METHOD OF ESTIMATING BIOGENIC METHANE PRODUCTION AT FILL SITES

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Abstract

Methane is found in areas where buried organic materials decompose in the absence of oxygen. It is produced when methanogenic microbes convert organic materials into methane and carbon dioxide. Biogenic methane is formed at relatively shallow depths by the bacteriological decomposition of organic matter in the soil (e.g., in landfills, fill operations, dairies). The primary mechanisms for methane migration in the subsurface are pressure driven flow and diffusion. Methane is an asphyxiant and a combustible gas. The geologic and geographic location of methane in the subsurface can affect the rate of decomposition and gas production. When decomposition gas containing methane is found at significant concentrations methane mitigation measures may be required. Methane gas emissions can be estimated using a theoretical first-order kinetic model of methane production. Site-specific data provides the length of biogenic methane production is available and alternatively rate constants for estimation purposes can be used. The methane concentration may rapidly decrease below regulatory limits and not require mitigation prior to construction. Conversely, if high concentrations persist, the duration of the mitigation can be estimated.

Keywords: soil, methane, methane generation rate, biogenic methane rate, empirical methane generation rate, methane rate constant

1. Introduction

Methane (CH_4) is found in areas where buried organic materials decompose in the absence of oxygen. It is produced when methanogenic microbes convert organic materials into methane and carbon dioxide. The composition of the gas mixture produced varies depending upon the nature of the organic material decomposed. Unaltered decomposition gas typically contains about 50%–55% methane, with the remainder composed of carbon dioxide and traces of other gases.

Methane is lighter than air, colorless, odorless, non-carcinogenic, and flammable. When methane is mixed with other gases such as carbon dioxide, the methane gas mixtures typically have densities comparable to, or less than, air. Methane occurs as natural gas in coal mines, oil and gas fields, and other geological formations; as a byproduct of petroleum refining; and as a product of decomposition of organic matter in natural settings (e.g., wetlands, marshes, swamps), and man-made settings (e.g., landfills, engineered fill, hydrocarbon waste, food processing facilities, sewer lines, septic systems, dairies, and concentrated animal feedlots).

There are two primary mechanisms by which methane is produced. These two mechanism are thermogenic and biogenic. Thermogenic methane is generated at depth under elevated pressure during and following the formation of petroleum (e.g., in oil fields). Biogenic methane is formed at relatively shallow depths by the bacteriological decomposition of organic matter in the soil (e.g., in landfills, engineered fill, dairies). It is rarely found under a pressure in excess of a few inches of water. The primary mechanisms for migration in the subsurface are advection and diffusion. Methane will migrate from areas of higher pressures or concentrations to areas of lower pressures or concentrations. Because methane is lighter than air, it has a tendency to rise from depth to the ground surface where it dissipates into the atmosphere. Where a relatively impermeable barrier (e.g., a concrete slab or geologic feature) is present at the ground surface, the potential exists for accumulation beneath that barrier. Methane may infiltrate through flooring material or cracks, accumulate under footings and in enclosed spaces (e.g., small rooms, vaults, wall spaces), and cause a fire or explosion when an ignition source (e.g., pilot flame, electrical spark, cigarette) is present.

Moreover, an indication of how rapidly decomposition gas is formed in the subsurface is its gas pressure. Large fluxes induce a greater potential for subsurface gas to migrate into nearby buildings and other structures. If significant subsurface pressures exist over an extended period of time, then subsurface gas migration by advection should be considered in addition to migration by dispersion and diffusion. In addition, geological conditions can dramatically affect the migration of decomposition gas. Where soil is homogeneous with low permeability, it is less likely that pressure gradients could drive decomposition gas long distances. However, where layers of relatively porous soils are covered by less porous ones, decomposition gas under pressure has the potential to move significant distances.

