TECHNICAL GUIDANCE DOCUMENT

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

Addressing Methane at Anaerobic Bioremediation Sites

Office of Land Quality

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Notice

The Technology Evaluation Group (TEG) composed this document to address the issue of appropriate methane monitoring/mitigation at bioremediation sites to avoid explosive hazards. This document is not meant to discuss using methane concentrations as a remediation performance measure during bioremediation.

This evaluation offers suggestions of what may be effective strategies for dealing with this issue. It does not approve any technology nor does it verify any technology's effectiveness in conditions not identified here. Mention of trade names or commercial products does not constitute endorsement or recommendation by IDEM for use.

Summary

Anaerobic conditions may produce methane and methane concentrations of 5-15% (50,000-150,000ppm v/v) are explosive. A site specific conceptual model should be developed, but in general methane ground water concentrations in excess of 10 mg/l or monitoring well/subsurface/ subslab gas concentrations in excess of 10% of the lower explosive limit (LEL) of 5% methane are a cause for concern and monitoring is needed to determine if adequate oxygenated vadose zone exists to mitigate the methane or if additional measures are necessary to protect any potential receptors.

Methanogenic conditions induced below a structure where oxygen is not as easily replenished present an added risk and soil gas monitoring and a mitigation contingency plan should be proposed. Sub slab gas concentrations exceeding 10% of the LEL indicate the need for mitigation. Likewise, if anaerobic conditions are induced in the vicinity of subsurface confined spaces, a mitigation contingency plan in addition to monitoring should be proposed.

Table 1 Suggested Screening Levels and Actions for Soil Gas Methane at Anaerobic Bioremediation Sites		
Sampled Medium	**Concentration**	**Action**
Ground water	>10 mg/L	Monitor Soil Gas
Soil Gas External	>10% of LEL	Check for receptors/ consider mitigation
Soil Gas Sub Slab	>10% of LEL	Mitigate
	<10% of LEL	Monitor
Indoor Air	>10% of LEL	Evacuate/ Mitigate

Background

Methane is a colorless, odorless gas which is non-toxic but extremely flammable and can also act as an asphyxiant if allowed to accumulate in closed spaces. The hazards of methane generation from landfills, sewers, wetlands and other familiar sources are well documented with accompanying regulatory strategies to alleviate issues. A relatively new methane issue is the elevated levels of methane generated in the subsurface at some anaerobic bioremediation sites. The consumption of organic carbon or electron donors used in bioremediation continually results in fermentation byproducts (e.g. volatile fatty acids) and end products such as carbon dioxide, methane and water until all the carbon is consumed. The organic carbon source leading to the high levels of methane production is <u>not</u> the chlorinated contaminants which are being remediatetd but rather the amendments used to evoke anaerobic conditions. The biogas produced by microbes in an anaerobic environment can be expected to be about half methane and half carbon dioxide. Methane concentrations will change dramatically as anaerobic activity increases, peaks then declines. At peak substrate usage, it is possible for methane to be present at or above the aqueous saturation limit and at concentrations causing advective flow of not only methane but other gases in the subsurface. Anaerobic processes usually proceed slowly and will vary at each site, but peak production of methane will generally occur weeks to months after injections.

The dynamic nature of methane production over time should be understood to address potential risk. Screening levels should account for the expected peak and monitoring should encompass broad time periods. While not described in this document, ethanol fuel releases (ex E85) can create the same anaerobic conditions as engineered anaerobic remediation sites and methane should be monitored at these sites because of accumulation hazards and also because it can reduce the oxygen available for biodegradation of aerobically degradable hydrocarbons allowing them to migrate further than would be expected. More information is available in the ITRC Petroleum Vapor Intrusion document (ITRC; 2014).

