrations and pressures may be inversely proportional. Methane volumes and pressures may be directly proportional. This is an evolving area and different consensus values may emerge in the future. The rules-of-thumb discussed here have been put forth by the authors in recent years and have been incorporated into standards by the State of California[13] and by ASTM[14] – standard currently being balloted.

Methane Concentration Regulations

Since the 1970's, the USEPA through its Resource Conservation and Recovery Act (RCRA) has allowed a maximum concentration of 5% by volume (50,000 ppmv) methane soil gas offsite, beyond the property line of sanitary landfills.[15] The regulation does not address gas pressure or gas volume, but is based upon the sound science[4] that methane concentrations below approximately 5% by volume in air cannot combust. No known verifiable methane incidents have occurred when compliance with this standard has been achieved. Eklund[2] has proposed not only that microbial methane concentrations in soil gas of <5% v/v are not a concern, but also that concentrations of 5% v/v to 30% v/v are only of concern if the ΔP exceeds some threshold.

Methane Concentrations in Structures

For indoor air, any value equaling or exceeding 1.25% calls for immediate action. The assumption is that if readings are that high at any given location, values above the LEL may be present elsewhere in the building and it is prudent to evacuate. Any values above 100 ppmv (0.01%) suggest a source of concern is present and merit further investigation. Indoor air values <100 ppmv generally are considered to be insignificant. Methane can be an asphyxiant, but action levels related to the combustibility of methane are far below levels at which asphyxiation would become an issue.

Methane Concentrations in Soil

Whole gas in soil may exhibit pressure. Diluted gas in soil does not exhibit inherent pressure. Practitioners should bear in mind the following:

High Concentrations

When large volumes of soil gas are produced in or introduced into soil, soil gas pressure results and is the strongest mechanism by which the soil gases travel away from the point of generation or introduction. Gas remains whole or undiluted only in a zone where gas is being generated or introduced into the soil at a sufficiently high rate to completely displace other gases from the soil in one-way pressurized flow.

Low Concentrations

When the rate of gas production in the soil or gas introduction into the soil from some remote source is small, the minor diffusive and advective push-pull forces work in both directions and the soil gases are found well diluted by air (oxygen and nitrogen). Where soil gas is diluted, the gas production or transport rate is assumed to be low. Low gas production/transport rates tend to be associated with low hazard potential.

Dilution

Microbial gas contains large amounts of both methane and carbon dioxide, and sometimes low levels of hydrogen sulfide and trace amounts of other chemicals. Thermogenic gas usually contains mostly methane and lesser amounts of higher order hydrocarbons plus some carbon dioxide and hydrogen sulfide. The amount of air (nitrogen plus oxygen) contained in a sample of soil gas is a reliable measure of dilution regardless of original soil gas composition or source. Practically speaking, inherent soil gas pressure may be expected at sites only where the air dilution of soil gas is zero to perhaps a few percent by volume. When air dilution in soil gas is as much as say 20 % air (oxygen plus nitrogen) by volume, soil gas pressure is unknown absent re-pressurization phenomena discussed earlier. At twenty percent air dilution, the methane content of thermogenic gas might be close to 80% by volume, and the methane content of microbial gas might be in the range of 40% to 60% by volume.

Suggested Guidance Concentraton

For added conservativeness, 30% can be used as a rule-of-thumb (rather than 40%) as a normally safe methane soil gas level. A methane concentration of 30% or less in soil gas indicates that the soil gas has been well diluted; that the gas will no longer exhibit pressure; and that the gas will not pose a methane hazard.

Volume

Widespread elevated methane soil gas concentrations suggest that the introduction of gas to the soil, whether from onsite microbial activity or through some pathway to a remote microbial or thermogenic source, is or has been significant. If a large reservoir of methane exists in the soil gas near a building, it may pose a potential hazard even if there is no on-going gas production or elevated differential pressure. Under certain circumstances, the methane can be induced to move (e.g., extremely low barometric pressure, methane flashing out of formerly confined groundwater, etc.). Therefore, if the soil gas surrounding a building is largely “whole” or undiluted biogas (e.g., if hydrocarbons + carbon dioxide are > 80 to 90% v/v), it would be prudent to mitigate even if the differential pressure is less than the 2” H_2O rule-of-thumb discussed elsewhere in this paper. Buildings where the elevated soil gas concentrations are present under only a portion of the building should be evaluated on a case-by-case basis, with consideration of soil gas generation or transport rates and pressure.

Differential Pressure

If significant gas production or gas introduction to the site soils is underway, elevated pressures will be observed. Fluid flows through soil according to $Q = kIA$.[16] Flow is dependent upon the hydraulic gradient $I = \Delta P/L$ as well as the soil permeability or k factor, and the available cross sectional area of flow A. For gas flow through soil, the soil moisture content is also important. Moisture can fill soil pore space and restrict vapor flow. Sepich[3] has proposed a soil gas ΔP screening value of 2” H_2O. This ΔP would result in a potential rate of gas transport that is about an order of magnitude greater than the rate due to diffusion in a typical soil matrix.

Pressures below this screening value are considered to be negligible and unlikely to result in significant gas transport rates. A more conservative screening level (e.g., 1” H_2O) may be more appropriate for more highly permeable soils or materials with low moisture content.

Pressures above this screening value require further consideration. In general, if the pressure exceeds 2” H_2O, methane soil gas control measures should be considered. In tight clay soils, however, even very small gas generation rates may result in relatively high ΔP values because there is little or no gas migration away from the source through the soil matrix. In such cases, unless some high permeability pathway cuts through the low permeability soil matrix, controls should not be needed.

Flux Rates

Finding methane in FID sweep monitoring, whether indoors or in the yard at a site, correlates to pressure-driven methane soil-gas flow and generally indicates that the site needs immediate mitigation.

Gas Origin / Genesis

Knowing whether the methane found in the soil or in a building interior is of biogenic or thermogenic origin can help in determining the source. Once the gas source is identified, it may be possible to measure or estimate source concentrations-volumes-pressures, determine pathways, calculate flows or flux rates, and estimate potential gas hazard at a receptor site or structure.

Interpretation of data from isotopic analysis, emission flux measurements, or column studies are beyond the scope of this paper.

SUMMARY

A number of tools are available for evaluating the potential hazard due to methane at VI sites. This paper summarizes the available tools and describes the current best practices for performing such evaluations. Methane soil gas hazard largely related to pressure in the soil gas. As previously noted, this is an evolving field of inquiry and new approaches and different rules-of-thumb may come to light in future years.

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KEYWORDS

Methane, hazard, vapor intrusion, pathways, soil gas, site characterization