The decomposition gas may be altered and attenuated as it reaches the surface soils. The most common way that carbon dioxide can be removed from decomposition gas is in the presence of moist or saturated soil conditions. Decomposition gas formed slowly beneath the water table will lose both methane and carbon dioxide as these gases dissolve in water. Because carbon dioxide is about 75 times more soluble than methane in water, much more carbon dioxide is lost. The resultant decomposition gas has relatively high methane and low carbon dioxide concentrations. The decomposition gas is also altered as it moves upward into the shallow aerated soil horizon. The methane component of decomposition gas is subject to dilution, oxidation, and microbial degradation in the aerated zone. When the gas is moving relatively slowly in the unsaturated soil zone, these mechanisms can significantly reduce methane concentrations. This may be one of the reasons that methane present at ambient pressures in the subsurface may not reach buildings constructed directly above even if no mitigation steps are implemented. Regulatory limits have been set by local and state regulatory agencies for investigation and subsequent mitigation of methane encountered at sites. Methane is combustible and potentially explosive when it is present at concentrations in excess of 53,000 parts per million by volume (ppmv) in the presence of oxygen. This concentration is known as the lower explosive limit (LEL) of methane. Government agencies use a fraction of the LEL as an action level to trigger investigation and mitigation of encountered methane.

Therefore, it is important to determine the nature of import soils, grading, or engineered fill at a site to evaluate for the presence of elevated total organic carbon (TOC). A fill site with large amounts of plant-derived materials, organic topsoil, or municipal solid waste will produce relatively large amounts of methane, often over decades. The rate of methane generation will decrease over time, with the rate of decrease determined by the nature of the decomposing materials and environmental conditions such as precipitation and temperature. Even “inert” fill soils can contain traces of roots, topsoil, and other organic materials. Soil fills, deeper than 10 feet thick where anaerobic conditions may be created, can create pockets of decomposition gas containing methane with these small amounts of organic materials. To prevent methane generation, a fill source with TOC of 0.5% by weight or above (DTSC, 2005) should not be used or a methane evaluation should be conducted at least 30 days after fill placement and compaction.

1.1 Biological Decomposition

Soil decomposition gas may be generated by biological decomposition of putrescible wastes. Biological decomposition is important in most active and closed landfills containing organic wastes, which decompose due to anaerobic microbial degradation. Generally, the amount of gas generated in a landfill is directly related to the amount of organic matter present. Waste type, in-situ characteristics, and conditions can affect biological decomposition. Under anaerobic conditions, organic wastes are primarily converted by microbial action into carbon dioxide and methane.

1.2 Physical Mechanisms

Several physical mechanisms describe the movement of decomposition gas through the subsurface. They are molecular diffusion and convection. Molecular diffusion occurs when there is a concentration difference between two different locations. Diffusive flow is in the direction of decreasing concentration. The density affects molecular diffusion, but the concentration will tend to overcome small differences in density. In the soil atmosphere, the diffusion coefficients are only relative indicators due to the tortuous path the gas must travel in the soil. Convection flow occurs when a pressure or temperature gradient exists between two locations. Gas will flow from an area of higher pressure to an area of lower pressure. Convection flow of gas will overcome the influence of molecular diffusion. This type of flow is usually associated with landfills with an active extraction system. Biodegradation processes, compaction effects, or methane generation drives vapors vertically and horizontally. Changes in barometric pressure will have an effect on convection flow. The rate of gas movement by convection is generally orders of magnitude greater than diffusion.

1.3 Geologic Factors

The geologic and geographic location of entry into the subsurface can affect the rate of decomposition and gas production. Soil permeability is an important factor in the movement of gas through soil. Soil permeability is the measure of the ease with which a gas or liquid can move through sediment, soil, or rock. It is related to the grain size and the amount of water in the soil. Soils with smaller grain sizes are less permeable. When soils contain clay size particles, soil gas movement is severely limited. Or if the soils become poorly sorted with increased fine-grained material, the pore space is decreased, water content increases and the rate of diffusion decreases. The most retarding layer dictates the rate of diffusion of gas in the vadose zone. Heterogeneous soil conditions across a site may interfere in the distribution of decomposition gas. Areas of horizontal low permeability area within the vadose zone may exhibit low concentrations when the level of contamination could be the same or higher than other areas. Conversely, high permeability areas in a low permeability area could exhibit an area of high concentration. The presence of moisture in the soil decreases gas migration. The soil airspace decreases as the volume of soil water increases, thereby inhibiting gas movement. In addition, soil moisture decreases the mass for transport by allowing the gas to partition into the pore water.