Once produced, the primary mechanisms for gas phase methane migration in the subsurface are pressure driven (advective) flow and diffusion. Methane will migrate from areas where it is present at higher concentrations or pressures to areas at lower concentrations or pressures. Since 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 an enclosed space (utility access, basement sump pit, dryer vent, etc.) is present at the ground surface, the potential exists for methane to accumulate. Methane attenuates readily if oxygen is present but when methane production rates are high enough, oxygen may be depleted allowing methane to reach receptors. Generally, a few feet of oxygenated vadose zone is enough to mitigate methane unless oxygen infiltration is impeded (for example by a structure). The goal of monitoring is to ensure that enough oxygen is present to degrade methane before it reaches a place where it can accumulate to explosive concentrations. EPA recommends reviewing readily ascertainable information for purposes of assessing whether non-occupied structures (including, but not limited to, sewers, pits, and subsurface drains) are present, which may also accumulate vapors, in addition to occupied and non-occupied buildings (USEPA; 2015 p 53). Separation distance from receptors along with methane and oxygen concentrations are important lines of evidence.

Screening Levels/Monitoring at Anaerobic Bioremediation Sites

Although excess amounts of soluble substrate amendments would be expected to produce methane at the greatest rate, some methane will be produced anytime anaerobic conditions exist regardless of which substrate is used. If methane concentrations at anaerobic bioremediation sites can reasonably be expected to reach 10% of the LEL at receptors, a proactive methane monitoring plan should be initiated and a methane mitigation contingency plan should be outlined. Sites which would be expected to meet this criteria include sites with shallow ground water where not enough oxygenated vadose zone height exists to dissipate methane, sites with preferential pathways (including utility corridors and Karst areas) to occupied structures or instances where methanogenic conditions are induced beneath a structure. The goal of screening is to make sure that methane attenuates before reaching an area where it can accumulate. Either dissolved ground water methane concentrations or soil gas concentrations could be measured to give an indication if concentrations are high enough to step out in the direction of receptors. Monitoring should be coordinated with an analysis of the site's geochemistry as time is required for methane production to peak once a system becomes anaerobic. The monitoring plan should include an appropriate response for exceedances. Further guidelines on methane monitoring programs are outlined in IDEM's non-rule policy document covering landfill methane monitoring (IDEM; 2007).

Ground Water

Ground water methane concentrations should be sampled at the injection/ remediation depth in the contaminant source area. Monitoring well caps with dedicated gas sampling ports should be considered at anaerobic bioremediation sites. Methane should be monitored according to RSK175 (Kampbell, 1998) or another appropriate method may be used. Ground water methane usually will not accumulate to levels higher than the source concentration so this would be a worst case scenario. The USGS recommends that ground water methane concentrations greater than 10 mg/l are an indication that methane concentrations may become a hazard (USGS, 2006). If ground water concentrations exceed screening levels (10 mg/l), soil gas monitoring points should be placed in the direction of receptors and in any preferential pathways (eg. utilities) that may act as corridors for soil-gas transport. Methane solubility in water is pressure and temperature dependent but is generally in 22-35 mg/l range. Any concentrations in excess of the ambient solubility indicate methane is being produced at rates that could lead to advective flow into areas where the methane could create a hazard.

Soil Gas

Soil gas concentrations in the remediation area can be measured either in the monitoring well head space or in dedicated vapor ports if available using a calibrated Flame Ionization Detector (FID), combustible gas meter or soil gas sampling. Care needs to be taken to ensure that well screens are not submerged as anomalously high readings would result from the gas trapped in the well tube which may not be indicative of actual soil gas concentrations. Soil gas concentrations exceeding 10% of the LEL indicate the need for continued monitoring and possible mitigation depending on the conceptual site model and the depth at which elevated concentrations exist. Multiple depth soil gas ports provide a line of evidence that methane is attenuating. Consider monitoring monthly and increase or decrease the frequency according to site specific lines of evidence indicating whether or not methane is an issue.

Anaerobic conditions induced beneath a structure are an added risk and methane concentrations should be measured beneath the structure. Sub slab soil gas concentrations exceeding 10% of the LEL indicate the need for mitigation. Responses less than 10% of the LEL in conjunction with groundwater exceeding 10 mg/L indicate the need for continued monitoring with the potential for mitigation depending on results. Likewise, if anaerobic conditions are induced in the vicinity of subsurface confined spaces a mitigation contingency plan in addition to monitoring should be proposed; if soil gas concentrations exceed 10% of the LEL, the mitigation plan should be implemented.