Two geologic factors that can lead to anomalies are barriers and conductive zones. Barriers to soil gas diffusion are obstructions, either anthropogenic or natural, which impede the movement of decomposition gas. The obstacles can be structures, blacktop, cement, landfill caps, clay layers, perched water, frozen soil, irrigated or recently disturbed soils. The location and extent of the barrier will dictate the direction of movement around the obstacle. Conductive zones are areas where gases will preferentially move because of the low resistance to movement. Conductive zones can be natural, such as old stream beds, gravel lenses, and fractures, or man made such as bedding around pipelines, French drains, and tunnels.

1.4 Methane Gas Mitigation

When methane decomposition gas is found at significant concentrations at a site above established regulatory threshold limits, methane mitigation measures are required. Several basic approaches to mitigation are available:

- Excavation of shallow or limited methane sources
- Methane monitoring program
- Methane collection and passive vent system (without membrane)
- Methane collection, membrane and passive vent system
- Methane collection, membrane and active vent system
- Air injection
- Alarms

The mitigation approach employed is designed to suit the particular circumstances of a site or development. Sites with large amounts of organic fill are candidates for more involved mitigation systems such as active vent systems. Whereas sites with small amounts of organic fill mitigation may require monitoring or installation of a simple passive system.

2. Materials and Methods

A well-established and accepted equation to calculate methane generation from putrescible matter is a first order differential equation. The algebraic solution for this equation is an exponential decay in AP 42 (USEPA, 1995) for the decomposition of refuse provides a decomposition rate constant (k). The k ranges from an estimated 0.02 year^{-1} for areas receiving 25 inches or more of rain per year to 0.04 year^{-1} for areas receiving less than 25 inches per year. In addition, the USEPA Landfill Gas Emissions Model (LandGem) also uses a default of 0.7 year^{-1} for a wet bioreactor situation (Alexander et al., 1995). The primary putrescible fraction in landfills and in typical fill soils is cellulose. However, the decomposition of cellulose is significantly higher in fill soils because of the smaller particle size of the material than that of a landfill. To evaluate this condition, a k value of 0.15 year^{-1} and 0.5 year^{-1} is considered. Such an evaluation does not consider the total amount of methane generated by the decomposition of the cellulose. It is unlikely that the methane concentration will remain as long as the model predicts using the U.S. EPA rate constants. The rate constants provided by the USEPA are for large landfill conditions. It is expected that higher rates of decay between 0.7 year^{-1} and 1.0 year^{-1} are more reasonable estimates for fill sites. Empirical rate of decomposition has not been studied to date for these conditions.

Therefore the uncontrolled emission of biogenic methane generation may be estimated by using a theoretical first-order kinetic model under anaerobic conditions (USEPA, 2004). The equation is as follows:

$$C_f = C_o \, e \, (-kt)$$

Where:

C_f = Final decayed methane concentration in ppmV;
C_o = Peak methane concentration in ppmV;
k = Rate constant year^{-1}; and
t = Time in years.

The uncontrolled generation of the methane can be modeled based on the theoretical first-order kinetic model for a number of sites where biogenic methane is detected in fill soils. The initial methane concentration is obtained by a soil gas survey during an environmental investigation at the site of interest. The rate constant can be estimated by empirical data obtained for a site from ongoing long-term monitoring. Alternatively, the rate constants provided in the USEPA AP 42 can also be used to estimate the length of methane production. The plot of initial concentration and several estimated rate constants provide an estimated length of methane generation for a final methane concentration below acceptable regulatory limits. Figure 1 shows the calculated future asymptotic methane concentrations in soil for an initial concentration of 200,000 ppmV. The initial concentration chosen is reflective of initial methane concentrations encountered at fill sites and dairy sites throughout the Southern California area.