Indoor Air

Methane is flammable at concentrations between 5 and 15%v/v (50,000-150,000 ppm). Reaching this concentration in household indoor air is unlikely as it would require an attenuation factor significantly larger than is usually observed. But if subslab concentrations beneath a structure or soil gas methane concentrations in preferential pathways approach 10% of the LEL, indoor air concentrations should be measured. Indoor air concentrations greater than 10% of the LEL should result in building evacuation until mitigation and a comprehensive methane monitoring plan are implemented. This level is also protective of situations which can lead to oxygen deficiency (33,000 ppm). These levels are aimed at ventilated commercial structures and are not meant to supersede regulations for other structures such as sewers or confined spaces. For example, OSHA prohibits entry into crawl spaces in excess of 10% of the LEL for methane.

Mitigation

The goal of mitigation is to eliminate the ability of methane to collect in an area where it is an explosion hazard. Mitigation measures need to be determined on a site specific basis in conjunction with an analysis of the risk presented by methane levels and receptors which are present. The presence of structures in conjunction with shallow anaerobic zones would tend to increase risk. Choosing an appropriate mitigation measure will require combining knowledge of site concentrations and the possible migration pathways into on-site structural features.

If no on-site structures or preferential pathways exist and it can be shown that an oxygenated layer of soil exists above the remediation zone, then the methane risk is minimal. IDEM solid waste rules (329 IAC 10-20-17) require that methane concentrations at the facility boundary do not exceed 25% of the LEL (IDEM, 2007); this would seem a reasonable precaution at remediation sites also. If 25% of the LEL is exceeded at the site boundary, an analysis of potential receptors should be incorporated into a decision to either monitor further or mitigate. When above ground structures, preferential pathways and subsurface structures are not present, venting would usually be an appropriate mitigation measure unless concentrations are extremely high site-wide. When concentrations of methane and other remediation byproducts (ex degradation byproducts or ethane gas) are present at elevated levels site-wide, an intrinsically safe Soil Vapor Extraction (SVE) system to collect vapors should be considered. Administrative measures, such as warning signs, and opening manholes and allowing them to degas and/or ventilating with an intrinsically safe fan would be protective of most subsurface structures but OSHA guidance should be consulted.

Anaerobic conditions beneath a structure would likely require a more active mitigation plan. If microbially reducing conditions are implemented under building floors, subslab depressurization or low flow ventilation should be incorporated to remove gases of concern (Suthersan and Payne, 2005). Table 1 and the soil gas screening section above provide more guidelines. This is especially important as methane is not the only hazardous gas which might be generated. Ethane, ethene, hydrogen sulfide and numerous other gases may exist. In all cases, remediation equipment needs to be intrinsically safe from explosion hazards and the goal of mitigation needs to be clear. While radon type mitigation systems may be appropriate depending on the mitigation goal, they will not eliminate the methane under a structure; they will simply stop methane from entering the structure through the sub slab. Only a properly screened collection system (such as SVE) will collect methane.

Routine inspection of mitigation system components during remediation duration should be specified. SVE and subslab systems should be equipped with system failure warning devices in areas where potential receptors are present.

Methane Monitoring Equipment

A Flame Ionization Detector (FID) should be used to detect methane because a Photoionization Detector (PID) will not measure methane.The high ionization energy of methane, 12.6eV, prevents the UV light source in a PID from ionizing methane. If samples are taken using a calibrated meter, care should be taken to avoid interference from petroleum or other organic compounds. Petroleum and chlorinated compounds cause high readings. A carbon filter which removes these, but not methane, will lead to more accurate readings. Meters are useful for screening and choosing sample placement and timing, but an analytical sample to confirm the readings should be considered if concentrations are close to screening levels (Jewel and Wilson, 2011). Appropriate analytical samples may be taken with Tedlar bags or summa type canisters.

Safety Issues

Methane buildup at remediation sites can lead to explosion hazards. Intrinsically safe remediation equipment should be used at anaerobic bioremediation sites.

Indiana Case Studies (or Use in Similar Environment)

Several sites in Indiana are utilizing chlorinated bioremediation with a wide variety of attention given to methane generation. Generally, sites in which remediation commenced some time ago do not consider methane migration hazards but more recent sites are cognizant of the need to address methane issues.

Industrial Site; Indianapolis

Remediation commenced in 2011. Methane in ground water is in excess of 30 mg/l with many wells consistently 10-20 mg/l on site including 7-13 mg/L at the property border. The highest methane concentrations are in the intermediate ground water range. The shallow zone ground water is from 3-14 ft bgs with the intermediate defined as around 12-22 ft bgs. The site is extremely heterogeneous and characterization has been difficult. Consultant indicated that ignition sources were removed from the wellhead with elevated methane concentrations and that the wellheads are vented and system components are explosion proof. The likelihood of elevated concentrations in soil gas and possible migration to on-site structures has not been addressed in spite of the high ground water concentrations. Mitigation measures including, at a minimum, a methane monitoring plan should be implemented.

Industrial Site; Connersville

Pilot test for chlorinated bioremediation commenced in June, 2003 with emulsified vegetable oil injections and lactate (10 mg/l goal) injections commencing in January, 2004 with Dehaloccoides (10^7 DHC/L) bacteria amendments in March 2004. Methane ground water concentrations were 0.25-12 mg/l with final methane at 1.3 mg/l. Ground water was at 23 ft bgs. Injection wells were screened at 19-29 ft bgs, 28-38 ft bgs and 37-47 ft bgs. Recirculation cells in addition to stoichiometric amendment addition have allowed mineralization without extremely elevated methane levels being present in ground water. Soil gas has not been measured but due to the depth to ground water, low levels of methane in the ground water and lack of preferential pathways, methane is likely dissipated before reaching receptors. Mitigation measures were not necessary.

Industrial Site; Columbus

Chlorinated solvent remediation using molasses injections commenced in 2011. Baseline ground water methane levels of 0.004 mg/L increased to 21 mg/l during remediation. Depth to water is around 22 ft bgs. Mitigation measures were implemented with the original plan. In addition to monitoring methane levels, an SVE system was put in place to capture methane and other remediation byproducts. The highest recorded ground water methane concentration at the perimeter of the system (to date) is 6.1 mg/L. In addition, soil gas concentrations in monitoring wells and gas ports were also monitored. Some initial soil gas concentrations were above the 5% LEL but as the SVE system operation has stabilized, soil gas methane concentrations have become negligible.

Conclusion

The hazards of methane are well documented and should be addressed at bioremediation sites where methane and other explosive gases may be generated. Due to the acute hazards associated with methane, methods will differ from traditional vapor intrusion investigations. If methane concentrations can reasonably be expected to reach 10% of the LEL, methane monitoring and/or mitigation may be necessary.

Further Information

If you have any additional information regarding this issue or any questions about the evaluation, please contact the Office of Land Quality, Science Services Branch at (317) 232.3215. IDEM TEG will update this technical guidance document periodically or on receipt of new information.