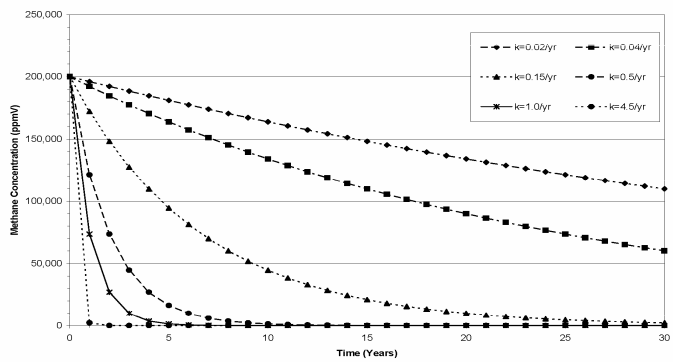

Figure 1. Methane Concentrations versus time for variable degradation rates.

The plot of the concentration versus various rate constants allows the estimation for the length of time for methane mitigation and whether site mitigation is necessary. The methane concentration may rapidly decrease below regulatory limits and not require mitigation prior to construction. Conversely, if high concentrations persist, the duration of the mitigation can be estimated. The estimation of the length of time for the anticipated mitigation system allows for cost analysis and the making of the related business decisions for current or future land development. Once a site is developed with landscaping and vegetation, the resultant addition of irrigation and organic nutrients may cause methane levels to increase as it adds to the biogenic formation of methane. However, such a rise in the biogenic production of methane levels off quickly, reaches a steady state, and the site quickly reverts back to the decreasing trends previously exhibited.

3. Results and Discussion

Based on empirical data from a site in Southern California, a k value between 0.7 $year^{-1}$ and 10 $year^{-1}$ has been observed for steady state conditions of biogenic methane generation as presented in Table 1. The average of the lowest two rate constant values provides a k value of 1.2 $year^{-1}$ whereas the average k is 4.5 $year^{-1}$. The site has been monitored for approximately two and a half years to date. The average k value of 1.2 $year^{-1}$ may be more representative of steady state conditions in comparison with the average k of 4.5 $year^{-1}$ as evidenced in its sharp decline of the methane concentration versus time as shown in Figure 1. Furthermore, this average k rate results in concentrations that will be asymptotic within the first year. This rate is too aggressive for the site and therefore a k rate of 1.0 $year^{-1}$ may provide a more realistic conservative estimate for steady state conditions. Ultimately the best estimates of the rate constant can be gathered by the use of site-specific long-term monitoring. Due to recent attention to biogenic methane in fill soils more sites and data will be available within the next few years for study. In the absence of site-specific data, an approximation of the length of biogenic methane production is available by the referenced figure using the site's initial methane concentrations.

Table 1. Observed Field Empirical Rate Constants for Probes and Vents

	Rate Constant ($year^{-1}$)
Below Ground Probes	
MP2-S	4.9
MP-4S	**0.7**
MP-4D	10
Passice Vents	
A1	**1.7**
A2	3.3
A3	4.5
A5	3.1
A6	5.3
A7	5.1
B1	6.8
B3	3.6
B4	6.6
R1	4.1
R2	3.9
Average	**4.5**

4. Conclusion

Methane is found in areas where buried organic materials decompose in the absence of oxygen. It is produced when methanogenic microbes convert organic materials into methane and carbon dioxide. Biogenic methane is formed at relatively shallow depths by the bacteriological decomposition of organic matter in the soil (e.g., in landfills, fill operations, dairies). The primary mechanisms for methane migration in the subsurface are pressure driven flow and diffusion. Methane is an asphyxiant and a combustible gas. The geologic and geographic location of methane in the subsurface can affect the rate of decomposition and gas production. When decomposition gas containing methane is found at significant concentrations methane mitigation measures may be required. Methane gas emissions can be estimated using a theoretical first-order kinetic model of methane production. Site-specific data provides the length of biogenic methane production is available and alternatively a figure with rate constants was provided for estimation purposes at similar biogenic methane production fill sites. The methane concentration may rapidly decrease below regulatory limits and not require mitigation prior to construction. Conversely, if high concentrations persist, the duration of the mitigation can be estimated. Based on empirical data from a site in Southern California, a k value of 1.0 year^{-1} can be used as a conservative estimate for steady state conditions of biogenic methane generation whereas the site average k was 4.5 year^{-1}.

5. References

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