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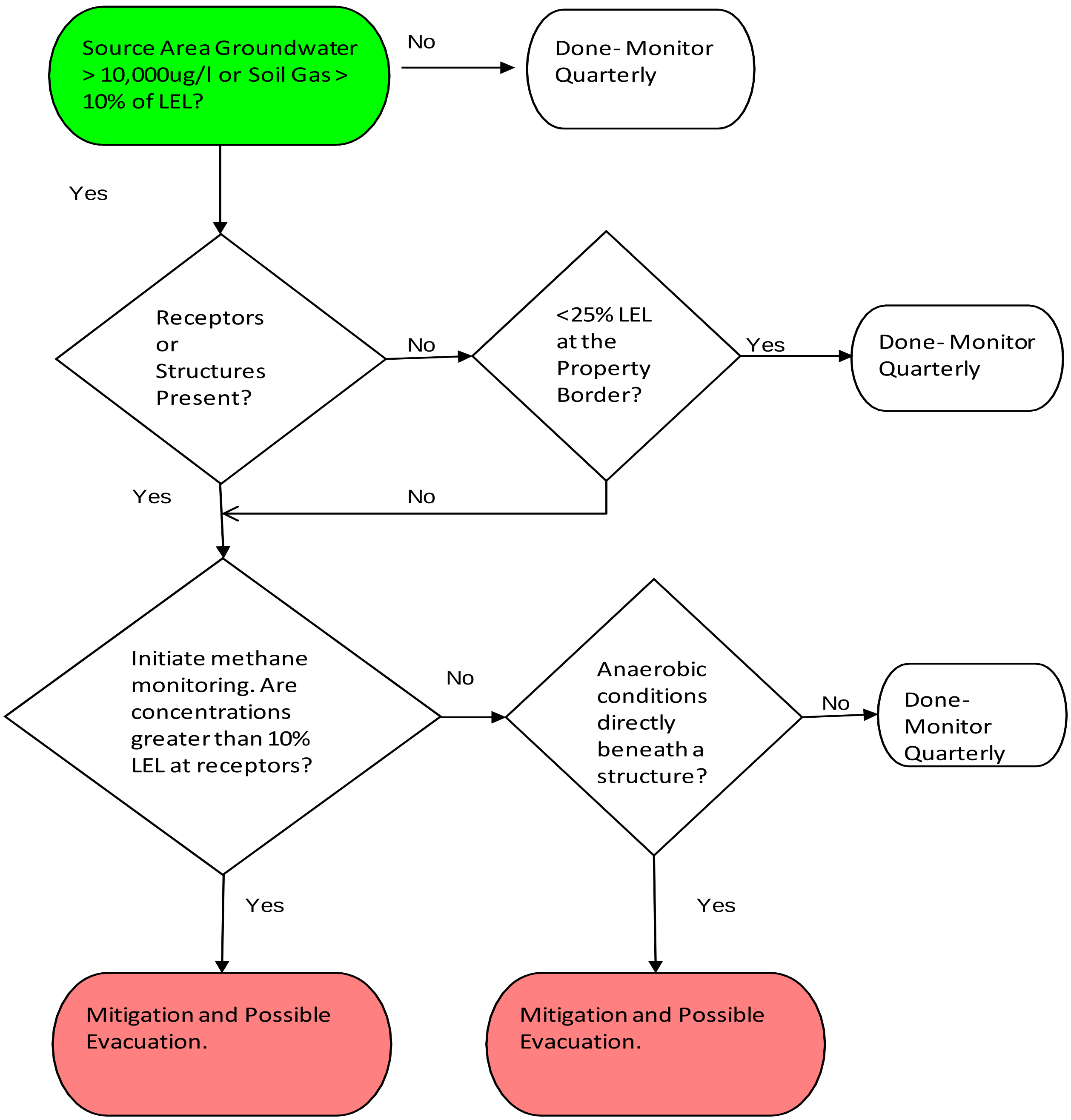
Suggested Process for Methane Monitoring at Anaerobic Bioremediation Sites



APPENDIX A and B

Appendix A – 25% of the LEL Explained

Methane is flammable from 5-10% per volume of air. In units of part per million, volume (ppmv), this converts to 50,000 ppmv because fifty thousand divided by a million is 5%. Further confusion sets in when regulatory screening levels are set at 25% of the LEL as a safety factor since a percent of a percent is not a frequently calculated characteristic. The screening level of 25% of the LEL is actually 25% of 5% which is 1.25% or 12,500 ppmv (12,500 is 1.25% of a million). Similarly, 10% of the LEL would be 0.5% methane or 5,000 ppmv.

Appendix B – Screening Level Explanation

Not enough data exists for a data-driven analysis of a ground water methane concentration screening level indicative of hazardous conditions. Henry's Law predicts 1-2 mg/L in the ground water could theoretically produce 5% methane (see below). However, using only Henry's Law does not account for any oxygen consumption of methane. USGS (2006) indicated 10 mg/L as a screening level but did not support the concentration with a stringent numerical analysis. Nevertheless, 10 mg/L is about half the solubility and seems like a reasonable indication that the site's microbial population is generating substantial ground water methane and soil gas methane should be investigated if receptors are present.